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Gaussian Tight Binding Study of Ultrafast Electron Dynamics

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Max Boleininger
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Declaration of originality

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Abstract

Computer simulations are invaluable for the study of ultrafast phenomena, as it is not possible to directly access the electronic and nuclear dynamics in experiments. We present an efficient method for simulating the time-dependent coupled electron-ion dynamics within the Ehrenfest picture in molecules under the influence of time-dependent electric fields, based on an extension of the density-functional tight binding model. We consider self-consistency in a self-multipole-consistent framework, expanding the electron density in terms of radial Gaussian and angular real cubic harmonic functions. This enables the efficient computation of the electrostatic interaction energy while retaining a physical description of charge transfer and ionic polarisation. We show that this Gaussian tight binding method produces molecular polarisabilities, time-dependent dipole moments, and electron densities in strong agreement with density-functional theory, but at a small fraction of the cost. This efficiency enables high-throughput ultrafast studies on molecules, which we demonstrate on the example of transient core-spectroscopy on polythiophene fragments.

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Recent advances in experimental techniques have made it possible to control and characterise the response from a range of small organic molecules to short intense laser pulses with sub-femtosecond resolution ($1\text{ fs} = 10^{-15}\text{ s}$).¹⁻⁴ The significance of this development can hardly be overstated: particularly the first femtoseconds following a photoionisation or photoexcitation event are considered the drivers for a diverse range of photochemical mechanisms, such as photosynthesis,⁵ photocatalysis,⁶ and biological damage.⁷⁻⁹ Understanding these processes on a fundamental level has far-reaching implications for future technology. After all, if we can truly characterise excited systems with atomic resolution in space and with attosecond resolution ($1\text{ as} = 10^{-18}\text{ s}$) in time, we can also hope to ultimately tune or even control this response to the benefit of technological applications.

Of particular interest is the response of conductive polymers to ultrafast pulses. Conductive polymers exhibit a diverse range of optoelectronic properties while also being highly tunable, for instance by structural changes or by chemical substitution. However, the response of large molecules to ultrafast pulses in general is still poorly understood due to the sheer number of electronic, vibrational, and structural degrees of freedom that characterise the system. Sudden photoionisation in molecules causes a simultaneous response in the form of non-trivially coupled charge flows and changes in the vibrational dynamics.^{10,11} Computational modelling holds the key to disentangle this interplay between electronic and nuclear dynamics and ultimately assist the experimental efforts.

We require computational methods with a reliable description of electronic excited states, as well as being sufficiently computationally efficient to enable demanding time-dependent simulations of molecules in condensed phases. Current computational methods,

whether based on density-functional or Hartree-Fock theory, require enormous computational resources to simulate these systems, severely limiting both system size as well as the variety of initial and boundary conditions which can be studied. This necessitates the development of faster but also more approximate electronic structure methods that still capture the essential physics.

The core topic of the work presented here is the development and testing of such an approximate method. We developed the Gaussian tight binding framework, an electronic structure method implemented in the PLATO software. We demonstrate this method to accurately compute the response of organic molecules to static and time-dependent electric fields at significantly less computational time than comparable methods. We furthermore model the coupled electronic and nuclear dynamics for systems in external time-dependent fields. This enables us to track the time-evolution of the electron density, as well as the non-adiabatic structural rearrangement of the molecule following an excitation. Finally we apply the method to simulate a basic pump-probe setup on thiophene fragments, allowing us to extract information on the internal electronic and vibrational dynamics of the system following photoexcitation.

1.1 From experiment to theory

Ultrafast dynamics experiments hold the potential to probe electron^{12–14} and nuclear dynamics^{15,16} with sub-femtosecond time-resolution,¹⁷ effectively probing chemistry on the femtosecond time scale.¹⁸ This is achieved by subjecting atoms or molecules to strong, low-frequency laser fields ($I > 10^{12}$ W/cm²)* of just a few femtoseconds duration and measuring the subsequent spectral response. In this section we shall attempt to give a most basic introduction to the subject.

Ultrafast dynamics experiments initially started out as the study of dilute atomic gas subjected to intense, short-pulsed laser pulses of low frequency.¹⁹ Provided the pulse was intense enough, it was observed that the atoms emitted coherent radiation at frequencies that are odd-numbered multiples of the laser frequency. The harmonic radiation was found to reach photon energies of 100 eV or more, well over the ionisation potential of the irradiated atoms. That is despite the energy of an individual photon of the laser field lying below the ionisation energy. This effect was named high-harmonic generation (HHG)

*Consider a field with peak intensity of $I_0 = 10^{15}$ W/cm² acting on a hydrogen atom. This corresponds to a field amplitude of $E_0 = 0.17 E_h/ea_0$ following $I_0 = c/(8\pi)E_0^2$. Hydrogen has an ionisation potential of $0.5 E_h$ and a classical radius of $1 a_0$. The external field energy $V_{ele} = eE_0a_0 = 0.17 E_h$ of the electron is therefore of comparable magnitude to the ionisation potential.

and was subsequently exploited to develop table-top sources of x-ray lasers.^{20–22} Still, the underlying physical mechanisms responsible for this effect were not fully understood.

Lewenstein et al. in 1994²³ first formulated a quantum-mechanical description of HHG using a series of approximations that are today summarised under the name of strong-field theory. This theoretical work considers electrons ionised by strong fields to move on a nearly free trajectory while accumulating further kinetic energy from the laser field. The far-field dipole radiation of the ionised electrons would subsequently emit radiation in odd multiples of the laser field frequency. Strong-field theory was found to be capable of predicting the most characteristic features of high-harmonic spectra.

While the original work neglected recombination and scattering interactions of the ionised electron with the cation, it was clear that such interactions would allow for a time-resolved probing of the internal dynamics of the ionised system. The recombination and scattering amplitudes of an ionised electron with a positively charged system is naturally dependent on the time-propagated quantum states of either system. The photoemission spectrum would therefore be modulated by these mechanisms, but in what way, and how strongly? One may then reverse the question, and ask: can the electronic and nuclear dynamics of the ionised molecule be inferred from the information contained in a time-resolved spectrum? In the following work we shall attempt to elucidate this question.

Experiments unfortunately only give limited access to the underlying dynamics. Depending on the setup, the primary observable is either the transmission-absorption spectrum or the spectrum of high-harmonic radiation.²⁴ We know that these spectra necessarily contain some information on the electronic and vibrational dynamics of the system. While it is possible to infer the dynamics in small systems from symmetry considerations of the molecular orbitals,²⁵ this approach relies on the studied system to have a very small number of degrees of freedom. This presents a strong opportunity for applying theoretical models that take the time-dependent response of a probed system into account. Computational modelling allows us to approach this problem from the opposite direction, as simulations grant us full access to the electronic and nuclear dynamics. We simulate the time-dependent electron density for a given system under the influence of a laser field, extract the time-dependent dipole moment, and finally compute the spectral function. We are thereby able to correlate changes in the spectral function with changes in the underlying electronic and nuclear dynamics.

1.2 Dissertation outline

We present in chapter 2 the fundamental concepts of quantum mechanics underlying this work, as well as various conventions and notations that will be used throughout the following chapters. We introduce the time-dependent N -body Schrödinger-equation, outline the basics of static- and time-dependent density-functional theory, and finally derive the density-functional tight binding equations.

In chapter 3 we outline the theoretical framework of a generalised self-multipole-consistent density-functional tight binding theory which we call Gaussian tight binding. This method allows for a more accurate description of the self-consistent electrostatic energy. We derive the self-consistent energy and force equations, and further give details on how we solve and numerically verify the integrals.

Chapter 4 contains benchmarks of the Gaussian tight binding method in comparison with density functional theory for electrostatic properties. We build a parametrisation for hydrogen, carbon, and sulfur atoms. We show that merely the addition of both polarisable basis functions and self-consistent dipole terms leads to a tight binding theory that is in excellent agreement with density-functional theory without any further empirical corrections. We further apply tight binding in conjunction with the point-polarisable dipoles model to estimate the internal fields of amorphous polythiophene subjected to external fields.

In chapter 5 we show how to solve the time-propagated tight-binding equations using the unitary projection approach and test the numerical integrator for energy conservation. We compute the optical response of trans-2,2'-bithiophene to external electric fields, and again find our tight binding method to be in strong agreement with density-functional theory. Furthermore we show directly by example that the time-dependent densities predicted by Gaussian tight binding and density functional theory are in excellent agreement.

In the penultimate chapter 6 we introduce the Ehrenfest equations of motion to allow the computation of forces in time-propagated simulations. The hydrogen, carbon, sulfur tight binding model is further extended by inclusion of core electrons. This enables us to compute transient core absorption spectra of molecular polythiophene fragments over various time delays. We find spectral signatures that can be associated with the dynamics of excited states and nuclei, offering a direct link between simulation and experiment.

Finally we conclude our work in chapter 7, summarising our key findings and offering a selection of potential avenues for future research.

Fermi and Thomas^{26,27} laid the foundations of density-functional theory (DFT) in their treatment of the simple electron gas, which was further formally expanded by Hohenberg and Kohn²⁸ in 1964. Kohn’s findings were most notably recognized with the Nobel Price in Chemistry in 1998 “for his development of the density-functional theory”.²⁹ The principal idea behind density-functional theory is to map the wave function of the interacting N -particle Schrödinger-equation to that of N non-interacting single-particle Schrödinger-equations under the influence of an additional fictitious potential that summarises the many-body effects. The problem of solving the correlated N -body quantum problem is hence replaced by the problem of finding appropriate approximations to this so-called Kohn-Sham potential which give physically sensible results.

Density-functional theory has seen a wide range of applications over the past half century since its conception, enabling simulations accessing much larger length- and time-scales than wave-function based quantum-chemistry methods. Indeed the method has become so widely applied, that an introduction almost seems redundant. We refer here to the excellent write-up on the history of density-functional theory by Jones,³⁰ and instead jump straight into the theory.

In the following section we start with the presentation of the time-dependent N -body Schrödinger equation. We next outline principles of ground-state and time-dependent density-functional theory, and finally introduce the approximate density-functional tight binding method as an efficient alternative to density-functional theory.

2.1 Time-dependent N-body Schrödinger equation

We shall in the following build upon the postulates of quantum mechanics.^{31,32} The state $|\Xi(t)\rangle$ in a quantum mechanical system propagates according to the time-dependent Schrödinger equation:

$$i\hbar \frac{\partial}{\partial t} |\Xi(t)\rangle = \hat{H} |\Xi(t)\rangle, \quad (2.1)$$

where $\hbar$ is the reduced Planck constant and i is the imaginary number. The Hamiltonian is here given by the total kinetic $\hat{T}$ and potential $\hat{V}$ energy operators of the system:

$$\hat{H} = \hat{T} + \hat{V} \quad (2.2)$$

The expectation value of the Hamiltonian is hence the total energy of the system: $E = \langle \Xi | \hat{H} | \Xi \rangle$. We note that both spin-polarisation and relativistic effects are neglected in this work, which are included in the Pauli³³ and Dirac³¹ equations respectively. Consider now the quantum system to be composed of N electrons with spatial coordinates $\{\vec{r}_i\} = \{\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N\}$, charge e , and mass m_e , as well as M ions (bare nuclei) with coordinates $\{\vec{R}_I\} = \{\vec{R}_1, \vec{R}_2, \dots, \vec{R}_M\}$, charges $\{Z_I\}$, and masses $\{M_I\}$ under the influence of a time-dependent, electric potential $\hat{V}_{ef}(t)$ caused by an electric field. The energy operators are now given as:

$$\hat{T} = \hat{T}_{ele} + \hat{T}_{ion} = - \sum_{i=1}^N \frac{\hbar^2}{2m_e} \vec{\nabla}_{\vec{r}_i}^2 - \sum_{I=1}^M \frac{\hbar^2}{2M_I} \vec{\nabla}_{\vec{R}_I}^2, \quad (2.3)$$

and

$$\hat{V} = \hat{W}_{ele-ele} + \hat{W}_{ion-ion} + \hat{W}_{ele-ion} + \hat{V}_{ef}. \quad (2.4)$$

The $\hat{W}$ operator here is defined as the Coulomb-interaction operator between the particles as noted in the subscript:

$$\hat{W}_{ele-ele} = \frac{e^2}{8\pi\epsilon_0} \sum_{i=1}^N \sum_{\substack{j=1 \\ j \neq i}}^N \frac{1}{\|\hat{\vec{r}}_i - \hat{\vec{r}}_j\|}, \quad (2.5)$$

$$\hat{W}_{ion-ion} = \frac{e^2}{8\pi\epsilon_0} \sum_{I=1}^M \sum_{\substack{J=1 \\ J \neq I}}^M \frac{Z_I Z_J}{\|\hat{\vec{R}}_I - \hat{\vec{R}}_J\|}, \quad (2.6)$$

$$\hat{W}_{ele-ion} = - \frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^N \sum_{J=1}^M \frac{Z_J}{\|\hat{\vec{r}}_i - \hat{\vec{R}}_J\|}, \quad (2.7)$$

where $\|\cdot\|$ denotes the Euclidean norm. We now proceed with the Born-Oppenheimer approximation, which separates the electronic and ionic degrees of freedom. While ions and electrons impart forces of comparable magnitude on one another, the ions have considerably

more mass than the electrons and as such move much slower. Electrons can hence be pictured to react instantaneously to changes in the nuclear coordinates. This allows us to separate out the nuclear wave-function $|\xi\rangle$, leaving the electronic wave-function $|\Psi\rangle$ merely parametrically dependent on the ionic coordinates:

$$\langle \vec{r}_N \vec{R}_M | \Xi(t) \rangle \approx \langle \vec{r}_N | \Psi(\vec{R}_M; t) \rangle \cdot \langle \vec{R}_M | \xi(t) \rangle. \quad (2.8)$$

All dependencies on the coordinates $\vec{r}_N$ and $\vec{R}_M$ shall further be omitted for clarity. We next consider the ions as classical point-charged particles. The consequence of this approximation is that only contributions including electronic degrees of freedom $\vec{r}_N$ remain in the now solely electronic Hamiltonian $\hat{H}_{ele}(t)$. The total energy of this system E is now given by the sum of the quantum-mechanical electron energy E_{ele} and the classical ion energy E_{ion} :

$$E = E_{ele} + E_{ion} = \langle \Psi | \hat{H}_{ele}(t) | \Psi \rangle + E_{ion}, \quad (2.9)$$

The ionic energy E_{ion} takes on the classical form, including the kinetic energy of motion T_{ion} , the Coulomb repulsion of the bare ionic nuclei $W_{ion-ion}$, and the interaction between the ions and the external electric potential V_{ef-ion} :

$$E_{ion} = T_{ion} + W_{ion-ion} + V_{ef-ion}, \quad (2.10)$$

where

$$T_{ion} = \frac{1}{2} \sum_{I=1}^M M_I \dot{\vec{R}}_I^2, \quad (2.11)$$

$$W_{ion-ion} = \frac{e^2}{8\pi\epsilon_0} \sum_{I=1}^M \sum_{\substack{J=1 \\ J \neq I}}^M \frac{Z_I Z_J}{||\vec{R}_I - \vec{R}_J||}, \quad (2.12)$$

and the external electric energy is found under the assumption that the charge distribution of the bare nuclei $n_{ion}(\vec{r})$ is concentrated at their respective centres:

$$\begin{aligned} V_{ef-ion} &= \int n_{ion}(\vec{r}) V_{ef}(\vec{r}) d^3r \\ &= \int \sum_I e Z_I \delta(\vec{r} - \vec{R}_I) V_{ef}(\vec{r}) d^3r = \sum_I e Z_I V_{ef}(\vec{R}_I). \end{aligned} \quad (2.13)$$

Here we refer to integration over the volume as $\int d^3r$. The time-dependent Schrödinger equation (2.1) then takes the form:

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = \hat{H}_{ele} |\Psi(t)\rangle, \quad (2.14)$$

where the electronic Hamiltonian is given by:

$$\hat{H}_{ele} = \hat{T}_{ele} + \hat{W}_{ele-ele} + \hat{W}_{ele-ion} + \hat{V}_{ef-ele}. \quad (2.15)$$

It is to note that $\hat{T}_{ele}$ and $\hat{W}_{ele-ele}$ merely depend on the electron number N and their trajectories $\{\vec{r}_i\}$. They are otherwise system-independent, and hence are commonly grouped into the *universal operator* $\hat{F}$:

$$\hat{F} \equiv \hat{T}_{ele} + \hat{W}_{ele-ele}. \quad (2.16)$$

We carry the $\hat{V}_{ele-ef}$ forward explicitly, as it is system-dependent through the form of the externally applied electric potential. The ionic coordinates equally only enter the electronic Hamiltonian parametrically in $\hat{W}_{ele-ion}$, which describes the effect of the bare ionic Coulomb potentials on the electrons. This operator is therefore commonly called the *external potential* $\hat{V}_{ext}$:

$$\hat{V}_{ext} = -\frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^N \sum_{J=1}^M \frac{Z_J}{||\hat{\vec{r}}_i - \vec{R}_J||}. \quad (2.17)$$

To summarise, the electronic Hamiltonian in the Born-Oppenheimer approximation is given by:

$$\hat{H}_{ele} = \hat{F} + \hat{V}_{ext} + \hat{V}_{ele-ef}. \quad (2.18)$$

We further note that electrons follow the Pauli exclusion principle, requiring the wave-function to be anti-symmetric with respect to any pairwise exchange of electron coordinates at any time:

$$\langle \vec{r}_1, \dots, \vec{r}_i, \dots, \vec{r}_j, \dots, \vec{r}_N | \Psi(t) \rangle = -\langle \vec{r}_1, \dots, \vec{r}_j, \dots, \vec{r}_i, \dots, \vec{r}_N | \Psi(t) \rangle. \quad (2.19)$$

These equations fully characterise the system's time-evolution given an initial condition $|\Psi(t_0)\rangle$. Unfortunately the Schrödinger equation can in practice neither be solved analytically, nor numerically for systems containing more than a few electrons, as the configurational space of the wave function $\langle \vec{r}_N | \Psi(t) \rangle$ scales factorial with the number of electrons N . We are left in a peculiar spot; this fundamental equation holds the answer to most practical problems of condensed matter theory, but cannot be solved practically due to its sheer complexity. This presents a pragmatic need to find approximate solutions capable of predicting physical properties accurately.

The past century has seen the development of many theories that solve the approximate N -electron Schrödinger equation, from empirical methods such as the linear-combination of atomic orbitals (LCAO) and tight binding (TB), to first principles methods such as Hartree-Fock (HF), density-functional theory (DFT), and GW, to name just a few. These methods give insight into the electronic structure of the system and are hence aptly called *electronic structure methods*.

2.1.1 Expectation values

We shall briefly recapture some properties of the wave-function and its operators. The concept of observables being functionally dependent on the electron density will become important in section 2.2.1, where we introduce density-functional theory.

2.1.1.1 Electron density

The state $|\Psi\rangle$ lies in the Hilbert space $\mathcal{H}$, a complex vector space with the inner product defined as:

$$\langle\alpha|\beta\rangle = \langle\beta|\alpha\rangle^* = \int \alpha^*(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \beta(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \prod_{i=1}^N d^3r_i, \quad (2.20)$$

where $|\alpha\rangle, |\beta\rangle \in \mathcal{H}$, z^* refers to the complex conjugate of z . Consider the N -body wave-function as defined by $\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \langle\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N|\Psi\rangle$ with the convention $\langle\Psi|\Psi\rangle = 1$. The expectation value of an operator $\hat{O}$ is defined as:

$$O = \langle\hat{O}\rangle = \langle\Psi|\hat{O}|\Psi\rangle = \int \Psi^*(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \hat{O} \Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \prod_{i=1}^N d^3r_i. \quad (2.21)$$

The electron density now is defined by the number operator $\hat{n}(\vec{r}) = \sum_{i=1}^N \delta(\vec{r} - \hat{\vec{r}}_i)$ as $\rho(\vec{r}) = \langle\hat{n}\rangle$:

$$\rho(\vec{r}) = \int \sum_{j=1}^N \Psi^*(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \delta(\vec{r} - \vec{r}_j) \Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \prod_{i=1}^N d^3r_i \quad (2.22)$$

$$= N \int \Psi^*(\vec{r}, \vec{r}_2, \dots, \vec{r}_N) \Psi(\vec{r}, \vec{r}_2, \dots, \vec{r}_N) \prod_{i=2}^N d^3r_i, \quad (2.23)$$

where the symmetry property of the wave-function has been used.

2.1.1.2 External field energy

We shall now show that the external field energy $E_{ext} = \langle\Psi|\hat{V}_{ext}|\Psi\rangle$ is a functional of the electron density. Consider the external field operator as given by Eq. (2.17):

$$\hat{V}_{ext} = -\frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^N \sum_{J=1}^M \frac{Z_J}{\|\hat{\vec{r}}_i - \vec{R}_J\|} = \sum_{i=1}^N v_{ext}(\hat{\vec{r}}_i), \quad (2.24)$$

where $v_{ext}(\hat{\vec{r}}_i)$ is the one-electron external potential operator as defined by:

$$v_{ext}(\hat{\vec{r}}_i) = -\frac{e^2}{4\pi\epsilon_0} \sum_{J=1}^M \frac{Z_J}{\|\hat{\vec{r}}_i - \vec{R}_J\|}. \quad (2.25)$$

The external field energy E_{ext} is therefore given by the expectation value:

$$E_{ext} = \langle \Psi | \hat{V}_{ext} | \Psi \rangle = \sum_{i=1}^N \langle \Psi | v_{ext}(\hat{r}_i) | \Psi \rangle = \int v_{ext}(\vec{r}) \sum_{i=1}^N \langle \Psi | \delta(\vec{r} - \hat{r}_i) | \Psi \rangle d^3r. \quad (2.26)$$

Applying the definition of the number operator, we identify this expression as:

$$E_{ext} = \langle \Psi | \hat{V}_{ext} | \Psi \rangle = \int v_{ext}(\vec{r}) \langle \hat{n}(\vec{r}) \rangle d^3r = \int v_{ext}(\vec{r}) \rho(\vec{r}) d^3r. \quad (2.27)$$

To summarize, the external field energy is a functional of the electron density $E_{ext}[\rho] = \langle \hat{V}_{ext} \rangle$. We shall later show that the expectation values of $\hat{W}$ and $\hat{T}$ appearing in the electronic Hamiltonian are equally functionals of the electron density.

2.2 Time-independent N -body Schrödinger equation

Propagating the time-dependent Schrödinger equation for time $t > t_0$ requires the initial solution $|\Psi_0\rangle = |\Psi(t_0)\rangle$ at time t_0 to be known. Most applications of the time-dependent problem in this work assume an initially unperturbed system. In this case the Hamiltonian is time-independent, allowing us to factor out the time-dependent function $\Theta(t)$ from the wave-function:

$$\langle \vec{r}_N | \Psi(\vec{R}_M; t) \rangle = \langle \vec{r}_N | \Psi(\vec{R}_M) \rangle \cdot \Theta(t). \quad (2.28)$$

For λ being the separation of variables constant, the Schrödinger equations now read:

$$\hat{H} |\Psi\rangle = \lambda |\Psi\rangle \quad (2.29)$$

$$i\hbar \frac{\partial}{\partial t} \Theta(t) = \lambda \Theta(t), \quad (2.30)$$

From Eq. (2.29) we obtain $\lambda = E = \langle \Psi | \hat{H} | \Psi \rangle$. Eq (2.30) has the solution $\Theta(t) = e^{-iEt/\hbar}$. This time-dependent phase does not contribute to expectation values and can hence be neglected. We are left to solve Eq. (2.29), the time-independent Schrödinger equation:

$$\hat{H} |\Psi\rangle = E |\Psi\rangle. \quad (2.31)$$

We refer here to section A.1 of the appendix for a derivation of the variational principle from which the definition of the electronic ground-state follows.

2.2.1 Hohenberg-Kohn theorem

Solving the time-independent Schrödinger equation of Eq. (2.31) is unfortunately an equally impossible feat as solving the time-dependent Schrödinger-equation for anything other than trivially simple systems. The central difficulty again lies in the vast configurational space

required to describe the all-electron wave-function $|\Psi\rangle$, which is a consequence of each electron's trajectory $\{\vec{r}_i\}$ in the system being correlated with all other electron trajectories $\{\vec{r}_{j \neq i}\}$ by both the electron-electron Coulomb repulsion and the Pauli exclusion principle. The Hohenberg-Kohn²⁸ theorems offer an elegant solution to this problem by reducing the dimensionality of the problem.

Theorem 1. Let $G : v_{ext}(\vec{r}) \rightarrow \rho_0(\vec{r})$ be the map from the one-particle potential $v_{ext}(\vec{r})$ to the ground-state electron density $\rho_0(\vec{r}) = \langle \Psi_0 | \hat{n} | \Psi_0 \rangle$. The map G is invertible up to an additive constant v_0 in $v_{ext}(\vec{r})$.

The number of electrons N and the external potential $v_{ext}(\vec{r}) + v_0$ therefore uniquely determine the ground-state density $\rho_0(\vec{r})$ of the system. Equally, any ground-state density of its corresponding external potential $v_{ext}(\vec{r})$ also defines the electron number $N = \int \rho_0(\vec{r}) d^3r$ and hence the functionals $F[\rho_0]$ and $|\Psi_0[\rho_0]\rangle$. We shall now define an energy functional $E_v[\rho_0]$ for an arbitrary external potential $v(\vec{r})$:

$$E_v[\rho_0] = \int \rho_0(\vec{r}) v(\vec{r}) d^3r + F[\rho_0]. \quad (2.32)$$

Theorem 2. Let $\mathcal{V}$ be the space of all v -representable electron densities* and E_0 the ground-state energy of N electrons in the external potential $v(\vec{r})$. Then it follows that

$$\forall_{\rho \in \mathcal{V}} E_v[\rho] \geq E_0, \quad (2.33)$$

where $E_v[\rho]$ is defined by Eq. (2.32).

We refer to section A.2 in the appendix for proof. To summarise, the ground-state density defines the external potential, and thus also defines the Hamiltonian. The major benefit lies in the representation of the solution, as we have reduced the dimensional space from $\mathbb{R}^{3N}$ of the wave-function to $\mathbb{R}^3$ of the electron density. At this point the expression is still exact, and the form of the universal functional $F[\rho]$ is not clear. Hohenberg and Kohn further suggest separating out the long-range Coulomb interaction energy from $F[\rho]$:

$$F[\rho] = \frac{e^2}{8\pi\epsilon_0} \int \frac{\rho(\vec{r})\rho(\vec{r}')}{||\vec{r} - \vec{r}'||} d^3r d^3r' + G[\rho], \quad (2.34)$$

where the first term is also called the Hartree energy $E_{Ha}[\rho]$, and $G[\rho] = F[\rho] - E_{Ha}[\rho]$ is another universal functional.

*Not all densities are v -representable,³⁴ however this condition can be relaxed by the Levi-construction,³⁵ where instead the ground-state electron density is defined as the lowest-energy density from the ensemble of all densities with an identical number of electrons N .

2.2.2 Kohn-Sham density-functional theory

At this point the density-functional theory equations cannot be solved as the form of $F[\rho]$ is unknown. One of the earliest attempts to use density-functionals was made by Thomas and Fermi for the electron gas,^{26,27} preceding the Hohenberg-Kohn theorems. Direct approximations to $F[\rho]$ however bring severe difficulties with them, as an accurate description of the kinetic energy functional is highly non-trivial. These schemes are called orbital-free density-functional theory, and are subject to current research.^{36–38} A more successful approach was first proposed by Kohn and Sham³⁹ in 1965. The idea is to express the system of interacting electrons as a system of non-interacting electrons under the influence of an external potential. This is based on splitting the universal functional into the contributions

$$F[\rho] = T_{KS}[\rho] + E_{Ha}[\rho] + E_{XC}[\rho], \quad (2.35)$$

where T_{KS} is the kinetic energy of the non-interacting system, E_{Ha} is the Hartree energy from Eq. (2.34), and $E_{XC}[\rho]$ is the exchange-correlation functional that includes the remaining, unknown many-body contributions and a correction to the kinetic energy:

$$E_{XC}[\rho] = (T[\rho] - T_{KS}[\rho]) + (W[\rho] - E_{Ha}[\rho]). \quad (2.36)$$

The total electronic energy is therefore given by:

$$E_{ele}[\rho] = F[\rho] + E_{ext}[\rho] = T_{KS}[\rho] + E_{Ha}[\rho] + E_{XC}[\rho] + E_{ext}[\rho] \quad (2.37)$$

$$= T_{KS}[\rho] + E_{KS}[\rho], \quad (2.38)$$

where $E_{ext}[\rho]$ is the external potential energy of Eq. (2.26) and where $E_{KS}[\rho]$ is defined as the Kohn-Sham energy functional. Let us now recall that the variation of a functional $J[f(x)]$ is defined as:⁴⁰

$$\delta J[f(x)] = \int_a^b \left(\frac{\delta J[f(x)]}{\delta f(x)} \right) \delta f(x) dx. \quad (2.39)$$

We apply the variational principle, see section A.1 in the appendix, to find the electron density which minimises the electronic energy under the constraint of electron number conservation:

$$\delta \left[E_{ele}[\rho] - \mu \left(\int \rho(\vec{r}) d^3r - N \right) \right] = 0. \quad (2.40)$$

The variable μ here is a Lagrange multiplier. For an arbitrary variation in density $\delta\rho(\vec{r})$ it must therefore follow:

$$\mu = \frac{\delta E_{ele}[\rho]}{\delta\rho(\vec{r})} = \frac{\delta T_{KS}[\rho]}{\delta\rho(\vec{r})} + \frac{\delta E_{KS}[\rho]}{\delta\rho(\vec{r})}. \quad (2.41)$$

We summarise the functional derivatives of the energy functionals with respect to their corresponding potentials as the Kohn-Sham potential $v_{KS}[\rho]$:

$$v_{KS}[\rho] = \frac{\delta E_{KS}[\rho]}{\delta \rho(\vec{r})} = \frac{\delta E_{Ha}[\rho]}{\delta \rho(\vec{r})} + \frac{\delta E_{XC}}{\delta \rho(\vec{r})} + \frac{\delta E_{ext}}{\delta \rho(\vec{r})} = v_{Ha}[\rho] + v_{XC}[\rho] + v_{ext}[\rho]. \quad (2.42)$$

The Lagrange multiplier (2.41) is therefore expressed as:

$$\mu = \frac{\delta T_{KS}[\rho]}{\delta \rho(\vec{r})} + v_{KS}[\rho]. \quad (2.43)$$

The key finding is that we would get the same expression as above if we were instead considering a non-interacting fermion gas in the presence of an external potential. We can therefore instead solve the Schrödinger-equation of the non-interacting system:

$$\left(-\frac{\hbar^2}{2m_e} \vec{\nabla}_r^2 + v_{KS}[\rho] \right) \Phi^{(n)}(\vec{r}) = \varepsilon^{(n)} \Phi^{(n)}(\vec{r}). \quad (2.44)$$

We shall refer to Eq. (2.44) as the time-independent Kohn-Sham equation. It is important to note here that $|\Phi^{(n)}\rangle$ does not represent the N -electron wave-function, but rather the one-electron orbitals of the fictitious non-interacting system. The eigenvalues $\varepsilon^{(n)}$ equally do not correspond to the real eigenvalues of the system, but to the eigenvalues of the corresponding n -th one-electron orbital. We shall refer to these as the Kohn-Sham wave-function and eigenvalues. The total electron density is constructed as the sum of the single-electron densities $\rho_n(\vec{r})$, weighted by their occupancy:

$$\rho(\vec{r}) = 2 \sum_{n=1}^{N_{KS}} f_n \rho_n(\vec{r}) = 2 \sum_{n=1}^{N_{KS}} f_n \Phi^{*(n)}(\vec{r}) \Phi^{(n)}(\vec{r}), \quad (2.45)$$

where the factor of 2 is for spin-degeneracy and f_n is the electron occupancy of the n -th Kohn-Sham orbital and N_{KS} is the number of Kohn-Sham states, i.e. the number of solutions to Eq. (2.44). The occupancy f_n takes on values of 0 or 1 for an electron temperature of 0 K, filling up the lower energy Kohn-Sham orbitals first according to the Aufbau principle. There are also schemes available that take the electron temperature into account.⁴¹

2.2.3 Kohn-Sham double counting

The Kohn-Sham eigenvalues do not sum up to the total electronic energy E_{ele} of the system, as they overaccount for the Hartree and exchange-correlation energies. We shall now derive the form of this double counting contribution from the solution of the Kohn-Sham equation. Let us start with the Kohn-Sham equation (2.44):

$$\left(\hat{T}_{KS} + \hat{v}_{KS}[\rho] \right) |\Phi^{(n)}\rangle = \varepsilon^{(n)} |\Phi^{(n)}\rangle. \quad (2.46)$$

Following the definition of the electron density in Eq. (2.45), we introduce the single-electron density ρ_n by multiplying Eq. (2.46) by $\langle \Phi^{(n)} |$ and integrating the resulting equation over the volume:

$$\int \Phi^{*(n)}(\vec{r}) \hat{T}_{KS} \Phi^{(n)}(\vec{r}) d^3r + \int v_{KS}[\rho] \rho_n(\vec{r}) d^3r = \varepsilon^{(n)}. \quad (2.47)$$

This equation is now weighted by the occupancy $2f_n$ and summed over all Kohn-Sham states n :

$$2 \sum_n f_n \int \Phi^{*(n)}(\vec{r}) \hat{T}_{KS} \Phi^{(n)}(\vec{r}) d^3r + \int v_{KS}[\rho] \rho(\vec{r}) d^3r = 2 \sum_n f_n \varepsilon^{(n)}. \quad (2.48)$$

Note that, due to the interchangeability of the non-interacting electrons in this picture, the Kohn-Sham potential is identical for each Kohn-Sham state. Identifying the left term as the Kohn-Sham kinetic energy functional, we arrive at:

$$T_{KS}[\rho] + \int v_{KS}[\rho] \rho(\vec{r}) d^3r = 2 \sum_n f_n \varepsilon^{(n)}. \quad (2.49)$$

Finally we substitute the kinetic energy functional of Eq. (2.49) into the electron energy of Eq. (2.37):

$$E_{ele}[\rho] = 2 \sum_n f_n \varepsilon^{(n)} + E_{KS}[\rho] - \int v_{KS}[\rho] \rho(\vec{r}) d^3r. \quad (2.50)$$

This additional contribution to the eigenvalue energies is called the double-counting energy $E_{dc}[\rho]$:

$$E_{dc}[\rho] = E_{KS}[\rho] - \int v_{KS}[\rho] \rho(\vec{r}) d^3r. \quad (2.51)$$

For the Kohn-Sham energy functional as defined in Eq. (2.37), the double counting energy takes on the common form:

$$E_{dc}[\rho] = -E_{Ha}[\rho] + E_{XC}[\rho] - \int v_{XC}[\rho] \rho(\vec{r}) d^3r. \quad (2.52)$$

To summarise, the total energy of the system is given by the sum of the classical ionic energy (2.10) and the Kohn-Sham energy (2.50):

$$E[\rho] = 2 \sum_n f_n \varepsilon^{(n)} + E_{KS}[\rho] - \int v_{KS}[\rho] \rho(\vec{r}) d^3r + E_{ion}. \quad (2.53)$$

It is at this point important to note that the Kohn-Sham potential is a functional of the density, hence the energy is minimised self-consistently according to the variational principle. So far the Kohn-Sham equation is exact and still requires knowledge of the exchange-correlation functional $E_{XC}[\rho]$. Its representation by the difference of the many-body and non-interacting terms however lends itself well to using approximate, analytically tractable forms. Weakly correlated systems can be well described by approximations to the many-body terms, as their contribution to the total energy may be small. In the following we shall assume that density-functional theory is employed with an approximate $E_{XC}[\rho]$.

2.2.4 Exchange-correlation functionals

The main difficulty in Kohn-Sham density-functional theory lies in finding approximate $E_{XC}[\rho]$ functionals that yield physically sensible and transferable results. Fortunately one of the more straightforward approaches yields surprisingly good results, and is hence the starting point for more sophisticated exchange-correlation functionals. The local-density-approximation (LDA) considers the many-body energy as that of an infinitely extended homogeneous electron gas, filled with a positive background charge to keep the system neutral. For a given position $\vec{r}_0$ and volume element d^3r , the functional $E_{XC}^{LDA}[\rho]$ takes on the exchange-correlation energy of the homogeneous electron gas with density $\rho(\vec{r}_0)$:

$$E_{XC}^{LDA}[\rho] = \int \varepsilon_{XC}^{LDA}(\rho(\vec{r}))\rho(\vec{r})d^3r. \quad (2.54)$$

The LDA functional is strictly local, as the potential $\varepsilon_{XC}^{LDA}(\rho(\vec{r}))$ only depends on the density at point $\vec{r}$. This leads to a slightly overestimated exchange-correlation energy for molecules as ε_{XC}^{LDA} is repulsive for all values of the density. The LDA subsequently overestimates bond-lengths in molecules, but works well in periodic metals. The functional cannot be found analytically, but has been parametrised with quantum Monte Carlo methods.⁴² Another common functional is based on the generalised-gradient approximation (GGA), where the gradient of the electron density also enters as a parameter:

$$E_{XC}^{GGA}[\rho] = \int \varepsilon_{XC}^{GGA}(\rho(\vec{r}), \vec{\nabla}\rho(\vec{r}))\rho(\vec{r})d^3r. \quad (2.55)$$

The addition of the density gradient as a parameter improves the description of molecules, making this the preferred functional over LDA. In this work we exclusively use a GGA functional.

2.3 Time-dependent density-functional theory

We are now able to find the ground-state of a given system. The Hohenberg-Kohn theorem however strictly assumes a time-independent Hamiltonian, and is hence not suitable for a time-dependent calculation. We shall here introduce the Runge-Gross theorem,⁴³ which is the equivalent to the Hohenberg-Kohn theorem for the time-dependent Schrödinger equation. The proof is involved and subject of many reviews, hence we shall only present the theorems:

Theorem 1. Let $G : v_{ext}(\vec{r}, t) \rightarrow \rho(\vec{r}, t)$ be the map from the one-particle potential $v_{ext}(\vec{r}, t)$ to the density $\rho(\vec{r}, t) = \langle \Psi(t) | \hat{n} | \Psi(t) \rangle$ found by solving the time-dependent Schrödinger equation starting with the initial state $|\Psi(t_0)\rangle$. The map G is invertible up to an additive time-dependent function $v_0(t)$ in $v_{ext}(\vec{r}, t)$.

Theorem 2. For any electron density $\rho(\vec{r}, t)$ following the solution of the interacting N -electron Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = \hat{H} |\Psi(t)\rangle, \quad (2.56)$$

there exists a time-dependent Kohn-Sham potential $v_{KS}[\rho](\vec{r}, t)$ such that the solutions of a fictitious non-interacting system

$$i\hbar \frac{\partial}{\partial t} \Phi^{(n)}(\vec{r}, t) = \left(-\frac{\hbar^2}{2m_e} \vec{\nabla}_r^2 + v_{KS}[\rho](\vec{r}, t) \right) \Phi^{(n)}(\vec{r}, t) \quad (2.57)$$

yield the same electron density constructed as

$$\rho(\vec{r}, t) = 2 \sum_{n=1}^{N_{KS}} f_n \Phi^{*(n)}(\vec{r}, t) \Phi^{(n)}(\vec{r}, t), \quad (2.58)$$

where f_n is the electron occupancy of the n -th Kohn-Sham orbital and N_{KS} is the number of Kohn-Sham states, i.e. the number of solutions to Eq. (2.57). The time-dependent Kohn-Sham potential is given as:

$$v_{KS}[\rho](\vec{r}, t) = v_{ext}[\rho](\vec{r}, t) + v_{Ha}[\rho](\vec{r}, t) + v_{XC}[\rho](\vec{r}, t), \quad (2.59)$$

where $v_{XC}[\rho](\vec{r}, t) = \delta A_{XC}[\rho](\vec{r}, t) / \delta \rho$ is the time-dependent exchange-correlation potential, and $A_{XC}[\rho](\vec{r}, t)$ is the time-dependent exchange-correlation energy functional.

We shall refer to Eq. (2.57) as the time-dependent Kohn-Sham equation. These theorems have far-reaching implications, as they enable time-dependent density-functional theory calculations, provided an approximation to the exchange-correlation potential $v_{XC}[\rho](\vec{r}, t)$ is chosen. The exchange-correlation potential is non-local in both time and space, as it causally depends on the history of the system. The physical consequences of this memory dependence is subject to current research,^{44–46} but non-adiabatic functionals have not yet seen wide usage. In most practical applications the adiabatic approximation is taken, assuming that the functional is local in time: $v_{XC}[\rho](\vec{r}, t) \approx v_{XC}[\rho(t)](\vec{r})$. Commonly used adiabatic time-dependent functionals are the adiabatic local-density approximation (ALDA) and the adiabatic generalised-gradient approximation (AGGA) functionals, which are respectively identical to LDA and GGA.

Another important point is that the Runge-Gross theorem assumes knowledge of the initial state $|\Psi(t_0)\rangle$. This knowledge can be retrieved from the ground-state density following the Hohenberg-Kohn theorem if $|\Psi(t_0)\rangle$ is the ground-state wave-function. This mapping however is not available if $|\Psi(t_0)\rangle$ is an arbitrary excited state, and would require knowledge of the full N -electron wave-function.

2.4 Density-functional tight binding

In the previous section we have outlined the Kohn-Sham density-functional theory. While density-functional theory has found widespread application, there are still serious challenges associated with accessing larger length- and time-scales. Recent research has seen the development of linear-scaling density-functional theory methods,^{47–49} for which the computational effort scales linearly with system size as opposed to the standard cubic scaling associated with solving eigensystems by direct diagonalisation. Linear scaling techniques commonly exploit the near-sightedness of electrons, effectively expressing the electron density matrix as sparse. However, this may lead to errors for systems with very small band-gaps as the interactions become long-ranged. Time-propagated calculations furthermore are still a challenge, as they require efficient computation of over thousands of steps. The challenge is hence to develop a theory with comparable predictive capabilities to density-functional theory, but with significantly reduced computational effort.

One very promising method which we shall employ in this work is the density-functional tight binding theory. Density-functional tight binding is capable of predicting geometries,⁵⁰ reaction energies,^{51,52} vibrational frequencies,^{51,53} and more, at a fraction of the cost of density-functional theory calculations. Extensions to time-dependent tight binding also enable the calculation of excited states^{54,55} and various ultrafast processes.^{56,57} The theoretical derivation of this method is firmly rooted in first principles, which enables the method to be systematically extended to describe the physical phenomena of interest more accurately.

In the following section we outline the basis of ground-state density-functional tight binding theory, see references^{58–61} for extensive reviews. The principle idea behind the tight binding approach is to save the computational costs associated with calculating the Kohn-Sham potential. This is achieved by a series of approximations that ultimately allow us to pre-compute the potential in the form of matrix elements, so that they can simply be looked up from a table. Further efficiency is gained by representing the one-electron wavefunction in terms of a small atomically-localised basis set, ideally without deteriorating the quality of the calculation.

2.4.1 Approximate Kohn-Sham theory

The solution of the Kohn-Sham equations requires the input of a trial density $\rho(\vec{r})$. The trial density is used to compute the initial guess for the Kohn-Sham potential. Solving the Kohn-Sham system yields a set of eigenvalues and eigenstates, from which a new trial density can be constructed for another solution of the updated Kohn-Sham system. This

process is repeated until energy convergence is achieved. Each iteration step requires constructing the Kohn-Sham potentials anew and solving again the updated eigensystem. This begs the question whether one could not instead choose a trial density $\rho^0(\vec{r})$ that represents the system sufficiently well and consider self-consistency only by the effect of small density deviations $\delta\rho(\vec{r})$ from the reference density $\rho^0(\vec{r})$. This is motivated by the idea that small density deviations allow us to express the density-functional theory energy by a series expansion in $\delta\rho(\vec{r})$. These terms only need to be considered approximately, speeding up the construction of the Kohn-Sham potential. A common choice for the reference density is the superposition of non-interacting, atomically-centered, and spherically symmetric densities $\rho^0(\vec{r}) = \sum_{I=1}^M \rho_I^0(\vec{r} - \vec{R}_I)$. In this picture it is only required to a-priori define a representative reference density per atomic species in the system and to place these atomic densities on the ionic sites $\vec{R}_I$.

Let us first remind ourselves of the definition of the functional series expansion. Let $J[f]$ be a functional dependent on the function $f(x)$. We smoothly apply the variation $f \rightarrow f + \kappa\eta$, where η is another function and $\kappa \in (0, 1)$. The series expansion of $J[f]$ is given by:⁴⁰

$$J[f + \kappa\eta] = J[f] + \left. \frac{dJ[f + \kappa\eta]}{d\kappa} \right|_{\kappa=0} \kappa + \frac{1}{2} \left. \frac{d^2 J[f + \kappa\eta]}{d\kappa^2} \right|_{\kappa=0} \kappa^2 + \mathcal{O}(\kappa^3). \quad (2.60)$$

Here the n -th variational derivative is defined by:

$$\left. \frac{d^n J[f + \kappa\eta]}{d\kappa^n} \right|_{\kappa=0} = \int \frac{\delta^n J[f]}{\delta f(x_1) \dots \delta f(x_n)} \eta(x_1) \dots \eta(x_n) dx_1 \dots dx_n. \quad (2.61)$$

We start the derivation with the total Kohn-Sham density-functional theory energy following Eqs. (2.9) and (2.37):

$$E = T_{KS}[\rho] + E_{KS}[\rho] + E_{ion} \quad (2.62)$$

Let us now take the functional expansion of $E_{KS}[\rho]$ with respect to the electron density variation $\delta\rho = \rho - \rho^0$ from a chosen reference density ρ^0 following Eq. (2.60):

$$\begin{aligned} E_{KS}[\rho^0 + \delta\rho] &= E_{KS}[\rho^0] + \int \frac{\delta E_{KS}[\rho^0]}{\delta \rho^0(\vec{r})} \delta\rho(\vec{r}) d^3r \\ &+ \frac{1}{2} \int \frac{\delta^2 E_{KS}[\rho^0]}{\delta \rho^0(\vec{r}) \delta \rho^0(\vec{r}')} \delta\rho(\vec{r}) \delta\rho(\vec{r}') d^3r d^3r' + \mathcal{O}(\delta\rho^3). \end{aligned} \quad (2.63)$$

Note that here we have omitted the use of the infinitesimal κ for brevity. A formally consistent way to arrive at this result would be to use the variation $\rho = \rho^0 + \kappa\Delta\rho$, and at the final step redefine $\kappa\Delta\rho \equiv \delta\rho$. This work considers the series expansion only up to second order in $\delta\rho$. We now take the functional power expansion for each term in

the Kohn-Sham potential individually, since the differentiation operator is linear. From Eq. (2.37)

$$E_{KS}[\rho^0] = E_{Ha}[\rho^0] + E_{XC}[\rho^0] + E_{ext}[\rho^0], \quad (2.64)$$

we consider the series expansion of the Hartree energy

$$E_{Ha}[\rho] = E_{Ha}[\rho^0] + \frac{e^2}{4\pi\epsilon_0} \int \frac{\rho^0(\vec{r})\delta\rho(\vec{r}')}{||\vec{r} - \vec{r}'||} d^3r d^3r' + \frac{e^2}{8\pi\epsilon_0} \int \frac{\delta\rho(\vec{r})\delta\rho(\vec{r}')}{||\vec{r} - \vec{r}'||} d^3r d^3r', \quad (2.65)$$

of the exchange-correlation energy

$$E_{XC}^{app}[\rho] = E_{XC}[\rho^0] + \int v_{XC}[\rho^0]\delta\rho(\vec{r})d^3r + \frac{1}{2} \int f_{XC}[\rho^0]\delta\rho(\vec{r})\delta\rho(\vec{r}')d^3r d^3r', \quad (2.66)$$

and the external potential energy

$$E_{ext}[\rho] = E_{ext}[\rho^0] + \int v_{ext}(\vec{r})\delta\rho(\vec{r})d^3r. \quad (2.67)$$

Note that the expansions of the Hartree energy and the external field energy are exact, while the approximate expansion $E_{XC}^{app}[\rho]$ of the exchange-correlation energy $E_{XC}[\rho]$ has been truncated at the second order in $\delta\rho(\vec{r})$. We define here f_{XC} as the second order functional derivative of the exchange-correlation energy:

$$f_{XC}[\rho](\vec{r}, \vec{r}') = \frac{\delta^2 E_{XC}[\rho]}{\delta\rho(\vec{r})\delta\rho(\vec{r}')}. \quad (2.68)$$

Now that we have derived an approximate expression for the Kohn-Sham energy, it remains to find the equivalent approximate expression for the Kohn-Sham potential. Following the same approach as for the Kohn-Sham double-counting energy in section 2.2.3, we find the approximate Kohn-Sham potential by taking the functional derivative of the approximate Kohn-Sham energy

$$E_{KS}^{app}[\rho] = E_{Ha}[\rho] + E_{XC}^{app}[\rho] + E_{ext}[\rho] \quad (2.69)$$

with respect to the density $\rho(\vec{r})$:

$$v_{KS}^{app}[\rho] = v_{Ha}[\rho] + v_{XC}^{app}[\rho] + v_{ext}[\rho]. \quad (2.70)$$

Note again that the Hartree and external potentials are exact, we merely represent them in terms of the density variation $\delta\rho = \delta\rho^0 + \delta\rho$. The potentials are found as:

$$v_{Ha}[\rho] = \frac{e^2}{4\pi\epsilon_0} \int \frac{\rho^0(\vec{r}')}{||\vec{r} - \vec{r}'||} d^3r' + \frac{e^2}{4\pi\epsilon_0} \int \frac{\delta\rho(\vec{r}')}{||\vec{r} - \vec{r}'||} d^3r' \quad (2.71)$$

$$v_{XC}^{app}[\rho] = v_{XC}[\rho^0] + \int f_{XC}[\rho^0]\delta\rho(\vec{r}')d^3r' \quad (2.72)$$

$$v_{ext}[\rho] = v_{ext}(\vec{r}). \quad (2.73)$$

The external potential $v_{ext}(\vec{r})$ was previously defined in Eq. (2.25). We have now all the required expressions to define the electronic energy of the approximate Kohn-Sham theory. For the n -th eigenvalue given as

$$\varepsilon^{(n)} = \langle \Phi^{(n)} | \hat{H}_{KS}^{app}[\rho] | \Phi^{(n)} \rangle = \langle \Phi^{(n)} | \hat{T} + v_{KS}^{app}[\rho] | \Phi^{(n)} \rangle, \quad (2.74)$$

the electronic energy follows from Eq. (2.50) as:

$$E_{ele}^{app}[\rho] = 2 \sum_n f_n \varepsilon^{(n)} + E_{KS}^{app}[\rho] - \int v_{KS}^{app}[\rho] \rho(\vec{r}) d^3r. \quad (2.75)$$

Substituting our previously derived expressions for $E_{KS}^{app}[\rho]$ in Eq. (2.69) and $v_{KS}^{app}[\rho]$ in Eq. (2.70) into (2.74), we arrive at:

$$\begin{aligned} E_{ele}^{app}[\rho] &= 2 \sum_n f_n \varepsilon^{(n)} - E_{Ha}[\rho] + E_{XC}[\rho^0] - \int v_{XC}[\rho^0] \rho^0(\vec{r}) d^3r \\ &\quad - \frac{1}{2} \int f_{XC}[\rho^0] \delta\rho(\vec{r}) \delta\rho(\vec{r}') d^3r d^3r' - \int f_{XC}[\rho^0] \rho^0(\vec{r}) \delta\rho(\vec{r}') d^3r d^3r'. \end{aligned} \quad (2.76)$$

The Hartree energy can also be expressed in terms of ρ^0 and $\delta\rho$ using Eq. (2.65):

$$\begin{aligned} E_{ele}^{app}[\rho] &= 2 \sum_n f_n \varepsilon^{(n)} - E_{Ha}[\rho^0] - \frac{e^2}{4\pi\varepsilon_0} \int \frac{\rho^0(\vec{r}) \delta\rho(\vec{r}')}{||\vec{r} - \vec{r}'||} d^3r d^3r' \\ &\quad - \frac{e^2}{8\pi\varepsilon_0} \int \frac{\delta\rho(\vec{r}) \delta\rho(\vec{r}')}{||\vec{r} - \vec{r}'||} d^3r d^3r' + E_{XC}[\rho^0] - \int v_{XC}[\rho^0] \rho^0(\vec{r}) d^3r \\ &\quad - \frac{1}{2} \int f_{XC}[\rho^0] \delta\rho(\vec{r}) \delta\rho(\vec{r}') d^3r d^3r' - \int f_{XC}[\rho^0] \rho^0(\vec{r}) \delta\rho(\vec{r}') d^3r d^3r'. \end{aligned} \quad (2.77)$$

We are left to add the classical ionic energy to form the total energy expression. The ionic energy, ignoring the external electric potential for now, is defined by Eq. (2.10):

$$E_{ion} = T_{ion} + W_{ion-ion} \quad (2.78)$$

The ion-ion Coulomb repulsion $W_{ion-ion}$ and the electronic energy terms only dependent on the reference density ρ^0 are commonly summarised in the so-called repulsive potential:

$$E_{rep}[\rho^0] = W_{ion-ion} - E_{Ha}[\rho^0] + E_{XC}[\rho^0] - \int v_{XC}[\rho^0] \rho^0(\vec{r}) d^3r. \quad (2.79)$$

The energy difference $W_{ion-ion} - E_{Ha}[\rho^0]$ of the Coulombic ion-ion repulsion and the Hartree electron-electron repulsion effectively describe the energy of the net neutral, electrostatically screened ions. To summarise,

$$\begin{aligned} E^{app}[\rho] &= 2 \sum_n f_n \varepsilon^{(n)} + T_{ion} + E_{rep}[\rho^0] - \frac{e^2}{4\pi\varepsilon_0} \int \frac{\rho^0(\vec{r}) \delta\rho(\vec{r}')}{||\vec{r} - \vec{r}'||} d^3r d^3r' \\ &\quad - \frac{e^2}{8\pi\varepsilon_0} \int \frac{\delta\rho(\vec{r}) \delta\rho(\vec{r}')}{||\vec{r} - \vec{r}'||} d^3r d^3r' - \frac{1}{2} \int f_{XC}[\rho^0] \delta\rho(\vec{r}) \delta\rho(\vec{r}') d^3r d^3r' \\ &\quad - \int f_{XC}[\rho^0] \rho^0(\vec{r}) \delta\rho(\vec{r}') d^3r d^3r' \end{aligned} \quad (2.80)$$

is the total approximate Kohn-Sham energy of a system with density $\rho = \rho^0(\vec{r}) + \delta\rho(\vec{r})$, where the energy change associated with the density variation $\delta\rho(\vec{r})$ is only considered to second order in $\delta\rho(\vec{r})$. The corresponding approximate Kohn-Sham Hamiltonian is given by:

$$\begin{aligned}\hat{H}_{KS}^{app}[\rho] &= \hat{T}_{KS} + v_{KS}^{app}[\rho](\vec{r}) \\ &= -\frac{\hbar^2}{2m_e}\vec{\nabla}_r^2 + \frac{e^2}{4\pi\epsilon_0} \int \frac{\rho^0(\vec{r}')}{||\vec{r} - \vec{r}'||} d^3r' + \frac{e^2}{4\pi\epsilon_0} \int \frac{\delta\rho(\vec{r}')}{||\vec{r} - \vec{r}'||} d^3r' \\ &\quad + v_{XC}[\rho^0](\vec{r}) + \int f_{XC}[\rho^0](\vec{r}, \vec{r}') \delta\rho(\vec{r}') d^3r' + v_{ext}(\vec{r}).\end{aligned}\tag{2.81}$$

These expressions lend themselves well to further approximations. At this point the theory is exact to second order in $\delta\rho$, no further approximations were made. We shall next introduce the density-functional tight-binding approximations that enable an efficient computation of the electronic structure.

2.4.2 Density-functional tight-binding approximations

The central principle of tight-binding theory lies in the exploitation of the electronic near-sightedness in conjunction with a localised basis set to deliver a highly efficient electronic structure theory that approaches density-functional theory in its accuracy. This is achieved by expressing the reference density $\rho^0(\vec{r})$ as a sum of atomically-centred and spherically symmetric atomic densities. The densities are further chosen such that the net charge associated with an ionic site is neutral. The Kohn-Sham potential can further be approximated to only depend on one- and two-body centred terms. The potentials can subsequently be expressed as a function of merely interatomic distance. The Hamiltonian is in practice precomputed and tabulated for a given choice of atomic reference densities and basis set, and for each simulation simply read out again from the table. This particular ‘flavour’ of tight binding is referred to as density-functional tight binding (DFTB). It is a systematically derived, formally first-principles method based on Kohn-Sham density-functional theory.

2.4.2.1 Self-consistent and static Hamiltonians

Consider the definition of the approximate Hamiltonian from Eq. (2.81):

$$\begin{aligned}\hat{H}_{KS}^{app}[\rho] &= -\frac{\hbar^2}{2m_e}\vec{\nabla}_r^2 + \frac{e^2}{4\pi\epsilon_0} \int \frac{\rho^0(\vec{r}')}{||\vec{r} - \vec{r}'||} d^3r' + \frac{e^2}{4\pi\epsilon_0} \int \frac{\delta\rho(\vec{r}')}{||\vec{r} - \vec{r}'||} d^3r' \\ &\quad + v_{XC}[\rho^0] + \int f_{XC}[\rho^0] \delta\rho(\vec{r}') d^3r' + v_{ext}(\vec{r}).\end{aligned}\tag{2.82}$$

Table 2.1: Real cubic harmonics in Cartesian coordinates up to octupole order. The convention $\vec{r} = (z, x, y)^T$ is used here.

harmonic indices		real cubic harmonics
l	m	$K_{lm}(x, y, z)$
0	0	1
1	0	z
	1	x
	2	y
2	0	$z^2 - \frac{1}{2}(x^2 + y^2)$
	1	$\sqrt{3}zx$
	2	$\sqrt{3}yz$
	3	$\frac{1}{2}\sqrt{3}(x^2 - y^2)$
	4	$\sqrt{3}xy$
3	0	$z^3 - \frac{3}{2}z(x^2 + y^2)$
	1	$-\frac{1}{2}\sqrt{\frac{3}{2}}x(x^2 + y^2 - 4z^2)$
	2	$-\frac{1}{2}\sqrt{\frac{3}{2}}y(x^2 + y^2 - 4z^2)$
	3	$\frac{1}{2}\sqrt{15}z(x^2 - y^2)$
	4	$\sqrt{15}xyz$
	5	$\frac{1}{2}\sqrt{\frac{5}{2}}x(x^2 - 3y^2)$
	6	$-\frac{1}{2}\sqrt{\frac{5}{2}}y(y^2 - 3x^2)$

We can split up the Hamiltonian into two terms, one dependent on the static reference density ρ^0 , and the other dependent on the density variation $\delta\rho$:

$$\hat{H}_{KS}^{app}[\rho] = \hat{H}_{KS}^0[\rho^0] + \hat{H}_{KS}^{scf}[\delta\rho], \quad (2.83)$$

where

$$\hat{H}_{KS}^0[\rho^0] = -\frac{\hbar^2}{2m_e}\vec{\nabla}_r^2 + \frac{e^2}{4\pi\epsilon_0} \int \frac{\rho^0(\vec{r}')}{||\vec{r} - \vec{r}'||} d^3r' + v_{XC}[\rho^0] + v_{ext}(\vec{r}) \quad (2.84)$$

is the static Hamiltonian, and

$$\hat{H}_{KS}^{scf}[\rho] = \frac{e^2}{4\pi\epsilon_0} \int \frac{\delta\rho(\vec{r}')}{||\vec{r} - \vec{r}'||} d^3r' + \int f_{XC}[\rho^0]\delta\rho(\vec{r}')d^3r'. \quad (2.85)$$

is the self-consistent Hamiltonian.

2.4.2.2 Atomically localised basis set

We shall next introduce the localised basis set, as it enables us to split the density into atomic contributions. We represent the Kohn-Sham orbitals in a real, non-orthogonal

atomic-type orbitals basis set $\{\phi_{I\alpha}\}$, where the atom on site I has an orbital $\phi_{I\alpha}$ attached to it. The Kohn-Sham orbital $\Phi^{(n)}$ is then expanded in the new basis set with the expansion coefficients $c_{I\alpha}^{(n)}$:

$$\Phi^{(n)}(\vec{r}) = \sum_{I\alpha} c_{I\alpha}^{(n)} \phi_{I\alpha}(\vec{r} - \vec{R}_I). \quad (2.86)$$

The atomic-type orbitals are localised, going to zero beyond a cut-off radius R_C :

$$\phi_{I\alpha}(\vec{r} - \vec{R}_I) = 0, \quad \text{if } \|\vec{r} - \vec{R}_I\| \geq R_C. \quad (2.87)$$

We shall internally consider the index α in $\phi_{I\alpha}$ to act as a map to an atomic-like orbital with the quantum numbers nlm . Following the naming convention of hydrogen wavefunctions, we consider an orbital with $l = 0$ to be an s -orbital, an orbital with $l = 1$ to be a p -orbital, continuing with $d, f, g, h, \dots$, and so on. We can also attach multiple orbitals with identical quantum numbers nlm to site I , but with varying radial functions. This allows the orbitals contributing to the quantum number nlm to vary flexibly in their radial extent, improving the overall accuracy. Such basis sets are called N -zeta basis-sets, where N refers to the multiplicity of nlm and ζ indexes the radial function. We therefore define the basis functions in terms of atomic-like radial and angular functions:

$$\phi_{I\alpha}(\vec{r}) \equiv \phi_{nlm}^{I,\zeta}(\vec{r}) = R_{nl}^{I,\zeta}(\|\vec{r}\|) K_{lm}(\vec{r}), \quad (2.88)$$

where we use the real cubic harmonics $K_{lm}(\vec{r})$ to avoid using a complex basis set:

$$\begin{aligned} K_{l,0}(r, \theta, \phi) &= \sqrt{\frac{4\pi}{2l+1}} r^l Y_l^0(\theta, \phi) \\ K_{l,2m}(r, \theta, \phi) &= -i \sqrt{\frac{2\pi}{2l+1}} r^l ((-1)^m Y_l^m(\theta, \phi) - Y_l^{-m}(\theta, \phi)) \\ K_{l,2m-1}(r, \theta, \phi) &= \sqrt{\frac{2\pi}{2l+1}} r^l ((-1)^m Y_l^m(\theta, \phi) + Y_l^{-m}(\theta, \phi)), \end{aligned} \quad (2.89)$$

and where Y_l^m are spherical harmonics of order l and degree m , with $-l \leq m \leq l$. We have chosen the principal axis to lie in the Cartesian $\hat{e}_z$ direction, hence: $\vec{r} = (K_{10}, K_{11}, K_{12})^T = (z, x, y)^T$. The real cubic harmonics up to octupole order are listed in table 2.1 in terms of the Cartesian coordinates. A MATHEMATICA script for the computation of the real cubic harmonics to arbitrary order is available in section A.7 in the appendix.

The shape of an atom's electron density is strongly dependent on its surrounding environment. A basis set needs to be flexible enough to accommodate such variations in the electron density. The size of the basis set and the shape of the radial functions $R_{nlm}^{I,\zeta}$ are therefore chosen such that the desired physical or chemical observables can be

computed with high precision. Hartree-Fock based methods from the field of Quantum Chemistry have led to the development of a vast family of basis sets, optimised to describe quantities such as correlation energy, polarisability, or delocalised excited states with high accuracy. This accuracy however comes at a cost; the computational effort in solving the self-consistent problem scales with the basis set size N_{basis} as $\mathcal{O}(N_{basis}^3)$. Practical applications require a trade-off between computational time and accuracy.

2.4.2.3 Electron density in the basis-set representation

The electron density in this representation follows from the substitution of Eq. (2.86) into the Kohn-Sham density of Eq. (2.45):

$$\rho(\vec{r}) = 2 \sum_n f_n \Phi^{*(n)}(\vec{r}) \Phi^{(n)}(\vec{r}) \quad (2.90)$$

$$= 2 \sum_n \sum_{I\alpha J\beta} f_n c_{I\alpha}^{*(n)} c_{J\beta}^{(n)} \phi_{I\alpha}(\vec{r} - \vec{R}_I) \phi_{J\beta}(\vec{r} - \vec{R}_J). \quad (2.91)$$

$$= \sum_{I\alpha J\beta} \rho_{I\alpha J\beta} \phi_{I\alpha}(\vec{r} - \vec{R}_I) \phi_{J\beta}(\vec{r} - \vec{R}_J), \quad (2.92)$$

where we have defined the one-electron density matrix as:

$$\rho_{I\alpha J\beta} = 2 \sum_n \sum_{I\alpha J\beta} f_n c_{I\alpha}^{*(n)} c_{J\beta}^{(n)}. \quad (2.93)$$

Note that this change in representation also changes the way we arrive at the solution of the Kohn-Sham problem. Instead of applying the variational principle of the Kohn-Sham energy with respect to density, we now have to apply the variation with respect to the basis set coefficients $\{c_{I\alpha}^{(n)}\}$ and their complex conjugate $\{c_{I\alpha}^{*(n)}\}$. The Kohn-Sham equation of Eq. (2.44) now reads:

$$\hat{H}_{KS}[\rho] \Phi^{(n)}(\vec{r}) = \varepsilon^{(n)} \Phi^{(n)}(\vec{r}) \quad (2.94)$$

$$\sum_{J\beta} \hat{H}_{KS}[\rho] c_{J\beta}^{(n)} \phi_{J\beta}(\vec{r} - \vec{R}_J) = \varepsilon^{(n)} c_{J\beta}^{(n)} \phi_{J\beta}(\vec{r} - \vec{R}_J). \quad (2.95)$$

This expression is cast into a matrix equation by multiplying $\phi_{I\alpha}(\vec{r} - \vec{R}_I)$ from the left, and subsequently integrating the expression over the volume:

$$\begin{aligned} & \sum_{J\beta} \int \phi_{I\alpha}(\vec{r} - \vec{R}_I) \hat{H}_{KS}[\rho] \phi_{J\beta}(\vec{r} - \vec{R}_J) d^3r c_{J\beta}^{(n)} \\ &= \sum_{J\beta} \varepsilon^{(n)} \int \phi_{I\alpha}(\vec{r} - \vec{R}_I) \phi_{J\beta}(\vec{r} - \vec{R}_J) d^3r c_{J\beta}^{(n)}. \end{aligned} \quad (2.96)$$

Defining the Hamiltonian matrix

$$H_{I\alpha J\beta}^{KS}[\rho] = \int \phi_{I\alpha}(\vec{r} - \vec{R}_I) \hat{H}_{KS}[\rho] \phi_{J\beta}(\vec{r} - \vec{R}_J) d^3r \equiv \langle \phi_{I\alpha} | \hat{H}_{KS}[\rho] | \phi_{J\beta} \rangle, \quad (2.97)$$

and the overlap matrix

$$S_{I\alpha J\beta} = \int \phi_{I\alpha}(\vec{r} - \vec{R}_I) \phi_{J\beta}(\vec{r} - \vec{R}_J) d^3r \equiv \langle \phi_{I\alpha} | \phi_{J\beta} \rangle, \quad (2.98)$$

the equation (2.96) is expressed as an eigensystem:

$$\sum_{J\beta} H_{I\alpha J\beta}^{KS}[\rho] c_{J\beta}^{(n)} = \varepsilon^{(n)} \sum_{J\beta} S_{I\alpha J\beta} c_{J\beta}^{(n)} \quad (2.99)$$

Instead of finding the Kohn-Sham potential, we are left to find the Kohn-Sham Hamiltonian matrix elements $H_{I\alpha J\beta}^{KS}[\rho]$. Solution of the eigensystem delivers the Kohn-Sham eigenvalues $\{\varepsilon^{(n)}\}$ and eigenvectors $\{c_{I\alpha}^{*(n)}\}$ from which the Kohn-Sham orbitals can be reconstructed following Eq. (2.86).

2.4.2.4 Atomic densities

The basis set representation also allows us to separate the electronic density $\rho(\vec{r})$ into atomically localised contributions:

$$\rho(\vec{r}) = \sum_I \rho_I(\vec{r}) = \sum_I \left(\sum_{\alpha J\beta} \rho_{I\alpha J\beta} \phi_{I\alpha}(\vec{r} - \vec{R}_I) \phi_{J\beta}(\vec{r} - \vec{R}_J) \right). \quad (2.100)$$

Considering that the basis functions $\{\phi_{I\alpha}\}$ are localised, the product $\phi_{I\alpha}(\vec{r} - \vec{R}_I) \phi_{J\beta}(\vec{r} - \vec{R}_J)$ vanishes if the interatomic distance is larger than the common orbital cut-off radius: $R_{IJ} = \|\vec{R}_I - \vec{R}_J\| \geq R_C$. We have here assumed that all orbitals share a common cut-off radius R_C for simplicity. This allows us to exactly decompose the total electron density of a system with M ions into M spherically confined parts. It is then a natural choice to represent the reference density $\rho^0(\vec{r})$ similarly by the superposition of atomically-centred, spherically symmetric, and charge neutral atomic densities:

$$\rho^0(\vec{r}) = \sum_I \rho_I^0(\vec{r} - \vec{R}_I), \quad (2.101)$$

with the properties:

$$1. \text{ charge neutral: } \int \rho_I^0(\vec{r} - \vec{R}_I) d^3r = Z_I \quad (2.102)$$

$$2. \text{ localised: } \rho_I^0(\vec{r} - \vec{R}_I) = 0, \quad \text{if } \|\vec{r} - \vec{R}_I\| \geq R_C \quad (2.103)$$

$$3. \text{ spherically symmetric: } \rho_I^0(\vec{r} - \vec{R}_I) = \rho_I^0(\|\vec{r} - \vec{R}_I\|) \quad (2.104)$$

The charge neutrality property in this case refers to the number of electrons Z_I in the atomic reference density ρ_0^I being equal to the ionic charge eZ_I on the ionic site I . The density variation $\delta\rho(\vec{r})$, defined as the difference between density and static density, can now equally be split into atomic contributions

$$\delta\rho(\vec{r}) = \sum_I \delta\rho_I(\vec{r} - \vec{R}_I) = \sum_I \rho_I(\vec{r} - \vec{R}_I) - \rho_0^I(\vec{r} - \vec{R}_I), \quad (2.105)$$

where each atomic contribution $\delta\rho_I(\vec{r} - \vec{R}_I)$ is confined within $\|\vec{r} - \vec{R}_I\| \leq R_C$.

2.4.2.5 Static Hamiltonian matrix elements

We would now like to pre-compute and store the matrix elements of the static Hamiltonian $H_{I\alpha J\beta}^{0-KS}[\rho^0] = \langle \phi_{I\alpha} | \hat{H}_{KS}^0[\rho^0] | \phi_{J\beta} \rangle$ to save the computational expense associated with computing the matrix elements. However, note that the Hamiltonian $\hat{H}_{KS}^0[\rho^0] = \hat{H}_{KS}^0[\sum_K \rho_K^0(\vec{r} - \vec{R}_K)]$ at this point is parametrically dependent on the ionic coordinates of the system $\{\vec{R}_K\}$. Following Eq. (2.84), the static Hamiltonian matrix elements are given by:

$$H_{I\alpha J\beta}^{0-KS}[\rho^0] = T_{I\alpha J\beta}^{KS} + V_{I\alpha J\beta}^{Ha}[\rho^0] + V_{I\alpha J\beta}^{XC}[\rho^0] + V_{I\alpha J\beta}^{ext}, \quad (2.106)$$

where the matrix elements are given by:

$$T_{I\alpha J\beta}^{KS} = -\frac{\hbar^2}{2m_e} \left\langle \phi_{I\alpha} \left| \vec{\nabla}_r^2 \right| \phi_{J\beta} \right\rangle \quad (2.107)$$

$$V_{I\alpha J\beta}^{Ha}[\rho^0] = \frac{e^2}{4\pi\epsilon_0} \sum_K \left\langle \phi_{I\alpha} \left| \int \frac{\rho_K^0(\vec{r}' - \vec{R}_K)}{\|\vec{r} - \vec{r}'\|} d^3r' \right| \phi_{J\beta} \right\rangle \quad (2.108)$$

$$V_{I\alpha J\beta}^{XC}[\rho^0] = \left\langle \phi_{I\alpha} \left| v_{XC} \left[\sum_K \rho_K^0(\vec{r} - \vec{R}_K) \right] \right| \phi_{J\beta} \right\rangle \quad (2.109)$$

$$V_{I\alpha J\beta}^{ext} = -\sum_K \frac{eZ_K}{4\pi\epsilon_0} \left\langle \phi_{I\alpha} \left| \frac{1}{\|\vec{r} - \vec{R}_K\|} \right| \phi_{J\beta} \right\rangle \quad (2.110)$$

We find that the kinetic energy is a two-body term, as it only depends on the ionic coordinates $\vec{R}_I$ and $\vec{R}_J$ of the basis functions. The term $T_{I\alpha J\beta}^{KS}$ can therefore trivially be precomputed for a given basis set, and stored for future use. This situation however looks different for the other matrix elements. The $V_{I\alpha J\beta}^{Ha}[\rho^0]$ and $V_{I\alpha J\beta}^{ext}$ terms are three-body terms, simultaneously dependent on three ionic coordinates $\vec{R}_I$, $\vec{R}_J$, and $\vec{R}_K$. The $V_{I\alpha J\beta}^{XC}[\rho^0]$ term is even dependent on the whole set of ionic coordinates $\{\vec{R}_K\}$, as the exchange-correlation potential is non-linear in density. We therefore need to approximate these matrix elements to only depend on two ionic coordinates at a time, otherwise it is not possible to tabulate these as a function of merely two ionic coordinates.

2.4.2.6 Two-body Hartree potential

Consider first the Hartree potential and the external potential. It makes sense to consider both of these potentials simultaneously, as they act contrary to one another and are both Coulombic; the external potential represents the attraction of the electron to the ionic nuclei at $\vec{R}_K$, whereas the Hartree potential represents the Coulomb repulsion of the electron from the atomically centred reference density $\rho_K^0(\vec{r} - \vec{R}_K)$. It is therefore common to summarise these potentials as the *neutral-atom potential* v_{NA} :

$$\begin{aligned} v_{NA}[\rho_0^K] &= v_{Ha}[\rho_0^K(\vec{r} - \vec{R}_K)] - \frac{eZ_K}{4\pi\epsilon_0} \frac{1}{||\vec{r} - \vec{R}_K||} \\ &\equiv v_{Ha}[\rho_0^K(\vec{r} - \vec{R}_K)] + v_{ext}^K(\vec{r} - \vec{R}_K) \\ &\equiv v_{NA}[\rho_0^K(\vec{r} - \vec{R}_K)]. \end{aligned} \quad (2.111)$$

Let us now consider for illustrative purposes the Hartree and Coulomb potentials of a single hydrogen. The density distributions of the Hydrogen electron and the proton both integrate to one over infinite volume, therefore the net, neutral-atom potential $v_{NA}[\rho^H(R)]$, defined as

$$\begin{aligned} v_{NA}[\rho^H(R)] &= v_{Ha}[\rho^H(R)] + v_{ext}^H(R) \\ &= \frac{e}{4\pi\epsilon_0} \int \frac{\rho^H(R)}{||\vec{r} - \vec{r}'||} d^3r' - \frac{e}{4\pi\epsilon_0} \frac{1}{R} \end{aligned} \quad (2.112)$$

goes to zero for $R \geq R_C$ by Gauss' theorem. The Coulomb potential diverges for $R \rightarrow 0$, where as the Hartree potential remains finite; the singularity therefore persists. The integral over neither potential does converge, as they fall off as $\sim 1/R$. One can however show that the neutral-atom potential decays considerably faster than either the Hartree or Coulomb potential. See figure 2.1 for a demonstration on the example of the hydrogen atom. This property motivates the *2-centre* approximation,^{59,61} in which we neglect all three-center contributions to the matrix elements:

$$V_{I\alpha J\beta}^{NA}[\rho^0] \approx V_{I\alpha J\beta}^{2C-NA}[\rho^0] = \begin{cases} \langle \phi_{I\alpha} | v_{NA}[\rho_I^0] + v_{NA}[\rho_J^0] | \phi_{J\beta} \rangle & I \neq J \\ \langle \phi_{I\alpha} | v_{NA}[\rho_I^0] | \phi_{I\beta} \rangle & I = J. \end{cases} \quad (2.113)$$

Note that the onsite matrix element $V_{I\alpha I\beta}^{NA}[\rho^0]$ is a simple one-body term; here we have further applied the *crystal-field* approximation, only considering the potential from the onsite density. The matrix elements $V_{I\alpha J\beta}^{2C-NA}[\rho^0]$ can now be tabulated as a function of interatomic distance $R_{IJ} = ||\vec{R}_I - \vec{R}_J||$ for each pair of interacting atomic species, following the two-centre parametrisation of Slater and Koster.⁶² This approximation seems rather crude, but it can be reasoned to be physically sensible due to the short range of the neutral atom potential.

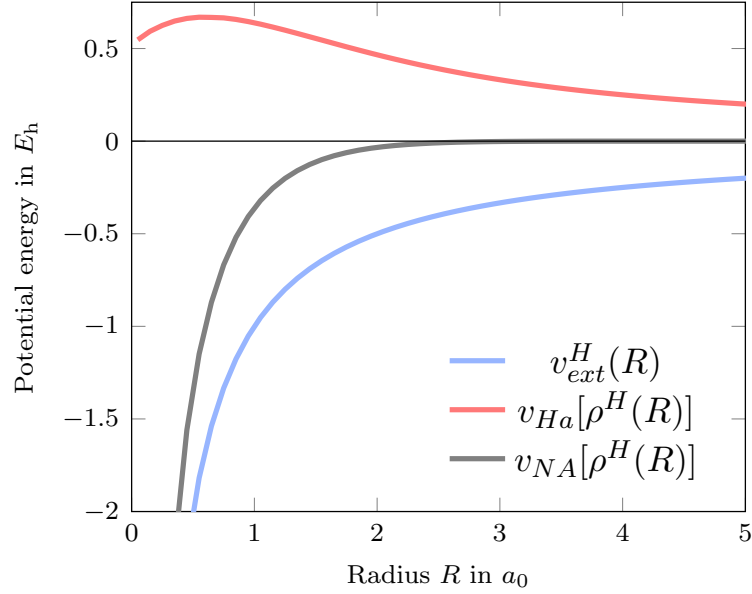


FIGURE 2.1: Electrostatic potentials of a single hydrogen atom. The neutral atom potential $v_{NA}[\rho^H(R)] = v_{Ha}[\rho^H(R)] + v_{ext}^H(R)$ falls off considerably faster than either of its constituents, and is therefore of shorter range.

2.4.2.7 Two-body exchange-correlation potential

We shall next consider the exchange-correlation potential. Here we are unable to split the potential into linear terms as with the Hartree potential, as $v_{XC}[\rho]$ is generally not linear in ρ . Instead, similar two-centre and crystal-field approximations are applied rather pragmatically, motivated a posteriori by their effectiveness in reproducing electronic structure with high accuracy. We start by a cluster expansion of the potential into many-body contributions:

$$v_{XC}[\rho^0] \approx \sum_K v_{XC}[\rho_K^0] + \frac{1}{2} \sum_{K \neq L} (v_{XC}[\rho_K^0 + \rho_L^0] - v_{XC}[\rho_K^0] - v_{XC}[\rho_L^0]) \quad (2.114)$$

The expansion is taken up to two-body terms only. The corresponding intersite matrix elements in the cluster approximation are:

$$V_{I\alpha J\beta}^{XC}[\rho^0] \approx \sum_K V_{I\alpha J\beta}^{XC}[\rho_K^0] + \frac{1}{2} \sum_{K \neq L} (V_{I\alpha J\beta}^{XC}[\rho_K^0 + \rho_L^0] - V_{I\alpha J\beta}^{XC}[\rho_K^0] - V_{I\alpha J\beta}^{XC}[\rho_L^0]). \quad (2.115)$$

We are here faced with a similar issue as in the Hartree potential. The matrix elements of the two-body cluster expansion lead to up to four-centre matrix elements. These cannot possibly be tabulated in a straight-forward manner as the coordinate space is of dimension $(\mathbb{R}^3)^4$, before symmetry reductions. Instead the two-center approximation is taken again,

neglecting the effect of all atomic densities neither centered on $\vec{R}_I$ nor $\vec{R}_J$.

$$V_{I\alpha J\beta}^{XC}[\rho^0] \approx V_{I\alpha J\beta}^{2C-XC}[\rho^0] = \begin{cases} \langle \phi_{I\alpha} | v_{XC}[\rho_I^0 + \rho_J^0] | \phi_{J\beta} \rangle & I \neq J \\ \langle \phi_{I\alpha} | v_{XC}[\rho_I^0] | \phi_{I\beta} \rangle & I = J. \end{cases} \quad (2.116)$$

The two-centre approximations impose a strict locality on our electronic structure. It is clear that the approximations outlined above become more accurate the more localised the atomic orbitals are. The two-body approximations therefore lead to the *tight-binding* theory. As the name suggests, tight-binding theory considers electrons to be tightly bound to the bare ions. This is synonymous with the assumptions that a strongly localised basis set is used, and that the atomic reference density is similarly localised. In summary, we arrive at the static tight-binding Hamiltonian by applying the two-centre and crystal field approximations to the static Kohn-Sham Hamiltonian (2.106):

$$H_{I\alpha J\beta}^{0-KS}[\rho^0] \approx H_{I\alpha J\beta}^{TB}[\rho^0] = T_{I\alpha J\beta}^{KS} + V_{I\alpha J\beta}^{2C-NA}[\rho^0] + V_{I\alpha J\beta}^{2C-XC}[\rho^0]. \quad (2.117)$$

2.4.2.8 Two-body repulsive energy

We are left to find an efficient expression for the repulsive energy $E_{rep}[\rho^0]$ from Eq. (2.79):

$$E_{rep}[\rho^0] = W_{ion-ion} - E_{Ha}[\rho^0] + E_{XC}[\rho^0] - \int v_{XC}[\rho^0] \rho^0(\vec{r}) d^3r. \quad (2.118)$$

While the Hartree energy is easily partitioned into products of atomic densities, the difficulty lies with the exchange-correlation terms $E_{XC}[\rho^0]$ and $v_{XC}[\rho^0]$. These terms are generally non-linear in density, and necessarily have to be approximated to arrive at a two-centre expression. While these approximations work well for the exchange-correlation potential, they do not seem to translate well to accurate forces. More accurate approximations to $E_{XC}[\rho^0]$ and $v_{XC}[\rho^0]$ are still subject to current research,^{63,64} however, we shall hence abandon the idea of first-principles forces and take the pragmatic approach. Sutton et al.⁶⁵ have shown that the repulsive potential can be approximated by a repulsive pair-potential U_{rep} which only depends on the ionic coordinates $\{\vec{R}_I\}$:

$$E_{rep}[\rho^0] \approx E_{rep}[\{\vec{R}_I\}] = \sum_I \varepsilon_0^I + \sum_{\substack{IJ \\ I \neq J}} U_{rep}(R_{IJ}), \quad (2.119)$$

where ε_0^I is the double-counting energy of the isolated neutral atom. Practical experience in building density-functional tight-binding method has shown that these repulsive potentials can be fitted to reproduce density-functional theory binding energies whilst being reasonably transferable between different systems. A further benefit to the fitting approach is that it also enables correction of systematic errors in the force due to the small basis set sizes

prevalent in tight binding. The reference density-functional theory calculations are for this purpose done with large basis sets.

2.4.3 Self-consistent electrostatics

Non-self-consistent tight-binding methods may work for a wide range of systems, nonetheless, systems in which a large amount of charge transfer occurs need to include the self-consistent contribution $\hat{H}_{KS}^{scf}[\rho]$ from Eq. (2.85). This is in particular the case when strong external fields are applied. We shall here outline one of the most common ways of treating self-consistency approximately in density-functional tight-binding, and as such lay the groundwork for an improved method.

Consider first the self-consistent energy contributions as given by Eq. (2.80):

$$E_{KS}^{scf}[\rho] = -\frac{e^2}{4\pi\epsilon_0} \int \frac{\rho^0(\vec{r})\delta\rho(\vec{r}')}{||\vec{r} - \vec{r}'||} d^3r d^3r' - \frac{e^2}{8\pi\epsilon_0} \int \frac{\delta\rho(\vec{r})\delta\rho(\vec{r}')}{||\vec{r} - \vec{r}'||} d^3r d^3r' \\ - \frac{1}{2} \int f_{XC}[\rho^0] \delta\rho(\vec{r})\delta\rho(\vec{r}') d^3r d^3r' - \int f_{XC}[\rho^0] \rho^0(\vec{r})\delta\rho(\vec{r}') d^3r d^3r'. \quad (2.120)$$

Density-functional tight-binding methods commonly only consider the self-consistent Hartree contributions,⁶⁰ as there are difficulties in efficiently evaluating the exchange-correlation integrals without the use of numerical integration. We therefore define the self-consistent tight-binding energy $E_{KS}^{scf}[\rho] \approx E_{TB}^{scf}[\rho]$ as:

$$E_{TB}^{scf}[\rho] = -\frac{e^2}{4\pi\epsilon_0} \int \frac{\rho^0(\vec{r})\delta\rho(\vec{r}')}{||\vec{r} - \vec{r}'||} d^3r d^3r' - \frac{e^2}{8\pi\epsilon_0} \int \frac{\delta\rho(\vec{r})\delta\rho(\vec{r}')}{||\vec{r} - \vec{r}'||} d^3r d^3r' \quad (2.121)$$

It can be reasoned that the exchange-correlation contribution behaves qualitatively similar to the Hartree energy at short range, and that no significant loss of accuracy is incurred by neglecting it. The above expression cannot be tabulated in a straight-forward manner, as the density variation $\delta\rho$ is not predetermined at the beginning of the simulation, unlike the reference density ρ^0 . We therefore require an efficient approximation that captures the essential physics while avoiding expensive integrals.

Let us next briefly consider the structure of the expression Eq. (2.121). We rewrite it as:

$$E_{TB}^{scf}[\rho] = E_{Ha}[\delta\rho] - \int v_{Ha}[\delta\rho] \rho(\vec{r}) d^3r. \quad (2.122)$$

This expression presents a clear strategy on how to approximate the self-consistent electrostatic interactions. First, let us define the variational Hartree energy $E_{Ha}^{var}[\rho]$ as a functional of the electron density:

$$E_{Ha}^{var}[\rho] = E_{Ha}[\delta\rho] \quad (2.123)$$

From here follows the variational Hartree potential as

$$v_{Ha}^{var}[\rho] = \frac{\delta E_{Ha}^{var}[\rho]}{\delta \rho(\vec{r})}, \quad (2.124)$$

which enters both the electronic energy as of Eq. (2.122),

$$E_{TB}^{scf}[\rho] = E_{Ha}^{var}[\rho] - \int v_{Ha}^{var}[\rho] \rho(\vec{r}) d^3r, \quad (2.125)$$

and the self-consistent Hamiltonian as of Eq. (2.85), where we too have neglected the exchange-correlation contribution:

$$\hat{H}_{KS}^{scf}[\rho] \approx \hat{H}_{TB}^{scf}[\rho] = v_{Ha}^{var}[\rho] \quad (2.126)$$

Summarising the approximations to the repulsive potential (2.119), the neglect of self-consistent exchange-correlation energy (2.121), and the introduction of an approximate treatment of the self-consistent Hartree energy (2.123) and potential (2.124), we arrive at the total energy of the self-consistent tight-binding model given by:

$$E^{TB}[\rho] = 2 \sum_n f_n \varepsilon^{(n)} + E_{Ha}^{var}[\rho] - \int v_{Ha}^{var}[\rho] \rho(\vec{r}) d^3r + E_{rep}[\{\vec{R}_I\}] + T_{ion}. \quad (2.127)$$

The self-consistent tight-binding Hamiltonian matrix is given by the static 2-centre Hamiltonian as derived in Eq. (2.117), plus the contribution from the approximate, variational Hartree potential:

$$H_{I\alpha J\beta}^{TB}[\rho] = T_{I\alpha J\beta}^{KS} + V_{I\alpha J\beta}^{2C-NA}[\rho^0] + V_{I\alpha J\beta}^{2C-XC}[\rho^0] + V_{I\alpha J\beta}^{var-Ha}[\rho] \quad (2.128)$$

given by:

$$V_{I\alpha J\beta}^{var-Ha}[\rho] = \langle \phi_{I\alpha} | v_{Ha}^{var}[\rho] | \phi_{J\beta} \rangle. \quad (2.129)$$

We are now left to find an appropriate approximation to the variational Hartree energy. Using the previously defined atomic densities of Eq. (2.105), the Hartree integral can be expressed in the pairwise form:

$$E_{Ha}^{var}[\rho] = \frac{e^2}{8\pi\epsilon_0} \sum_{IJ} \int \frac{\delta\rho_I(\vec{r})\delta\rho_J(\vec{r}')}{||\vec{r} - \vec{r}'||} d^3r d^3r'. \quad (2.130)$$

While this integral can in principle be solved exactly, as is done in many density-functional theory codes, we would like to minimise the computational effort. It is clear from Eq. (2.105) that $\delta\rho$ contains N_{basis}^2 basis function products, hence N_{basis}^4 integrals need to be solved to evaluate $E_{Ha}^{var}[\rho]$. The computational costs can be made more manageable by truncating the Hartree integrals in range, yet a direct evaluation of this expression would be a bottleneck in the performance of any tight binding method. We therefore require an effective approximation to $E_{Ha}^{var}[\rho]$ that significantly reduces the computational effort required to evaluate the Hartree energy of Eq. (2.130). This will be discussed in the next chapter 3.

2.4.4 Electric field interaction

The equations we have derived so far consider the electrons to be only under the influence of the electronic and ionic potentials. We shall here introduce an external electric potential $V_{ef}(\vec{r})$ to the approximate Kohn-Sham potential as originally outlined in Sec. 2.1. The electric potential first contributes to the ionic energy, following Eq. (2.13):

$$V_{ef-ion} = \sum_I eZ_I V_{ef}(\vec{R}_I), \quad (2.131)$$

and secondly, it also contributes to the electronic energy similarly in form of the electric field energy $V_{ef-ele}[\rho]$:

$$V_{ef-ele}[\rho] = \int V_{ef}(\vec{r}) n_{ele}(\vec{r}) = -e \int V_{ef}(\vec{r}) \rho(\vec{r}) d^3r, \quad (2.132)$$

where $n_{ele}(\vec{r})$ is the electronic charge density. The electric field contribution to the Kohn-Sham Hamiltonian is easily found as:

$$v_{ef-ele}[\rho] = \frac{\delta V_{ef-ele}[\rho]}{\delta \rho(\vec{r})} = -e V_{ef}(\vec{r}). \quad (2.133)$$

Following the definition of the Kohn-Sham double-counting energy in Eq. (2.51), we find that the electric potential does not contribute to the double-counting energy:

$$E_{dc}^{ef-ele}[\rho] = V_{ef-ele}[\rho] - \int v_{ef-ele}[\rho] \rho(\vec{r}) d^3r = 0. \quad (2.134)$$

Last but not least, we define the electric-potential matrix elements:

$$V_{I\alpha J\beta}^{ef} = \langle \phi_{I\alpha} | v_{ef-ele} | \phi_{J\beta} \rangle = -e \int \phi_{I\alpha}(\vec{r} - \vec{R}_I) V_{ef}(\vec{r}) \phi_{J\beta}(\vec{r} - \vec{R}_J) d^3r. \quad (2.135)$$

Note that for the special case of $V_{ef}(\vec{r})$ being a dipole field

$$V_{ef}(\vec{r}) = \vec{E} \cdot \vec{r}, \quad (2.136)$$

the matrix elements can be expressed in terms of the dipole moments:

$$V_{I\alpha J\beta}^{ef} = -e \vec{E} \cdot \int \phi_{I\alpha}(\vec{r} - \vec{R}_I) \vec{r} \phi_{J\beta}(\vec{r} - \vec{R}_J) d^3r. \quad (2.137)$$

In summary, the total self-consistent tight-binding Hamiltonian (2.128) for a system under the influence of an electric field is given by:

$$H_{I\alpha J\beta}^{TB}[\rho] = T_{I\alpha J\beta}^{KS} + V_{I\alpha J\beta}^{2C-NA}[\rho^0] + V_{I\alpha J\beta}^{2C-XC}[\rho^0] + V_{I\alpha J\beta}^{var-Ha}[\rho] + V_{I\alpha J\beta}^{ef}. \quad (2.138)$$

There is no additional double-counting contribution, but the ionic energy is increased by the ion-field interaction Eq. (2.131). It is interesting that the contribution of the electric field to the Hamiltonian is not a functional of the density, and is therefore part of the static Hamiltonian.

2.4.5 Tight-binding forces

We shall next derive the ionic forces following the Hellman-Feynman theorem. Starting with the total tight-binding energy from Eq. (2.127), including the electric field energy of Eq. (2.131):

$$E^{TB}[\rho] = 2 \sum_n f_n \varepsilon^{(n)} + E_{TB}^{scf}[\rho] + E_{rep}[\{\vec{R}_I\}] + T_{ion} + V_{ef-ion}. \quad (2.139)$$

Here $E_{TB}^{scf}[\rho]$ is the variational double-counting energy as defined in Eq. (2.122). We find the force acting on the ion at site K by differentiation of the total energy with respect to the ionic coordinate $\vec{R}_K$:

$$\vec{F}_K = -\frac{dE^{TB}[\rho]}{d\vec{R}_K} = -\frac{\partial E^{TB}[\rho]}{\partial \rho(\vec{r})} \vec{\nabla}_{R_K} \rho(\vec{r}) - \vec{\nabla}_{R_K} E^{TB}[\rho]. \quad (2.140)$$

We note here that the total energy is for one explicitly dependent on the ionic coordinates through the change of the Hamiltonian, and also implicitly dependent through the electron density. The derivative with respect to the electron density however vanishes, as we assume the system to be in an eigenstate of the Hamiltonian. We are left with:

$$\begin{aligned} \vec{F}_K &= -\vec{\nabla}_{R_K} E^{TB}[\rho] \\ &= -2 \sum_n f_n \vec{\nabla}_{R_K} \varepsilon^{(n)} - \vec{\nabla}_{R_K} E_{Ha}^{SCF}[\rho] \\ &\quad - \vec{\nabla}_{R_K} E_{rep}[\{\vec{R}_I\}] - \vec{\nabla}_{R_K} V_{ef-ion}. \end{aligned} \quad (2.141)$$

We shall next consider the gradient of each term individually, starting with the static Hamiltonian.

2.4.5.1 Eigenvalue gradient

For the purpose of this derivation it is helpful to express the eigenvalues in the Hamiltonian representation. First recall the eigenvalue expression of Eq. (2.74). This expression equally holds within the tight-binding approximations:

$$2 \sum_n f_n \varepsilon^{(n)} = 2 \sum_n f_n \langle \Phi^{(n)} | \hat{H}^{TB}[\rho] | \Phi^{(n)} \rangle, \quad (2.142)$$

where $\hat{H}^{TB}[\rho]$ is the self-consistent tight binding Hamiltonian under the influence of an external electric field, see Eq. (2.138). Let us consider now the gradient of the Kohn-Sham eigenvalues. We again apply the Hellman-Feynman theorem as we consider the system to be in a stationary state:

$$\vec{\nabla}_{R_K} \varepsilon^{(n)} = \vec{\nabla}_{R_K} \langle \Phi^{(n)} | \hat{H}^{TB}[\rho] | \Phi^{(n)} \rangle = \langle \Phi^{(n)} | \vec{\nabla}_{R_K} \hat{H}^{TB}[\rho] | \Phi^{(n)} \rangle \quad (2.143)$$

Consider the expression above represented by local orbitals:

$$\vec{\nabla}_{R_K} \varepsilon^{(n)} = \sum_{I\alpha J\beta} c_{I\alpha}^{*(n)} c_{J\beta}^{(n)} \langle \phi_{I\alpha} | \vec{\nabla}_{R_K} \hat{H}^{TB}[\rho] | \phi_{J\beta} \rangle \quad (2.144)$$

Note that we cannot directly compute the $\langle \phi_{I\alpha} | \vec{\nabla}_{R_K} \hat{H}^{TB}[\rho] | \phi_{J\beta} \rangle$ matrix elements as we only have access to $\vec{\nabla}_{R_K} \langle \phi_{I\alpha} | \hat{H}^{TB}[\rho] | \phi_{J\beta} \rangle = \vec{\nabla}_{R_K} H_{I\alpha J\beta}^{TB}[\rho]$ from the tabulated Slater-Koster integrals[†]. We can however transform the expressions into one another using the product rule:

$$\begin{aligned} \vec{\nabla}_{R_K} H_{I\alpha J\beta}^{TB}[\rho] &= \langle \vec{\nabla}_{R_K} \phi_{I\alpha} | \hat{H}^{TB}[\rho] | \phi_{J\beta} \rangle \\ &+ \langle \phi_{I\alpha} | \vec{\nabla}_{R_K} \hat{H}^{TB}[\rho] | \phi_{J\beta} \rangle \\ &+ \langle \phi_{I\alpha} | \hat{H}^{TB}[\rho] | \vec{\nabla}_{R_K} \phi_{J\beta} \rangle. \end{aligned} \quad (2.145)$$

Substitution of Eq. (2.145) into Eq. (2.144) yields:

$$\begin{aligned} \vec{\nabla}_{R_K} \varepsilon^{(n)} &= \sum_{I\alpha J\beta} c_{I\alpha}^{*(n)} c_{J\beta}^{(n)} \left(\vec{\nabla}_{R_K} H_{I\alpha J\beta}^{TB}[\rho] \right. \\ &\quad \left. - \langle \vec{\nabla}_{R_K} \phi_{I\alpha} | \hat{H}^{TB}[\rho] | \phi_{J\beta} \rangle - \langle \phi_{I\alpha} | \hat{H}^{TB}[\rho] | \vec{\nabla}_{R_K} \phi_{J\beta} \rangle \right). \end{aligned} \quad (2.146)$$

We next apply the Hamiltonian to the Kohn-Sham states

$$\begin{aligned} \vec{\nabla}_{R_K} \varepsilon^{(n)} &= \sum_{I\alpha J\beta} c_{I\alpha}^{*(n)} c_{J\beta}^{(n)} \left(\vec{\nabla}_{R_K} H_{I\alpha J\beta}^{TB}[\rho] \right. \\ &\quad \left. - \varepsilon^{(n)} \langle \vec{\nabla}_{R_K} \phi_{I\alpha} | \phi_{J\beta} \rangle - \varepsilon^{(n)} \langle \phi_{I\alpha} | \vec{\nabla}_{R_K} \phi_{J\beta} \rangle \right), \end{aligned} \quad (2.147)$$

and summarise the result following the product rule:

$$\vec{\nabla}_{R_K} \varepsilon^{(n)} = \sum_{I\alpha J\beta} c_{I\alpha}^{*(n)} c_{J\beta}^{(n)} \left(\vec{\nabla}_{R_K} H_{I\alpha J\beta}^{TB}[\rho] - \varepsilon^{(n)} \vec{\nabla}_{R_K} S_{I\alpha J\beta} \right). \quad (2.148)$$

2.4.5.2 Hamiltonian matrix element gradient

The Hamiltonian contains contributions from several sources given by Eq. (2.138):

$$H_{I\alpha J\beta}^{TB}[\rho] = H_{I\alpha J\beta}^{TB}[\rho^0] + V_{I\alpha J\beta}^{var-Ha}[\rho] + V_{I\alpha J\beta}^{ef}. \quad (2.149)$$

In section 2.4.2 we have shown that the static Hamiltonian matrix elements can be expressed purely as a function of pairwise nuclear coordinates $\{\vec{R}_I\}$:

$$H_{I\alpha J\beta}^{TB}[\rho^0] \equiv H_{I\alpha J\beta}^{TB}[\rho^0](\vec{R}_I - \vec{R}_J) \equiv H_{I\alpha J\beta}^{TB}[\rho^0](\vec{R}_{IJ}). \quad (2.150)$$

[†]This is not necessarily true for the self-consistent contributions, but these are also easily computed this way.

The gradient is therefore given as:

$$\vec{\nabla}_{R_K} H_{I\alpha J\beta}^{TB}[\rho^0] = \vec{\nabla}_{R_{IJ}} H_{I\alpha J\beta}^{TB}[\rho^0] (\delta_{IK} - \delta_{JK}). \quad (2.151)$$

The static Hamiltonian matrix is not only hermitian, but even symmetric: $H_{I\alpha J\beta}^{TB}[\rho^0] = H_{J\beta I\alpha}^{TB}[\rho^0]$. Using Eq. (2.151), the static contribution to the sum simplifies to:

$$\sum_{I\alpha J\beta} \rho_{I\alpha J\beta} \vec{\nabla}_{R_K} H_{I\alpha J\beta}^{TB}[\rho^0] = 2 \sum_{\alpha J\beta} \rho_{K\alpha J\beta} \vec{\nabla}_{R_{KJ}} H_{K\alpha J\beta}^{TB}[\rho^0]. \quad (2.152)$$

The gradient of the self-consistent contribution and the external field coupling depend on the treatment of self-consistency and at this stage cannot be further simplified. We shall therefore factor these contributions out of the Hamiltonian gradient:

$$\begin{aligned} \sum_{I\alpha J\beta} \rho_{I\alpha J\beta} \vec{\nabla}_{R_K} H_{I\alpha J\beta}^{TB}[\rho] &= 2 \sum_{\alpha J\beta} \rho_{K\alpha J\beta} \vec{\nabla}_{R_{KJ}} H_{K\alpha J\beta}^{TB}[\rho^0] \\ &+ \sum_{I\alpha J\beta} \rho_{I\alpha J\beta} \vec{\nabla}_{R_K} \left(V_{I\alpha J\beta}^{var-Ha}[\rho] + V_{I\alpha J\beta}^{ef} \right). \end{aligned} \quad (2.153)$$

2.4.5.3 Overlap gradient

Just like the static Hamiltonian matrix elements, the overlap matrix elements are only dependent on the pairwise interatomic distances. We can therefore express these as:

$$\vec{\nabla}_{R_K} S_{I\alpha J\beta} = \vec{\nabla}_{R_{IJ}} S_{I\alpha J\beta} (\delta_{IK} - \delta_{JK}). \quad (2.154)$$

2.4.5.4 Variational double-counting gradient

Following the definition of $E_{TB}^{scf}[\rho] = E_{Ha}^{var}[\rho] - \int v_{Ha}^{var}[\rho] \rho(\vec{r}) d^3r$ it becomes apparent that the gradient of the v_{Ha}^{var} integral cancels out with the previously derived contribution of the self-consistent potential to the Hamiltonian gradient: this is not surprising, as that is generally the purpose of the double-counting terms. We are merely left to evaluate $\vec{\nabla}_K E_{Ha}^{var}[\rho]$.

2.4.5.5 Repulsive pair-potential gradient

Consider the repulsive pair-potential as given by Eq. (2.119). The gradient is easily found as:

$$\vec{\nabla}_{R_K} E_{rep}[\{\vec{R}_I\}] = \sum_{\substack{IJ \\ I \neq J}} \vec{\nabla}_{R_K} U_{rep}(R_{IJ}) = 2 \sum_{\substack{J \\ J \neq K}} U'_{rep}(R_{JK}) \hat{R}_{JK}, \quad (2.155)$$

where $\hat{R}_{JK}$ is the unit vector: $\hat{R}_{JK} = (\vec{R}_J - \vec{R}_K) / \|\vec{R}_J - \vec{R}_K\|$.

2.4.5.6 Electric field energy gradient

The gradient of the electric field-ion energy as given by Eq. (2.131) is also easily found as:

$$\vec{\nabla}_{R_K} V_{ef-ion} = \sum_I e Z_I \vec{\nabla}_{R_K} V_{ef}(\vec{R}_I) = e Z_K \vec{\nabla}_{R_K} V_{ef}(\vec{R}_K). \quad (2.156)$$

2.4.5.7 Total tight-binding force

In summary the total tight-binding force on the ion at site K is given as:

$$\begin{aligned} \vec{F}_K[\rho] = & -2 \sum_{\alpha J \beta} \rho_{K\alpha J \beta} \left(\vec{\nabla}_{R_{KJ}} H_{K\alpha J \beta}^{TB}[\rho^0] - \varepsilon^{(n)} \vec{\nabla}_{R_{KJ}} S_{K\alpha J \beta} \right) \\ & - \sum_{I\alpha J \beta} \rho_{I\alpha J \beta} \vec{\nabla}_{R_K} V_{I\alpha J \beta}^{ef} - \vec{\nabla}_{R_K} E_{Ha}^{var}[\rho] \\ & - 2 \sum_{\substack{J \\ J \neq K}} U'_{rep}(R_{JK}) \hat{R}_{JK} - e Z_K \vec{\nabla}_{R_K} V_{ef}(\vec{R}_K). \end{aligned} \quad (2.157)$$

We can split the force into a static contribution, only dependent on pairwise interatomic distances and on the choice of the reference density $\rho^0(\vec{r})$, and into a self-consistent contribution, dependent on the total electron density $\rho(\vec{r})$:

$$\vec{F}_K[\rho] = \vec{F}_K^0[\rho^0] + \vec{F}_K^{scf}[\rho], \quad (2.158)$$

where

$$\vec{F}_K^{scf}[\rho] = -\vec{\nabla}_{R_K} E_{Ha}^{var}[\rho], \quad (2.159)$$

and $\vec{F}_K^0[\rho^0]$ contains all remaining terms. We will show how to evaluate the gradient of the static, tabulated Hamiltonian matrix elements using the Slater-Koster tables in section 2.4.6. The self-consistent force contribution $\vec{F}_K^{scf}[\rho]$ explicitly depends on the way we approximate the variational Hartree energy, and shall be treated later in section 3.3. We will also consider $\vec{\nabla}_{R_K} V_{I\alpha J \beta}^{ef}$ in section 3.3.1.

2.4.6 Slater-Koster tables

We have shown in section 2.4.2 that the static Hamiltonian matrix elements can be approximated to only depend on the interatomic displacements $\vec{R}_{IJ} = \vec{R}_I - \vec{R}_J$. While the matrix elements could already be precomputed at this stage, it would be too cumbersome as we are not yet accounting for any bond symmetries.

2.4.6.1 Bond integrals

We shall here return to the basis-set notation of Eq. (2.88) introduced in section 2.4.2.2, where the orbital $\phi_{I\alpha}$ refers to an orbital with quantum numbers nlm :

$$\phi_{I\alpha}(\vec{r}) \equiv \phi_{nlm}^I(\vec{r}) = R_{nl}^I(|\vec{r}|)K_{lm}(\vec{r}). \quad (2.160)$$

For brevity we consider a single-zeta basis set. Consider now the simplest case of two interacting s -orbitals:

$$\begin{aligned} \phi_{I\alpha}(\vec{r} - \vec{R}_I) &= \phi_{n00}^I(\vec{r} - \vec{R}_I) \\ \phi_{J\beta}(\vec{r} - \vec{R}_J) &= \phi_{n'00}^J(\vec{r} - \vec{R}_J). \end{aligned} \quad (2.161)$$

The s -orbitals are spherically symmetric around their respective ionic site, therefore the dependency on their interatomic displacement $\vec{R} = \vec{R}_I - \vec{R}_J$ can be reduced to a dependency on the interatomic distance, or bond length, $R = \|\vec{R}\|$. One can now simply express the matrix element of a two-centre operator $\hat{O}$ as an integral solely dependent on the bond length:

$$O_{I\alpha J\beta} = O_{n00n'00}^{IJ} = O(R) = \langle \phi_{n00}^I(\vec{r}) | \hat{O} | \phi_{n'00}^J(\vec{r} - R\hat{e}_z) \rangle. \quad (2.162)$$

This integral can be precomputed over a range of bond lengths R and stored for future use. We have here chosen $\hat{e}_z$ as the bond direction for historical reasons. The bond integral $O(R)$ is commonly written as $R_{ss\sigma}(R)$, referencing the interaction between two s -orbitals showing a σ -symmetry around the bond direction $\hat{e}_z$. Note that each combination of nn' , and possibly $\zeta\zeta'$ for N -zeta basis sets, requires a separate set of tabulated bond integrals.

The situation becomes a bit more complicated for orbitals of higher shells. Higher shells have polarised orbitals, thereby introducing angular dependencies to the matrix elements. Still, the general procedure remains the same; two-centre matrix elements can always be expressed in terms of rotated bond integrals, each representing a unique bonding configuration. We refer to figure 2.2 for a visualisation of the unique bond integrals and their symmetry properties. The matrix elements are constructed from the integrals depending on the rotation of the displacement vector $\vec{R}$ from $\hat{e}_z$. This is represented in terms of the direction cosines:

$$\begin{aligned} l &= R_x/R \\ m &= R_y/R \\ n &= R_z/R. \end{aligned} \quad (2.163)$$

This representation follows the original work of Slater and Koster,⁶² who have first expressed the two-centre matrix elements in terms of bond integrals $R_{ll'\alpha}(R)$, interatomic distance R , and direction cosines l, m, n . The Slater-Koster table for interactions up to

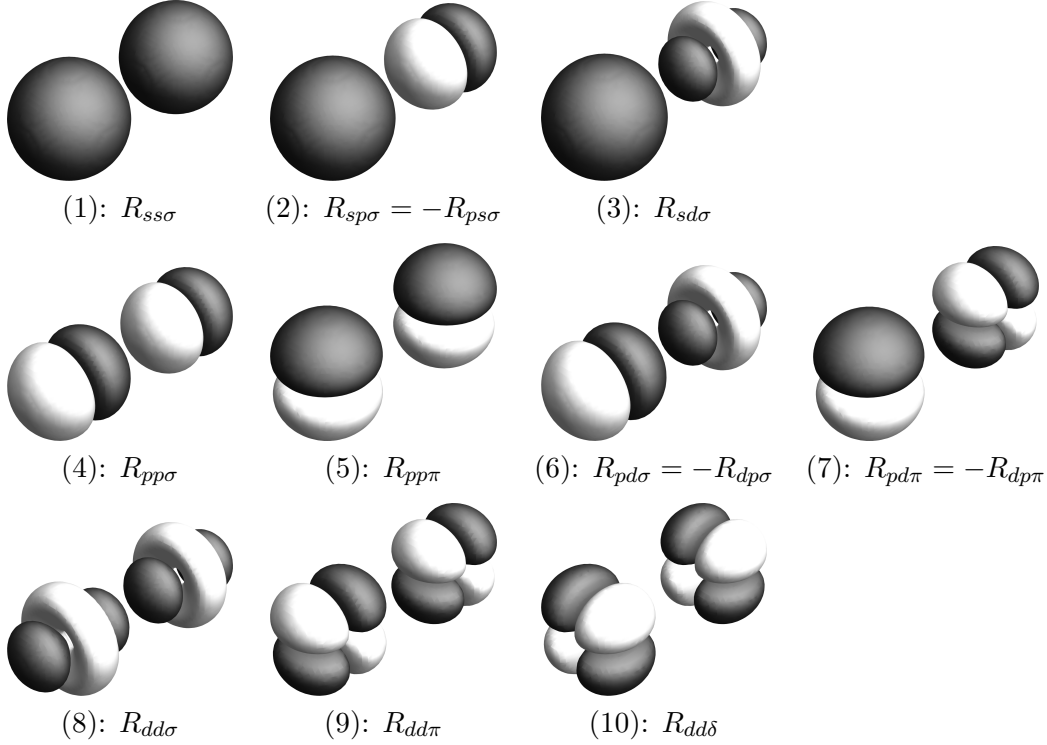


FIGURE 2.2: The unique Slater-Koster integrals $R_{ll'\alpha}$ and their corresponding orbital configurations up to the $l = 2$, or d -orbital, case. The orbitals are aligned along the $\hat{e}_z$ axis. The bond integrals are either even or odd with respect to the inversion $R_{ll'\alpha} = \pm R_{l'l\alpha}$. Integrals with odd symmetry are marked as such in the captions.

d - d orbitals is listed in table 2.2. Slater-Koster tables for higher angular momenta are also available.^{66–68} The Slater-Koster tables are also coded up in a MATHEMATICA script, given in section A.7 in the appendix.

The Slater-Koster representation is crucial for an efficient implementation of tight-binding simulation software, as it merely involves the parametrisation or computation of the few unique bond integrals. These are tabulated over a range of interatomic distances for all occurring bonding scenarios in the system and stored for future use.

2.4.6.2 Slater-Koster derivatives

We have derived the expressions for the tight-binding force in section 2.4.5. The static tight-binding force requires the evaluation of the matrix-element derivatives with respect to the ionic coordinates $\{\vec{R}_I\}$:

$$d\vec{H}_{I\alpha J\beta}^{TB}[\rho_0] \equiv \vec{\nabla}_{R_{IJ}} H_{I\alpha J\beta}^{TB}[\rho_0]. \quad (2.164)$$

We have shown in section 2.4.6.1 that any two-centre matrix element can be expressed in terms of bond integrals and the direction cosines (2.163) following the Slater-Koster tables.

Table 2.2: Slater-Koster table for s , p , and d orbitals. The bond integrals $R_{ll'\alpha}$ are implied to depend on the interatomic distance $R = ||\vec{R}_I - \vec{R}_J||$. We refer to figure 2.2 for the symmetry behaviour with respect to inversion: $R_{ll'\alpha} = \pm R_{l'l\alpha}$. The missing entries can be inferred by permutation of the indices $(n, l, m) \rightarrow (l, m, n) \rightarrow (m, n, l) \rightarrow (n, l, m)$. The harmonics K_{lm} are shown without prefactors as defined in table 2.1.

K_{lm}	$K_{l'm'}$	matrix element $O_{nlm,n'l'm'}^{IJ}$
1	1	$R_{ss\sigma}$
1	x	$lR_{sp\sigma}$
x	x	$l^2 R_{pp\sigma} + (1 - l^2) R_{pp\pi}$
x	y	$lm (R_{pp\sigma} - R_{pp\pi})$
x	z	$ln (R_{pp\sigma} - R_{pp\pi})$
1	xy	$\sqrt{3}lmR_{sd\sigma}$
1	$x^2 - y^2$	$\frac{1}{2}\sqrt{3}(l^2 - m^2) R_{sd\sigma}$
1	$3z^2 - r^2$	$(n^2 - \frac{1}{2}(l^2 - m^2)) R_{sd\sigma}$
x	xy	$\sqrt{3}l^2 m R_{pd\sigma} + m(1 - 2l^2) R_{pd\pi}$
x	yz	$\sqrt{3}lmn R_{pd\sigma} - 2lmn R_{pd\pi}$
x	zx	$\sqrt{3}l^2 n R_{pd\sigma} + n(1 - 2l^2) R_{pd\pi}$
x	$x^2 - y^2$	$\frac{1}{2}\sqrt{3}l(l^2 - m^2) R_{pd\sigma} + l(1 - l^2 + m^2) R_{pd\pi}$
y	$x^2 - y^2$	$\frac{1}{2}\sqrt{3}m(l^2 - m^2) R_{pd\sigma} - m(1 + l^2 - m^2) R_{pd\pi}$
z	$x^2 - y^2$	$\frac{1}{2}\sqrt{3}n(l^2 - m^2) R_{pd\sigma} - n(l^2 - m^2) R_{pd\pi}$
x	$3z^2 - r^2$	$l(n^2 - \frac{1}{2}(l^2 + m^2)) R_{pd\sigma} - \sqrt{3}ln^2 R_{pd\pi}$
y	$3z^2 - r^2$	$m(n^2 - \frac{1}{2}(l^2 + m^2)) R_{pd\sigma} - \sqrt{3}mn^2 R_{pd\pi}$
z	$3z^2 - r^2$	$n(n^2 - \frac{1}{2}(l^2 + m^2)) R_{pd\sigma} + \sqrt{3}n(l^2 + m^2) R_{pd\pi}$
xy	xy	$3l^2 m^2 R_{dd\sigma} + (l^2 + m^2 - 4l^2 m^2) R_{dd\pi} + (n^2 + l^2 m^2) R_{dd\delta}$
xy	yz	$3lm^2 n R_{dd\sigma} + ln(1 - 4m^2) R_{dd\pi} + ln(m^2 - 1) R_{dd\delta}$
xy	zx	$3l^2 mn R_{dd\sigma} + mn(1 - 4l^2) R_{dd\pi} + mn(l^2 - 1) R_{dd\delta}$
xy	$x^2 - y^2$	$\frac{3}{2}lm(l^2 - m^2) R_{dd\sigma} + 2lm(m^2 - l^2) R_{dd\pi} + \frac{1}{2}lm(l^2 - m^2) R_{dd\delta}$
yz	$x^2 - y^2$	$\frac{3}{2}mn(l^2 - m^2) R_{dd\sigma} - mn(1 + 2(l^2 - m^2)) R_{dd\pi} + mn(1 + \frac{1}{2}(l^2 - m^2)) R_{dd\delta}$
zx	$x^2 - y^2$	$\frac{3}{2}nl(l^2 - m^2) R_{dd\sigma} + nl(1 - 2(l^2 - m^2)) R_{dd\pi} - nl(1 - \frac{1}{2}(l^2 - m^2)) R_{dd\delta}$
xy	$3z^2 - r^2$	$\sqrt{3}lm(n^2 - \frac{1}{2}(l^2 + m^2)) R_{dd\sigma} - 2\sqrt{3}lmn^2 R_{dd\pi} + \frac{1}{2}\sqrt{3}lm(1 + n^2) R_{dd\delta}$
yz	$3z^2 - r^2$	$\sqrt{3}mn(n^2 - \frac{1}{2}(l^2 + m^2)) R_{dd\sigma} + \sqrt{3}mn(l^2 + m^2 - n^2) R_{dd\pi} - \frac{1}{2}\sqrt{3}mn(l^2 + m^2) R_{dd\delta}$
zx	$3z^2 - r^2$	$\sqrt{3}ln(n^2 - \frac{1}{2}(l^2 + m^2)) R_{dd\sigma} + \sqrt{3}ln(l^2 + m^2 - n^2) R_{dd\pi} - \frac{1}{2}\sqrt{3}ln(l^2 + m^2) R_{dd\delta}$
$x^2 - y^2$	$x^2 - y^2$	$\frac{3}{4}(l^2 - m^2)^2 R_{dd\sigma} + (l^2 + m^2 - (l^2 - m^2)^2) R_{dd\pi} + (n^2 + \frac{1}{4}(l^2 - m^2)^2) R_{dd\delta}$
$x^2 - y^2$	$3z^2 - r^2$	$\frac{1}{2}\sqrt{3}(l^2 - m^2)(n^2 - \frac{1}{2}(l^2 + m^2)) R_{dd\sigma} + \sqrt{3}n^2(m^2 - l^2) R_{dd\pi} + \frac{1}{4}\sqrt{3}(1 + n^2)(l^2 - m^2) R_{dd\delta}$
$3z^2 - r^2$	$3z^2 - r^2$	$(n^2 - \frac{1}{2}(l^2 + m^2))^2 R_{dd\sigma} + 3n^2(l^2 + m^2) R_{dd\pi} + \frac{3}{4}(l^2 + m^2)^2 R_{dd\delta}$

This enables us to find the gradient of any matrix element directly by differentiating the Slater-Koster expressions. Consider for instance the derivative of the $O_{n00n'00}^{IJ}$ matrix element with respect to R_z :

$$\partial_{R_z} O_{n00n'00}^{IJ} = \partial_{R_z} O_{ss\sigma}(R) = \frac{R_z}{R} O'_{ss\sigma}(R) = n O'_{ss\sigma}(R). \quad (2.165)$$

The direction cosines are also affected by the derivative as they are functions of $\vec{R}$. Consider the example of $O_{n10n'00}^{IJ}$:

$$\partial_{R_z} O_{n10n'00}^{IJ} = \partial_{R_z} (n O_{sp\sigma}(R)) = (1 - n^2) O_{sp\sigma}(R)/R + n^2 O'_{sp\sigma}(R). \quad (2.166)$$

The same principle can be applied to find the second-order derivatives of the matrix elements, which we will show later in section 6.1 to appear in the non-adiabatic equations of motion. A MATHEMATICA script for the automatic determination of the first and second order derivatives and their onsite limits of the Slater-Koster table up to d - d integrals is presented in section A.7 in the appendix. The onsite limits of the Slater-Koster elements can be found by series expansion following Tong.⁶⁹

2.4.7 Tight Binding models and parameters

We have derived an approximate Kohn-Sham theory which only depends on two-body terms. This tight-binding theory enables us to compute electronic structure simply by reading out the Hamiltonian and overlap matrix elements from the tabulated bond integrals. As described in sec. 2.4.6, these are the set of the symmetrically unique Hamiltonian and overlap integrals in the bond reference frame. The integrals are a function of interatomic distance $\vec{R}_{IJ}$ and of the chosen the atomic reference densities $\rho_I^0(\vec{r} - \vec{R}_I)$. By this virtue the theory is very efficient, saving the computational effort associated with solving the integrals on-the-fly as is usually done in density-functional theory. However, we have not yet described how this atomic reference density can be found.

2.4.7.1 Empirical tight binding

In principle it is not necessary to use a basis set and atomic reference densities to construct the bond integrals. Empirical tight-binding models fit the bond integrals to reproduce either experimental or higher-level theory reference data.^{70,71} Such models have been highly successful in predicting all kinds of properties, but the fitting is generally a very labour intensive endeavour. In particular the introduction of new elements into empirical models is difficult, as there is little a-priori knowledge available about their interspecies interaction. These models furthermore cannot easily be improved upon, as neither a distinction between the different contributions in the Hamiltonian, nor an underlying basis set are available. Empirical tight binding models therefore commonly do not grant access to the electron density.

2.4.7.2 Density-functional tight-binding

The alternative is to keep with the first-principles approach, using density-functional theory to generate reference densities $\rho_I^0(\vec{r} - \vec{R}_I)$. The atomic reference densities are found by solving the DFT problem of the single atom on a radial grid. We note that, within the introduced approximations in this chapter, the DFT and tight-binding models

are equivalent in their description of single atoms. The wave-function is described in a basis of atomically-localised functions $\psi_{nlm}^{I,\zeta}$ on a radial grid. The solution of the one-atom eigenproblem is found self-consistently, optimising the shape of the wave-functions $\psi_{nlm}^{I,\zeta}$ and therefore the electron density $\rho_I^0(\vec{r})$, yielding the eigenvalues $\varepsilon^{(n)}$. The eigenvalues are assigned to the onsite Hamiltonian matrix elements directly, following the neglect of the crystal-field potential, while the wave-functions $\psi_{nlm}^{I,\zeta}$ are used to compute the onsite overlap elements. The wave-functions $\psi_{nlm}^{I,\zeta}$ also define the atomically-localised basis-set of Eq. (2.88):

$$\phi_{nlm}^{I,\zeta} \equiv \psi_{nlm}^{I,\zeta}, \quad (2.167)$$

enabling us to explicitly compute and tabulate the Slater-Koster integrals for the atomic DFT reference densities. This theory would be considered a first-principles method, with the exception of the repulsive pair potential commonly being fitted to better predict forces. Such density-functional tight-binding models are called *semi-empirical*; while the electronic structure follows from first principles, the pair potential is in practice described by an empirical fit.

The solution of the single-atom DFT problem therefore yields the basis set. In practice it was found that orbitals from the free atom could become too delocalised to be of practical use, invalidating the crystal field and two-centre approximations. Eschrig and Bergert in 1978⁷² first suggested the use of a radially confining potential to the atom, for instance of the form:

$$V_C(R) = V_0 \left(\frac{R}{R_0} \right)^n. \quad (2.168)$$

This approach has been widely used in the DFTB community^{52,60,73,74} for $V_0 = 1.0 E_h$ and $n = 2$, only leaving R_0 as a free optimisation parameter. Horsfield and Kenny in 2000⁷⁵ formulated a first-principles DFTB model with polarisation orbitals, using $V_0 = 1.0 E_h$ and $n = 6$.

The semi-empirical approach has the major advantage over the empirical method that it grants direct access to the underlying orbitals, the electron density, and the separate contributions to the Hamiltonian matrix elements like the kinetic energy or Kohn-Sham potential. It is trivial to introduce interactions between new atomic species by applying this scheme. Merely the repulsive pair-potentials remain to be fitted. Despite these benefits, the creation of tight-binding models still requires a significant amount of human involvement. We show this by example in section 4.1.

2.5 Summary

In this chapter we have given an introduction to density-functional theory. We presented a derivation of the density-functional tight binding method, which is an approximate electronic structure framework that can be implemented as a first-principles, semi-empirical, or fully empirical method. The approximations inherent in density-functional tight binding theory allow us to save significantly on computational effort, while still offering a quantum-mechanical description of the system. The trade-off however is that the empirical, and to some extent the semi-empirical, tight binding methods require a parametrisation chosen specific to the problem at hand. We shall in the following section present an extension to the density-functional tight binding model aimed to improve the description of electrostatic and electrodynamic response to external electric fields.

Non-self-consistent density-functional tight binding, as outlined in Sec. 2.4, is capable of predicting many ground-state properties correctly. However, the inclusion of self-consistent electrostatics is required for an accurate description of non-stationary states. Current DFTB models include self-consistent electrostatics by considering the atomic density variation $\delta\rho_I(\vec{r} - \vec{R}_I)$ as spherically symmetric around $\vec{R}_I$. While these so-called *self-charge-consistent* models (SCC-DFTB) offer a basic description of charge transfer, they are also severely limited; this becomes particularly clear when strong external fields are involved, as is the case in ultrafast experiments. Various empirical extensions to tight binding with a self-consistent description of ion polarisability have previously been formulated and tested, such as the polarisable-ion tight-binding model,^{76,77} or parametrically extended DFTB^{78–81} models.

We present a systematically improvable model derived from first-principles within the DFTB formalism. We have developed a generalised self-multipole-consistent model, allowing us to treat the self-consistent electrostatics with significantly improved accuracy. This is achieved by multipole expansion of the density variation into electrostatically interacting Gaussian distributions, which is why we call this method Gaussian tight binding (GTB). This multipole framework is the natural extension of the widely used SCC-DFTB model to a more generalised description without introducing any additional empirical parameters. The leading monopole order recovers the SCC-DFTB model, while the addition of higher dipole and quadrupole terms leads to an overall improved picture of the static and time-dependent electronic response.

The methodology presented here, including the solution of the electrostatic integrals as

presented in section 3.5, is implemented in the PLATO tight binding software, completely replacing the previously self-charge-consistent formulation of electrostatic energy, force, and field-coupling with its self-multipole-consistent equivalent.

3.1 Limitations of density-functional tight binding

We shall briefly recapture the major approximations underlying self-charge-consistent tight binding, and how they may affect the accuracy when applied to ultrafast dynamics simulations in comparison to time-dependent Kohn-Sham theory.

1. **Series expansion in density.** The Kohn-Sham energy is expanded to second order in the density variation $\delta\rho$ with respect to the reference density ρ^0 . As with any series expansion, this expression is only accurate if the expansion variable $\delta\rho$ remains small relative to the reference ρ^0 . This seems to be the case in the majority of covalently bound systems. Issues will naturally arise if the electron density variation becomes strongly localised, for instance in protonation reactions.⁸² Recent developments on a third-order expansion in $\delta\rho$ demonstrated strongly improved protonation energies and higher transferability.⁵² We expect a similar issue to arise for molecules ionised by strong fields. A localised electron hole equally represents a large, negative density variation and could hence lead to inaccuracies due to the series expansion.
2. **Two-center approximation.** From Eq. (2.116), the matrix element for the static exchange-correlation potential is approximated as:

$$V_{I\alpha J\beta}^{XC}[\rho^0] \approx V_{I\alpha J\beta}^{2C-XC}[\rho^0] = \begin{cases} \langle \phi_{I\alpha} | v_{XC}[\rho_I^0 + \rho_J^0] | \phi_{J\beta} \rangle & I \neq J \\ \langle \phi_{I\alpha} | v_{XC}[\rho_I^0] | \phi_{I\beta} \rangle & I = J. \end{cases} \quad (3.1)$$

The matrix elements for the static Hartree potential are approximated similarly in Eq. (2.113). We effectively neglect the influence of all other densities ρ_K^0 , for $K \neq I$ or J , to the neutral atom and exchange-correlation interactions. Tight binding schemes incorporating these additional three-centre and crystal field contributions have shown improved transferability and band-structures by comparison with density-functional theory.^{83–86} The evaluation of three-centre terms takes additional computational time and is difficult to implement, hence we shall be careful to validate our two-centre model for molecular systems.

3. **Approximate self-consistency.** The self-consistent contribution to the electronic energy is approximated as

$$E_{KS}^{scf}[\rho] \approx E_{TB}^{scf}[\rho] = E_{Ha}^{var}[\delta\rho] - \int v_{Ha}^{var}[\delta\rho]\rho(\vec{r})d^3r \quad (3.2)$$

from Eq. (2.121), while the self-consistent contribution to the Kohn-Sham potential is similarly approximated as

$$\hat{H}_{KS}^{scf}[\rho] \approx \hat{H}_{TB}^{scf}[\rho] = v_{Ha}^{var}[\delta\rho] \quad (3.3)$$

from Eq. (2.126). The self-consistent tight-binding contributions are for one characterised by the neglect of exchange-correlation terms, and secondly, by the use of an approximate Hartree energy and potential.* The accuracy of this approximation is mostly determined by the quality of the Hartree approximation, as it can be reasoned that the exchange-correlation potential does not play a significant role. A commonly used approach is the self-charge-consistent DFTB model, in which the density variation of an atomic site is considered as spherically symmetric. The variational electron density can hence redistribute amongst the ionic sites, but is not able to deviate from the spherical shape and polarise. Self-charge-consistent models show therefore show an erroneous response to external fields.

4. **Minimal basis sets.** Strong electric fields are capable of inducing large molecular dipole moments. A single-valence basis set might be insufficient to accurately describe polarisation effects. Small basis sets furthermore offer an inaccurate description of the unoccupied Kohn-Sham orbitals, as they are commonly optimised to accurately reproduce ground-state properties. We hence expect excited states to be poorly described in a single-valence basis set. Strongly localised basis sets are also unable to describe ionisation in strong fields, our theory is therefore limited to field strengths below which significant ionisation occurs.

We shall in the following address the self-consistent Hartree approximation and the minimal basis set, points 3 and 4. Higher order expansions of the Kohn-Sham energy and three-centre terms might also play an important role, however we shall not consider these in the present work. We refer to the work of Giese and York⁷⁸ for a systematic investigation of the density-functional tight binding approximations. Our model presented in the following is based on an extension of standard DFTB, and shall therefore be carefully validated in comparison with standard density-functional theory.

*Some self-consistent schemes may indirectly take exchange-correlation contributions into account by modifying the variational onsite Hartree contributions.

3.2 Multipole expansion

We present here a computationally efficient approximation to the self-consistent Hartree energy based on a multipole expansion of the atomic densities. The multipole expansion framework offers a natural extension to the self-charge-consistent tight-binding models in the sense that we now not only consider charge density monopoles, but also charge density dipoles, and beyond if required.

3.2.1 Electron density moments

Consider the variational Hartree energy from Eq. (2.130):

$$E_{Ha}^{var}[\rho] = \frac{e^2}{8\pi\epsilon_0} \sum_{IJ} \int \frac{\delta\rho_I(\vec{r})\delta\rho_J(\vec{r}')}{||\vec{r} - \vec{r}'||} d^3r d^3r'. \quad (3.4)$$

There are several established ways to reduce the computational load, for instance by Resolution of the Identity approximation or by density fitting.⁸⁷ We want to capture the essential physics of electrostatic interaction, while keeping the computational time to a minimum. Similar to Elstner et al.,⁶⁰ we employ an expansion into spherical harmonic functions. As we have previously done in section 2.4.2.2 in our definition of the basis set, we again employ real cubic harmonics K_{lm} to avoid using a complex basis set:

$$\begin{aligned} K_{l,0}(r, \theta, \phi) &= \sqrt{\frac{4\pi}{2l+1}} r^l Y_l^0(\theta, \phi) \\ K_{l,2m}(r, \theta, \phi) &= -i\sqrt{\frac{2\pi}{2l+1}} r^l ((-1)^m Y_l^m(\theta, \phi) - Y_l^{-m}(\theta, \phi)) \\ K_{l,2m-1}(r, \theta, \phi) &= \sqrt{\frac{2\pi}{2l+1}} r^l ((-1)^m Y_l^m(\theta, \phi) + Y_l^{-m}(\theta, \phi)), \end{aligned} \quad (3.5)$$

where Y_l^m are spherical harmonics of order l and degree m , with $-l \leq m \leq l$. We retain the convention $\vec{r} = (K_{10}, K_{11}, K_{12})^T = (z, x, y)^T$. We express the harmonics in Cartesian coordinates to make integration easier, see table 2.1. Note that real cubic harmonics follow the orthogonality condition:

$$\int K_{lm}(\vec{r}) K_{l'm'}(\vec{r}) d\Omega = \delta_{ll'} \delta_{mm'}, \quad (3.6)$$

where the integral is taken over the solid angle: $d\Omega = \sin\theta d\theta d\phi$. The density variation is now expressed as a series of radial and angular components by a multipole expansion:

$$\delta\rho_I(\vec{r} - \vec{R}_I) = \sum_{lm} a_{Ilm} (||\vec{r} - \vec{R}_I||) K_{lm}(\vec{r} - \vec{R}_I), \quad (3.7)$$

where $\{l, m\}$ are the multipole coefficients of the real cubic harmonics $K_{lm}(\vec{r})$, and $a_{Ilm}(r)$ is the radial distribution function of the electron density associated with the ionic site

I . We wish to express $a_{I lm}(r)$ by a set of radial functions $f_{I lm}(r)$ for which there is a straight-forward integrable solution of the electrostatic integral of Eq. (3.4). We approach this problem by defining the electron density moments $Q_{I lm}$ as the expansion coefficients of the radial functions $f_{I lm}(r)$:

$$\delta\rho_I(\vec{r} - \vec{R}_I) = \sum_{lm} Q_{I lm} f_{I lm}(|\vec{r} - \vec{R}_I|) K_{lm}(\vec{r} - \vec{R}_I). \quad (3.8)$$

Here we have defined the electron density moments $Q_{I lm}$ in terms of the cubic harmonics:

$$Q_{I lm} = \int \delta\rho_I(\vec{r} - \vec{R}_I) K_{lm}(\vec{r} - \vec{R}_I) d^3r. \quad (3.9)$$

Using $\delta\rho_I = \rho_I - \rho_I^0$ and the definition for $\rho(\vec{r})$ from Eq. (2.90), we find:

$$Q_{I lm} = -Z_I \delta_{l0} \delta_{m0} + \sum_{\alpha J \beta} \rho_{I \alpha J \beta} \int \phi_{I \alpha}(\vec{r} - \vec{R}_I) K_{lm}(\vec{r} - \vec{R}_I) \phi_{J \beta}(\vec{r} - \vec{R}_J) d^3r. \quad (3.10)$$

The nuclear charge number Z_I here comes from the integration of $\int \rho_0^I(\vec{r}) d^3r = Z_I$. We define the multipole integrals $M_{I \alpha J \beta}^{lm}$ as:

$$M_{I \alpha J \beta}^{lm} = \int \phi_{I \alpha}(\vec{r}) K_{lm}(\vec{r}) \phi_{J \beta}(\vec{r} - \vec{R}_{IJ}) d^3r, \quad (3.11)$$

where $\vec{R}_{IJ} = \vec{R}_I - \vec{R}_J$. We also note that the monopole moment is equal to the overlap matrix: $M_{I \alpha J \beta}^{00} = S_{I \alpha J \beta}$. This yields a compact expression for the electron density moment $Q_{I lm}$:

$$Q_{I lm} = -Z_I \delta_{l0} \delta_{m0} + \sum_{\alpha J \beta} \rho_{I \alpha J \beta} M_{I \alpha J \beta}^{lm}. \quad (3.12)$$

It is important to note that the multipole moments $M_{I \alpha J \beta}^{lm}$ correspond to a multipole expansion centred on the ionic site I . The moments are hence generally not symmetric with respect to an inversion of indices: $M_{I \alpha J \beta}^{lm} \neq M_{J \beta I \alpha}^{lm}$, but can easily be transformed into one-another. We refer to section A.3 in the appendix for a set of expressions relating $M_{J \beta I \alpha}^{lm}$ and $M_{I \alpha J \beta}^{lm}$, as well as their gradients, to one another. Furthermore we call $Q_{I lm}$ electron density moments, but they are strictly speaking electron density *variation* moments, as we have defined them in terms of the density variation $\delta\rho_I = \rho_I - \rho_I^0$. An isolated, unperturbed atom will hence have all moments $Q_{I lm}$ equal to zero.

Let us now return to Eq. (3.8). The substitution at this point is still exact. We have merely factored out the electron density moments $Q_{I lm}$ out of the radial distribution function $a_{I lm}$, as the density moments give us an intuitive description of the electron density distribution. It is also clear that as a consequence our radial functions $f_{I lm}(r)$ need to be normalised. We find the normalisation condition for $f_{I lm}$ by substituting the

variational density (3.8) into the density moments (3.9) and applying the orthogonality condition for the solid harmonics:

$$\int f_{Ilm}(|\vec{r}|) |K_{lm}(\vec{r})|^2 d^3r = 1. \quad (3.13)$$

The variational density (3.8) is now substituted into the second order correction of the Hartree energy of Eq. (3.4), using the convention $\vec{r}_A = \vec{r} - \vec{R}_A$:

$$E_{Ha}^{var}[\rho] = \frac{e^2}{8\pi\epsilon_0} \sum_{\substack{Ilm \\ J'l'm'}} Q_{Ilm} Q_{J'l'm'} \cdot \int \frac{f_{Ilm}(|\vec{r}_I|) K_{lm}(\vec{r}_I) f_{J'l'm'}(|\vec{r}'_J|) K_{l'm'}(\vec{r}'_J)}{|\vec{r} - \vec{r}'|} d^3r d^3r'. \quad (3.14)$$

The electrostatic integral is defined as the Madelung structure constant $B_{IlmJ'l'm'}$:

$$B_{Ilm,J'l'm'} = \frac{e^2}{4\pi\epsilon_0} \int \frac{f_{Ilm}(|\vec{r}_I|) K_{lm}(\vec{r}_I) f_{J'l'm'}(|\vec{r}'_J|) K_{l'm'}(\vec{r}'_J)}{|\vec{r} - \vec{r}'|} d^3r d^3r', \quad (3.15)$$

leading to the compact expression:

$$E_{Ha}^{var}[\rho] = \frac{1}{2} \sum_{\substack{Ilm \\ J'l'm'}} Q_{Ilm} Q_{J'l'm'} B_{Ilm,J'l'm'}. \quad (3.16)$$

Note that the density moments Q_{Ilm} depend on the density and the ionic coordinates, while the Madelung matrix $B_{Ilm,J'l'm'}$ only depends on the ionic coordinates. This formalism enables us to express $E_{Ha}^{var}[\rho]$ as a function of the electron density moments Q_{Ilm} (3.9). The total energy can hence be self-consistently minimized with respect to the moments Q_{Ilm} , which are functionals of the electron density due to their dependence on the density matrix $\rho_{I\alpha J\beta}$ in Eq. (3.12).

3.2.2 Self-consistent-field Hamiltonian

We are left to find the potential $v_{Ha}^{var}[\rho]$ of the variational Hartree energy $E_{Ha}^{var}[\rho]$. Note that in the previous Sec. 3.2.1 we have defined the charge density moments Q_{Ilm} both in terms of the atomic density variation $\delta\rho_I(\vec{r} - \vec{R}_I)$ in Eq. (3.9), and in terms of the density matrix elements $\rho_{I\alpha J\beta}$ in Eq. (3.12). We are left in a minor dilemma; the variational principle considers the variation with respect to the complete density $\rho(\vec{r})$, not its atomic constituents $\rho_I(\vec{r} - \vec{R}_I)$ which we have defined via the density matrix in Eq. (2.100). One could of course formulate a variational principle in terms of the density matrix, but we shall present here an alternative approach.

3.2.2.1 Density mask function

We approach this problem by applying a work-around, offering an alternative definition of the atomic density variation:

$$\rho_I(\vec{r} - \vec{R}_I) = \delta\rho(\vec{r} - \vec{R}_I) + \rho_I^0(\vec{r} - \vec{R}_I) = \rho(\vec{r})\Omega^I(\vec{r} - \vec{R}_I) + \rho_I^0(\vec{r} - \vec{R}_I) \quad (3.17)$$

where $\Omega^I(\vec{r} - \vec{R}_I)$ is a mask function, weighting parts of the density such that we arrive at a definition of the atomic density consistent with Eq. (2.100). This allows us to express the charge density moments (3.9) as a functional of the total density:

$$Q_{Ilm}[\rho] = \int \left(\rho(\vec{r})\Omega^I(\vec{r} - \vec{R}_I) - \rho_I^0(\vec{r} - \vec{R}_I) \right) K_{lm}(\vec{r} - \vec{R}_I) d^3r. \quad (3.18)$$

We shall now further characterise $\Omega^I(\vec{r} - \vec{R}_I)$. First, the above expression can be simplified under the assumption that the atomic reference density $\rho_0^I(\vec{r} - \vec{R}_I)$ is spherically symmetric. We apply the charge-neutrality condition of Eq. (2.102):

$$Q_{Ilm}[\rho] = \int \rho(\vec{r})\Omega^I(\vec{r} - \vec{R}_I) K_{lm}(\vec{r} - \vec{R}_I) d^3r - Z_I \delta_{l0} \delta_{m0}. \quad (3.19)$$

Next we express the density $\rho(\vec{r})$ in terms of the local basis set (2.100), and equate it with the previously derived expression for Q_{Ilm} in terms of $\rho_{I\alpha J\beta}$ (3.12):

$$Q_{Ilm}[\rho] \equiv Q_{Ilm}(\rho_{I\alpha J\beta}), \quad (3.20)$$

leading to:

$$\begin{aligned} & \sum_{K\alpha J\beta} \rho_{K\alpha J\beta} \int \phi_{K\alpha}(\vec{r} - \vec{R}_K) \Omega^I(\vec{r} - \vec{R}_I) K_{lm}(\vec{r} - \vec{R}_I) \phi_{J\beta}(\vec{r} - \vec{R}_J) d^3r - Z_I \delta_{l0} \delta_{m0} \\ & \equiv \sum_{\alpha J\beta} \rho_{I\alpha J\beta} \int \phi_{I\alpha}(\vec{r} - \vec{R}_I) K_{lm}(\vec{r} - \vec{R}_I) \phi_{J\beta}(\vec{r} - \vec{R}_J) d^3r - Z_I \delta_{l0} \delta_{m0}. \end{aligned} \quad (3.21)$$

For the above expression to be true for all $\{I, l, m\}$, it must hold:

$$\begin{aligned} & \int \phi_{K\alpha}(\vec{r} - \vec{R}_K) \Omega^I(\vec{r} - \vec{R}_I) K_{lm}(\vec{r} - \vec{R}_I) \phi_{J\beta}(\vec{r} - \vec{R}_J) d^3r \\ & = \delta_{IK} \int \phi_{I\alpha}(\vec{r} - \vec{R}_I) K_{lm}(\vec{r} - \vec{R}_I) \phi_{J\beta}(\vec{r} - \vec{R}_J) d^3r \\ & = \delta_{IK} M_{I\alpha J\beta}^{lm}. \end{aligned} \quad (3.22)$$

This relation allows us to link the mask function to the multipole moments. We can now define the functional derivative trivially:

$$\frac{\delta Q_{Ilm}[\rho]}{\delta \rho(\vec{r})} = \Omega^I(\vec{r} - \vec{R}_I) K_{lm}(\vec{r} - \vec{R}_I). \quad (3.23)$$

The mask function therefore enables us to express the derivative of our atomically localised density moments Q_{Ilm} with respect to the total electron density $\rho(\vec{r})$. We can now apply the variational principle to our self-consistent equations to arrive at the variational Hamiltonian.

3.2.2.2 Variational Hamiltonian

We have previously defined the density moments as functionals of the density: $Q_{Ilm} \equiv Q_{Ilm}[\rho(\vec{r})]$. The variational Hartree energy of Eq. (3.16) can now be equally expressed as a density functional:

$$E_{Ha}^{var}[\rho] = \frac{1}{2} \sum_{\substack{Klm \\ Ll'm'}} Q_{Klm}[\rho] Q_{Ll'm'}[\rho] B_{Klm, Ll'm'}. \quad (3.24)$$

The summation indices have been changed for clarity with the next steps in mind. We arrive at the variational Hartree potential by taking the functional derivative:

$$v_{Ha}^{var}[\rho] = \frac{\delta E_{Ha}^{var}[\rho]}{\delta \rho(\vec{r})}. \quad (3.25)$$

Reordering the indices and applying Eq. (3.23), we arrive at:

$$\begin{aligned} v_{Ha}^{var}[\rho] &= \frac{1}{2} \sum_{\substack{Klm \\ Ll'm'}} Q_{Klm}[\rho] \left(\frac{\delta Q_{Ll'm'}[\rho]}{\delta \rho(\vec{r})} \right) (B_{Klm, Ll'm'} + B_{Ll'm', Klm}) \\ &= \frac{1}{2} \sum_{\substack{Klm \\ Ll'm'}} Q_{Klm}[\rho] \Omega^L(\vec{r} - \vec{R}_L) K_{l'm'}(\vec{r} - \vec{R}_L) (B_{Klm, Ll'm'} + B_{Ll'm', Klm}). \end{aligned} \quad (3.26)$$

We can now find the matrix elements $V_{I\alpha J\beta}^{Ha-var}[\rho]$ of the self-consistent Hamiltonian, applying the rule of Eq. (3.22):

$$\begin{aligned} V_{I\alpha J\beta}^{Ha-var}[\rho] &= \langle \phi_{I\alpha} | v_{Ha}^{var}[\rho] | \phi_{J\beta} \rangle \\ &= \frac{1}{2} \sum_{\substack{Klm \\ Ll'm'}} Q_{Klm}[\rho] \left(\delta_{IL} M_{I\alpha J\beta}^{l'm'} \right) (B_{Klm, Ll'm'} + B_{Ll'm', Klm}) \\ &= \frac{1}{2} \sum_{\substack{Klm \\ l'm'}} Q_{Klm}[\rho] M_{I\alpha J\beta}^{l'm'} (B_{Klm, Il'm'} + B_{Il'm', Klm}). \end{aligned} \quad (3.27)$$

Note that the density mask function does not appear in the final expression. It was merely used to define the differentiation of the atomically localised densities $\rho_I(\vec{r} - \vec{R}_I)$ with respect to the total density $\rho(\vec{r})$. To summarise, the complete tight-binding Hamiltonian matrix of Eq. (2.138) is given by:

$$\begin{aligned} H_{I\alpha J\beta}^{TB}[\rho] &= H_{I\alpha J\beta}^{TB}[\rho^0] + V_{I\alpha J\beta}^{Ha-var}[\rho] \\ &= T_{I\alpha J\beta}^{KS} + V_{I\alpha J\beta}^{2C-NA}[\rho^0] + V_{I\alpha J\beta}^{2C-XC}[\rho^0] + V_{I\alpha J\beta}^{Ha-var}[\rho] + V_{I\alpha J\beta}^{ef} \end{aligned} \quad (3.28)$$

Note that at this stage the variational Hartree energy is still exact, assuming the multipole expansion is taken to infinite order. We will later introduce approximations to the Madelung matrix $B_{Ilm,Jl'm'}$ to make this expression computationally efficient.

3.2.2.3 Variational double-counting energy

It is left to derive the contribution of the variational Hartree energy to the double-counting energy $E_{TB}^{scf}[\rho]$. We have previously derived the following expression in Eq. (2.125):

$$E_{TB}^{scf}[\rho] = E_{Ha}^{var}[\rho] - \int v_{Ha}^{var}[\rho] \rho(\vec{r}) d^3r. \quad (3.29)$$

Let us first consider the integral over the variational Hartree potential, defined as of Eq. (3.26):

$$\begin{aligned} \int v_{Ha}^{var}[\rho] \rho(\vec{r}) d^3r &= \frac{1}{2} \sum_{\substack{Klm \\ Ll'm'}} Q_{Klm}[\rho] (B_{Klm,Ll'm'} + B_{Ll'm',Klm}) \\ &\quad \cdot \int \Omega^L(\vec{r} - \vec{R}_L) K_{l'm'}(\vec{r} - \vec{R}_L) \rho(\vec{r}) d^3r. \end{aligned} \quad (3.30)$$

Applying the definition of the mask function (3.19), we can evaluate the integrals and arrive at:

$$\begin{aligned} \int v_{Ha}^{var}[\rho] \rho(\vec{r}) d^3r &= \frac{1}{2} \sum_{\substack{Klm \\ Ll'm'}} Q_{Klm}[\rho] (B_{Klm,Ll'm'} + B_{Ll'm',Klm}) Q_{Ll'm'}[\rho] \\ &\quad + \frac{1}{2} \sum_{\substack{Klm \\ Ll'm'}} Q_{Klm}[\rho] (B_{Klm,Ll'm'} + B_{Ll'm',Klm}) (\delta_{l'0} \delta_{m'0} Z_L), \end{aligned} \quad (3.31)$$

which simplifies further to:

$$\begin{aligned} \int v_{Ha}^{var}[\rho] \rho(\vec{r}) d^3r &= \frac{1}{2} \sum_{\substack{Klm \\ Ll'm'}} Q_{Klm}[\rho] (B_{Klm,Ll'm'} + B_{Ll'm',Klm}) Q_{Ll'm'}[\rho] \\ &\quad + \frac{1}{2} \sum_{\substack{Klm \\ L}} Q_{Klm}[\rho] (B_{Klm,L00} + B_{L00,Klm}) Z_L. \end{aligned} \quad (3.32)$$

The variational double-counting energy is finally found as:

$$E_{TB}^{scf}[\rho] = -E_{Ha}^{var}[\rho] - \frac{1}{2} \sum_{\substack{Klm \\ L}} Q_{Klm}[\rho] Z_L (B_{Klm,L00} + B_{L00,Klm}). \quad (3.33)$$

3.2.2.4 Electric field dipole interaction

We have formulated a model for the electrostatic interaction by multipole expansion. This scheme requires the computation of the multipole moments $M_{I\alpha J\beta}^{lm}$, which is to great

benefit for the electric field interaction as derived in Sec. 2.4.4. Let us here revisit the matrix elements for the electric dipole field of Eq. (2.137).

$$V_{I\alpha J\beta}^{ef} = -e \sum_{\nu} (\vec{E})_{\nu} \int \phi_{I\alpha}(\vec{r} - \vec{R}_I) (\vec{r})_{\nu} \phi_{J\beta}(\vec{r} - \vec{R}_J) d^3r. \quad (3.34)$$

Using the expansion $\vec{r} = (\vec{r} - \vec{R}_I) + \vec{R}_I$, the expression can be recast into the following:

$$V_{I\alpha J\beta}^{ef} = -e \sum_{\nu} (\vec{E})_{\nu} \left(M_{I\alpha J\beta}^{1\nu} + (\vec{R}_I)_{\nu} M_{I\alpha J\beta}^{00} \right). \quad (3.35)$$

Note that $M_{I\alpha J\beta}^{00} \equiv S_{I\alpha J\beta}$. This expression shows clearly that the dipole moments $M_{I\alpha J\beta}^{1\nu}$ are required for an exact treatment of electric field coupling. The electric field coupling can also be approximated under the neglect of the dipole moments $M_{I\alpha J\beta}^{1\nu} \approx 0$ as is commonly done in SCC-DFTB. This approximation therefore completely removes ionic polarisation, which we will show later to lead to large errors in polarisability calculations.

3.2.3 Summary

The total self-consistent tight-binding energy as of Eq. (2.127) is given by:

$$E^{TB}[\rho] = 2 \sum_n f_n \varepsilon^{(n)} + E_{TB}^{scf}[\rho] + E_{rep}[\{\vec{R}_I\}], \quad (3.36)$$

where $E_{TB}^{scf}[\rho]$ follows from Eq. (3.33):

$$E_{TB}^{scf}[\rho] = -E_{Ha}^{var}[\rho] - \frac{1}{2} \sum_{\substack{Klm \\ L}} Q_{Klm}[\rho] Z_L (B_{Klm,L00} + B_{L00,Klm}), \quad (3.37)$$

and $E_{Ha}^{var}[\rho]$ follows from Eq. (3.16):

$$E_{Ha}^{var}[\rho] = \frac{1}{2} \sum_{\substack{Ilm \\ J'l'm'}} Q_{Ilm} Q_{J'l'm'} B_{Ilm,J'l'm'}. \quad (3.38)$$

The repulsive energy $E_{rep}[\{\vec{R}_I\}]$ is approximated by an empirically parametrised pair-potential as of Eq. (2.119):

$$E_{rep}[\{\vec{R}_I\}] = \sum_{I \neq J} U_{rep}(R_{IJ}). \quad (3.39)$$

The eigenvalues and the electron density are found by solving the eigensystem of Eq. (2.99):

$$\sum_{J\beta} H_{I\alpha J\beta}^{TB}[\rho] c_{J\beta}^{(n)} = \varepsilon^{(n)} \sum_{J\beta} S_{I\alpha J\beta} c_{J\beta}^{(n)}, \quad (3.40)$$

where the self-consistent tight-binding Hamiltonian matrix elements $H_{I\alpha J\beta}^{TB}[\rho]$ are defined in Eq. (3.28), the overlap matrix elements $S_{I\alpha J\beta}$ are defined in Eq. (2.98), and the eigenvectors $\{c_{J\beta}^{(n)}\}$ are defined in Eq. (2.86). Once the ground-state eigenvectors have been found after self-consistent minimisation, the eigenvalues can also be retrieved from:

$$\varepsilon^{(n)} = \langle \Psi^{(n)} | \hat{H}^{TB}[\rho] | \Psi^{(n)} \rangle. \quad (3.41)$$

Note also that the multipole expansion allows for an exact treatment of electric-field coupling as in Eq. (3.52), given that the dipole matrix elements $M_{I\alpha J\beta}^{1\nu}$ are explicitly computed.

3.3 Self-consistent-field tight-binding force

We have previously derived the total force acting on the ion at site I in section 2.4.5, expressed as a static $\vec{F}_K^0[\rho^0]$ and variational force $\vec{F}_K^{scf}[\rho]$:

$$\vec{F}_K[\rho] = \vec{F}_K^0[\rho^0] + \vec{F}_K^{scf}[\rho], \quad (3.42)$$

where $\vec{F}_K^0[\rho^0]$ is given by Eq. (2.158), and $\vec{F}_K^{scf}[\rho]$ by:

$$\vec{F}_K^{scf}[\rho] = -\vec{\nabla}_{R_K} E_{Ha}^{var}[\rho]. \quad (3.43)$$

Consider now our variational Hartree energy as expressed in the multipole expansion:

$$E_{Ha}^{var}[\rho] = \frac{1}{2} \sum_{\substack{Ilm \\ J'l'm'}} Q_{Ilm} Q_{J'l'm'} B_{Ilm, J'l'm'}. \quad (3.44)$$

The self-consistent force contribution to the ion on site K is given as:

$$\begin{aligned} \vec{F}_K^{scf} &= -\vec{\nabla}_{R_K} E_{Ha}^{var}[\rho] \\ &= -\frac{1}{2} \sum_{\substack{Ilm \\ J'l'm'}} Q_{Ilm} \left(\vec{\nabla}_{R_K} Q_{J'l'm'} \right) (B_{Ilm, J'l'm'} + B_{J'l'm', Ilm}) \\ &\quad - \frac{1}{2} \sum_{\substack{Ilm \\ J'l'm'}} Q_{Ilm} Q_{J'l'm'} \left(\vec{\nabla}_{R_K} B_{Ilm, J'l'm'} \right). \end{aligned} \quad (3.45)$$

We have here neglected the gradient of the density matrix as in section 2.4.5, seeing that we consider the system to be in an eigenstate of the Hamiltonian. The gradient of the energy with respect to the density is therefore already zero. We shall next find the analytic expression for the derivatives, where the electron density moments are given by Eq. (3.12):

$$\begin{aligned} \vec{\nabla}_{R_K} Q_{Ilm} &= \vec{\nabla}_{R_K} \left(-Z_I \delta_{l0} \delta_{m0} + \sum_{\alpha J\beta} \rho_{I\alpha J\beta} M_{I\alpha J\beta}^{lm} \right) \\ &= \sum_{\alpha J\beta} \rho_{I\alpha J\beta} \vec{\nabla}_{R_K} M_{I\alpha J\beta}^{lm} \end{aligned} \quad (3.46)$$

Using the definition of the multipole moments from Eq. (3.11), the gradient is found as:

$$\begin{aligned}\vec{\nabla}_{R_K} M_{I\alpha J\beta}^{lm}(\vec{R}_{IJ}) &= (\delta_{KI} - \delta_{KJ}) \vec{\nabla}_{R_{IJ}} M_{I\alpha J\beta}^{lm} \\ &\equiv (\delta_{KI} - \delta_{KJ}) d\vec{M}_{I\alpha J\beta}^{lm}.\end{aligned}\quad (3.47)$$

Here we have defined the derivative of the moment as $d\vec{M}_{I\alpha J\beta}^{lm} = \vec{\nabla}_{R_{IJ}} M_{I\alpha J\beta}^{lm}$. Substituting Eq. (3.47) into Eq. (3.46), we arrive at:

$$\vec{\nabla}_{R_K} Q_{Ilm} = \sum_{\alpha J\beta} \rho_{I\alpha J\beta} (\delta_{KI} - \delta_{KJ}) d\vec{M}_{I\alpha J\beta}^{lm}. \quad (3.48)$$

We equally find the derivative of the Madelung matrix:

$$\vec{\nabla}_{R_K} B_{Ilm, J'l'm'} = (\delta_{KI} - \delta_{KJ}) d\vec{B}_{Ilm, J'l'm'}, \quad (3.49)$$

where $d\vec{B}_{Ilm, J'l'm'} = \vec{\nabla}_{R_{IJ}} \vec{B}_{Ilm, J'l'm'}(\vec{R}_{IJ})$. Substituting Eq. (3.48) and Eq. (3.49) into Eq. (3.45), we receive the self-consistent force contribution after several simplification steps:

$$\begin{aligned}\vec{F}_K^{scf} &= \frac{1}{2} \sum_{I\alpha J\beta} \sum_{\substack{lm \\ l'm'}} Q_{Ilm} \rho_{K\alpha J\beta} \cdot \left(d\vec{M}_{J\beta K\alpha}^{l'm'} (B_{Ilm, J'l'm'} + B_{J'l'm', Ilm}) \right. \\ &\quad \left. - d\vec{M}_{K\alpha J\beta}^{l'm'} (B_{Ilm, K'l'm'} + B_{K'l'm', Ilm}) \right) \\ &\quad + \frac{1}{2} \sum_I \sum_{\substack{lm \\ l'm'}} Q_{Ilm} Q_{K'l'm'} \left(d\vec{B}_{Ilm, K'l'm'} - d\vec{B}_{K'l'm', Ilm} \right).\end{aligned}\quad (3.50)$$

This self-consistent force contributes directly to the force of the static reference densities. Calculating the force requires knowledge of the multipole derivatives $d\vec{M}_{I\alpha J\beta}^{lm}$ and the Madelung derivatives $d\vec{B}_{Ilm, Jlm}$, which we shall introduce in the implementation section 3.5, as well as the total ground-state density $\rho(\vec{r})$. The self-consistent solution of the eigensystem therefore necessarily precedes the force calculation.

3.3.1 External field forces

The multipole expansion enables us to account for anisotropy in the electron density variation. This becomes particularly important for the coupling with external fields, as the ionic dipole moments interact directly with constant fields. We shall now evaluate the external field coupling force of Eq. (2.157) for the case of a dipole field:

$$\vec{F}_K^{ef-ele} = - \sum_{I\alpha J\beta} \rho_{I\alpha J\beta} \vec{\nabla}_{R_K} V_{I\alpha J\beta}^{ef}, \quad (3.51)$$

where the matrix elements $V_{I\alpha J\beta}^{ef}$ are defined as of Eq. (3.52):

$$V_{I\alpha J\beta}^{ef} = -e \sum_{\nu} \left(\vec{E} \right)_{\nu} \left(M_{I\alpha J\beta}^{1\nu} + \left(\vec{R}_I \right)_{\nu} M_{I\alpha J\beta}^{00} \right). \quad (3.52)$$

Using the differentiation rule of Eq. (3.47):

$$\vec{\nabla}_{R_K} M_{I\alpha J\beta}^{lm}(\vec{R}_{IJ}) = (\delta_{KI} - \delta_{KJ}) d\vec{M}_{I\alpha J\beta}^{lm}, \quad (3.53)$$

we proceed to take the derivative, and after a few steps arrive at the expression:

$$\begin{aligned} \vec{F}_K^{ef-ele} = e \sum_{\alpha J\beta} \rho_{K\alpha J\beta} \left(\sum_{\nu} E_{\nu} \left(d\vec{M}_{K\alpha J\beta}^{1\nu} - d\vec{M}_{J\beta K\alpha}^{1\nu} \right) + \vec{E} M_{K\alpha J\beta}^{00} \right. \\ \left. + \left(\vec{E} \cdot \vec{R}_K \right) d\vec{M}_{K\alpha J\beta}^{00} - \left(\vec{E} \cdot \vec{R}_J \right) d\vec{M}_{J\beta K\alpha}^{00} \right). \end{aligned} \quad (3.54)$$

3.4 Gaussian approximation

The electrostatic multipole formalism derived so far is exact. While we have derived the self-consistent expressions for the electrostatic multipole energy, Hamiltonian, and forces, we have not yet made any attempts at making the solution of the multipole and Madelung integrals more tractable. We will here introduce the Gaussian approximation, in which the electron density radial functions are described by single Gaussians, severely reducing the computational effort to solve compute the Madelung matrix at the cost of accuracy.

3.4.1 Scaling considerations

The multipole expression of the Hartree energy in Eq. (3.16)

$$E_{Ha}[\rho] = \frac{1}{2} \sum_{\substack{Ilm \\ J'l'm'}} Q_{Ilm} Q_{J'l'm'} B_{Ilm, J'l'm'} \quad (3.55)$$

already scales much more favourably than the original expression of Eq. (2.130). Here the total number of products is proportional to $\mathcal{O}(N_{multipoles}^2 N_{atom}^2)$ as opposed to the previous $\mathcal{O}(N_{basis}^4)$. N_{atom} is certainly smaller than N_{basis} , by about an order of magnitude, while $N_{multipole}$ depends on the chosen multipole expansion order: for up to monopole order it is 1, for up to dipole order it is 4, and for up to quadrupole order it is 9. Consider for instance a system of 20 atoms with 4 basis functions each. The number of total Hartree energy products is $(20 \cdot 4)^4 = 4 \times 10^7$, while the number of multipole $l = 1$ products is only $(20 \cdot 4)^2 = 6 \times 10^3$. Needless to say, this is a much smaller amount of integrals. Note that as this estimation is before symmetry reductions and distance truncations, one would in practice need to evaluate significantly fewer Hartree integrals.

Still, many practical solutions avoid taking on the full Hartree integral; the Resolution of Identity approach for instance is conceptually similar to the multipole expansion, reducing the number of integrals by fitting the atomic densities $\rho_I(\vec{r} - \vec{R}_I)$ with an auxiliary basis set. Other methods completely avoid evaluating the Hartree integration in real space, solving it instead numerically in reciprocal space by Fourier transform. We shall illustrate this by example in section 3.5.1.4.

3.4.2 Gaussian radial functions

We remember the density expansion of Eq. (3.8):

$$\delta\rho_I(\vec{r} - \vec{R}_I) = \sum_{lm} Q_{lm} f_{lm}(|\vec{r} - \vec{R}_I|) K_{lm}(\vec{r} - \vec{R}_I), \quad (3.56)$$

and the normalisation condition of Eq. (3.13):

$$\int f_{lm}(|\vec{r}|) |K_{lm}(\vec{r})|^2 d^3r = 1. \quad (3.57)$$

While we could explicitly compute the radial function $f_{lm}(r)$ in terms of the radial density distribution function $a_{lm}(r)$ of Eq. (3.7), we need to remember that the radial functions will be used to evaluate the Madelung integral of Eq. (3.15) after all:

$$B_{lm, l'm'} = \frac{e^2}{4\pi\epsilon_0} \int \frac{f_{lm}(|\vec{r}_I|) K_{lm}(\vec{r}_I) f_{l'm'}(|\vec{r}'_J|) K_{l'm'}(\vec{r}'_J)}{|\vec{r} - \vec{r}'|} d^3r d^3r', \quad (3.58)$$

where we defined $\vec{r}_A = \vec{r} - \vec{R}_A$ for brevity. For this reason it makes sense to take the pragmatic approach and approximate the radial function $f_{lm}(r)$ in such a way that the Madelung integral can be solved analytically in an efficient manner. The quality of this approximation improves the closer $f_{lm}(r)$ matches the true radial distribution function $a_{lm}(r)$. Past work in the self-charge-consistent approximation has shown decaying functions for $f_{lm}(r)$ to perform well.^{60,88} We will show that Gaussian functions in particular lend themselves well to solving the Madelung integral, which motivates us to pursue this approach here. We choose

$$f_{lm}(r) \approx k_{lm} e^{-\alpha_{lm} r^2}, \quad (3.59)$$

where k_{lm} is the normalisation constant introduced to satisfy equation (3.13). The normalisation up to quadrupole order is found as follows:

$$\begin{aligned} k_{I00} &= \left(\frac{\alpha_{I00}}{\pi} \right)^{3/2} \\ k_{I1m} &= 2 \alpha_{I1m} \cdot \left(\frac{\alpha_{I1m}}{\pi} \right)^{3/2} \\ k_{I2m} &= \frac{4}{3} \alpha_{I2m}^2 \cdot \left(\frac{\alpha_{I2m}}{\pi} \right)^{3/2}, \end{aligned} \quad (3.60)$$

or by analytical integration generally as:

$$k_{Ilm} = \frac{2^l}{(2l-1)!!} \frac{(\alpha^{Ilm})^{3/2+l}}{\pi^{3/2}}. \quad (3.61)$$

The constant α_{Ilm} represents the inverse square width of the Gaussian charge distribution associated with site I and angular momentum $\{l, m\}$. In practice we use the same Gaussian width α_I over all momenta for each atomic species, thereby reducing the normalisation constant k_{Ilm} to k_{Il} . This width can be associated with the Hubbard parameter U_I of the atomic species as shown by Elstner et al.⁶⁰ We follow this approach here, using:

$$\alpha_I = \frac{\pi}{8} \left(\frac{U_I}{\hbar c} \right)^2. \quad (3.62)$$

While this value can be calculated from first principles, we leave it as an adjustable parameter and use U_I from the mio-1-1 density-functional tight binding parameter set,⁶⁰ averaged over all angular momenta.

Substituting the Gaussian expression for $f_{Ilm}(r)$ (3.59) into the Madelung integral (3.58), we arrive at the approximate integral:

$$B_{Ilm, J'l'm'} \approx \frac{e^2 k_{Il} k_{J'l'}}{4\pi\epsilon_0} \int \frac{e^{-\alpha_I \|\vec{r}_I\|^2} K_{lm}(\vec{r}_I) e^{-\alpha_J \|\vec{r}'_J\|^2} K_{l'm'}(\vec{r}'_J)}{\|\vec{r} - \vec{r}'\|} d^3r d^3r'. \quad (3.63)$$

3.5 Implementation

We shall in the following outline how to efficiently solve the approximate multipole integrals. Our current implementation constructs the multipole moments on-the-fly explicitly from the Gaussian basis set. While this is not a significant expense for single-point calculations, it represents about 3/4 of the computational effort in time-dependent runs with forces (PLATO implementation). However, we emphasize that the multipole integrals can also be obtained from tabulated, Slater-Koster-like tables. This would likely significantly reduce the overhead associated with constructing the integrals. We furthermore implemented a simple extrapolation scheme that significantly reduces the computational overhead for Ehrenfest dynamics runs, see section 6.2.2.6.

3.5.1 Gaussian electrostatic integrals

Consider now the simplest case, the monopole integral:

$$B_{I00, J00} = \frac{e^2}{4\pi\epsilon_0} k_{I0} k_{J0} \int \frac{e^{-\alpha_I \|\vec{r}_I\|^2} e^{-\alpha_J \|\vec{r}'_J\|^2}}{\|\vec{r} - \vec{r}'\|} d^3r d^3r'. \quad (3.64)$$

The above integral is widely solved in literature. We refer to Helgaker:⁸⁹

$$B_{I00,J00} = \frac{e^2}{4\pi\epsilon_0} \cdot \frac{\operatorname{erf}\left(\sqrt{\frac{\alpha_I\alpha_J}{\alpha_I+\alpha_J}}\|\vec{R}_I - \vec{R}_J\|\right)}{\|\vec{R}_I - \vec{R}_J\|}. \quad (3.65)$$

The monopole integral can be used to compute the higher orders by differentiation. For example,

$$\begin{aligned} \partial_{Z_I} B_{I00,J00} &= \frac{e^2}{4\pi\epsilon_0} k_{I0} k_{J0} \int \frac{\left(\partial_{Z_I} e^{-\alpha_I\|\vec{r}_I\|^2}\right) e^{-\alpha_J\|\vec{r}'_J\|^2}}{\|\vec{r} - \vec{r}'\|} d^3r d^3r' \\ &= \frac{e^2}{4\pi\epsilon_0} k_{I0} k_{J0} \int \frac{2\alpha_I z_I e^{-\alpha_I\|\vec{r}_I\|^2} e^{-\alpha_J\|\vec{r}'_J\|^2}}{\|\vec{r} - \vec{r}'\|} d^3r d^3r' \\ &= B_{I10,J00}. \end{aligned} \quad (3.66)$$

Having solved the monopole integral analytically, we can therefore differentiate $B_{I00,J00}$ with respect to $\vec{R}_I$ and $\vec{R}_J$ to arrive at any higher order of the Madelung matrix. However, care needs to be taken with the quadrupole terms and above; the second order derivatives do not form the quadrupole Madelung matrices in a straight-forward way, but rather need to be formed by a linear combination of derivatives. We shall next outline how to automate this process to any order of $\{l, m, l', m'\}$.

3.5.1.1 Primitive Cartesian electrostatic integrals

We shall in the following borrow heavily from the McMurchie-Davidson scheme for solving Coulomb integrals as outlined by Helgaker.⁸⁹ Consider first that each real cubic harmonic can be expressed as a polynomial in the form of:

$$K_{lm}(\vec{r}_A) = \sum_{tuv}^{t+u+v \leq l} C_{tuv}^{lm} x_A^t y_A^u z_A^v, \quad (3.67)$$

where $\vec{r}_A = \vec{r} - \vec{R}_A$. The electrostatic integral of Eq. (3.63) is therefore given by:

$$B_{Ilm,Jl'm'} = \frac{e^2 k_{Il} k_{Jl'}}{4\pi\epsilon_0} \sum_{\substack{tuv \\ t'u'v'}}^{t+u+v \leq l, t'+u'+v' \leq l'} C_{tuv}^{lm} C_{t'u'v'}^{l'm'} \int \frac{x_I^t y_I^u z_I^v e^{-\alpha_I\|\vec{r}_I\|^2} x_J^{t'} y_J^{u'} z_J^{v'} e^{-\alpha_J\|\vec{r}'_J\|^2}}{\|\vec{r} - \vec{r}'\|} d^3r d^3r'. \quad (3.68)$$

Defining the primitive Cartesian electrostatic integrals as

$$K_{IJ}(\alpha, \beta)_{t'u'v'}^{tuv} = \int \frac{x_I^t y_I^u z_I^v e^{-\alpha\|\vec{r}_I\|^2} x_J^{t'} y_J^{u'} z_J^{v'} e^{-\beta\|\vec{r}'_J\|^2}}{\|\vec{r} - \vec{r}'\|} d^3r d^3r', \quad (3.69)$$

we write Eq. (3.68) in the compact form:

$$B_{Ilm,Jl'm'} = \frac{e^2 k_{Il} k_{Jl'}}{4\pi\epsilon_0} \sum_{\substack{t+u+v \leq l \\ t'u'+v' \leq l'}}^{tuv} C_{tuv}^{lm} C_{t'u'v'}^{l'm'} K_{IJ}(\alpha_I, \alpha_J) |_{t'u'v'}^{tuv}. \quad (3.70)$$

The strategy is clear; first we construct the primitive Cartesian integrals up to order (l, l') . Subsequently we construct the Madelung matrix elements following Eq. (3.70).

3.5.1.2 Electrostatic Hermite integrals

In Quantum-Chemistry methods the primitive Cartesian integrals are commonly constructed from Hermite Gaussians:

$$V_{IJ}(\alpha, \beta) |_{t'u'v'}^{tuv} = \int \frac{\Lambda_{tuv}^I(\alpha) \Lambda_{t'u'v'}^J(\beta)}{||\vec{r} - \vec{r}'||} d^3r d^3r', \quad (3.71)$$

where the Hermite Gaussians are defined as:

$$\begin{aligned} \Lambda_{tuv}^I(\alpha) &= \partial_{R_I^x}^t \partial_{R_I^y}^u \partial_{R_I^z}^v e^{-\alpha ||\vec{r}_I||^2} = \left(\partial_{R_I^x}^t e^{-\alpha x_I^2} \right) \left(\partial_{R_I^y}^u e^{-\alpha y_I^2} \right) \left(\partial_{R_I^z}^v e^{-\alpha z_I^2} \right) \\ &\equiv \Lambda_t^{xI}(\alpha) \Lambda_u^{yI}(\alpha) \Lambda_v^{zI}(\alpha). \end{aligned} \quad (3.72)$$

It is highly beneficial to express the Coulomb integral in terms of Hermite Gaussians, as these can be easily constructed using very efficient recursion relations. We already have found the monopole Hermite Gaussian integral $V_{IJ}(\alpha, \beta) |_{000}^{000}$ in Eq. (3.65) as:

$$V_{IJ}(\alpha, \beta) |_{000}^{000} = \frac{\pi^3}{\alpha^{3/2} \beta^{3/2}} \cdot \frac{\text{erf} \left(\sqrt{\frac{\alpha\beta}{\alpha+\beta}} ||\vec{R}_I - \vec{R}_J|| \right)}{||\vec{R}_I - \vec{R}_J||}. \quad (3.73)$$

All higher orders can now easily be found by differentiating the solution with respect to $\vec{R}_I$ and $\vec{R}_J$. In practice we construct the Hermite Gaussian integrals via the relation:

$$V_{IJ}(\alpha, \beta) |_{t'u'v'}^{tuv} = (-1)^{t+t'+u+u'+v+v'} \frac{2\pi^{5/2}}{\alpha\beta\sqrt{\alpha+\beta}} R_{IJ} |^{t+t',u+u',v+v'}(\alpha, \beta), \quad (3.74)$$

Here $R_{IJ} |^{tuv}(\alpha, \beta)$ is defined as the Hermite integral, given by:

$$R_{IJ} |^{tuv}(\alpha, \beta) = \partial_{R_{IJ}^x}^t \partial_{R_{IJ}^y}^u \partial_{R_{IJ}^z}^v F^0(\alpha\beta(\alpha+\beta)^{-1} ||R_{IJ}||^2), \quad (3.75)$$

where $F^0(x)$ is the incomplete Gamma function:

$$F^0(x) = \int_0^1 e^{-xt^2} dt = \sqrt{\frac{\pi}{4x}} \text{erf}(\sqrt{x}). \quad (3.76)$$

The above expressions can be derived with the Hermite Gaussian recursion relations. We refer here to a complete derivation by Helgaker.⁸⁹ We can now construct the Hermite

Gaussian integrals (3.71) in terms of the Hermite integral (3.75). The Hermite integrals are found by successively differentiating the incomplete Gamma function (3.76). However, we still need to express the primitive Cartesian integrals in terms of the Hermite Gaussian integral. First, consider that every Cartesian integrand $C_{tuv}^I(\alpha) = x_I^t y_I^u z_I^v e^{-\alpha \|\vec{r}_I\|^2}$ can be split up into a product of three components:

$$C_{tuv}^I(\alpha) = \left(x_I^t e^{-\alpha x_I^2}\right) \left(y_I^u e^{-\alpha y_I^2}\right) \left(z_I^v e^{-\alpha z_I^2}\right) \equiv C_t^{xI}(\alpha) C_u^{yI}(\alpha) C_v^{zI}(\alpha). \quad (3.77)$$

Second, the Cartesian components follow the recursion relations with respect to the q -th order derivatives:

$$\partial_a^{(q+1)} C_t^a(\alpha) = 2\alpha \cdot \partial_a^{(q)} C_{t+1}^a(\alpha) - t \cdot \partial_a^{(q)} C_{t-1}^a(\alpha) \quad (3.78)$$

Third, since $C_0^a(\alpha) = \Lambda_0^a(\alpha)$, it is also clear that

$$\partial_a^{(q)} C_0^a(\alpha) = \partial_a^{(q)} \Lambda_0^a(\alpha) \quad (3.79)$$

is valid for all orders q . We can therefore construct the Cartesian components in terms of Hermite components of equal or lower order:

$$C_{tuv}^I(\alpha) = \sum_{\substack{a \leq t, \\ b \leq u, \\ c \leq v}} q_{abc}^{tuv} \cdot \Lambda_{abc}^I(\alpha), \quad (3.80)$$

where q_{abc}^{tuv} is a composite polynomial coefficient that is found using the recursion relations (3.78) and (3.79). This enables us to relate the primitive Coulomb integrals to the solutions of the electrostatic Hermite integrals $V_{IJ}(\alpha, \beta)|_{t'u'v'}^{tuv}$ of Eq. (3.71):

$$K_{IJ}(\alpha, \beta)|_{t'u'v'}^{tuv} = \sum_{\substack{a \leq t \\ b \leq u \\ c \leq v}} \sum_{\substack{a' \leq t' \\ b' \leq u' \\ c' \leq v'}} q_{abc}^{tuv} \cdot q_{a'b'c'}^{t'u'v'} \cdot V_{IJ}(\alpha, \beta)|_{t'u'v'}^{tuv}. \quad (3.81)$$

We define the joint composite variable $q_{abc|a'b'c'}^{tuv|t'u'v'} = q_{abc}^{tuv} \cdot q_{a'b'c'}^{t'u'v'}$ and abbreviate the summation indices as $\{abc\}$, writing expression Eq. (3.81) in a more compact form:

$$K_{IJ}(\alpha, \beta)|_{t'u'v'}^{tuv} = \sum_{\{abc\}} q_{abc|a'b'c'}^{tuv|t'u'v'} \cdot V_{IJ}(\alpha, \beta)|_{t'u'v'}^{tuv}. \quad (3.82)$$

We have now all ingredients ready to construct any Madelung integral. Consider the matrix element $B_{Ilm, J'l'm'}$. The multipole order is (l, l') . We first construct all Hermite integrals from $R_{IJ}|^{000}$ up to $R_{IJ}|^{tuv}$, where $t + u + v \leq l + l'$. We next follow Eq. (3.74) to construct all Hermite Gaussian electrostatic integrals $V_{IJ}(\alpha_I, \alpha_J)|_{t'u'v'}^{tuv}$, where $t + u + v \leq l$ and $t' + u' + v' \leq l'$. The Hermite Gaussians are translated to the primitive Cartesian

integrals via Eq. (3.82), and are finally used to build the Madelung matrix elements following Eq. (3.70).

The Hermite integrals can in principle be built from recursion relations. We have written a MATHEMATICA code to construct $R_{IJ}|^{tuv}$ up to arbitrary order by differentiation, and transfer the resulting symbolic expressions to our tight-binding code for compilation. This leads to an overall speed-up compared to the recursive scheme, as it avoids evaluating the lengthy recursion relations for the incomplete Gamma function for every matrix element. The coefficients $q_{abc}^{tuv}|_{a'b'c'}^{t'u'v'}$ can easily be found following the definition of the solid harmonics. We constructed these algebraically in MATHEMATICA. We refer to section A.7 in the appendix for the MATHEMATICA code.

3.5.1.3 Gradient of the Madelung matrix

We have derived the self-consistent force in section 3.3. Evaluation of this force requires knowledge of the gradient of the Madelung matrix elements:

$$d\vec{B}_{Ilm,Jl'm'} = \vec{\nabla}_{R_{IJ}} B_{Ilm,Jl'm'}. \quad (3.83)$$

Using Eq. (3.70), it can be shown that this derivative can be constructed from the gradient of the primitive Cartesian integrals:

$$d\vec{B}_{Ilm,Jl'm'} = \frac{e^2 k_{Il} k_{Jl'}}{4\pi\epsilon_0} \sum_{\substack{t+u+v \leq l \\ t'u'v' \leq l'}}^{tuv} C_{tuv}^{lm} C_{t'u'v'}^{l'm'} d\vec{K}_{IJ}(\alpha_I, \alpha_J)|_{t'u'v'}^{tuv}. \quad (3.84)$$

The gradient of the Cartesian integrals follows from Eq. (3.82):

$$d\vec{K}_{IJ}(\alpha, \beta)|_{t'u'v'}^{tuv} = \sum_{\substack{abc \\ a'b'c'}} q_{abc}^{tuv}|_{a'b'c'}^{t'u'v'} \cdot d\vec{V}_{IJ}(\alpha, \beta)|_{t'u'v'}^{tuv}, \quad (3.85)$$

while the gradient of the Hermite Gaussian integrals follows from Eq. (3.74):

$$d\vec{V}_{IJ}(\alpha, \beta)|_{t'u'v'}^{tuv} = (-1)^{t+t'+u+u'+v+v'} \frac{2\pi^{5/2}}{\alpha\beta\sqrt{\alpha+\beta}} d\vec{R}_{IJ}|^{t+t',u+u',v+v'}(\alpha, \beta). \quad (3.86)$$

Following the definition of the Hermite integral in Eq.(3.75):

$$R_{IJ}|^{tuv}(\alpha, \beta) = \partial_{x_{IJ}}^t \partial_{y_{IJ}}^u \partial_{z_{IJ}}^v F^0(\alpha\beta(\alpha+\beta)^{-1} ||R_{IJ}||^2), \quad (3.87)$$

we find the derivatives of the Hermite integral trivially as:

$$\begin{aligned} \partial_{x_{IJ}} R_{IJ}|^{tuv}(\alpha, \beta) &= R_{IJ}|^{t+1,u,v}(\alpha, \beta) \\ \partial_{y_{IJ}} R_{IJ}|^{tuv}(\alpha, \beta) &= R_{IJ}|^{t,u+1,v}(\alpha, \beta) \\ \partial_{z_{IJ}} R_{IJ}|^{tuv}(\alpha, \beta) &= R_{IJ}|^{t,u,v+1}(\alpha, \beta). \end{aligned} \quad (3.88)$$

One therefore merely needs to construct the Hermite integrals to order $t + u + v \leq l + l' + 1$ to readily obtain the gradient of the Madelung matrix elements.

3.5.1.4 Numerical integration

In the previous section we have outlined our implementation of the Madelung matrix elements. It is now left to verify the analytical integration in an independently implemented numerical integration. We will use two atoms in this test case; one located at the origin with a Gaussian exponent of α , the other located at $\vec{R}$ with an exponent of β . Note here that the integration is over the volume elements $d^3r d^3r'$, e.g. $\mathbb{R}^6$, we therefore cannot do a simple integration over a numerical grid.

We will here briefly outline how the electrostatic integral can be solved numerically using the Fourier transform. Let us first define the harmonic Gaussian for the sake of brevity as:

$$\Omega_{lm}^\alpha(\vec{r}_I) = k_{lm} e^{-\alpha \|\vec{r}_I\|^2} K_{lm}(\vec{r}_I), \quad (3.89)$$

where $\vec{r}_I = \vec{r} - \vec{R}_I$. The electrostatic potential of the density at the origin is:

$$v_{Ha}[\Omega_{lm}^\alpha](\vec{r}) = \int \frac{\Omega_{lm}^\alpha(\vec{r}')}{\|\vec{r} - \vec{r}'\|} d^3r', \quad (3.90)$$

which enables us to express the Madelung integral in terms of an integration over $\mathbb{R}^3$:

$$B_{lm,Jl'm'} = \int v_{Ha}[\Omega_{lm}^\alpha](\vec{r}) \Omega_{Jl'm'}^\beta(\vec{r}_J) d^3r. \quad (3.91)$$

We could now proceed to evaluate the density over a finite box, and find the corresponding potential by virtue of the Fourier transform of Poisson's equation. Note however that the Fourier transform over a finite space considers the charge density to be periodically repeated, such an approach would therefore yield incorrect results in our case.

Instead we follow Onida et al⁹⁰ and truncate the charge density Ω_{lm}^α in real space by application of a radial Heaviside-function $\theta(\|\vec{r}\| - R_C)$ with a cut-off radius R_C . This ensures that the electrostatic potential reaches zero at the edges of the finite box. The truncated charge density at the origin is defined as:

$$(\Omega_t)_{lm}^\alpha(\vec{r}) = \Omega_{lm}^\alpha(\vec{r}) \cdot \theta(\|\vec{r}\| - R_C) \quad (3.92)$$

This enables us to express the electrostatic potential of the truncated charge density in terms of the convolution:

$$v_{Ha}[(\Omega_t)_{lm}^\alpha](\vec{r}) = (\Omega_{lm}^\alpha \otimes \Theta)(\vec{r}) \quad (3.93)$$

where we define the truncation function as:

$$\Theta(\vec{r}) = \frac{\theta(\|\vec{r}\| - R_C)}{\|\vec{r}\|}. \quad (3.94)$$

Consider now the Fourier transform of Eq. (3.93):

$$\tilde{v}_{Ha}[(\Omega_t)_{ilm}^\alpha](\vec{k}) = \tilde{\Omega}_{ilm}^\alpha(\vec{k}) \cdot \tilde{\Theta}(\vec{k}). \quad (3.95)$$

Note that the convolution has been transformed to a product. We apply the Fourier transform once more to return to real space:

$$v_{Ha}[(\Omega_t)_{ilm}^\alpha](\vec{r}) = \mathfrak{F}_r \left(\tilde{\Omega}_{ilm}^\alpha(\vec{k}) \cdot \tilde{\Theta}(\vec{k}) \right). \quad (3.96)$$

This expression is numerically much more tractable than the direct integration over real space. We only need to find the Fourier transforms of the density and the radial truncation function, and transform their product back to real space. This is numerically extremely efficient by virtue of the Fast-Fourier-Transform. The resulting potential is used to find the Madelung integral by a trivial numerical integration following Eq. (3.91).

We also note that the Fourier transform of the truncation function (3.94) is evaluated analytically to avoid the singularity for $\lim_r \Theta(\vec{r}) \rightarrow 0$ as:

$$\tilde{\Theta}(\vec{k}) = \frac{1 - \cos(\|\vec{k}\| R_C)}{\|\vec{k}\|^2} \quad (3.97)$$

for $\|\vec{k}\| > 0$, with the limit: $\lim_{k \rightarrow 0} \tilde{\Theta}(\vec{k}) = R_C^2/2$.

We summarise the steps we take to compute the Madelung matrix element below:

1. For a given box-length of L_C and resolution of δr , generate a cubic (x, y, z) -grid centred at the origin with a padded box-length $L_D = (1 + \sqrt{3})L_C$. The padding improves the convergence behaviour of the truncated density at the box edges.
2. Compute the truncation function $\tilde{\Theta}(\vec{k})$ of Eq. (3.97) on the reciprocal (k_x, k_y, k_z) of the cubic grid, using the truncation radius $R_C = \sqrt{3}L_C/2$.
3. Take the Fast-Fourier-Transform of $\Omega_{ilm}^\alpha(\vec{r})$ and evaluate the product $\tilde{v}_{Ha}[(\Omega_t)_{ilm}^\alpha](\vec{k}) = \tilde{\Omega}_{ilm}^\alpha(\vec{k}) \cdot \tilde{\Theta}(\vec{k})$ of Eq. (3.95).
4. Evaluate the density $\Omega_{Jl'm'}^\beta(\vec{r}_J)$ on the padded (x, y, z) -grid.[†]
5. Take the Fast-Fourier-Transform of $\tilde{v}_{Ha}[(\Omega_t)_{ilm}^\alpha](\vec{k})$ and evaluate the Madelung integral by summation over the product $\Omega_{Jl'm'}^\beta(\vec{r}_J) \cdot v_{Ha}[(\Omega_t)_{ilm}^\alpha](\vec{r})$ following Eq. (3.91).

[†]Electronic structure codes may only compute the density on the L_C -sized grid, and subsequently transfer the density to the larger, padded L_D -sized grid just for the computation of the electrostatic energy to save computational effort.

Table 3.1: Analytical and numerical Madelung intersite matrix elements $B_{Ilm,Jl'm'}$ in E_h up to quadrupole order. The benchmark system is a carbon-oxygen system with displacement vector $\vec{R} = (0.6, 0.4, 0.2)a_0$. The rows show $0lm$, while the columns show $1l'm'$.

	analytical								
	00	10	11	12	20	21	22	23	24
00	0.416 644	-0.023 451	-0.015 634	-0.007 813	0.000 926	0.000 308	0.000 463	0.000 386	-0.000 490
10	0.023 451	0.036 679	-0.001 603	-0.000 801	-0.001 429	0.000 038	-0.000 714	-0.002 267	0.001 276
11	0.015 634	-0.001 603	0.038 015	-0.000 534	-0.002 239	-0.000 746	0.000 038	0.001 574	0.000 851
12	0.007 813	-0.000 801	-0.000 534	0.038 817	0.000 038	-0.001 530	-0.002 295	0.000 016	-0.000 910
20	0.000 926	0.001 429	0.002 239	-0.000 038	0.001 996	-0.000 053	-0.000 033	0.000 002	0.000 123
21	0.000 308	-0.000 038	0.000 746	0.001 530	-0.000 053	0.002 137	-0.000 108	0.000 037	-0.000 022
22	0.000 463	0.000 714	-0.000 038	0.002 295	-0.000 033	-0.000 108	0.002 046	-0.000 053	-0.000 033
23	0.000 386	0.002 267	-0.001 574	-0.000 016	0.000 002	0.000 037	-0.000 053	0.001 991	0.000 051
24	-0.000 490	-0.001 276	-0.000 851	0.000 910	0.000 123	-0.000 022	-0.000 033	0.000 051	0.002 125

	numerical								
	00	10	11	12	20	21	22	23	24
00	0.412 292	-0.023 206	-0.015 470	-0.007 735	0.000 916	0.000 305	0.000 458	0.000 382	-0.000 485
10	0.023 206	0.036 296	-0.001 587	-0.000 793	-0.001 414	0.000 037	-0.000 707	-0.002 243	0.001 263
11	0.015 470	-0.001 587	0.037 618	-0.000 529	-0.002 215	-0.000 738	0.000 037	0.001 558	0.000 842
12	0.007 735	-0.000 793	-0.000 529	0.038 412	0.000 037	-0.001 514	-0.002 271	0.000 016	-0.000 901
20	0.000 916	0.001 414	0.002 215	-0.000 037	0.001 975	-0.000 052	-0.000 033	0.000 002	0.000 122
21	0.000 305	-0.000 037	0.000 738	0.001 514	-0.000 052	0.002 114	-0.000 107	0.000 037	-0.000 022
22	0.000 458	0.000 707	-0.000 037	0.002 271	-0.000 033	-0.000 107	0.002 025	-0.000 053	-0.000 033
23	0.000 382	0.002 243	-0.001 558	-0.000 016	0.000 002	0.000 037	-0.000 053	0.001 971	0.000 051
24	-0.000 485	-0.001 263	-0.000 842	0.000 901	0.000 122	-0.000 022	-0.000 033	0.000 051	0.002 103

We refer to section A.7 in the appendix for a MATHEMATICA script written to compute the numerical integrals.

In our benchmarks we use $L_C = 14a_0$, and $\delta r = 0.2a_0$. We place a carbon atom with $\alpha = 0.22214a_0^{-2}$ at the origin, and an oxygen atom with $\beta = 0.40753a_0^{-2}$ at $\vec{R} = (0.6, 0.4, 0.2)a_0$. The widths are taken from the mio-1-1 parameter-set Hubbard constants using Eq. (3.62). We compute the onsite and intersite Madelung matrix elements numerically following the procedure outlined above and analytically following the procedure outlined in the previous section. The results are listed in tables 3.1 and 3.2. The values lie in good agreement with one another, we conclude that the analytical integrals have been implemented correctly.

3.5.2 Multipole moments

The multipole expression of the Hartree energy in Eq. (3.16)

$$E_{Ha}[\rho] = \frac{1}{2} \sum_{\substack{Ilm \\ Jl'm'}} Q_{Ilm} Q_{Jl'm'} B_{Ilm,Jl'm'} \quad (3.98)$$

Table 3.2: Analytical and numerical Madelung onsite matrix elements $B_{Ilm,Jl'm'}$ in E_h up to quadrupole order for carbon and oxygen.

method\l	carbon onsite			oxygen onsite		
	0	1	2	0	1	2
analytical	0.752 125	0.055 694	0.002 474	1.018 705	0.138 383	0.011 279
numerical	0.745 272	0.055 187	0.002 452	1.009 420	0.137 122	0.011 176

requires evaluation of the electron density moments Q_{Ilm} as defined in Eq. (3.12):

$$Q_{Ilm} = -Z_I \delta_{l0} \delta_{m0} + \sum_{\alpha J \beta} \rho_{I\alpha J \beta} M_{I\alpha J \beta}^{lm}, \quad (3.99)$$

where the multipole moment matrix element $M_{I\alpha J \beta}^{lm}$ is defined as of Eq (3.11):

$$M_{I\alpha J \beta}^{lm} = \int \phi_{I\alpha}(\vec{r}_I) K_{lm}(\vec{r}_I) \phi_{J\beta}(\vec{r}_J) d^3r, \quad (3.100)$$

where $\vec{r}_A = \vec{r} - \vec{R}_A$. We shall in the following section outline a strategy on how to construct the multipole moments given a Gaussian-type basis set $\{\phi_{I\alpha}\}$ as defined in the following section 3.5.2.1.

3.5.2.1 Gaussian-Type-Orbital basis sets

The multipole moment integral in Eq. (3.100) requires us to integrate over the basis orbitals $\{\phi_{I\alpha}\}$. We shall here go into more detail on our basis set description. We have previously introduced the atomically localised basis set (2.88) in section 2.4.2.2:

$$\phi_{I\alpha}(\vec{r}) \equiv \phi_{nlm}^{I,\zeta}(\vec{r}) = R_{nl}^{I,\zeta}(\|\vec{r}\|) K_{lm}(\vec{r}), \quad (3.101)$$

where the index α maps to the quantum numbers nlm , ζ indexes orbitals of the same quantum number nlm but with different radial functions $R_{nl}^{I,\zeta}(r)$, and $K_{lm}(\vec{r})$ are the real solid harmonics as introduced in section 2.4.2.2.

Similar to Quantum Chemistry basis sets, we shall here utilise a basis of Gaussian-Type Orbitals (GTO), where each radial function is described by a superposition of multiple Gaussians:

$$R_{nl}^{I,\zeta}(r) = \sum_{\nu} c_{nl}^{I,\zeta \nu} e^{-a_{nl}^{I,\zeta \nu} r^2}, \quad (3.102)$$

leading to the full GTO expression:

$$\phi_{I\alpha}(\vec{r}) \equiv \phi_{nlm}^{I,\zeta}(\vec{r}) = \sum_{\nu} c_{nl}^{I,\zeta \nu} e^{-a_{nl}^{I,\zeta \nu} \|\vec{r}\|^2} K_{lm}(\vec{r}). \quad (3.103)$$

The recursive nature of Gaussians makes possible a very efficient and analytical solution of many integrals, as previously demonstrated on the example of the electrostatic integrals. We will here show how a Gaussian basis set can be used to build the Cartesian multipole moments efficiently.

3.5.2.2 Primitive cartesian multipole moments

Consider the Gaussian-Type Orbitals $\phi_{I\alpha}(\vec{r})$ as introduced in sec 3.5.2.1. The multipole moment integral (3.100) in this representation is given by:

$$\begin{aligned} M_{I\alpha J\beta}^{l^\gamma m^\gamma} &= \sum_{\nu\nu'} c_{nl}^{I\zeta\nu} c_{n'l'}^{J\zeta'\nu'} \int e^{-a_{nl}^{I\zeta\nu} \|\vec{r}_I\|^2} K_{lm}(\vec{r}_I) K_{l''m''}(\vec{r}_I) e^{-a_{n'l'}^{J\zeta'\nu'} \|\vec{r}_J\|^2} K_{l'm'}(\vec{r}_J) d^3r \\ &\equiv \sum_{\nu\nu'} c_{nl}^{I\zeta\nu} c_{n'l'}^{J\zeta'\nu'} \cdot M_{IJ}(a_{nl}^{I\zeta\nu}, a_{n'l'}^{J\zeta'\nu'}) \Big|_{l'm'}^{l''m''} \\ &\equiv M_{IJ}^{\zeta\zeta'} \Big|_{n'l'm'}^{l''m''}. \end{aligned} \quad (3.104)$$

We will for added clarity use α, β as explicit superscripts to the quantum numbers nlm and ζ instead of $nlm, n'l'm'$. The index γ refers to the harmonic indices of the multipole expansion. This makes it easier to distinguish different orbitals as they appear in a product. We are left to solve the general integral $M_{IJ}(\alpha, \beta) \Big|_{l^\beta m^\beta}^{l^\gamma m^\gamma}$. While this expression certainly does not look very encouraging, we can break it down further into manageable pieces. Consider first the real solid harmonics. Each harmonic can be expressed as a polynomial in the form of:

$$K_{lm}(\vec{r}_A) = \sum_{tuv}^{t+u+v \leq l} C_{tuv}^{lm} x_A^t y_A^u z_A^v. \quad (3.105)$$

We can therefore write the triple product of cubic harmonics as:

$$\begin{aligned} &K_{l^\alpha m^\alpha}(\vec{r}_I) K_{l^\gamma m^\gamma}(\vec{r}_I) K_{l^\beta m^\beta}(\vec{r}_J) \\ &\quad \sum_{\substack{t+u+v \leq l^\alpha \\ t'+u'+v' \leq l^\gamma \\ t''+u''+v'' \leq l^\beta}} C_{tuv}^{l^\alpha m^\alpha} C_{t'u'v'}^{l^\gamma m^\gamma} C_{t''u''v''}^{l^\beta m^\beta} x_I^{t+t'} y_I^{u+u'} z_I^{v+v'} x_J^{t''} y_J^{u''} z_J^{v''}, \\ &= \sum_{\substack{tuv \\ t'u'v' \\ t''u''v''}} C_{tuv}^{l^\alpha m^\alpha} \Big|_{t'u'v'}^{l^\gamma m^\gamma} \Big|_{t''u''v''}^{l^\beta m^\beta} x_I^{t+t'} y_I^{u+u'} z_I^{v+v'} x_J^{t''} y_J^{u''} z_J^{v''}, \end{aligned} \quad (3.106)$$

where we defined the composite polynomial coefficient:

$$C_{tuv}^{l^\alpha m^\alpha} \Big|_{t'u'v'}^{l^\gamma m^\gamma} \Big|_{t''u''v''}^{l^\beta m^\beta} = C_{tuv}^{l^\alpha m^\alpha} C_{t'u'v'}^{l^\gamma m^\gamma} C_{t''u''v''}^{l^\beta m^\beta}. \quad (3.107)$$

The composite coefficients can be found either by hand or more easily by any symbolic mathematics software. The important revelation of this decomposition is that we can

express the multipole integral in terms of primitive Cartesian overlap integrals:

$$M_{IJ}(\alpha, \beta) \Big|_{l^\beta m^\beta}^{l^\gamma m^\gamma} = \sum_{\{tuv\}} C \Big|_{tuv}^{l^\alpha m^\alpha} \Big|_{t'u'v'}^{l^\gamma m^\gamma} \Big|_{t''u''v''}^{l^\beta m^\beta} S_{IJ}(\alpha, \beta) \Big|_{t''u''v''}^{t+t', u+u', v+v'}, \quad (3.108)$$

where

$$S_{IJ}(\alpha, \beta) \Big|_{def}^{abc} = \int x_I^a y_I^b z_I^c e^{-\alpha \|\vec{r}_I\|^2} x_J^d y_J^e z_J^f e^{-\beta \|\vec{r}_J\|^2} d^3r \quad (3.109)$$

is the primitive primitive Cartesian overlap integral, and the $\{tuv\}$ summation runs over the indices as in Eq. (3.106). The multipole moment matrix elements can in summary be found by:

$$M_{I\alpha J\beta}^{l^\gamma m^\gamma} \equiv \sum_{\{tuv\}} C \Big|_{tuv}^{l^\alpha m^\alpha} \Big|_{t'u'v'}^{l^\gamma m^\gamma} \Big|_{t''u''v''}^{l^\beta m^\beta} \sum_{\nu\nu'} c_{I\alpha}^{\nu\zeta} c_{J\beta}^{\nu'\zeta'} S_{IJ}(a_{n\alpha l\alpha}^{I\zeta\nu}, a_{n\beta l\beta}^{J\zeta'\nu'}) \Big|_{t''u''v''}^{t+t', u+u', v+v'}. \quad (3.110)$$

This expression shows that the multipole integrals can be constructed from primitive overlap integrals of higher powers.

3.5.2.3 Constructing the multipole matrix elements

A clear strategy follows for the construction of the multipole moments. Consider $M_{IJ}^{\zeta\zeta'} \Big|_{l^\beta m^\beta}^{l^\gamma m^\gamma}$, i.e. the multipole moment of order l_γ, m_γ of the orbitals $\phi_{In\alpha l\alpha m\alpha}^{\zeta\alpha}(\vec{r})$ and $\phi_{Jn\beta l\beta m\beta}^{\zeta\beta}(\vec{r})$. First, determine the maximum angular momentum $(l_\alpha + l_\gamma, l_\beta)$ for the primitive Cartesian overlap integrals $S_{IJ}(\alpha, \beta) \Big|_{def}^{abc}$ that need to be constructed, see table A.2. Next, construct all primitive Cartesian overlap integrals up to the maximum angular momentum $(l_\alpha + l_\gamma, l_\beta)$, consulting table A.1 for the list of all unique Cartesian integrals.

Note that for the construction of the primitive Cartesian integrals of $(l_\alpha + l_\gamma, l_\beta)$ the Gaussian widths $\{a_{I\alpha}^{\nu\zeta}\}$ and amplitudes $\{c_{I\alpha}^{\nu\zeta}\}$ follow the orbital shell numbers l_α and l_β . Their order is not increased by the multipole shell number l_γ . Finally the multipole moment matrix elements can be constructed using Eq. (3.110).

3.5.2.4 Recursion relations for the primitive Cartesian overlap integrals

We are left to find an expression for the primitive Cartesian overlap integrals $S_{IJ}(\alpha, \beta) \Big|_{def}^{abc}$ of Eq. (3.109). Consider first the zeroth-order integral:

$$S_{IJ}(\alpha, \beta) \Big|_{000}^{000} = \int e^{-\alpha \|\vec{r}_I\|^2} e^{-\beta \|\vec{r}_J\|^2} d^3r = \frac{\pi^{3/2}}{(\alpha + \beta)^{3/2}} e^{-\left(\frac{\alpha\beta}{\alpha+\beta}\right) \|\vec{R}_I - \vec{R}_J\|^2}. \quad (3.111)$$

Consider now the alternative notation:

$$I_{\mu\mu' \dots \mu''''}^{\nu\nu' \dots \nu''''} = \int \left(r_I^\nu r_I^{\nu'} \dots r_I^{\nu''''} \right) e^{-\alpha \|\vec{r}_I\|^2} \left(r_J^\mu r_J^{\mu'} \dots r_J^{\mu''''} \right) e^{-\beta \|\vec{r}_J\|^2} d^3r. \quad (3.112)$$

The number of indices ν refers to the order in $\vec{r}_I$, while those of μ refer to the order in $\vec{r}_J$. Here r_I^ν refers to $(\vec{r}_I)_\nu$, with ν taking on values of x, y , or z . The integral $S_{IJ}(\alpha, \beta)|_{013}^{101}$ for example would in this notation be written as I_{yzzz}^{xx} . Defining the set $\{\nu\} = \{\nu, \nu', \dots, \nu'''\dots\}$, we present the follow recursion relations:

$$I_{\{\mu\}}^{\{\nu\} \cup \nu^i} = -2\beta\lambda(\vec{R}_{IJ})_{\nu^i} I_{\{\mu\}}^{\{\nu\}} + \lambda \left(\sum_{\nu^j \in \{\nu\}} \delta_{\nu^i \nu^j} I_{\{\mu\}}^{\{\nu\} \setminus \nu^j} + \sum_{\mu^j \in \{\mu\}} \delta_{\nu^i \mu^j} I_{\{\mu\}}^{\{\nu\} \setminus \mu^j} \right) \quad (3.113)$$

$$I_{\{\mu\} \cup \mu^i}^{\{\nu\}} = 2\alpha\lambda(\vec{R}_{IJ})_{\mu^i} I_{\{\mu\}}^{\{\nu\}} + \lambda \left(\sum_{\nu^j \in \{\nu\}} \delta_{\nu^i \nu^j} I_{\{\mu\}}^{\{\nu\} \setminus \nu^j} + \sum_{\mu^j \in \{\mu\}} \delta_{\nu^i \mu^j} I_{\{\mu\}}^{\{\nu\} \setminus \mu^j} \right),$$

where $\lambda = 1/(2(\alpha + \beta))$, $\cup$ refers to the union, and $\setminus$ to the exclusion to the set of indices. These recursion relations can be derived from the Obara-Saika recursion scheme.⁸⁹ The PLATO manual also has the lower order integrals explicitly listed.

3.5.2.5 Multipole moment gradient

We have derived the self-consistent force in section 3.3. Evaluation of this force requires knowledge of the multipole gradient matrix elements:

$$d\vec{M}_{I\alpha J\beta}^{lm} = \vec{\nabla}_{R_{IJ}} M_{I\alpha J\beta}^{lm}. \quad (3.114)$$

Using Eq. (3.110), it can be shown that these depend on the gradient of the overlap integrals:

$$d\vec{M}_{I\alpha J\beta}^{l^\gamma m^\gamma} \equiv \sum_{\{tuv\}} C_{tuv}^{l^\alpha m^\alpha | l^\gamma m^\gamma | l^\beta m^\beta} \sum_{\nu\nu'} c_{I\alpha}^{\nu\zeta} c_{J\beta}^{\nu'\zeta'} \vec{\nabla}_{R_{IJ}} S_{IJ}(a_{I\alpha}^{\nu\zeta}, a_{J\beta}^{\nu'\zeta'})|_{t^{+t'}, u^{+u'}, v^{+v'}}^{t+t', u+u', v+v'}. \quad (3.115)$$

We are left to find the overlap derivatives. Consider the primitive Cartesian integral as given by Eq. (3.109):

$$S_{IJ}(\alpha, \beta)|_{def}^{abc} = \int x_I^a y_I^b z_I^c e^{-\alpha\|\vec{r}_I\|^2} x_J^d y_J^e z_J^f e^{-\beta\|\vec{r}_J\|^2} d^3r \quad (3.116)$$

We apply the substitution $\vec{r} \rightarrow \vec{r} + \vec{R}_I$, leading to the expression:

$$S_{IJ}(\alpha, \beta)|_{def}^{abc} = \int x^a y^b z^c e^{-\alpha\|\vec{r}\|^2} x_I^d y_I^e z_I^f e^{-\beta\|\vec{r}_{IJ}\|^2} d^3r. \quad (3.117)$$

We find the derivatives as:

$$\begin{aligned} \partial_{x_{IJ}} S_{IJ}(\alpha, \beta)|_{def}^{abc} &= d \cdot S_{IJ}(\alpha, \beta)|_{d-1, e, f}^{abc} - 2\beta \cdot S_{IJ}(\alpha, \beta)|_{d+1, e, f}^{abc} \\ \partial_{y_{IJ}} S_{IJ}(\alpha, \beta)|_{def}^{abc} &= e \cdot S_{IJ}(\alpha, \beta)|_{d, e-1, f}^{abc} - 2\beta \cdot S_{IJ}(\alpha, \beta)|_{d, e+1, f}^{abc} \\ \partial_{z_{IJ}} S_{IJ}(\alpha, \beta)|_{def}^{abc} &= f \cdot S_{IJ}(\alpha, \beta)|_{d, e, f-1}^{abc} - 2\beta \cdot S_{IJ}(\alpha, \beta)|_{d, e, f+1}^{abc} \end{aligned} \quad (3.118)$$

It is therefore possible to express the multipole gradients in terms of higher order primitive Cartesian overlap integrals.

3.5.2.6 Numerical tests

In practice we construct all primitive Cartesian integrals up to $(l_\alpha + l_\gamma + 1, l_\beta)$ order between all pairs of atoms within cut-off distance to one another. These Cartesian integrals are then used to construct the matrix elements $M_{I\alpha J\beta}^{lm}$ and $d\vec{M}_{I\alpha J\beta}^{lm}$. Given the sheer amount of steps involved in this implementation, it is highly advisable to verify the accuracy of the integrals by independent numerical integration.

We compute the multipole moments $M_{I\alpha J\beta}^{lm}$ between a pair of atoms I and J as of Eq. (3.104) up to quadrupole order by numerical integration over a finite, regular grid $\{x_i, y_i, z_i\}$. The integration volume is chosen by the minimum bounding box of the sites $\vec{R}_I$ and $\vec{R}_J$ including a buffer region of $8a_0$ thickness. The grid spacing is chosen as $0.08a_0$. In this example we place a Carbon atom at $\vec{R}_I = (0, 0, 0)a_0$ and an Oxygen atom at $\vec{R}_J = (1, 3, 2)a_0$. Both atoms use a polarisable single-zeta valence basis set which we will introduce in section 4.1.1. Each atom has therefore 9 orbitals, leading to 81 monopole, 243 dipole, and 405 quadrupole matrix elements.

The evaluated multipole moments are listed in table A.3. We find good agreement between the analytical and numerical results. The total absolute error over all matrix elements is 1×10^{-4} , with the mean absolute error being 2×10^{-7} . The largest absolute error is 1×10^{-5} . We attribute this deviation to inaccuracies in the numerical integration and conclude that the integration scheme is working effectively.

Having confirmed the accuracy of the analytical multipole matrix elements, we next check the accuracy of the multipole derivatives $d\vec{M}_{I\alpha J\beta}^{lm}$. Here we employ a finite-difference scheme. The oxygen atom J is first placed at $\vec{R}_J + \delta x \hat{e}_x$, where we compute $M_{I\alpha J\beta}^{lm}|^+$. Next we place the atom at $\vec{R}_J - \delta x \hat{e}_x$, where we compute $M_{I\alpha J\beta}^{lm}|^-$. The derivative $\partial_{x_{IJ}} M_{I\alpha J\beta}^{lm}$ is subsequently found by the finite-difference scheme:

$$\partial_{x_{IJ}} M_{I\alpha J\beta}^{lm} = \frac{M_{I\alpha J\beta}^{lm}|^+ - M_{I\alpha J\beta}^{lm}|^-}{2\delta x} \quad (3.119)$$

We choose a displacement of $\delta x = 1 \times 10^{-5} a_0$ and find the absolute deviation between any numerically and analytically differentiated matrix elements to lie below 1×10^{-8} . The procedure is repeated for y and z derivatives with consistent results. We conclude that the analytical multipole moment derivatives are implemented correctly.

3.6 Summary

We have extended the self-charge-consistent description of electrostatics in density-functional tight binding by a self-multipole-consistent description. The Gaussian tight binding framework accesses the Gaussian basis set underlying the density-functional tight binding parametrisation to construct the multipole moments, while approximating the variational density for the electrostatic integrals in terms of a multipole expansion. We have implemented the model up to quadrupole order, and shall next parametrise and benchmark the method in comparison to density-functional theory.

The Gaussian tight binding (GTB) formalism offers a physically more complete treatment of self-consistent electrostatics than self-charge-consistent tight binding. In this chapter we shall derive a GTB model for hydrocarbons including sulfur for the treatment of conducting polymers, with a single-valence-basis set including polarisation orbitals optimised to deliver accurate molecular polarisabilities and band gaps.

The accuracy of the SVP-GTB model is assessed by the agreement with DFT using the Perdew-Becke-Ernzerhof⁹¹ (PBE) exchange-correlation functional and experimental data for various hydrocarbons' mean polarisabilities. The Gaussian tight binding model is found to give molecular polarisabilities in excellent agreement with the reference data. Finally we use GTB in conjunction with the classical polarisable-point-dipoles method to estimate the internal electric fields of amorphous bulk Poly(3-hexylthiophene-2,5-diyl) under the influence of an external field. We find that $\approx 2/3$ of the externally applied field at any polymer site is screened by the polarisation field of neighbouring polymers.

4.1 Model benchmarks

We seek to clarify two points. First we shall investigate how the band gaps and the molecular polarisabilities of a small representable set of molecules are affected by the choice of the basis set and the confining potential, as outlined in section 2.4.7. Next we shall assess the accuracy and transferability of the GTB method by comparison with data from DFT and experiments. Our physical observable of interest is molecular polarisability, which we will show to strongly depend on the multipole order of the self-consistent Hartree energy.

Table 4.1: Basis set size of the single-valence (SV) and the single-valence-polarisable (SVP) basis set for the elements H, C, and S in the Gaussian tight binding model.

species	SV basis configuration	SVP basis configuration
H	$1s^1$	$1s^1 2p^0$
C	$2s^2 2p^2$	$2s^2 2p^2 3d^0$
S	$3s^2 3p^4$	$3s^2 3p^4 3d^0$

4.1.1 Creating the tight-binding models

While minimal single-valence basis sets are sufficiently accurate for a wide range of ground-state properties, an accurate description of polarisation effects requires the use of extended, polarisable basis sets. Here we outline the derivation of the polarisable basis set used in this work.

The externally confined single-atom DFT problem is solved for every atomic species included in the model using the PBE exchange-correlation functional with Goedecker, Teter, and Hutter pseudo-potentials⁹² as outlined in section 2.4.7. We use the confining potentials

$$V_C^I(R) = 1 E_h (R/R_C^I)^6, \quad (4.1)$$

where R_C^I are the confinement radii. The density and orbitals are constrained to zero beyond a radius of $5.5 a_0$. The problem of creating a tight binding model is hence reduced to finding the confinement radii R_C^I that yield the most accurate and transferable model.

The density ρ_0^I and numerical orbitals ψ_{nlm}^I are further fitted by Gaussian-type-orbitals (GTOs) to enable fast and noise free analytical integration of the Slater-Koster tables for the Hamiltonian and overlap integrals. The Hamiltonian onsite elements are directly taken from the solution of the single atom. The GTOs are also used to explicitly compute the multipole moment integrals required for the GTB method as outlined in section 3.5.

We test single-valence (SV) and single-valence-polarisable (SVP) basis sets, e.g. 1-zeta, for the elements hydrogen, carbon, and sulfur. The polarisation orbitals are of one angular momentum higher than the highest angular momentum of each respective atom’s valence shell: we add $2p^0$ orbitals for hydrogen, and $3d^0$ orbitals for carbon and sulfur. The electronic configuration of the basis set is listed in table 4.1.

4.1.2 Reference structures

We leave sulfur aside for now to simplify our parameter space. We test the hydrocarbon molecules listed in figure 4.1. The geometries of the benchmark molecules are optimized

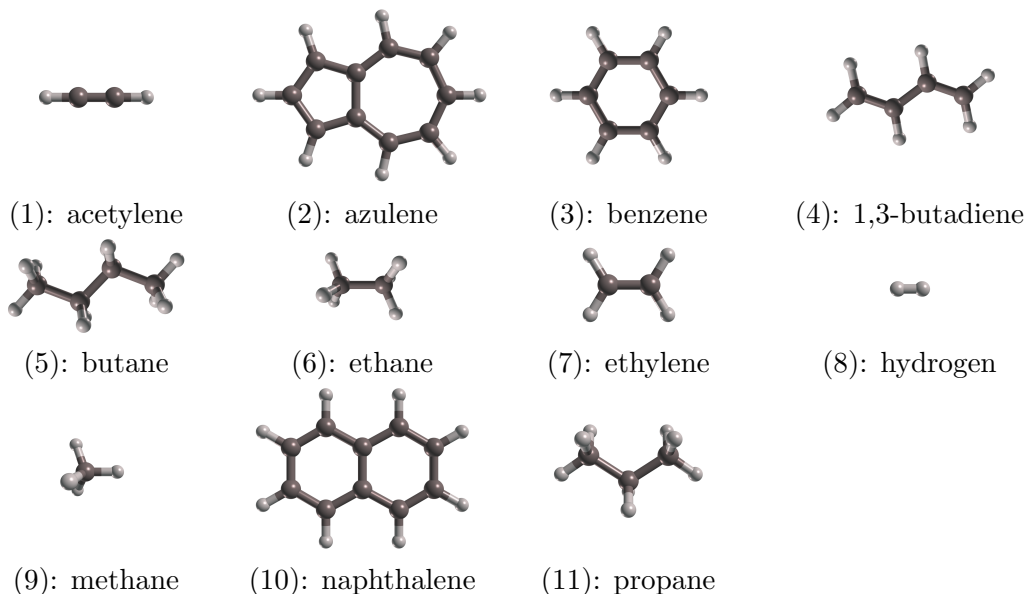


FIGURE 4.1: Benchmark hydrocarbons. All geometries are optimised in PBE-DFT with the cc-pVTZ basis set.

in all-electron PBE-DFT using the Gaussian 09 software⁹³ with the correlation-consistent basis set cc-pVTZ.⁹⁴

4.1.3 HOMO-LUMO gaps

The SV-GTB and SVP-GTB models are constructed for a range of confining radii R_C^C and R_C^H , with each radius being independently varied from $2.5 a_0$ to $5.0 a_0$ in steps of $0.5 a_0$. The SVP-GTB model uses the Hamiltonian onsite values of the single confined atom, while we consider the SV-GTB model first using the Hamiltonian onsite values from the single confined atom, and second from the single free atom.

The electronic structure of each molecule in the test set is solved self-consistently in DFT and GTB. We compare the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The energy gap error is a very preliminary quality measure for our tight binding models. It is a necessary condition for our tight binding model that the energy gap agrees with DFT to a certain extent, as otherwise the optical properties could be wildly inaccurate. We assume an electron temperature of 0 K for our simulations to enable a clear identification of the highest and lowest occupied molecular orbitals.

Figure 4.2 displays the mean signed errors of the tight binding HOMO-LUMO gaps with respect to PBE-DFT with the cc-pVDZ basis set over the range of confinements. We note that smaller molecules in the test set generally have a larger absolute band gap

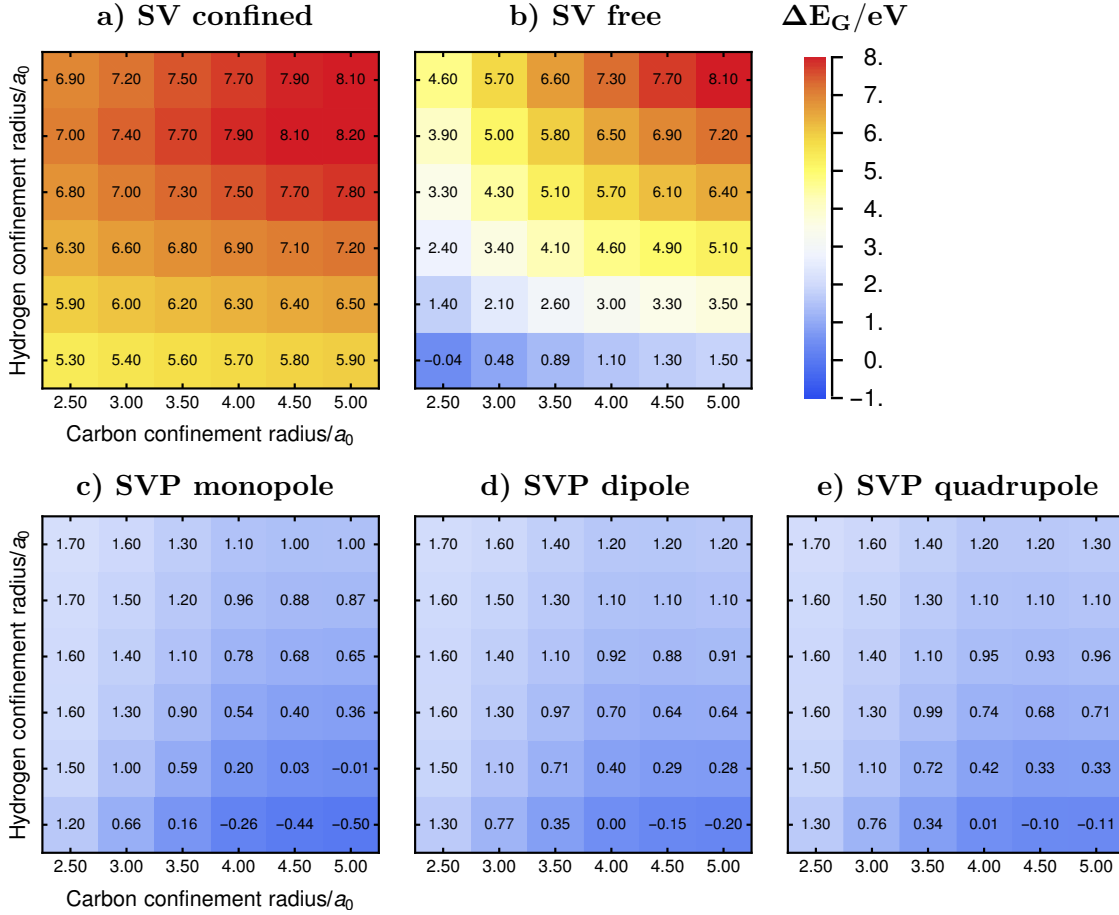


FIGURE 4.2: HOMO-LUMO gap benchmarks over a range of carbon and hydrogen external potential confinement radii. Each data point represents the mean signed error of the Gaussian tight binding HOMO-LUMO gap with respect to PBE-DFT with the cc-pVDZ basis set (in eV), averaged over the molecules in figure 4.1. The single-valence basis (SV) is tested to monopole order with Hamiltonian onsite values from **a)** confined atoms and **b)** free atoms. The single-valence-polarisation basis (SVP) is tested to **c)** monopole order, **d)** dipole order, and **e)** quadrupole order with Hamiltonian onsite values from confined atoms.

compared to big molecules, and as such contribute more to the mean signed errors.

The SV-GTB models using the Hamiltonian onsite values from the confined atoms (**a**) are found to severely overestimate the gaps by 5 eV on average or more. In contrast, the SV-GTB models using the Hamiltonian onsite values from the free atoms (**b**) yield much more favourable results; a strong confinement radius of about $2a_0$ to $3a_0$ for both hydrogen and carbon gives band gaps with significantly reduced absolute error, however the results are strongly dependent on the confinement radii. The SVP-GTB models (**c-e**) finds gaps in acceptable agreement with DFT, while displaying a comparatively weak

dependence of the errors on the confinement radii and the order of self-consistency.

These results feature a number of important points to consider when creating tight binding models:

- 1. Basis set size.** A small basis set is not able to describe the LUMO to a high degree of accuracy. Small basis sets are commonly optimised for ground-state properties, and therefore do not have the required flexibility to describe the electronic structure of higher energy molecular orbitals. Polarisation orbitals in particular are an important component of the unoccupied states. It is therefore unsurprising that SVP-GTB performs considerably better than SV-GTB. This effect is more severe for small molecules such as H_2 or methane.
- 2. Hamiltonian onsite elements.** The neglect of the crystal-field potential, see section 2.4.2.6, leads to an overall overestimation of the onsite Hamiltonian matrix elements for bonded systems. An atom in a confining external potential becomes excited, raising the value of the Hamiltonian matrix elements; this further exacerbates the overestimation of the onsite Hamiltonian. A workaround for SV-GTB lies in using a strongly confining external potential, but replacing the onsite Hamiltonian matrix elements with those belonging to the free unconfined atom. While this approach has proven to yield accurate models in the 2-centre SCC-DFTB level of theory it requires a sophisticated choice of the confining radii.
- 3. Order of self-consistency in GTB.** The multipole expansion order has an overall small effect on the error. We see a trend in the gap increasing with higher GTB order. Comparing monopole to quadrupole GTB, the magnitude of this shift is small at strong confinements (≈ 0.1 eV), and larger at weak confinements (≈ 0.3 eV). The energy difference between dipole and quadrupole GTB gaps is at most 0.1 eV.
- 4. Confinement radius.** The confinement radius is the defining parameter for the performance of the SV-GTB models. SV-GTB performs best at strong confinements, while SVP-GTB model in contrast shows a much weaker dependence on the confinement.

We would also like to emphasise that the DFT energies are strongly dependent on the choice of the basis set. Switching from cc-pVDZ to the diffusion-function augmented aug-cc-pVQZ basis set, which is practically size-converged, lowers the gaps by approximately 1 eV. A single-valence-polarisable basis set in PBE-DFT would similarly shift gaps to higher energies. With this in mind we accept the SVP-GTB errors as a consequence of using a 1-zeta basis set and choose the confining radii $R_C^C = 4.5 a_0$ and $R_C^H = 4.0 a_0$ for the

SVP-GTB model. For direct comparison we also define the SV-GTB model with identical confining radii. While better agreement with DFT is reached for a stronger confinement of hydrogen, we are reluctant to over-fit our basis to this very specific measure.

We further fit and benchmark pair-potentials for the hydrogen-carbon-sulfur SVP-GTB model to density-functional theory reference data, see appendix A.5. The resulting model is found to reproduce molecular geometries well, but needs further fine-tuning for vibrational frequencies, particularly for those involving carbon-sulfur bonds.

4.1.4 Polarisability benchmarks

We have arrived at the SV-GTB and SVP-GTB models for Gaussian tight binding theory, see section 4.1.3. Returning to our original intention, we shall now test whether Gaussian tight binding is capable of describing static molecular polarisation accurately in direct comparison with density-functional theory.

4.1.4.1 Molecular multipole moments

Let us formally define the molecular multipole moments. Consider a molecule under the influence of a constant uniform electric field $\vec{E}$. The electron density will rearrange, forming net molecular dipole p_μ and quadrupole $Q_{\mu\nu}$ moments given by the linear relations:⁹⁵

$$\begin{aligned} p_\mu &= p_\mu^0 + \sum_\nu \alpha_{\mu\nu} E_\nu \\ Q_{\mu\nu} &= Q_{\mu\nu}^0 + \sum_\xi a_{\xi\mu\nu} E_\xi, \end{aligned} \tag{4.2}$$

where α is the 3×3 dipole polarisability matrix, and a is the $3 \times 3 \times 3$ dipole-quadrupole polarisability tensor. The static dipole and quadrupole moments are respectively given by p_μ^0 and $Q_{\mu\nu}^0$. The moments are computed by integration over the total charge density including ionic charges $n(\vec{r})$:

$$\begin{aligned} p_\mu &= \int n(\vec{r}) r'_\mu d^3r \\ Q_{\mu\nu} &= \frac{1}{2} \int n(\vec{r}) \left(3 r'_\mu r'_\nu - \delta_{\mu\nu} \|\vec{r}'\|^2 \right) d^3r, \end{aligned} \tag{4.3}$$

where $r'_\mu = r_\mu - r_\mu^0$, with r_μ^0 being the chosen multipole origin. This definition is similar to that of the atomically-expanded charge density moments (3.9), however we now compute the total charge moments of the molecule. The dipole moment is independent of origin provided the molecule has no net charge, which is the case here. The quadrupole moments however do depend on the choice of origin if a net dipole moment is present.⁹⁶ The

molecular multipole moments are in practice computed in GTB from the charge density moments.

4.1.4.2 Polarisability calculation and reference data

Our GTB implementation in PLATO does not currently support the calculation of polarisabilities by linear response theory. We therefore apply external fields up to $\pm 0.0039 E_h/ea_0$ strength to each molecule. The dipole polarisabilities $\alpha_{\mu\nu}$ and dipole-quadrupole polarisabilities $a_{\xi\mu\nu}$ are subsequently extracted from the slope of a linear fit to q_μ and $Q_{\mu\nu}$ over external field strength.

The PBE-DFT dipole polarisabilities $\alpha_{\mu\nu}$ are computed by linear response over a range of basis sets, using the correlation-consistent series cc-pVXZ⁹⁴ and the diffuse-function augmented series aug-cc-pXDZ, where X=(D,T,Q) stands for double-, triple-, and quadruple-zeta. The DFT dipole polarisability simulations are carried out with the Resolution of the Identity approximation (RI-J)⁸⁷ (with the exception of H₂) using the software ORCA.⁹⁷ The PBE-DFT dipole-quadrupole polarisability simulations are carried out with Gaussian 09⁹³ for a finite electric field, just as previously described for GTB. We also compare the dipole polarisabilities to a mixture of experimentally determined static^{98–100} and dynamic¹⁰¹ polarisabilities.

4.1.4.3 Dipole polarisabilities

The PBE-DFT mean polarisability volumes $\alpha_m = \text{Tr}(\alpha^V)/3$ are listed along with experimental values in table 4.2. The polarisability volumes are related to the polarisabilities as $\alpha_{\mu\nu}^V = \alpha_{\mu\nu}/(4\pi\epsilon_0)$. The errors relative to experiment are given by the mean relative error $\Delta\alpha_m = \langle (\alpha_m^{\text{sim}} - \alpha_m^{\text{exp}})/\alpha_m^{\text{exp}} \rangle$ and the mean relative absolute error $|\Delta\alpha| = \langle |(\alpha_m^{\text{sim}} - \alpha_m^{\text{exp}})/\alpha_m^{\text{exp}}| \rangle$. The addition of diffuse functions has a significant effect on convergence, however the converged values overestimate polarisability considerably. This is a known issue for DFT using local or semi-local exchange-correlation functionals.¹⁰²

The GTB mean polarisabilities are listed in table 4.3. Standard monopole-order SV-GTB severely underestimates polarisabilities by about 50% on average, which is corrected by the addition of polarisation orbitals in SVP-GTB. Including the dipole order improves the agreement to the point where SVP-GTB performs comparably to DFT with the cc-pVTZ basis set. Additional quadrupole terms do not notably influence the polarisabilities. The large error in the monopole-order polarisability can be attributed to its lacking description of out-of-plane polarisability $\alpha_\perp$ in planar molecules, for instance in benzene or azulene. In these cases the polarisation is driven by atomic polarisation rather

Table 4.2: Basis set convergence of mean polarisability volumes $\alpha_m = \text{Tr}(\alpha^V)/3$ in $\text{\AA}^3$ for various hydrocarbons in PBE-DFT. The mean relative error and mean relative absolute errors compared to experiment are given as $\Delta\alpha$ and $|\Delta\alpha|$.

	cc-pVXZ			aug-cc-pVXZ			exp.
	D	T	Q	D	T	Q	
acetylene	2.39	2.92	3.20	3.47	3.56	3.58	3.49 ⁹⁸
azulene	17.0	18.38	19.11	19.85	19.89	19.89	15.52 ⁹⁹
benzene	8.69	9.53	9.98	10.48	10.52	10.52	9.9 ¹⁰¹
butadiene	7.08	7.83	8.23	8.70	8.74	8.75	8.10 ¹⁰⁰
butane	7.14	7.88	8.14	8.30	8.33	8.33	7.69 ⁹⁸
ethane	3.68	4.16	4.32	4.45	4.48	4.48	4.23 ⁹⁸
ethylene	3.21	3.66	3.90	4.20	4.25	4.26	4.19 ⁹⁸
H ₂	0.45	0.62	0.70	0.84	0.86	0.86	0.79 ⁹⁸
methane	1.99	2.33	2.46	2.60	2.62	2.63	2.45 ⁹⁸
naphthalene	15.71	16.98	17.65	18.31	18.35	18.40	16.6 ¹⁰¹
propane	5.41	6.02	6.23	6.37	6.39	6.40	5.92 ⁹⁸
$\Delta\alpha$	-0.15	-0.04	0.02	0.08	0.09	0.09	
$ \Delta\alpha $	0.17	0.08	0.07	0.08	0.09	0.09	

than by charge migration, making monopole-order tight binding unable to describe this effect.

4.1.4.4 Dipole-quadrupole polarisabilities

Table 4.4 refers to the errors in the dipole-quadrupole polarisabilities $a_{\xi\mu\nu}^V = a_{\xi\mu\nu}/(4\pi\epsilon_0)$ between GTB and DFT. Only tensor elements larger than $0.5 \text{ \AA}^4$ are considered for the errors, so as not to include large relative errors from quadrupole moments that vary only little with field strength. With the previous results of the dipole polarisability benchmark in mind, it is unsurprising that the SVP-GTB model performs well compared to PBE-DFT with the cc-pVTZ basis set.

4.1.5 Conclusion

The polarisability benchmarks indicate that SVP-GTB in the dipole order describes the static electronic response of molecules to external fields with an accuracy comparable to PBE-DFT. This is particularly satisfying due to the simplicity of multipole expansion employed in this method. Inclusion of the quadrupole terms does not generally improve

Table 4.3: Gaussian tight binding calculations of mean polarisability volumes $\alpha_m = \text{Tr}(\alpha^V)/3$ in $\text{\AA}^3$ for single-valence (SV) and polarisable (SVP) basis sets, as well as various orders of multipole expansion. The mean relative error and mean relative absolute errors compared to experiment are given as $\Delta\alpha$ and $|\Delta\alpha|$.

	SV-GTB, order			SVP-GTB, order			exp.
	0	1	2	0	1	2	
acetylene	1.35	1.50	1.47	1.91	3.10	3.04	3.49 ⁹⁸
azulene	12.31	11.87	11.92	17.17	17.57	17.58	15.52 ⁹⁹
benzene	5.80	5.34	5.32	9.06	9.18	9.13	9.9 ¹⁰¹
butadiene	4.76	4.43	4.40	7.28	7.75	7.71	8.10 ¹⁰⁰
butane	4.39	2.80	2.81	9.05	7.20	7.22	7.69 ⁹⁸
ethane	2.25	1.45	1.46	4.50	3.92	3.94	4.23 ⁹⁸
ethylene	1.96	1.73	1.72	3.27	3.71	3.68	4.19 ⁹⁸
H ₂	0.18	0.18	0.18	0.20	0.90	0.90	0.79 ⁹⁸
methane	1.16	0.75	0.77	2.28	2.28	2.30	2.45 ⁹⁸
naphthalene	11.01	10.27	10.30	16.43	16.11	16.12	16.6 ¹⁰¹
propane	3.31	2.12	2.13	6.68	5.54	5.56	5.92 ⁹⁸
$\Delta\alpha$	-0.47	-0.55	-0.55	-0.11	-0.03	-0.04	
$ \Delta\alpha $	0.47	0.55	0.55	0.20	0.08	0.08	

the description of the dipole and dipole-quadrupole polarisability, hence we shall proceed with dipole-order SVP-GTB for the next set of simulations.

The dipole polarisability errors of the GTB method are similar as reported for the chemical-potential equalisation DFTB method,^{78,79} though we have not considered ionic molecules in the present work.

The HOMO-LUMO gap analysis further demonstrates the quality of the SVP-GTB model to be only weakly dependent on the choice of the confining external potential. With this in mind, we augment our hydrocarbon model with sulfur, imposing the same confinement radius of $R_C^S = 4.5 a_0$ as for carbon.

4.2 Induced fields in amorphous P3HT

The performance benefits of GTB make it an efficient choice for computing the properties of large molecules. We demonstrate this on the example of an amorphous bulk polymer under the influence of an external field. This system is especially challenging to model with electronic structure methods due to the polymers' large molecular size as well as their

Table 4.4: Errors of GTB quadrupole-dipole polarisability volumes $a_{\xi\mu\nu}^V$ to DFT for single-valence (SV) and polarisable (SVP) basis sets, as well as various orders of multipole expansion. The mean relative error and mean relative absolute errors are given as $\Delta\alpha$ and $|\Delta\alpha|$.

	GTB-SV, order			GTB-SVP, order		
	0	1	2	0	1	2
errors relative to cc-pVTZ DFT						
$\Delta\alpha$	0.39	0.44	0.43	0.03	0.03	0.02
$ \Delta\alpha $	0.40	0.53	0.55	0.33	0.06	0.08
errors relative to aug-cc-pVTZ DFT						
$\Delta\alpha$	0.42	0.46	0.46	0.13	0.09	0.09
$ \Delta\alpha $	0.46	0.60	0.60	0.29	0.15	0.16

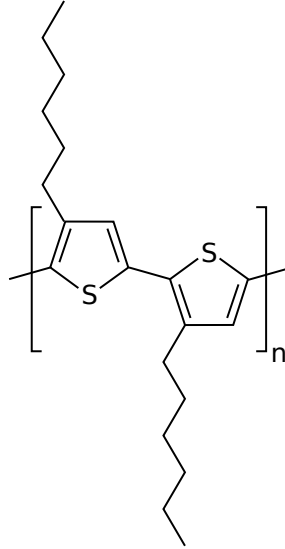


FIGURE 4.3: A P3HT dimer. The polymers in this work were chosen to be 20 monomers long ($n = 10$), giving them a mass of 3.3 kDa and an end-to-end length of about 70 Å. The simulation cell is cubic with a cell length of 95.42 Å and a density of 1017 kg/m³.

close proximity to one another. We aim to estimate the total electric fields at each polymer site for a given point in time, using solely input from isolated strand GTB calculations in conjunction with structural data from classical molecular dynamics. This will enable future time-dependent simulations of molecular fragments in external fields to take into account the electrostatic screening by the neglected surrounding material.

With future applications in mind, we choose the polymer Poly(3-hexylthiophene-2,5-diyl), P3HT, see figure (4.3). The polymer strands considered here are 20 monomers

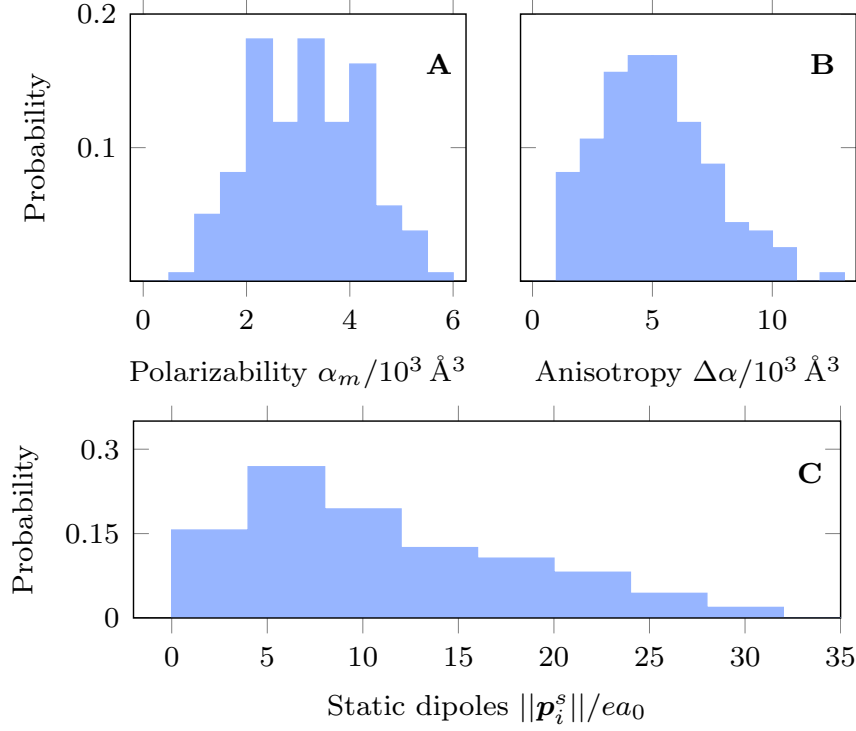


FIGURE 4.4: Electrostatic properties of isolated P3HT strands from the amorphous phase: histograms of mean polarisability volume α_m (**A**) and polarisability anisotropy $\Delta\alpha$ (**B**) in $10^3 \text{ \AA}^3$, and static dipole moments $\|\vec{p}_i^s\|$ (**C**) in ea_0 . Here $\Delta\alpha$ is defined by $2\Delta\alpha^2 = (\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2$.

long, and as such contain 500 atoms each. We use classical molecular dynamics data from a simulation box representing 160 P3HT strands in an amorphous configuration at a temperature of 360 K. The molecular dynamics simulations were carried out by A.A.Y. Guilbert, more information is available elsewhere.^{103,104}

The polarisability of every whole chain in isolation is computed in dipole-order SVP-GTB by applying external fields of $\pm 0.0005 E_h / ea_0$, as outlined in section 4.1. The polarisabilities, static dipole moments (figure 4.4), and geometries act as input for a damped Polarisable-Point-Dipoles (PPD) model,^{105–107} which approximates the polymer strands as classical polarisable particles. This enables efficient calculation of the induced fields at any point of the system. We shall briefly outline the PPD model as used in this approach.

4.2.1 Polarisable-point-dipoles model

Consider an interacting polymer strand on site i to have a mean ionic position $\vec{R}_i$, a dipole moment $\vec{p}_i = \vec{p}_i^s + \vec{p}_i^i$ given by the sum of static $\vec{p}_i^s$ and induced $\vec{p}_i^i$ dipole moments, and

an anisotropic polarisability tensor $\hat{\alpha}_i$. The strands are considered as charge neutral, hence only intermolecular dipole interactions are taken into account. The total electrostatic energy U_{ele} is then given as:

$$U_{ele} = U_{d,d} + U_{d,pol} + U_{d,ext} \\ = - \sum_{i,j>i} \vec{p}_i \cdot (\hat{T}_{ij} \vec{p}_j) + \frac{1}{2} \sum_i \vec{p}_i \cdot (\hat{\alpha}_i^{-1} \vec{p}_i) + \sum_i \vec{p}_i \cdot \vec{E}_{ext}. \quad (4.4)$$

The first term is the interaction between total dipole moments on different strands; the second term is the energy associated with polarising each strand; the final term is the interaction of the total dipoles with the external field. The sum is taken over all interacting dipoles in the system. Here $\hat{T}_{ij}$ is the 3×3 electrostatic dipole-dipole interaction tensor, defined by the second-order derivative of the damping function $s_0(\vec{r})$,¹⁰⁷

$$\left(\hat{T}_{ij} \right)_{\mu\nu} = \partial_{r_\mu} \partial_{r_\nu} (s_0(\vec{r})/r) \Big|_{\vec{r}=\vec{R}_{ij}} \quad (4.5)$$

which depends on the normalized charge distribution n_i of the polarisable particles:

$$s_0(\vec{R}_{ij}) = R_{ij} \int \frac{n_i(\vec{r} - \vec{R}_i) n_j(\vec{r}' - \vec{R}_j)}{||\vec{r} - \vec{r}'||} d\vec{r} d\vec{r}'. \quad (4.6)$$

We shall recast (4.4) into a more convenient form, defining the matrices:

$$A_{ij} = \hat{\alpha}_i^{-1} \delta_{ij}, \quad T_{ij} = \hat{T}_{ij}, \quad J_{ij} = A_{ij} - T_{ij}, \quad (4.7)$$

where $T_{ii} = 0$. The site-dependent vectors are further written into single columns, e.g. $P = (\vec{p}_1 \ \vec{p}_2 \ \dots \ \vec{p}_N)^T$. The total electrostatic energy is then given as:

$$U_{ele} = -\frac{1}{2} P^T T P + \frac{1}{2} (P^i)^T A P^i + P^T E^{ext}. \quad (4.8)$$

The total dipole moments P are found by the stationary condition $\partial_P U_{ele} = 0$, which follows from minimizing U_{ele} , and which gives:

$$P = J^{-1} A P^s + J^{-1} E^{ext}. \quad (4.9)$$

The super-polarisability matrix¹⁰⁵ of the simulation cell is hence identified as $\hat{\alpha}_{tot} = \sum_{ij} (J^{-1})_{ij}$, from which the dielectric constant can be derived. We can now formulate an expression for the site-dependent internal fields. Consider again each dipole to be given by a static and induced component. The induced component on site i is determined by the total internal field on site i , following the relation $\vec{p}_i^i = \hat{\alpha}_i \vec{E}_i^{tot}$. Thus the internal fields are given as $E^{tot} = A P^i$:

$$E^{tot} = A (J^{-1} A - \mathbb{I}) P^s + A J^{-1} E^{ext}, \quad (4.10)$$

where $\mathbb{I}$ is the $N \times N$ identity matrix. The total fields hence depend linearly on the applied external field, with an initial value determined by the static dipoles.

The choice of $n_i(\vec{r})$ needs to be addressed next. The PPD model makes the assumption that the charge distributions of the interacting particles are of small spatial extent compared to their distance to one another. Violation of this condition can lead to a break-down of the model; this is called the *polarisation catastrophe*.¹⁰⁵ In this case the J-matrix is not positive definite, which means U_{ele} does not have a minimum solution.¹⁰⁵ The damping function $s_0(\vec{r})$ acts to reduce the overlap between close particles by assigning a localized charge distribution $n_i(\vec{r})$ to them, subsequently lowering their contribution to the electrostatic energy. The optimal choice of the damping function has been, and still is, the subject of extensive research.^{105,108,109} In this work we choose a Gaussian PPD model:^{106,107,110}

$$n_i(\vec{r}) = \left(\frac{\kappa}{\pi}\right)^{3/2} e^{-\kappa\vec{r}^2}, \quad (4.11)$$

for its ease of implementation and its simple reciprocal representation for periodic boundary conditions.

P3HT polymer strands have a particularly anisotropic shape, which makes this system very sensitive to a breakdown of the dipole approximation. We shall therefore test two models that avoid this problem:

1G model. Each strand is described by a single Gaussian-damped polarisable particle (figure 4.5). A very generous smearing of at least $\kappa = 0.001/a_0^2$ was required to keep the J-matrix positive definite. This corresponds to a Gaussian full-width half-maximum (FWHM) of $52.7 a_0$, or 30% of the simulation box length.

NG model. Each polymer strand is split into N_ν individually polarisable beads, with the strand polarisability $\hat{\alpha}_i$ and static dipole $\vec{p}_i^s$ evenly divided amongst the beads (figure 4.6). Beads within the same strand do not interact with each other, though they do interact with dipoles on other strands. The Gaussians are centered on the sulfur atoms at $\vec{R}_\nu$, as these follow the polymer backbone well. Using this approach, a damping of $\kappa = 0.0022/a_0^2$ was found to give stable results, which corresponds to a FWHM of $35.5 a_0$, or 20% of the simulation box length.

4.2.2 Simulation of internal fields

The damped PPD models are run with xyz-periodic boundary conditions, evaluating the $\hat{T}_{ij}$ matrix elements by Ewald Summation with “tin foil” surface conditions ($\varepsilon_{Surface} \rightarrow \infty$).¹⁰⁶ The dielectric constant ε_r is found to be 3.32 for 1G and 3.41 for NG. This is consistent with

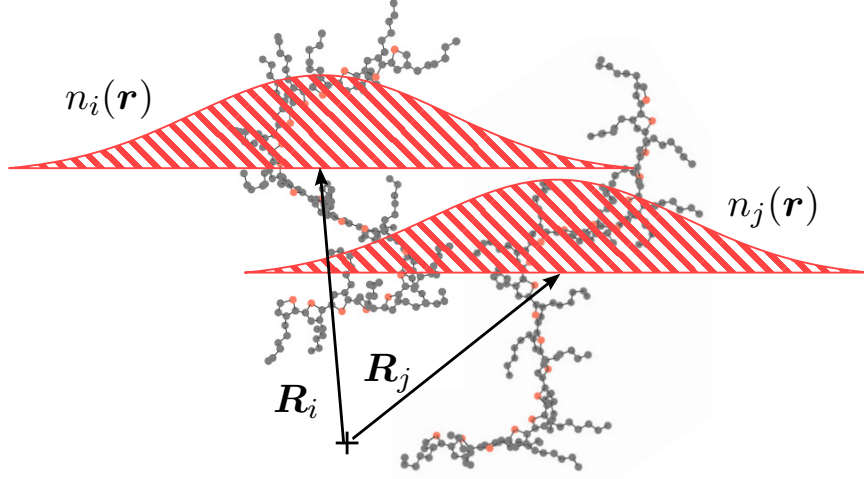


FIGURE 4.5: Coordinate system in the 1G model. Each P3HT strand is described as one polarisable particle. The charge distribution of a strand is approximated by a diffuse Gaussian (patterned area).

$\varepsilon_r \approx 3$ chosen for P3HT models¹¹¹ and $\varepsilon_r \approx 2.9$ for film measurements,¹¹² considering the simple form of the electrostatic model. DFTB has furthermore a tendency to overestimate polarisabilities of large conjugated chain molecules, similar to DFT.¹¹³

The total internal field equation (4.10) can furthermore be cast into self- and externally-induced components

$$\vec{E}_i^{\text{tot}} = \vec{E}_i^{\text{self}} + \hat{\gamma}_i \vec{E}^{\text{ext}}, \quad (4.12)$$

where

$$\vec{E}_i^{\text{self}} = \sum_j (\mathbf{A} (\mathbf{J}^{-1} \mathbf{A} + \mathbb{I}))_{ij} \vec{p}_j^s \quad (4.13)$$

is the self-induced internal field produced by the system's static dipoles, and

$$\hat{\gamma}_i = \sum_j (\mathbf{A} \mathbf{J}^{-1})_{ij} \quad (4.14)$$

is defined as the screening matrix, which determines both magnitude and direction of the externally-induced field $\hat{\gamma}_i \vec{E}^{\text{ext}}$. The screening matrix is generally asymmetric and anisotropic. We present histograms (figure 4.7) of the angular-averaged screening

$$\langle \hat{\gamma}_i \rangle_{\Omega} = 1/4\pi \int \|\hat{\gamma}_i \cdot \hat{e}_r(\theta, \phi)\| d\Omega, \quad (4.15)$$

which measures the screening of the magnitude of an external unit field averaged over all angular directions, and the angular screening anisotropy

$$\sigma_{\hat{\gamma}_i} = \left(1/4\pi \int \|\hat{\gamma}_i \cdot \hat{e}_r(\theta, \phi)\|^2 d\Omega - \langle \hat{\gamma}_i \rangle_{\Omega}^2 \right)^{1/2}, \quad (4.16)$$

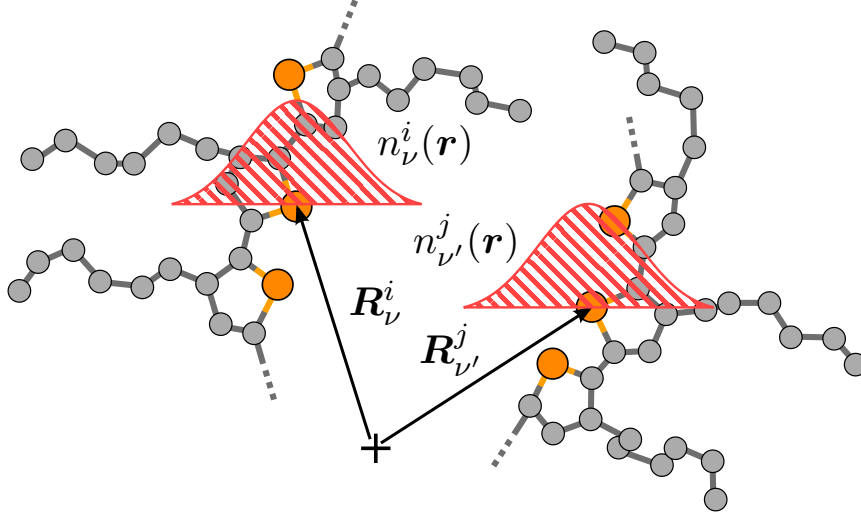


FIGURE 4.6: Coordinate system in the NG model. The P3HT strands are split into beads centered on the sulfur atoms (orange). The charge distribution of a bead is approximated by a diffuse Gaussian (patterned area). The polarisability and static dipole of a strand are evenly split amongst the beads.

which is the standard-deviation of the angular-averaged screening and as such measures the anisotropy of the screening with respect to the direction of an external unit field.

We find the screening properties to vary considerably over the polymer sites, see figure 4.7. The 1G model yields narrower distributions which is consistent with the use of wide Gaussian densities. Interactions between close strands are damped strongly, subsequently less site-dependence is expected. The NG model in contrast retains more interaction with the immediate environment of a strand, hence the screening properties follow a more irregular distribution. This is no surprise as the isolated strands show very strong variations in polarisability, see figure 4.4. A key result is that both expectation values $\mathbb{E}[\langle \hat{\gamma}_i \rangle_{\Omega}]$ and $\mathbb{E}[\sigma_{\hat{\gamma}_i}]$ are very similar between the 1G and NG models. The statistically averaged screening behavior is thus not particularly sensitive to the choice of the model; the NG model however differentiates site-resolved properties better.

For illustrative purposes we select a representative P3HT site j with $\langle \hat{\gamma}_j \rangle_{\Omega} = 0.27$ and $\sigma_{\hat{\gamma}_j} = 0.08$ close to the expectation values. A strong external field of 0.1 (in E_h/ea_0) leads to an angular-averaged externally-induced field of 0.027, with directionally dependent variations of $\sigma = 0.08$. The self-induced fields in this case are negligible, as their magnitude reaches at most 0.001, see figure 4.7. The total induced field at the representative P3HT site is listed in table 4.5 over various field strengths in the $\hat{e}_x$ direction for the NG model. A key observation is that the internal field direction does not fully align with the external

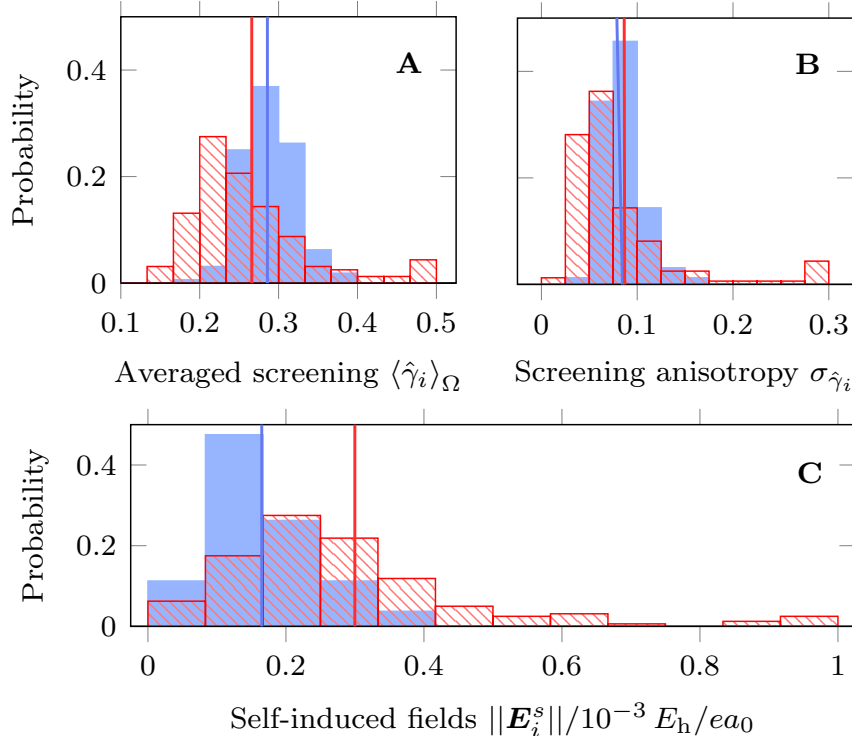


FIGURE 4.7: Internal field properties of amorphous P3HT in the 1G (blue, solid fill) and NG (red, patterned fill) models: histograms of angular-averaged screening $\langle \hat{\gamma}_i \rangle_\Omega$ (A), angular screening anisotropy $\sigma_{\hat{\gamma}_i}$ (B), and the self-induced fields $\|\vec{E}_i^s\|$ (C) in $10^{-3} E_h/ea_0$. The expectation values (vertical lines) in the 1G (NG) model are $\mathbb{E}[\langle \hat{\gamma}_i \rangle_\Omega] = 0.29$ (0.27), $\mathbb{E}[\sigma_{\hat{\gamma}_i}] = 0.08$ (0.09), and $\mathbb{E}[\|\vec{E}_i^s\|] = 0.16$ (0.3) $10^{-3} E_h/ea_0$.

field direction, but rather converges to a site-dependent constant angle for large fields. This effect is a direct consequence of the electrostatic coupling between polymer strands, and is reflected in the anisotropy of the screening-matrices. Figure (4.8) shows the self- and externally-induced fields for a slice through the simulation cell.

In summary, the approach taken here gives us an estimate on the internal field of a molecule in the midst of an extended system in a static external field. The site-resolved internal fields are found by using solely MD structural data and GTB data of isolated strands as an input. The screening matrices and the self-induced fields are an intuitive way to characterize the intermolecular interactions, allowing a basic description of the electrostatic environment in isolated strand simulations. More accurate values can likely be found by using a coarse-grained charge-equilibration model,¹¹⁴ though its parametrisation would require considerably more effort than the straightforward NG model outlined in this work. The PPD model can be further extended to include time-dependent external fields by using frequency-dependent polarisabilities from GTB; this would enable simulation of

Table 4.5: Total induced fields in E_h/ea_0 of an example strand site j in amorphous P3HT for various external fields in $\hat{e}_x$ direction. The angle between external and total internal field $\angle(\hat{e}_x, \vec{E}_j^{tot})$ gradually converges to a limit of 5.10° for very large fields (not shown). The screening factor for this direction is found as 0.27.

$(\vec{E}^{ext})_x$	$\vec{E}_j^{tot}$			$\angle(\hat{e}_x, \vec{E}_j^{tot})$
0.000	-0.00017	0.00034	-0.00019	114.00
0.001	0.00010	0.00033	-0.00017	75.43
0.005	0.00118	0.00028	-0.00008	13.98
0.010	0.00254	0.00022	0.00020	5.10
0.050	0.01339	-0.00023	0.00088	3.88
0.100	0.02695	-0.00080	0.00194	4.47

the extended system in conditions similar to those encountered in laser experiments.

4.2.3 Error analysis

We would like to emphasise that LDA and GGA-DFT are known to severely overestimate the polarisability of extended conjugated systems, such as polythiophene,¹¹⁵ due to the self-interaction error.¹¹⁵ GTB, as an approximate PBE-DFT method, inherits this limitation.¹¹⁶ We demonstrate this by computing the polarisabilities of a P3HT strand for chain lengths of varying monomer count n , where $n = 20$ corresponds to a full P3HT chain. The chain segments are terminated with hydrogen. Our methods of choice are MP2 in the RIJCOSX approximation¹¹⁷ and PBE-DFT using the 6-31G* basis-set,¹¹⁸ and dipole order SVP-GTB. We compare the relative error r_α in the isotropic polarisabilities of GTB and DFT to those of MP2 over monomer count n .

It is found that while GTB starts with a relative error of 11 % for $n = 1$, the error linearly increases up to 25 % for $n = 10$. We extrapolate the GTB polarisability error by a linear fit to 44 % for $n = 20$. The same behaviour is seen for PBE-DFT, where $r_\alpha = 6$ % for $n = 1$, 33 % for $n = 10$, and we extrapolate $r_\alpha = 62$ % for $n = 20$. This error is less severe than previously reported values¹¹⁵ of 100 % for polythiophene at $n = 8$, possibly due to the non-planar structure of the polymer strand used here and the addition of propane side-chains.

Next we assess the effect of this error on the computed bulk properties of P3HT. We rescale the GTB strand polarisabilities by a factor of $2/3$ (≈ 44 % overestimation). The

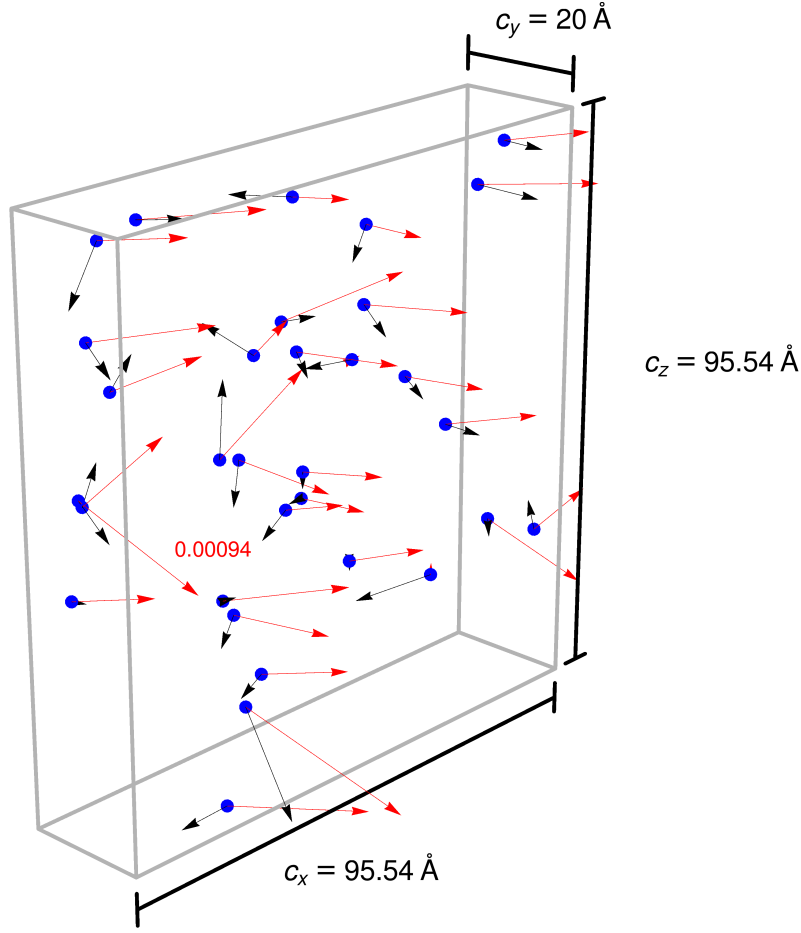


FIGURE 4.8: Internal fields of amorphous P3HT with applied external field (red arrows) of $\vec{E}^{ext} = 0.002 E_h/ea_0 \hat{e}_x$ and without field (black arrows) in the NG model. The dots represent the mean position of P3HT strands. The largest internal field $\vec{E}_i^{tot} = 0.00094 E_h/ea_0$ is marked for reference. A slice of $20 \text{ \AA}$ width is shown for improved visibility.

1G (NG) model now predicts a dielectric constant of 2.98 (3.00), and an angular-averaged mean screening of 0.26 (0.25). We note that the screening remains mostly unchanged. A smaller Gaussian density smearing can be used in the PPD model as a consequence of the polarisability reduction, which increases the dielectric constant and therefore largely negates the previous changes. This makes clear the need for future research on efficient self-interaction correction methods^{116,119,120} for tight binding in conjunction with the electrostatic multipoles model. We refer to the recently developed long-range corrected DFTB method¹¹⁶ as a possible solution.

4.3 Summary

We have formulated the SVP-GTB method which is a polarisable-ion tight-binding theory systematically derived from DFT, with a polarisable basis set optimised to describe molecular polarisabilities with high accuracy. The GTB method improves upon standard self-consistent tight binding by a more accurate estimation of the second-order variation in the Hartree energy. This is achieved by an on-the-fly multipole expansion of the atomic densities into Gaussian-type functions, and only requires a single adjustable parameter for the atomic hardness per atomic species. GTB computes molecular polarisabilities with PBE-DFT accuracy, but with considerably less computational time due to the usual tight-binding approximations.

We have applied GTB in conjunction with data from classical molecular dynamics and the polarisable-point-dipoles model to give an estimate of the internal fields in bulk amorphous P3HT as a function of an applied external field. We found a strong site-dependence in the field screening strength, which is consistent with the large variety of isolated strand polarisabilities displayed. The field screening serves as a useful input in future dynamical GTB simulations to correct for the missing electrostatic environment.

The GTB method delivers reliable electrostatic polarisabilities for small systems, however as in PBE-DFT, the polarisability of conjugated extended systems is strongly overestimated. This presents the need to implement approximate self-interaction corrections in GTB for a reliable description of electrostatics on all length-scales.

We emphasise at this point again that the GTB model was designed to offer an effective description of electrostatic properties. It remains to be seen how well GTB performs as an all-purpose tight binding model for a more varied ensemble of properties, such as vibrational frequencies, reaction enthalpies, hydrogen bonding, electrostatic forces, and others.

We have previously shown Gaussian tight binding theory to be capable of predicting the static polarisability of molecules with accuracy comparable to density-functional theory. A majority of optical properties however stem from a response of a given system to an external *time-dependent* perturbation. This is especially true in the systems encountered in ultrafast dynamics experiments. While sophisticated time-propagated density-functional theory (TP-DFT) codes for ultrafast dynamics simulations are available,^{121–123} we seek to directly test in this chapter whether the significantly faster Gaussian tight binding method is capable of reproducing the very same physical features.

We shall first outline the solution of the time-dependent Kohn-Sham equation in the Gaussian tight binding framework. We formulate a numerical integration scheme that preserves the orthonormality of the wave-functions and verify its effectiveness by monitoring energy conservation over time. The resulting time-propagated Gaussian tight binding method (TP-GTB) is directly compared to TP-DFT on the example of a trans-2,2'-bithiophene molecule under the influence of an external electric field. TP-GTB is found to deliver an accurate description of the electron dynamics.

5.1 Time-dependent Kohn-Sham equations with a localised basis set

Density-functional theory enables a computationally feasible treatment of a time-dependent many-body system by solution of the time-dependent Kohn-Sham equation given by (2.57):

$$i\hbar\dot{\Phi}^{(n)}(\vec{r}, t) = \left(-\frac{\hbar^2}{2m_e} \vec{\nabla}_r^2 + v_{KS}[\rho](\vec{r}) \right) \Phi^{(n)}(\vec{r}, t). \quad (5.1)$$

Computing time and memory constraints dictate that a numerical solution requires a finite representation of the Kohn-Sham orbitals $|\Phi^{(n)}(t)\rangle$. This could for instance be a real-space grid-based representation $\{x_i, y_j, z_k\}$. The benefits of using a spatial grid lie in its flexibility, as no particular shape is enforced on the wave-function other than the extent and the resolution of the simulation box, and in the ease in which the workload can be distributed over multiple cores. On the other hand this approach requires the use of millions of grid points to converge the eigenvalues with respect box size and resolution, and as such requires considerable computational effort even for a small system. Examples of real-space grid-based TP-DFT codes are OCTOPUS¹²¹ and EDAMAME.¹²³

Density-functional tight binding methods necessarily represent the Kohn-Sham states in terms of the atomically-localised basis functions $|\phi_{I\alpha}\rangle$ as introduced in section 2.4.2.2:

$$\Phi^{(n)}(\vec{r}, t) = \sum_{I\alpha} c_{I\alpha}^{(n)}(t) \phi_{I\alpha}(\vec{r} - \vec{R}_I(t)), \quad (5.2)$$

where $\{c_{I\alpha}^{(n)}(t)\} \in \mathbb{C}$ are the expansion coefficients of the n -th time-dependent Kohn-Sham state. We will next derive the matrix representation of Eq. (5.1) in the local basis set formalism.

We multiply the orbital $\phi_{J\beta}(\vec{r} - \vec{R}_J)$ to Eq. (5.1) from the left and integrate over the volume:

$$i\hbar \langle \phi_{J\beta} | \dot{\Phi}^{(n)} \rangle = \langle \phi_{J\beta} | \hat{H}^{KS} | \Phi^{(n)} \rangle. \quad (5.3)$$

Next the basis expansion from Eq. (5.2) is substituted:

$$i\hbar \sum_{I\alpha} \left(\dot{c}_{I\alpha}^{(n)}(t) \langle \phi_{J\beta} | \phi_{I\alpha} \rangle + c_{I\alpha}^{(n)}(t) \langle \phi_{J\beta} | \dot{\phi}_{I\alpha} \rangle \right) = \sum_{I\alpha} c_{I\alpha}^{(n)}(t) \langle \phi_{J\beta} | \hat{H}^{KS} | \phi_{I\alpha} \rangle. \quad (5.4)$$

We remember the definition of the overlap matrix $S_{I\alpha J\beta} = \langle \phi_{I\alpha} | \phi_{J\beta} \rangle$, the Hamiltonian matrix $H_{I\alpha J\beta}^{KS} = \langle \phi_{I\alpha} | \hat{H}^{KS} | \phi_{J\beta} \rangle$, and define the overlap derivative matrix $P_{I\alpha J\beta} = \langle \phi_{I\alpha} | \dot{\phi}_{J\beta} \rangle$. We can then write Eq. (5.4) as:

$$i\hbar \sum_{I\alpha} \left(S_{J\beta I\alpha} \dot{c}_{I\alpha}^{(n)}(t) + P_{J\beta I\alpha} c_{I\alpha}^{(n)}(t) \right) = \sum_{I\alpha} H_{J\beta I\alpha}^{KS} c_{I\alpha}^{(n)}(t) \quad (5.5)$$

$$i\hbar \left(S \dot{C}(t) + P C(t) \right) = H C(t), \quad (5.6)$$

Where $C_{I\alpha, n}(t) = c_{I\alpha}^{(n)}(t)$ is the time-dependent states matrix. This expression can be rearranged as:

$$\dot{C}(t) = -\frac{i}{\hbar} S^{-1} (H + i\hbar P) C(t), \quad (5.7)$$

where the initial states matrix $C(t_0)$ is taken from the solution of the time-independent problem. Note that this is only the equation of motion for the electronic states. The ionic equation of motion is presented at a later stage in section 6.1.

Consider first the intersite case, that is $I \neq J$. The basis orbitals in this representation are implicitly time-dependent through their pinning to the ionic coordinates. The matrix P therefore takes on the form:

$$\begin{aligned} P_{I\alpha J\beta} &= \int \phi_{I\alpha}(\vec{r} - \vec{R}_I(t)) \frac{\partial}{\partial t} \phi_{J\beta}(\vec{r} - \vec{R}_J(t)) d^3r \\ &= \dot{\vec{R}}_J \cdot \int \phi_{I\alpha}(\vec{r} - \vec{R}_I(t)) \vec{\nabla}_{R_J} \phi_{J\beta}(\vec{r} - \vec{R}_J(t)) d^3r \\ &= \dot{\vec{R}}_J \cdot \vec{\nabla}_{R_J} S_{I\alpha J\beta}. \end{aligned} \quad (5.8)$$

We exploit that the overlap matrix elements are only a function on the interatomic displacements $\vec{R}_{IJ} = \vec{R}_I - \vec{R}_J$:

$$\vec{\nabla}_{R_K} S_{I\alpha J\beta}(\vec{R}_{IJ}) = -\vec{\nabla}_{R_{IJ}} S_{I\alpha J\beta}(\vec{R}_{IJ}) (\delta_{IK} - \delta_{JK}), \quad (5.9)$$

therefore for $K = J$ it follows for Eq. (5.8):

$$P_{I\alpha J\beta} = \dot{\vec{R}}_J \cdot \vec{\nabla}_{R_{IJ}} S_{I\alpha J\beta}(\vec{R}_{IJ}). \quad (5.10)$$

This expression is evaluated in tight binding by differentiating the Slater-Koster integrals as outlined in section 2.4.6.2. We also note that P becomes zero if the ionic coordinates are held fixed, that is if $\dot{\vec{R}}_J = 0$. The onsite case is treated separately as the limit of $\vec{R}_J \rightarrow \vec{R}_I$ following Tong.⁶⁹

$$P_{I\alpha I\beta} = \dot{\vec{R}}_I \cdot \left(\lim_{\vec{R}_J \rightarrow \vec{R}_I} \vec{\nabla}_{R_{IJ}} S_{I\alpha J\beta}(\vec{R}_{IJ}) \right). \quad (5.11)$$

5.2 Propagation scheme

We are left to solve the time-dependent Kohn-Sham equation (5.7). This equation cannot be solved analytically; the explicit time-dependence of the Hamiltonian through the external electric field, as well as the implicit time-dependence of the Hamiltonian through it being a functional of the time-dependent density demand a numerical solution. We are left to apply a numerical integration scheme, propagating the system from a starting point t_0 to an endpoint t_f in finite steps of δt .

The computational cost associated with propagating the time-dependent problem is two-fold. For one, the Hamiltonian needs to be rebuilt after every time step due to its time-dependence. While this is a significant effort in density-functional theory methods, this cost carries little weight in tight binding methods, as the construction of the matrices is extremely fast by virtue of the two-centre approximations (section 2.4.2) and the Slater-Koster look-up tables (section 2.4.6). The other major cost lies in the overlap matrix

inversion required to propagate Eq. (5.7). The computational effort to invert a matrix scales as $\mathcal{O}(N_{\text{basis}}^3)$, hence it is of interest to keep the number of basis functions as low as possible without sacrificing too much accuracy.

5.2.1 Runge-Kutta algorithm

We use the 4th-order Runge-Kutta (RK4) integration algorithm due to its robustness and ease of implementation.¹²⁴ A single RK4 step requires four trial steps; while being robust, the method also requires a large number of function evaluations.

The RK4 algorithm however does not preserve unitarity, which means that the electron number changes over time and our system suffers from an energy drift. We avoid this problem by projecting the approximate, non-unitary solution provided by RK4 back onto the set of unitary matrices. This *projected unitary integrators* approach follows Dieci et al.¹²⁵

5.2.1.1 Unitarity condition

The time-dependent Kohn-Sham equation (5.1) conserves the orthonormality of the Kohn-Sham states. This condition can be made more mathematically tractable. Consider the norm of two eigenstates:

$$\langle \Psi^{(n)} | \Psi^{(m)} \rangle = \sum_{I\alpha J\beta} c_{I\alpha}^{*(n)}(t) c_{J\beta}^{(m)}(t) S_{I\alpha J\beta} = (C^\dagger(t) S C(t))_{nm} \stackrel{!}{=} \delta_{nm}, \quad (5.12)$$

hence:

$$C^\dagger(t) S C(t) = \mathbb{I}. \quad (5.13)$$

For an orthonormal basis set we have $S = \mathbb{I}$, the above relation therefore reduces to the form $C^\dagger(t) C(t) = \mathbb{I}$. The condition that the orthonormality of the wave-function is conserved becomes equal to the condition that the states matrix is unitary, that is $C^{-1}(t) = C^\dagger(t)$.

For a non-orthogonal basis set the states matrix $C(t)$ itself is not unitary and we need to recast Eq. (5.13) further. Consider next a Cholesky decomposition of the overlap matrix S into upper triangular matrices, $S = U U^\dagger$:

$$C(t)^\dagger S C(t) = C^\dagger(t) U U^\dagger C(t) = (U^\dagger C(t))^\dagger (U^\dagger C(t)) \equiv B^\dagger(t) B(t) = \mathbb{I}. \quad (5.14)$$

The new matrix $B(t)$ is unitary. The time-dependent Kohn-Sham equations using a non-orthogonal basis-set hence preserve the unitarity of $B(t) = U^\dagger C(t)$. The RK4 algorithm however does not consider the unitarity explicitly — unitarity is violated as the eigenvectors' equation of motion is evolved.

Table 5.1: Projected unitary Runge-Kutta method. This algorithm describes how to numerically integrate the time-dependent Kohn-Sham equation while conserving the norm using a *projected unitary integrator* approach. Here $t_{i+1} = t_i + \delta t$.

-
-
1. Use RK4 to find the norm-violating approximation $\tilde{C}(t_{i+1})$ from $C(t_i)$.
 2. Apply Cholesky decomposition for $S = UU^\dagger$ to find $\tilde{B}(t_{i+1}) = U^\dagger \tilde{C}(t_{i+1})$.
 $\tilde{B}(t_{i+1})$ is the non-unitary approximation of the unitary solution B_{i+1} .
 3. Use QR -factorisation for $\tilde{B}(t_{i+1}) = QR$ to find the unitary matrix Q .
 Q is the unitary projected solution $B(t_{i+1})$.
 4. Solve $B(t_{i+1}) = U^\dagger C(t_{i+1})$ for the norm-conserving solution $C(t_{i+1})$.
-
-

5.2.1.2 Unitarity projection

We discuss two kinds of approaches to solving the equations of motion while conserving the unitarity of the solution B . One could use *automatic unitarity integrators* which are carefully constructed to conserve the unitarity of the solution. One drawback is that these integrators have to be chosen carefully depending on the problem. We refer here to Lubich¹²⁶ for a write-up on various unitary integration schemes.

We are left with the second possibility of using a *projected unitary integrator*. In this approach we consider the non-unitary integration scheme to deliver a non-unitary solution $\tilde{B}$ as an approximation to the true unitary solution B . We then proceed to project $\tilde{B}$ back onto the space of unitary matrices to correct this error, for instance via QR -factorisation. This approach is based on the Lemma 4.2 from Dieci et al. in 1994.¹²⁵

Lemma. Suppose that $\tilde{B} \in \mathbb{C}^{n \times n}$ and assume that for some p and $\delta t_0 > 0$, $\tilde{B}^\dagger \tilde{B} = \mathbb{I} + \mathcal{O}(\delta t^p)$ for $0 < \delta t < \delta t_0$. The unique QR -factorisation of $\tilde{B}$ such that $\tilde{B} = QR$, $Q \in \mathcal{U}^{n \times n}$ (unitary), $R \in \mathcal{T}^{n \times n}$ (triangular) and $R_{ii} > 0$ satisfies $R = \mathbb{I} + \mathcal{O}(\delta t^p)$.

The Q matrix is then accepted as the unitary solution B . The deviation of R from the identity matrix $\mathbb{I}$ is at most of the order of $\mathcal{O}(\delta t^p)$, which is of the same order as the norm error of the approximate solution B . The QR -factorisation hence does not further degrade the accuracy of the solution, but in turn restores its unitarity. Our algorithm proceeds as outlined in table 5.1. We have implemented this algorithm in PLATO using a series of modules from the linear algebra package LAPACK.¹²⁷

5.2.2 Energy conservation tests

We test the effectiveness of the numerical propagation scheme in the dipole-order SVP-GTB model. The test system is a benzene molecule in the ground-state with fixed ionic coordinates. A time-dependent perturbation is applied in the form of a short external field pulse:

$$\vec{E}(t) = E_0 \hat{e}_x e^{-(t-t_0)^2/2\sigma^2}, \quad (5.15)$$

where $E_0 = 0.0015 E_h/ea_0$, $t_0 = 0.05$ fs, and $\sigma = 0.01$ fs. The time-propagation is started at a time of 0 fs for a duration of 30 fs using the RK4 scheme with various time steps. We run the simulation using the default norm-violating Runge-Kutta integration, as well as Runge-Kutta with a unitary projection applied once every $f = 20, 10, 5, 2$, or 1 time-steps. We monitor the total energy conservation over time for $t > 0.1$ fs, which is after the external field pulse has passed. The simulation outcomes are presented in figure 5.1.

The native Runge-Kutta integrator with a time step of $\delta t = 0.002$ fs leads to an accumulated absolute energy error of $3 \times 10^{-3} E_h$. This error corresponds to an energy shift of about 0.1 eV, which is of significant concern for longer simulations. Simulations with a time-step of $\delta t = 0.001$ fs lead to an error of about an order of magnitude smaller. Applying the unitary projection after every time step ($f = 1$) improves the energy conservation dramatically: a time step of $\delta t = 0.002$ fs leads to an accumulated error of $1 \times 10^{-6} E_h$. This excellent energy conservation is still preserved when the unitary projection frequency is reduced, even when as many as $f = 20$ Runge-Kutta steps lie between the projections. A reduction of the projection frequency also introduces artificial energy oscillations at every f -th step. These energy oscillations are found to alter the behaviour of the time-dependent molecular dipole moment as defined by:

$$\vec{p}(t) = \int n(\vec{r}, t) \vec{r} d^3r, \quad (5.16)$$

where $n(\vec{r}, t)$ is the time-dependent total charge density. Assuming $f = 1$ to yield more or less numerically exact results, we compute the maximum relative deviation of the dipole moments defined as:

$$\Delta p = \max \left| \frac{p_{f=1}(t) - p_f(t)}{\sigma_t(p_{f=1}(t))} \right|_{t \in (1 \text{ fs}, 30 \text{ fs})}, \quad (5.17)$$

where $p_f(t)$ corresponds to the norm of the time-dependent dipole moment using the Runge-Kutta integrator with unitary projection every f steps, and $\sigma_t(\cdot)$ is the standard-deviation over the duration. We refer to table 5.2 for results.

The native Runge-Kutta integrator leads to maximal deviation of over 100 %. This can be largely attributed to a constant shift entering the dipole-moment as the energy conservation is increasingly violated. Introduction of the unitary projection mends this

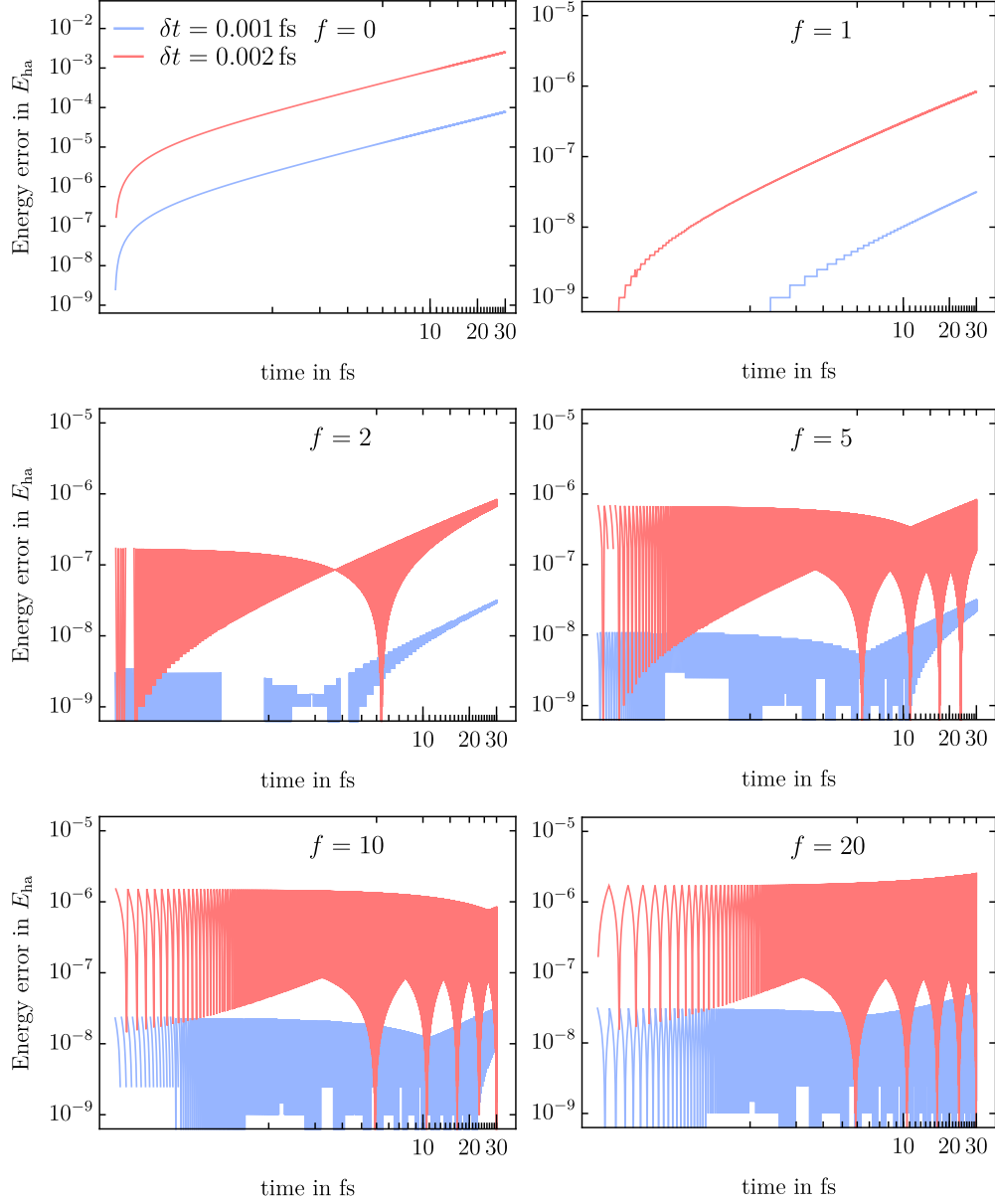


FIGURE 5.1: Energy conservation error over time $|E(t) - E(t_0 = 0.1 \text{ fs})|$ for a perturbed benzene. The system is propagated in dipole-order SVP-GTB for the indicated time steps. Every f time-steps a unitary projection is applied, where $f = 0$ corresponds to native Runge-Kutta. The solid areas correspond to rapid energy oscillations.

issue significantly. While the energy is well conserved for the $f = 20$ and $\delta t = 0.002 \text{ fs}$ case, there is a large relative deviation of up to 5 % in the time-dependent dipole moment. The unitary projection is capable of enforcing energy conservation, however it seems that it is unable to retain the dynamics accurately if applied at an insufficient rate, or with an insufficiently small time-step.

Table 5.2: Maximum relative dipole deviation Δp in % for various unitary projection intervals f and time-steps.

time-step $\delta t/\text{fs}$	f -value				
	2	5	10	20	RK4
0.001	0.013	0.033	0.049	0.46	457.14
0.002	0.117	0.457	1.340	4.92	217.34

We further note that simulations with time steps larger than 0.002 fs diverge rapidly. It might be possible to run larger time steps if the unitary projection is applied after every Runge-Kutta trial step instead of the complete step, however the computational effort associated with a QR -factorisation scales as $\mathcal{O}(N_{basis}^3)$. The performance gain from using a larger time-step therefore needs to be weighted against the performance loss from applying the projection more frequently.

5.3 Spectral observables

We have arrived at a method capable of accurately solving the time-dependent Kohn-Sham equation in the TP-GTB framework. It is left to define how the dipole moment is connected to the experimentally observable photon spectra.

5.3.1 Fourier transform of the dipole moment

Consider first the photo-absorption spectrum characterised by the absorption cross section $\sigma(\omega)$. In the semi-classical picture, the photo-absorption spectrum is a measure of a system's transition probability from the ground-state into the ensemble of higher-lying excited states if an electric field with frequency ω is applied. This probability is contained in the time-dynamics of the system, provided the wave-function samples the complete ensemble of excited states.

5.3.1.1 Instantaneous perturbation

We assume the system to be in the ground-state for $t < 0$. At time $t \geq 0$ an instantaneous perturbation in the form of an electric dipole field is applied, polarised in the $\hat{e}_f$ direction:

$$\vec{E}(t) = E_0 \delta(t) \hat{e}_f. \quad (5.18)$$

The Fourier transform of the Dirac delta-distribution $\delta(t)$ contains a constant real component over all frequencies: $\mathfrak{F}_\omega[\delta(t)] = 1$. The perturbed system therefore instantaneously

gains a phase in its Kohn-Sham orbitals following perturbation theory.* The time-dependent molecular dipole moment subsequently samples the oscillation dynamics and enables extraction of the underlying absorption cross-section $\sigma(\omega)$. Let us define the dipole moment of the system subjected to the $\hat{e}_f$ -polarised field as $\vec{p}^f$, where $f \in \{x, y, z\}$. The Fourier transform of the dipole moment

$$\tilde{p}_\mu^f(\omega) = \mathfrak{F}_\omega \left[p_\mu^f(t) \right] = \int_0^T \left(p_\mu^f(t) - p_\mu^f(0) \right) e^{i\omega t} dt, \quad (5.19)$$

where $\mu \in \{x, y, z\}$ and T is the duration of the finite dipole-moment measurement, is related to the dynamic polarisability tensor $\alpha_{\mu\nu}(\omega)$ by the polarisability-field convolution relation:

$$\tilde{p}_\mu^f(\omega) = \mathfrak{F}_\omega \left[\sum_\nu (\alpha_{\mu\nu} * E_\nu)(t) \right] = \sum_\nu \tilde{\alpha}_{\mu\nu}(\omega) \tilde{E}_\nu(\omega) = E_0 \sum_\nu \tilde{\alpha}_{\mu\nu}(\omega) (\hat{e}_f)_\nu, \quad (5.20)$$

where (5.18) was substituted in the final step. Consider now that three perturbing fields are applied with linearly independent polarisation directions, for instance along the Cartesian axes. For $f = x$ we gain the dipole moment $\vec{p}^x$, for $f = y$ we gain $\vec{p}^y$, and for $f = z$ we gain $\vec{p}^z$. This enables us to characterise the dynamic polarisability tensor completely by the relations:

$$\begin{aligned} \tilde{\alpha}_{\mu x}(\omega) &= \tilde{p}_\mu^x(\omega) / E_0 \\ \tilde{\alpha}_{\mu y}(\omega) &= \tilde{p}_\mu^y(\omega) / E_0 \\ \tilde{\alpha}_{\mu z}(\omega) &= \tilde{p}_\mu^z(\omega) / E_0. \end{aligned} \quad (5.21)$$

from which the cross section follows from the optical theorem:

$$\sigma_{\mu\nu}(\omega) = \frac{4\pi\omega}{c} \tilde{\alpha}_{\mu\nu}(\omega), \quad (5.22)$$

where c is the speed of light. The cross section is a tensor as it characterises the response of a generally anisotropic system in the μ direction to a perturbation along the ν direction. We note that the imaginary component of the cross-section is commonly used as a measure for the photo-absorption cross-section following the Beer-Lambert law, as a positive imaginary cross-section leads a decrease in photon intensity for light passing through the medium. Experimental photo-absorption spectra are further often measured in gaseous or liquid phase, which can be described by an ensemble of randomly aligned molecules. Such a measurement compares to the directionally averaged cross section:

$$\sigma^{abs.}(\omega) = \frac{1}{3} \Im [\sigma_{xx}(\omega) + \sigma_{yy}(\omega) + \sigma_{zz}(\omega)], \quad (5.23)$$

*Consider the time-evolution operator applied to the ground-state wave-function, bringing it from $t = 0^-$ to $t = 0^+$: $|\Psi(0^+)\rangle = \hat{U}(0^+, 0^-) |\Psi(0^-)\rangle = \exp(\frac{i}{\hbar} \int_{0^-}^{0^+} dt \hat{H}[\rho_0] + E_0 \delta(t) \hat{r} \cdot \hat{e}_f) |\Psi(0^-)\rangle \approx \exp(\frac{i}{\hbar} E_0 \hat{r} \cdot \hat{e}_f) |\Psi(0^-)\rangle$.

where $\Im$ is the imaginary component. Note that $\sigma(\omega)$ is independent on the molecular alignment, as the sum over the diagonal components of $\sigma_{\mu\nu}(\omega)$ is equal to the trace of the matrix, and therefore a rotationally invariant quantity.

5.3.1.2 Time-dependent perturbation

The expression for the photo-absorption cross section (5.22) is contingent on the validity of the linear-response approximation, which is violated for instance if the applied field causes a higher-order response in the dipole moment, if the field is of too long duration such that it keeps interacting with the perturbed system, or if the ions rearrange non-adiabatically under the electronic response. Consider now the external field perturbation $\vec{E}(t)$ to act over an extended amount of time. In that case the dynamic polarisability tensor is modulated by the external field spectrum:

$$\begin{aligned}\tilde{\alpha}_{\mu x}(\omega) &= \tilde{p}_{\mu}^x(\omega)/\tilde{E}_x(\omega) \\ \tilde{\alpha}_{\mu y}(\omega) &= \tilde{p}_{\mu}^y(\omega)/\tilde{E}_y(\omega) \\ \tilde{\alpha}_{\mu z}(\omega) &= \tilde{p}_{\mu}^z(\omega)/\tilde{E}_z(\omega)\end{aligned}\tag{5.24}$$

Previous work in strong-field theory commonly consider the photo-absorption spectrum directly dependent on the dipole moment spectrum, and similarly photo-emission spectrum dependent on the dipole acceleration spectrum.^{128,129} We shall therefore not consider the field modulation in the cross-section and instead compute the dipole moment power spectrum as a blanket measure for the system's response:

$$||\sigma(\omega)|| \sim \frac{1}{3} ||\tilde{p}_x^x(\omega) + \tilde{p}_y^y(\omega) + \tilde{p}_z^z(\omega)||.\tag{5.25}$$

5.3.2 Fast Fourier transform, Hann window, and smoothing

We shall here briefly outline the steps that lead to the cross section $\sigma(\omega)$. Consider first that a time-propagated simulation is run, yielding the dipole moment $\vec{p}$. The dipole-moment $\vec{p}(t)$ is represented as a binned signal of finite duration $T = t_f - t_0$ with a time-resolution given by the simulation time-step δt . We track in particular the dipole moment change $\Delta\vec{p}(t) = \vec{p}(t) - \vec{p}(t_0)$.

We introduce a pragmatically chosen filter function $W(t)$ to the dipole moment:

$$\Delta\vec{p}_w(t) = W(t)\Delta\vec{p}(t),\tag{5.26}$$

which acts to reduce numerical noise caused by discrete jumps in the dipole moment at the start and the end of the simulation. In practice we found the Hann window to be effective:

$$W(t) = \frac{1}{2}(1 - \cos(2\pi(t - t_0)/T)),\tag{5.27}$$

where T is the simulation duration. The Hann window smoothly scales the dipole moment to zero at the beginning and the end of the simulation, reducing the noise in the spectral function for a small trade-off in energy resolution.

Next we apply the fast-Fourier transform (FFT) on $\Delta\vec{p}_w(t)$ to arrive at $\tilde{\vec{p}}(\omega)$. The bin resolution of the FFT signal is given as $\delta E = 2\pi\hbar/T$. The simulation length T and the energy resolution of the spectrum are therefore inversely linked. For instance $T = 10$ fs leads to $\delta E = 0.42$ eV, $T = 20$ fs leads to $\delta E = 0.21$ eV, and $T = 30$ fs leads to $\delta E = 0.14$ eV.

We further may apply a Gaussian broadening to the spectrum by convolution. This approximates the spectral broadening as it would appear in an experiment due to thermal vibrations in a collection of molecules, making the theoretical spectrum more comparable to the experimental one. Most importantly it makes the phenomenological detection of spectral features by visual inspection easier.

5.4 Trans-2,2-bithiophene benchmarks

We shall now assess the performance of the SVP-GTB method on time-dependent calculations in comparison with time-dependent DFT. For this purpose we shall compute the time-dependent molecular dipole moment $\vec{p}(t)$ and electron density $\rho(\vec{r}, t)$ of a model system for a variety of external field frequencies. We use the following software for the simulations: PLATO¹³⁰ for GTB, ORCA⁹⁷ for time-independent basis-set DFT, and OCTOPUS¹²¹ for time-propagated grid-based DFT. We also test the mio-1-1 DFTB parametrization⁶⁰ in our monopole-order GTB model, which is self-charge-consistent and only includes polarisation orbitals for sulfur.⁷⁴ This parameter set has been shown to be highly accurate and transferable for a wide range of properties. Nonetheless, mio-1-1 DFTB is expected to underestimate static molecular polarisabilities due to the lack of the atomic dipole terms and polarisation orbitals as found in chapter 4 for monopole-order SV-GTB. In the following we shall refer to monopole-order SVP-GTB as GTB-0, and to dipole-order SVP-GTB as GTB-1.

5.4.1 Linear response

Our system of choice is trans-2,2'-bithiophene, pictured in figure 5.2, as we eventually aim to apply our method on larger polythiophene-based polymers. We first investigate the linear response of the molecule to an external field.

The bithiophene geometry is optimized in PBE-DFT using the cc-pVTZ basis set.⁹⁴ This molecule is not planar; we find a torsional angle of 17.61° , which is in agreement with

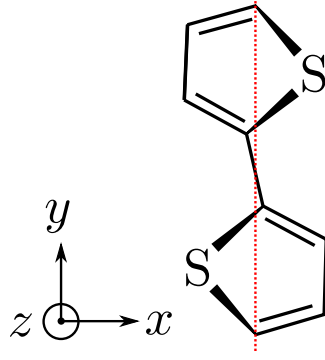


FIGURE 5.2: Trans-2,2'-bithiophene molecule. The outer-most carbons are aligned parallel to the y -axis. We apply time-dependent external electric fields along the x , y and z directions.

Table 5.3: Static polarisability-matrix eigenvalues $\alpha_{\lambda i}$ in $e^2 a_0^2 / E_h$ and HOMO-LUMO gap E_G (eV) of trans-2,2'-bithiophene for various density-functional theory (DFT) and tight binding (TB) models. $\langle \alpha_\lambda \rangle = (\alpha_{\lambda 1} + \alpha_{\lambda 2} + \alpha_{\lambda 3}) / 3$ is the mean polarisability.

method	$\alpha_{\lambda 1}$	$\alpha_{\lambda 2}$	$\alpha_{\lambda 3}$	$\langle \alpha_\lambda \rangle$	ΔE
mio-1-1 DFTB	183.69	108.78	3.36	98.61	2.71
SVP GTB-0	231.08	126.43	4.01	119.06	3.06
SVP GTB-1	202.24	128.18	61.49	130.64	3.21
PBE-DFT*	207.98	132.15	62.21	134.12	2.88
PBE-DFT [†]	218.37	140.28	80.62	146.42	2.85
B3LYP-DFT [†]	210.86	138.88	80.28	143.34	4.08

¹basis: cc-pVTZ⁹⁴

²basis: aug-cc-pVTZ⁹⁴

findings from a previous DFT study¹³¹ using the B3LYP functional^{132,133} which includes a fraction of the exact exchange energy from Hartree-Fock theory. We align the molecule such that the furthestmost carbon atoms lie along the y -axis and the sulfur atoms span a vector parallel to the xy -plane, see figure 5.2.

5.4.1.1 Static polarisability

We compute the molecular polarisability matrix in the electrostatic limit following the approach outlined in chapter 4. The eigenvalues $\alpha_{\lambda i}$ are listed in table 5.3 for a variety of methods.

We note that the self-charge-consistent methods mio-1-1 DFTB and GTB-0 mostly only account for polarisation in the molecular plane ($\alpha_{\lambda 3} \approx 0$ in table 5.3). The GTB-1 method in contrast also yields polarisation perpendicular to the molecular plane due to the inclusion of atomic dipole terms. We further note that GTB-1 predicts polarisabilities

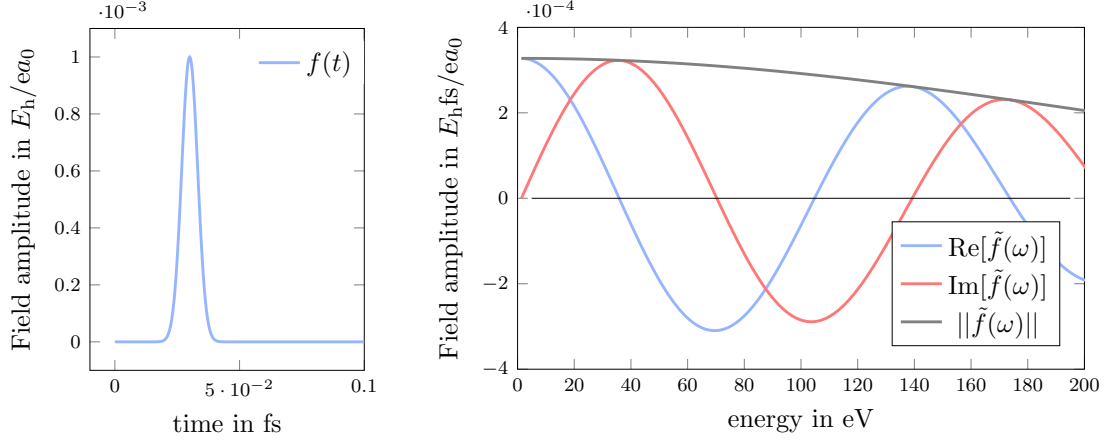


FIGURE 5.3: Time-dependent electric field amplitude in the time domain $f(t)$ (left) and in the frequency domain $\tilde{f}(\omega)$ as found by Fourier transform (right). This pulse is used to probe the linear response spectrum of trans-2,2'-bithiophene.

consistent with DFT using the cc-pVTZ basis set, which reaffirms our previous findings from chapter 4.

5.4.1.2 Photoabsorption spectrum

Next we compute the photon absorption spectrum in a time-dependent calculation as outlined in section 5.3. For this purpose we apply an external perturbation in the form of a linearly polarised, time-dependent dipole-field:

$$\vec{E}_{ext}(t) = E_0 \hat{e}_k e^{-(t-t_0)^2/2\sigma^2}, \quad (5.28)$$

where $k = x, y$, or z , and $E_0 = 0.001 E_h/ea_0$, $t_0 = 0.03$ fs and $\sigma = 0.0032$ fs, see figure 5.3. We note that the chosen field carries a significant complex component in frequency space, which is in contrast to an instantaneous perturbation at time $t = 0$.

All simulations are run for 30 fs. The dipole moment is sampled from 0.5 fs on, with a Hann window applied from 0.5 fs to 30 fs. The energy resolution of the Fourier transformed signal follows as $\Delta E = 2\pi\hbar/29.5$ fs = 0.14 eV, however we note that the application of the Hann window has a slight broadening effect in the frequency domain. No convolution is applied here.

We run TP-GTB simulations in PLATO with the GTB-0, GTB-1, and mio-1-1-DFTB models with a time-step of $\delta t = 0.002$ fs. The unitary projection is applied after every iteration step. We further run TP-DFT simulations in OCTOPUS using the PBE-functional with a time-step of 0.000 66 fs and a simulation box spanned by the union of atomically-centered spheres with a radius of 7 Å. The grid resolution is chosen as 0.18 Å, as for

Table 5.4: Five lowest-lying resonance energies in eV for a trans-2,2'-bithiophene excited by a narrow Gaussian pulse for various density-functional theory (DFT) and tight binding (TB) methods. The energy resolution is 0.14 eV.

method	x_1	x_2	x_3	x_4	x_5
mio-1-1 DFTB	3.45	4.00	5.38	5.79	6.34
SVP GTB-0	3.72	4.55	n/A	5.93	6.48
SVP GTB-1	4.00	4.69	5.79	6.20	6.89
PBE-DFT*	3.72	4.55	5.79	6.07	6.62

*grid-based, with a bounding-spheres radius of 7 Å and a 0.18 Å resolution.

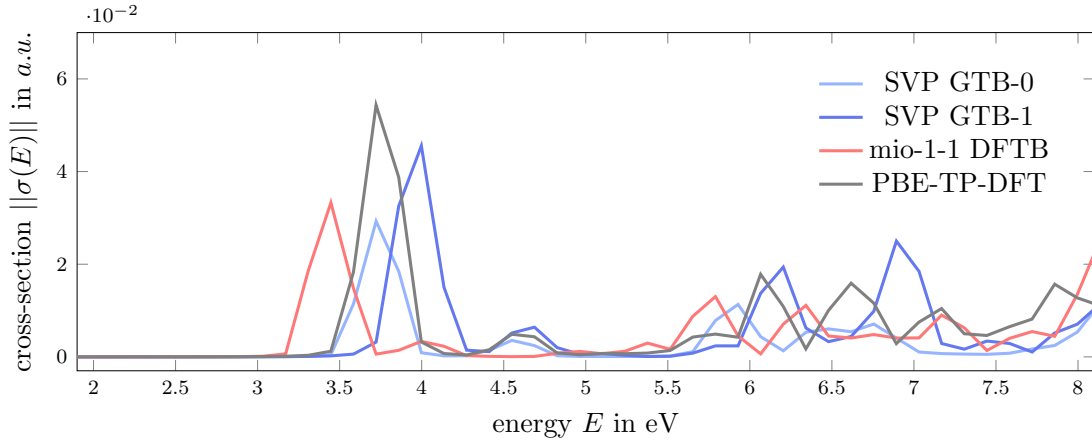


FIGURE 5.4: Norm of the dipole cross-section of trans-2,2'-bithiophene following an excitation with a narrow Gaussian pulse. We plot the spectra for various density-functional theory and tight binding models.

smaller resolutions the Kohn-Sham eigenvalues were found to deviate by more than 0.1 eV. We further apply absorbing boundary conditions.

The directionally averaged cross-sections are obtained following the procedure described in section 5.3.1.2. We compare the first few lowest-lying excitations of the TP-GTB and TP-DFT models, see figure 5.4 for a plot of the cross-sections and table 5.4 for a comparison of the excited states energies.

All methods are found to yield comparable results. The mio-1-1 model underestimates all excitation energies in comparison with the DFT results, with the absolute deviation being consistent with previous findings in the linear-response picture.⁵⁴ This result is improved by the inclusion of the polarisable orbitals in SVP-GTB. While there is no immediately obvious benefit to including the self-consistent dipole terms with SVP-GTB-1, one can in figure 5.4 see that the resonance-peak heights are in better agreement with the PBE-DFT result.

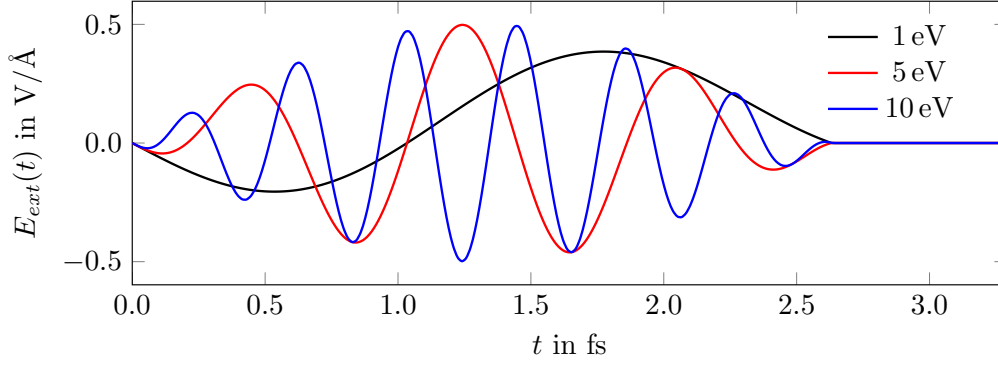


FIGURE 5.5: Time-dependent external fields $E_{ext}(t)$ in $\text{V}/\text{\AA}$. The envelopes are identical, but three different carrier frequencies are used, equivalent to the photon energies of 1 eV, 5 eV, and 10 eV.

5.4.2 Time-dependent response

We shall next study the response of the system to a short time-dependent external field $E_{ext}(t)$ of the form:

$$\vec{E}_{ext}(t) = \begin{cases} E_0 \hat{e}_k \cos(\omega t) \cos(\pi t/\tau + \pi/2) & 0 \leq t \leq \tau \\ 0 & \text{otherwise} \end{cases} \quad (5.29)$$

once for $k = y$, and once for $k = z$. We choose an amplitude of $E_0 = 0.0097 E_h/ea_0$, an envelope duration $\tau = 2.63$ fs, and three different carrier frequencies ω of 1.52 fs^{-1} , 7.59 fs^{-1} , and 15.19 fs^{-1} . This corresponds to a field amplitude of $0.5 \text{ V}/\text{\AA}$ and photon energies of 1 eV, 5 eV, and 10 eV. The laser peak intensity corresponds to $3.32 \times 10^{12} \text{ W}/\text{cm}^2$. The time-dependent field amplitudes are shown in figure 5.5.

The time-dependent simulations are run for 3.29 fs with a time-step of 0.001 fs using GTB and 0.00066 fs using TP-DFT. We use the same TP-DFT simulation box as before. Our tests have shown the TP-DFT dipole moment of this system to vary by less than one percent with box size for the 1 eV field, hence we consider the mesh as sufficiently large. We show the time-dependent molecular dipole moments for the following cases: p_x and p_y for the y -polarised fields in figures 5.6 and 5.7, and p_z for the z -polarised fields in figure 5.8. The time-dependent density change in the xy -plane $\Delta\rho(x, y, t) = \int (\rho(\vec{r}, t) - \rho(\vec{r}, 0)) dz$ for the y -polarised 10 eV field is shown for GTB-1 and TP-DFT in figure 5.9.

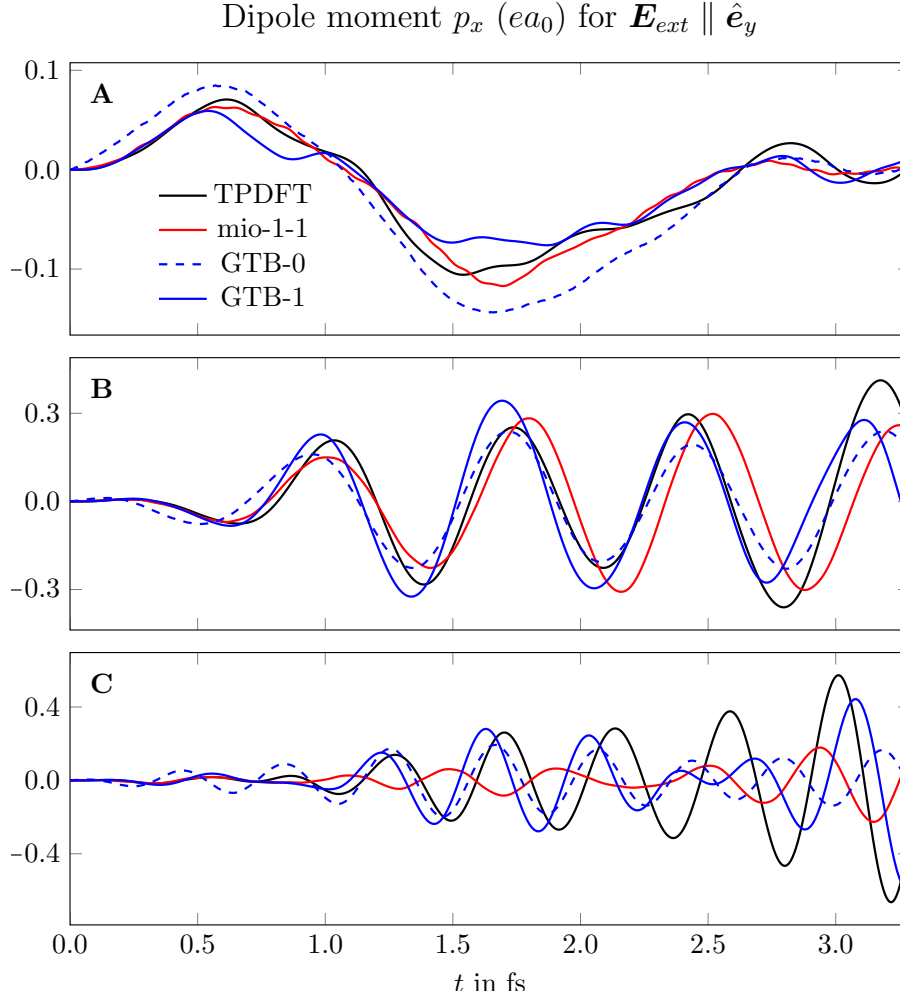


FIGURE 5.6: Time-dependent dipole moment $p_x(t)$ of trans-2,2'-bithiophene for an applied y -polarised field of 3.29 fs duration with a photon energy of (A) 1 eV, (B) 5 eV, (C) 10 eV, in TP-DFT, mio-1-1 DFTB, GTB-0, and GTB-1.

5.4.3 Discussion

Overall the level of agreement between TP-DFT and the tight-binding methods is favorable. The mio-1-1 DFTB model performs surprisingly well, considering that it has not been optimized for electrostatic response properties. The model becomes inaccurate at high field frequencies (10 eV), as the lack of polarisation orbitals leads to an insufficient description of higher excited states. Furthermore, both mio-1-1 DFTB and GTB-0 can only account for in-plane polarisation as they are self-charge-consistent theories, hence $p_z(t) = 0$. This is apparent for the polarisabilities in the electrostatic limit, see table 5.3. Only GTB-1 is capable of describing polarisation perpendicular to the molecular plane direction, see figure 5.8. The GTB-0 model shows the addition of polarisation orbitals to improve the

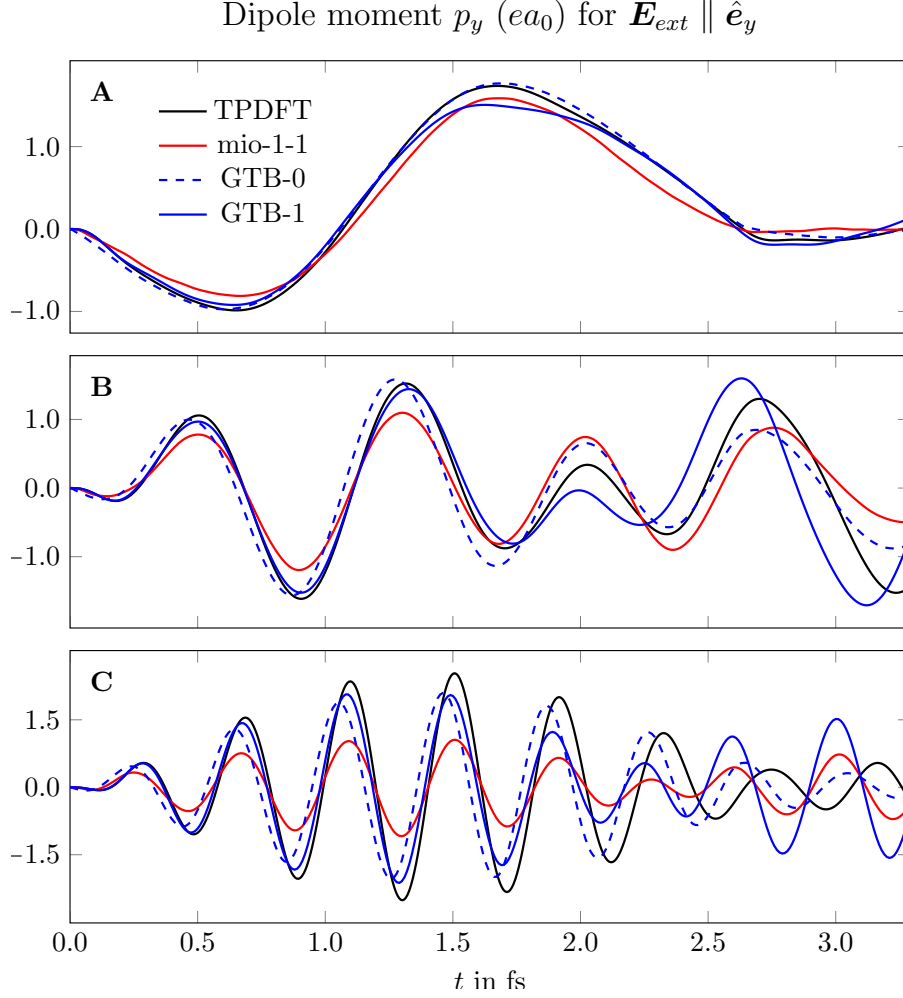


FIGURE 5.7: Time-dependent dipole moment $p_y(t)$ of trans-2,2'-bithiophene for an applied y -polarised field of 3.29 fs duration with a photon energy of (A) 1 eV, (B) 5 eV, (C) 10 eV, in TP-DFT, mio-1-1 DFTB, GTB-0, and GTB-1.

high-frequency result, however the $p_x(t)$ moment is described qualitatively wrong for the first femtosecond for all frequencies.

The GTB-1 model gives overall the best agreement with TP-DFT due to the inclusion of the dipole terms. The GTB-1 $p_x(t)$ and $p_y(t)$ moments deviate from TP-DFT in the 10 eV-case from around 2.0 fs on. This is likely because GTB-1 predicts a larger HOMO-LUMO gap energy than PBE-DFT, see table 5.3. The larger gap causes the GTB-1 dipole moments to oscillate at a higher frequency, preceding TP-DFT's dipole moment, which eventually causes a discrepancy as the field attenuates. Including exact-exchange in DFT with the B3LYP-functional increases the gap considerably, see table 5.3, in which case we would expect the time-dependent dipole moment to oscillate even faster. The

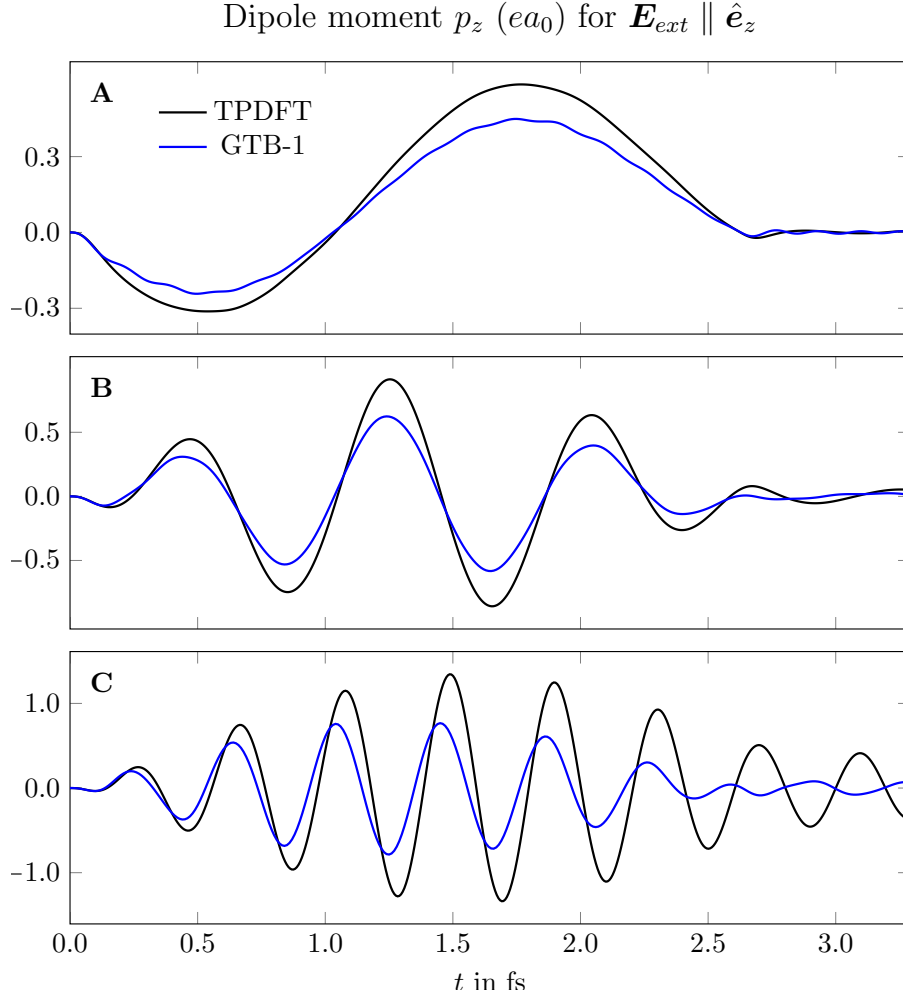


FIGURE 5.8: Time-dependent dipole moment $p_z(t)$ of trans-2,2'-bithiophene for an applied z-polarised field of 3.29 fs duration with a photon energy of (A) 1 eV, (B) 5 eV, (C) 10 eV, in TP-DFT and GTB-1.

perpendicular moment $p_z(t)$ follows TP-DFT qualitatively, but is overall underestimated. We attribute this to the lack of diffuse orbitals in the SVP basis set, as DFT with the cc-pVTZ set yields a similarly underestimated static polarisability.

The density change $\Delta\rho(x, y, t)$ between GTB-1 and TP-DFT agrees remarkably well, see figure 5.9. The tight binding model predicts features of the electron density on par with the TP-DFT model. This key result affirms our assumption that the GTB-1 density can indeed be used to investigate electron dynamics in ultrafast systems. Our analysis of the dipole moments is only indicative of the electron dynamics; the electron density however fundamentally confirms that our model is in strong agreement with TP-DFT.

5.5 Summary

We have implemented a numerical integration scheme for the propagation of the time-dependent Kohn-Sham equation based on the unitary projection approach. The integrator is numerically stable and conserves energy well. We have further shown time-propagated Gaussian tight binding (TP-GTB) to reproduce optical properties in strong agreement with time-propagated density-functional theory (TP-DFT) using the PBE functional. A direct comparison of the electron densities confirms that despite the simplicity of the tight binding model, it is capable of offering a qualitatively correct description of the time-dependent response on the example of trans-2,2'-bithiophene. The GTB model further offers quantitative accuracy comparable to PBE-DFT with the cc-pVTZ basis set at a significantly reduced cost, both for static and time-dependent calculations.

However, we also have to keep the limitations of the tight binding method in mind. Strong time-dependent fields can excite electrons to continuum states, which a method using solely localized orbitals would be unable to describe. One should hence consider whether ionization is a likely scenario on a system-by-system basis. Furthermore we are restricted to semi-local functionals such as the local spin-density approximations (LDA) or generalized gradient approximations (GGA), which are known to underestimate band gaps due to the self-interaction error. This could be amended for instance by including exact exchange or by the self-interaction correction schemes.¹²⁰

The GTB treatment of self-consistency is effective but crude, as we have approximated the atomic charge densities by single Gaussians, see equations (3.8) and (3.59). We have yet to find a clear example where this approximation breaks down before any of the aforementioned other tight binding approximations lead to failure.

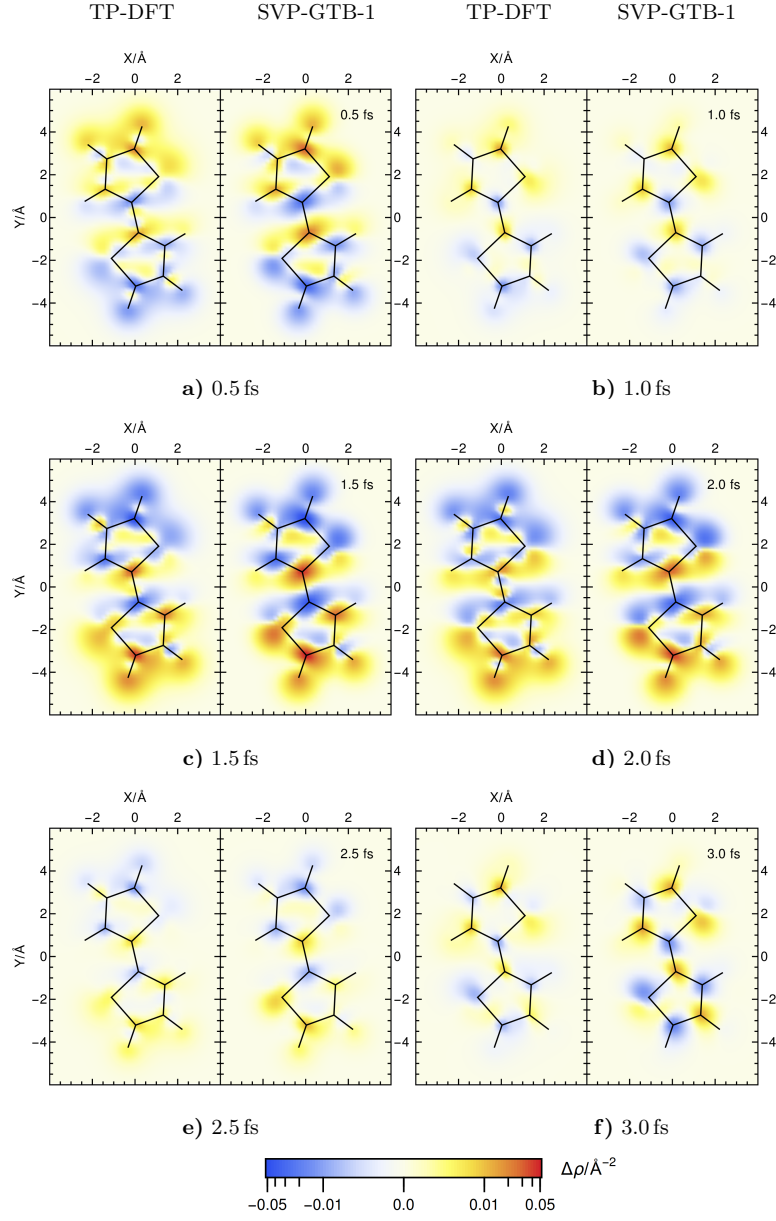


FIGURE 5.9: Time-dependent electron density change $\Delta\rho(x, y, t) = \int (\rho(x, y, z, t) - \rho(x, y, z, 0)) dz$ in $1/\text{\AA}^2$ of trans-2,2'-bithiophene in GTB-1 and TP-DFT under the influence of a time-dependent external field polarised in y -direction (figure 5.5, 1 eV). The Gaussian tight binding model is in strong agreement with TP-DFT, reproducing characteristic features of the electron density.

We have confirmed the effectiveness of Gaussian tight binding for both time-independent and time-dependent problems, but have so far only tested systems with fixed atoms. In this chapter we introduce the Ehrenfest equations of motion, which describe the motion of ions under the influence of the electronic mean-field. This introduces a basic non-adiabatic coupling between ionic and electronic motion. We further show how the performance benefits of Gaussian tight binding can be applied to explicitly simulate an experimental pump-probe setup to gain new insight without the heavy computing required by density-functional theory.

We start by presenting the Ehrenfest equations of motion for tight-binding using an atomically localised, non-orthogonal basis set. Next we construct an all-electron tight binding model based on the findings in chapter 4, and apply the model to simulate transient core-absorption experiments on a thiophene fragment with fixed and with moving ions, producing large volumes of data that would be prohibitively expensive to reach with standard density-functional theory methods. We identify signatures with characteristic time-scales in the pump-probe spectra and relate them to the time-dependent excitation dynamics of the molecule.

6.1 Ehrenfest dynamics

We have so far worked within the Born-Oppenheimer approximation (section 2.1), in which the bare nuclei are considered to behave as classical point-particles. This approximation is based on the assumption that the nuclei move so slowly that the electrons are considered to relax to their ground-state instantaneously. How should one however treat explicit

time-dependence in this semi-classical picture?

Systems in ultrafast dynamics studies are potentially subject to external electric fields of strong magnitude and bandwidths, and as such may be excited over a wide range of excitation states simultaneously. Each excitation state gives rise to a different potential energy surface. This raises the question on how to describe the coupling of this potential energy landscape to the classical ions.

The Ehrenfest approach in principle offers an answer to exactly that question: the ions are treated as classical particles, but their dynamics are coupled to the time-dependent evolution of the occupied electronic molecular orbitals. This is equivalent to the ions moving on a mean potential energy landscape, where the mean is taken over all adiabatic electronic states weighted by their corresponding electron occupancy. This approach is appropriate when no single virtual molecular orbital dominates the excitation, as it may be the case for systems resonantly excited by single photons. Such systems would be better described by the surface hopping method.^{134,135}

We outline below a brief derivation of the Ehrenfest equations of motion for the atomically-localised basis set as it has been implemented in PLATO as part of this project.

6.1.1 Equations of motion

We refer to the extensive work by Todorov¹³⁶ on time-dependent tight binding. The starting point is the semi-classical mean-field Lagrangian $\mathcal{L}$ in the tight binding picture:

$$\mathcal{L} = 2i\hbar \sum_n f_n \langle \Psi^{(n)} | \dot{\Psi}^{(n)} \rangle - 2 \sum_n f_n \langle \Psi^{(n)} | \hat{H}^{TB}[\rho](t) | \Psi^{(n)} \rangle + E_{ion}, \quad (6.1)$$

where $\hat{H}^{TB}[\rho](t)$ is the full self-consistent Gaussian tight binding Hamiltonian including an external time-dependent electric field, and E_{ion} is the ionic energy given by the sum of kinetic ion energy T_{ion} , Coulombic ion-ion repulsion $W_{ion-ion}$, and ion-external field interaction V_{ef-ion} as outlined in section 2.1:

$$E_{ion} = T_{ion} + W_{ion-ion} + V_{ef-ion}. \quad (6.2)$$

The Lagrangian can be recast into the matrix formalism:

$$\mathcal{L} = 2 \sum_{n, I\alpha J\beta} f_n c_{I\alpha}^{*(n)}(t) \left(i\hbar S_{I\alpha J\beta} \dot{c}_{J\beta}^{(n)}(t) + (H_{I\alpha J\beta}^{TB}[\rho] + i\hbar P_{I\alpha J\beta}) c_{J\beta}^{(n)}(t) \right) + E_{ion}, \quad (6.3)$$

where f_n is the electron occupancy of the n -th Kohn-Sham state, $c_{I\alpha}^{(n)}$ are the basis set expansion coefficients (2.86), $S_{I\alpha J\beta}$ is the overlap matrix (2.98), $H_{I\alpha J\beta}^{TB}$ is the tight-binding Hamiltonian matrix (3.28), and $P_{I\alpha J\beta}$ is the overlap derivative matrix (5.10).

Next the Lagrangian equations of motions are solved. Note that the dynamical parameters in this system are the state vectors and their complex conjugate $\{c_{I\alpha}^{(n)}, c_{I\alpha}^{*(n)}\}$, as well as the ionic coordinates $\{\vec{R}_I\}$. The equation of motion with respect to the state vectors yield the time-dependent Schrödinger-equation, which we have previously treated in chapter 5. We are now interested in the ionic equation of motion given by:

$$\frac{d}{dt} \left(\vec{\nabla}_{\dot{R}_k} \mathcal{L} \right) - \vec{\nabla}_{R_k} \mathcal{L} = 0. \quad (6.4)$$

Note that the only terms dependent on the ionic velocities $\{\dot{\vec{R}}_K\}$ are the overlap derivative matrix $P_{I\alpha J\beta} = \dot{\vec{R}}_J \cdot \vec{\nabla}_{R_{IJ}} S_{I\alpha J\beta}$ and the ionic kinetic energy $T_{ion} = \sum_I M_I \dot{\vec{R}}_I^2 / 2$. The Ehrenfest equation of motion is found after lengthy derivation as:

$$\begin{aligned} \vec{F}_K^{EF} = M_K \ddot{\vec{R}}_K = & -2 \sum_{n, \gamma I\alpha} f_n \left(c_{I\alpha}^{*(n)}(t) \vec{\nabla}_{R_{IK}} H_{I\alpha K\gamma}^{TB}[\rho] c_{K\gamma}^{(n)}(t) + \text{c.c.} \right) \\ & + 2i\hbar \sum_{n, \gamma I\alpha} f_n \left(\dot{c}_{I\alpha}^{*(n)}(t) \vec{\nabla}_{R_{IK}} S_{I\alpha K\gamma} c_{K\gamma}^{(n)}(t) - \text{c.c.} \right) \\ & - 2i\hbar \sum_{n, \gamma I\alpha} f_n \left(c_{I\alpha}^{*(n)}(t) \vec{\nabla}_{R_{IK}} (\dot{\vec{R}}_{IK} \cdot \vec{\nabla}_{R_{IK}} S_{I\alpha K\gamma}) c_{K\gamma}^{(n)}(t) - \text{c.c.} \right) \\ & - Z_K \vec{\nabla}_{R_K} V_{ef}(\vec{R}_K) \end{aligned} \quad (6.5)$$

where c.c. refers to the complex conjugate of the respective preceding term. The time-derivative of the states are given by the expression derived in section 5.1, see Eq. (5.7):

$$\dot{c}_{I\alpha}^{(n)}(t) = -\frac{i}{\hbar} \sum_{J\beta K\gamma} (S^{-1})_{I\alpha J\beta} (H_{J\beta K\gamma}^{TB}[\rho] + i\hbar P_{J\beta K\gamma}) c_{K\gamma}^{(n)}(t). \quad (6.6)$$

We have previously derived the analytical form of the first line in Eq. (6.5) in section 2.4.5, see Eq. (2.141). The difference here is that we consider the time-dependent and generally complex-valued electron density in the Hamiltonian instead of the self-consistent and real-valued electron density. We refer to this contribution therefore as the time-dependent Born-Oppenheimer contribution*:

$$\vec{F}_K^{BO}[\rho(t)] \equiv - \sum_{\gamma I\alpha} \left(\rho_{I\alpha K\gamma}(t) \vec{\nabla}_{R_{IK}} H_{I\alpha K\gamma}^{TB}[\rho] + \text{c.c.} \right) - Z_K \vec{\nabla}_{R_K} V_{ef}(\vec{R}_K) \quad (6.7)$$

The exact Ehrenfest forces contain two velocity-dependent contributions. One is explicitly shown in the third row of Eq. (6.5), and another one is implicitly contained in the time-derivative of the state in the form of $P_{J\beta K\gamma}$, see equations (6.6) and (5.8).

*The name is not quite fitting, as the full Born-Oppenheimer force also contains the $\varepsilon^{(n)} \vec{\nabla} S.c^{(n)}$ contribution, see section 2.4.5. This is contained in Eq.(6.6) in the form of $S^{-1}.H.c^{(n)}$.

We shall refer to these as *Pulay terms* following Todorov, in a reference to the *Pulay forces* as they appear would appear for forces of non-stationary states. While the Pulay terms do not contribute to the overall total energy of the system, their consideration is required if the total momentum of the system is to be conserved. Evaluation of the Pulay terms involves the rather elaborate construction of the second-order derivatives of the overlap matrix. The second-order derivatives are analytically tractable, however their efficient implementation is not straight-forward. We refer to section A.7 in the appendix for a MATHEMATICA script that computes the first- and second-order Slater-Koster table derivatives.

6.1.2 Approximate Ehrenfest dynamics

Density-functional tight binding codes commonly ignore the Pulay terms for the benefit of performance. There are several approaches on how to treat the Ehrenfest equations of motion approximately. First, one could assume that the ionic velocities are small. In this case all terms proportional to $\{\dot{\vec{R}}_I\}$ vanish, and we find the approximate Ehrenfest force by substituting Eq. (6.6) into Eq. (6.5). This is basically the Born-Oppenheimer force, but instead of using the ground-state density we use the time-propagated density. We refer to this approximation as approximate Ehrenfest (AE) dynamics:

$$\begin{aligned} \vec{F}_K^{AE} \approx & 2 \sum_{n, \gamma I \alpha} f_n \left(\left(\sum_{J \beta G \mu} (S^{-1})_{I \alpha J \beta} H_{G \mu J \beta}^{GTB} c_{G \mu}^{*(n)}(t) \right) \vec{\nabla}_{R_{IK}} S_{I \alpha K \gamma} c_{K \gamma}^{(n)}(t) + \text{c.c.} \right) \\ & + \vec{F}_K^{BO}[\rho(t)]. \end{aligned} \quad (6.8)$$

This result also follows if the forces are derived following the energy-conservation argument, that is $\dot{E} = 0$, as the Pulay forces do not apply work. Alternatively, the explicitly velocity-dependent term in Eq. (6.6) can be retained, which allows reusing of the time derivative $\{\dot{c}_{I \alpha}^{(n)}(t)\}$ from the state-propagation for an efficient computation of the forces. We refer to this expression as partial Pulay-Ehrenfest (PPE) dynamics:

$$\vec{F}_K^{PPE} \approx 2i\hbar \sum_{n, \gamma I \alpha} f_n \left(\dot{c}_{I \alpha}^{*(n)}(t) \vec{\nabla}_{R_{IK}} S_{I \alpha K \gamma} c_{K \gamma}^{(n)}(t) - \text{c.c.} \right) + \vec{F}_K^{BO}[\rho(t)]. \quad (6.9)$$

AE and PPE dynamics have been implemented in PLATO, while implementation of Ehrenfest dynamics with full Pulay forces is in progress.

6.1.3 Pulay forces benchmarks

Consider the total momentum P of the system to be given by the sum of the electronic and ionic momentum:¹³⁶

$$\vec{P} = -i\hbar \sum_{I\alpha J\beta} \rho_{I\alpha J\beta} \vec{\nabla}_{R_{IJ}} S_{I\alpha J\beta} + \sum_I M_I \dot{\vec{R}}_I(t) \quad (6.10)$$

We are interested in finding the degree to which the total momentum is violated as the approximate Ehrenfest equations of motions are propagated in time.

6.1.3.1 Moving hydrogen

Let us consider a single moving hydrogen atom with mass $M \approx 1836 m_e$ within the Ehrenfest picture for illustrative purposes. This system is particularly tractable, as the force-term depending on the second-order derivatives of the overlap matrix vanishes. The Ehrenfest time-evolution of this system is therefore treated exactly using PPE dynamics within the GTB picture.

Consider first the hydrogen at rest and in the ground-state for $t < 0$. At $t = 0$ we instantaneously apply a velocity of $\vec{v} = 1 a_0 E_h / \hbar \hat{e}_x$ to the nucleus. The velocity now feeds into the onsite $P_{I\alpha I\beta}$ matrix, see Eq. (5.11), and as such also into the time-derivative of the electronic state vector after Eq. (6.6). While the momenta of electron and ion are in constant exchange, the net momentum should remain conserved as $\vec{P} = M\vec{v} = 1836 \hbar / a_0 \hat{e}_x$. The electronic response should therefore slow down the ionic momentum as the electron is dragged by the ion through the Coulomb attraction.

We have simulated the hydrogen atom in AE and PPE-dynamics, using a time-step of $\delta t = 0.001$ fs without QR -projection. We refer to figure 6.1 for a plot of the time-dependent momenta in $\hat{e}_x$ -direction for the AE-dynamics simulation. We find that the ionic and electronic momenta oscillate in phase with one another, almost exactly cancelling out. The total momentum is found to decay, however the total momentum loss is many orders of magnitude smaller than the total momentum: we are comparing here a loss of $\Delta P \approx 10^{-5} \hbar / a_0$ to a net momentum of $P \approx 1836 \hbar / a_0$. The PPE-dynamics (not shown) are found to be exact as expected; no loss of momentum is found within 11 digits of numerical precision.

6.1.3.2 Polarised methane

Next we shall consider a small molecule under slightly different conditions: the ions are set to be initially resting, while the electrons are given an initial momentum. We do this by polarising the molecule with an external electric field at $t < 0$. The field is released for

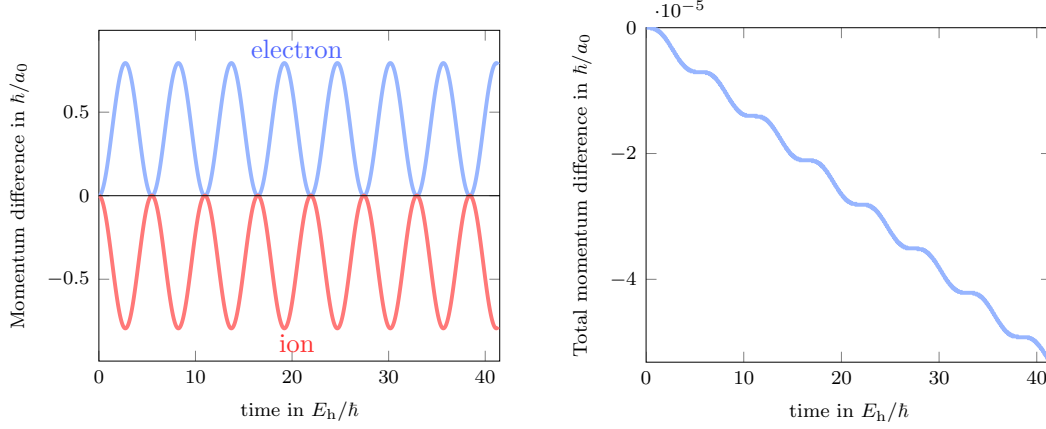


FIGURE 6.1: Left figure: electronic and ionic momentum differences over time t for a perturbed hydrogen atom, given by e.g. $\Delta P_{ele}(t) = P_{ele}(t) - P_{ele}(0)$. Right figure: total momentum difference over time $\Delta P(t) = \Delta P_{ele}(t) + \Delta P_{ion}(t)$ using approximate Ehrenfest dynamics without unitary projection.

$t \geq 0$ which causes the electrons to begin exchanging their potential energy for kinetic energy, while equivalently exchanging their momentum for ionic momentum, and oscillating around the common centre of mass.[†]

We set the simulation up by first relaxing the geometry of methane in the SVP-GTB dipoles model. We next fix the ionic coordinates and solve for the electronic structure self-consistently while a field of $\vec{E} = 0.1 E_h/ea_0 \hat{e}_x$ is applied. Subsequently we remove the field and release the ions, propagating the simulation for 20 fs using AE- and PPE-dynamics with a time-step of 0.001 fs and a unitary projection applied after every integration step. We refer to figure 6.2 for plots of the momentum over time.

We find the error in momentum to have significantly increased: the error reaches values on the order of 0.1 % for AE-dynamics and 0.3 % for PPE-dynamics. While the inclusion of a Pulay contribution in PPE-dynamics leads to exact results in the case of a single atom, it leads to significantly larger errors for molecules.

6.1.4 Summary

We have formulated the Ehrenfest equations of motion which describe the coupled electronic-ionic system in the mean-field picture. The validity of the approximate Ehrenfest approach was confirmed by monitoring the momentum conservation in the test systems of a single

[†]This picture is not fully accurate as some of the initial potential energy is converted to motion that does not contribute to the net momentum of the system, such as electronic density spreading and ions moving along the bonds. This becomes clear when integrating the momenta over time to find the effective electronic and ionic displacements: the subsequent maximum displacements always fall short of the initial dipole displacement by at least $\approx 20\%$.

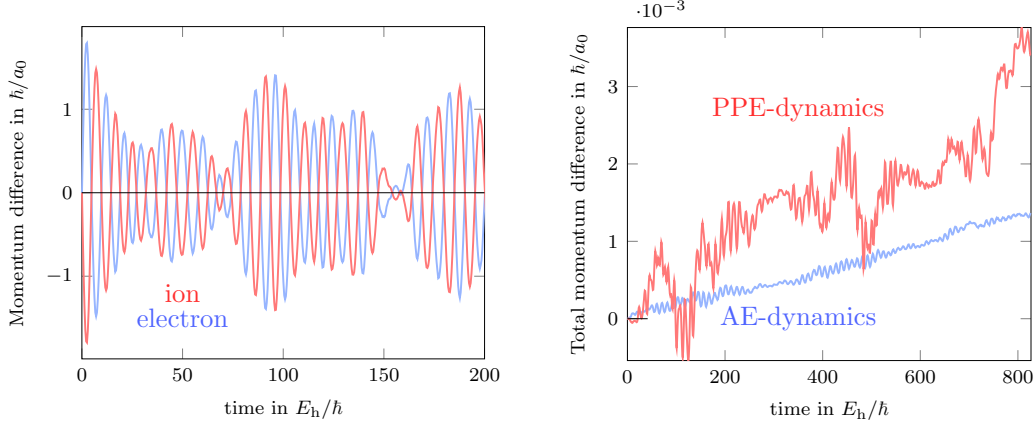


FIGURE 6.2: Left: electronic and ionic momentum for a perturbed methane molecule using approximate Ehrenfest dynamics (AE). Right: total momentum difference over time using approximate Ehrenfest dynamics (AE) and partial Pulay Ehrenfest dynamics (PPE). The unitary projection is applied at every step.

moving hydrogen and a strongly polarised methane molecule. We found that inclusion of one of the two Pulay terms does not significantly alter the result, while considerably eroding the quality of the momentum conservation in the case of methane. The overall momentum error however is small compared to the total momentum, even in the extreme cases benchmarked here. Having quantified the error, we choose the AE-dynamics method for future simulations in good confidence.

We have previously established that Gaussian tight binding accurately predicts electrostatic and time-dependent response, and the Ehrenfest equations of motion presented above allow to some degree for a physically sensible propagation of the ionic forces in time. We are now in a good position to tackle a system of experimental relevance.

While the Ehrenfest approach yields the exact non-adiabatic forces on the classical ions, one must also be aware that this semi-classical picture necessarily leaves out certain physical details. In the Ehrenfest picture the ions interact with the mean electron density, which enables hot ions to excite the electronic system and thus transfer energy. The electrons however can not reverse this process, for one because the ions are treated classically while the electrons are not, and for the other because the electronic ensemble-averaging represented by the mean-field approximation removes any microscopic perturbations within the density that could couple to the ions.¹³⁷ As a consequence the electronic system retains coherence over an unphysically long time-scale.¹³⁸ We refer to the review by Horsfield et al.¹³⁷ for a more in-depth discussion.

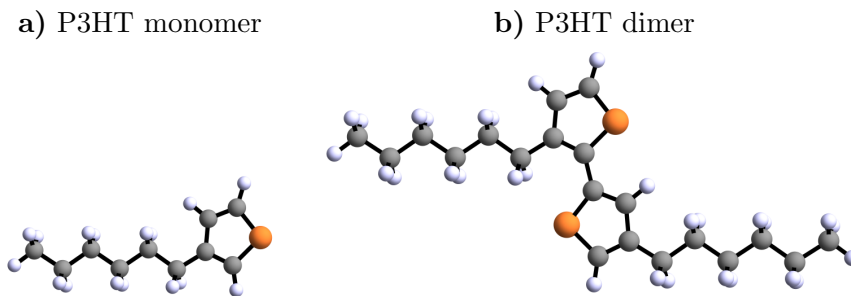


FIGURE 6.3: Monomer and dimer fragments of Poly(3-hexylthiophene-2,5-diyl), P3HT.

6.2 Transient core absorption spectroscopy

The in-situ resolution of time-dependent electronic and ionic dynamics is a key objective in the field of ultrafast dynamics. The general approach is to sample a system's response to laser fields of time profiles and to measure the resulting absorption, emission, or transmission spectra in an attempt to infer the underlying electronic and ionic dynamics. It is clear that this becomes more complicated the less symmetric and the larger the molecule. Computer simulations allow us to tackle the problem directly at the fundamental level, as we have full access to the simulated electronic and ionic dynamics, as well as the experimentally equivalent observables in the form of spectral functions. We seek to understand to which degree the spectra enable inference on the underlying dynamics. Going even further, we may ask: what conclusions can we make in advance on the feasibility of an upcoming experiment?

We will here investigate the time-dependent behaviour of the Poly(3-hexylthiophene-2,5-diyl), monomer and dimer, see figure 6.3, under the influence of strong external fields, and ultimately see if it is possible to extract information on the time-dependent response from multiple time-integrated absorption spectra.

6.2.1 Theory of transient core spectroscopy

Consider a system in the ground-state, with the (Kohn-Sham) molecular orbitals occupied as:

$$2f_n^{ground} = \{\overset{core}{2.00 \ 2.00 \ \dots \ 2.00} \ \overset{valence}{2.00 \ 2.00 \ 2.00} \ \overset{conduction}{0.00 \ 0.00 \ 0.00 \ 0.00 \ \dots}\}, \quad (6.11)$$

following the Aufbau principle. We now apply a highly energetic broad-band laser field, with the pulse shape chosen such that the pulse carries a significant amplitude over the energy range of 50 eV to > 500 eV. Application of this field partially depletes the core

states while occupying the conduction states, for instance:

$$2f_n^{perturbed} = \{\overset{core}{1.96} \overset{core}{1.94} \dots \overset{valence}{2.00} \overset{valence}{2.00} \overset{valence}{2.00} \overset{conduction}{0.03} \overset{conduction}{0.04} \overset{conduction}{0.02} \overset{conduction}{0.01} \dots\}. \quad (6.12)$$

Depleted states are highlighted in red, and newly occupied (pumped) states in blue. We consider the valence states as largely unaffected since the broad-band laser field carries no amplitude at lower energies. This further requires the assumption that the transition matrix elements between the valence states and very high-lying conduction states are low, which is the case if the conduction states are highly delocalised: a fair assumption for excitation energies above 50 eV. The field is further assumed to be too weak to cause a significant degree of ionisation.

Consider now the system to be in an initially excited state:

$$2f_n^{excited} = \{\overset{core}{2.00} \overset{core}{2.00} \dots \overset{valence}{2.00} \overset{valence}{1.96} \overset{valence}{1.74} \overset{conduction}{0.00} \overset{conduction}{0.20} \overset{conduction}{0.10} \overset{conduction}{0.00} \dots\}. \quad (6.13)$$

Application of the broad-band laser field acts similarly as before, with the exception that the now partially occupied valence states act as new transition channels:

$$2f_n^{perturbed} = \{\overset{core}{1.94} \overset{core}{1.92} \dots \overset{valence}{2.00} \overset{valence}{1.98} \overset{valence}{1.76} \overset{conduction}{0.03} \overset{conduction}{0.24} \overset{conduction}{0.12} \overset{conduction}{0.01} \dots\}. \quad (6.14)$$

These transition channels should therefore become noticeable by the appearance of additional peaks in the absorption spectrum, corresponding to the newly opened core to valence state transitions.

We can from here see how this phenomena can be exploited to resolve transitions directly in time. Consider a system in the ground-state to which at time $t = 0$ a pump-pulse in the form of a laser field is applied, exciting the valence electrons into the previously unoccupied ensemble of excited states. The laser frequency is in resonance with the first excited state of the system. The laser field is applied over a duration of several femtoseconds to avoid broadening of the spectral signal, and as such avoid excitation of higher-lying states. The pump field should further perturb the system in the linear response regime to avoid excitation of higher harmonics. The perturbed system subsequently evolves in time, with both the ions and the partially excited electrons moving under the influence of the laser field. The time-dependent state can also be described as a super-position of molecular orbitals with varying, time-dependent occupancies.

After a delay time $\tau > 0$ a probe-pulse in the form of a broad-band XUV laser field is applied. The pulse shape is chosen such that the pulse carries a significant amplitude over the energy range of 50 eV to 500 eV: the field therefore excites the core electrons from the carbon K -series (≈ 280 eV) and the sulfur L -series (≈ 160 eV) directly into the partially occupied molecular orbitals, while not adding any further excitations from the

HOMO-orbital to any lower lying molecular orbitals. Note that the probe-pulse should be ultra short, with a duration of $T < 1$ fs: this enables the pulse to nearly instantaneously sample the electron density within a snapshot of $\tau < t < \tau + T$. The absorption spectrum for a delay of τ will therefore contain information on the transition amplitudes around τ , sampling the partial occupancies in the molecular orbital picture. Subsequent repetition of this experiment for various time-delays τ hence enables reconstruction of the time-evolution of the molecular states.

6.2.2 Pump-probe simulations of P3HT fragments

The experimental setup would consider a thin film of long P3HT chains in the crystalline phase. We are here undertaking this study in a setup that we believe to behave qualitatively similar to the extended periodic system.

It is first important to mention that time-dependent density-functional theory cannot be applied to periodic systems in a straight-forward manner: electric field are expected to induce macroscopic currents into bulk systems, which requires a more specialised treatment, such as time-dependent current-density-functional theory. We shall therefore restrict ourselves to simulating molecular P3HT fragments in vacuum.

The modelling of core electrons in time-dependent density-functional theory bring additional difficulties. For one, core electrons may have enough kinetic energy that the non-relativistic approximation inherent to the Schrödinger-equation becomes inaccurate.¹³⁹ This necessitates the introduction of relativistic effects, for instance in the Dirac-Kohn-Sham picture.¹⁴⁰ Local or semi-local functionals further perform poorly for core-excitations due to the self-interaction error, which is certainly the case for LDA and GGA functionals. The self-interaction error can for instance be amended by inclusion of a short-ranged exact-exchange correction.¹⁴¹ Incomplete localised basis sets further do not describe continuum states well, which manifests itself as the appearance of additional unphysical peaks beyond the absorption edge. Our neglect of diffuse functions only exacerbates this issue. These effects in combination lead to errors in the eigenstates of tens of electronvolts or more; we are left with a theory that is of qualitative, rather than quantitative, character.

We are further restricted in system size as our present time-propagated Gaussian tight binding (TP-GTB) implementation is neither linear-scaling nor parallelised.[‡] On the other hand, the computational efficiency of tight binding makes it particularly suitable for running many concurrent independent simulations of small molecules, as the computational load can be trivially distributed amongst multiple processors.

[‡]We refer to the work by O'Rourke and Bowler^{142, 143} on linear-scaling TP-DFT. Similar techniques have also been applied to time-propagated tight binding.^{144, 145}

6.2.2.1 P3HT fragment geometries

Our fragments of choice are therefore the P3HT monomer and dimer, with geometries taken from the periodic system. We follow the findings of the DFT-study by Xie et al.,¹⁴⁶ arranging two P3HT dimers into an orthorhombic cell with dimensions (17.24, 7.70, 7.80) Å such that the rings stack up evenly. The ionic coordinates are relaxed using SCC-DFTB with the mio-1-1 parametrisation with a force tolerance of $0.0005 E_h/a_0$. Only the Γ -point is considered. We refer to figure 6.4 for the relaxed structure. The monomer and dimer reference geometries are taken from the relaxed box. We terminate the ends by placing hydrogen at the under-coordinated carbons at a distance of 1.09 Å.

We shall later propagate the molecular fragments at room temperature using Ehrenfest dynamics. A physically sensible treatment of molecular vibrations can be obtained by choosing the initial conditions for the ionic dynamics from thermally equilibrated Born-Oppenheimer molecular dynamics simulations of the crystal structure. We run 10 separate simulations starting with the relaxed crystal, propagating the system over a time of 40 ps using a time-step of $\delta t = 0.5$ fs within SCC-DFTB mio-1-1. The initial velocities are randomly generated according to the Maxwell-Boltzmann distribution, however every simulation uses a different random-number seed. This ensures that the ion dynamics between the different simulations decouple as the systems equilibrate. No thermostat is used, however whenever the temperature falls outside an interval of $290 \text{ K} \pm 90 \text{ K}$ the ionic velocities are rescaled such that the new temperature becomes 290 K.

Finally we extract molecular fragment snapshots from the dynamic crystal simulations every 4 ps, ignoring the first snapshot as equilibration takes place during that time-interval, and terminate the under-coordinated carbons following the procedure above.

6.2.2.2 All-electron tight-binding

The description of core states in tight binding obviously requires an explicit treatment of core electrons as opposed to the pseudo-potential treatment used in the single-valence-polarised (SVP) basis set. The time-propagation of an all-electron model however also requires a significantly smaller time-step, as electrons in the deep core states are oscillating much more rapidly than valence electrons. We shall exploit that the pump-probe setup outlined here does not access the deepest sulfur states at $\approx -2.5 \text{ keV}$, allowing us to treat the sulfur $1s^2$ -state by a pseudo-potential.

We build a (mostly) All-Electron (AE) tight binding model for hydrogen, carbon, and sulfur with the same confinement potential parameters as for the SVP model: $R_C^H = 4 a_0$, $R_C^C = R_C^S = 4.5 a_0$, with the electronic configuration given in table 6.1. Our model is not

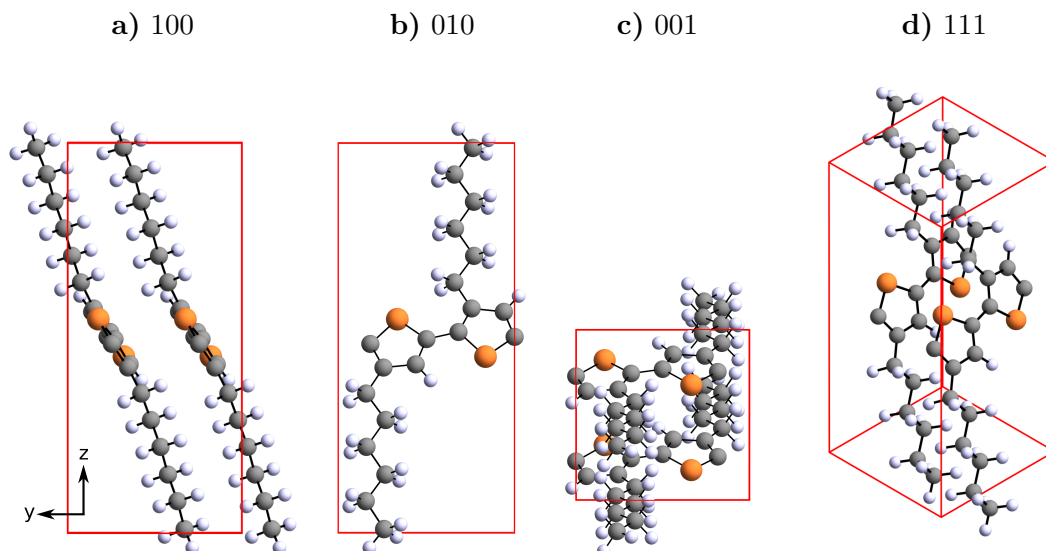


FIGURE 6.4: Simulation cell for the periodic P3HT structure, shown from four different crystallographic viewpoints. The geometry is optimised using SCC-DFTB with the mio-1-1 parametrisation.

truly all-electron as we construct a Goedecker, Teter, and Hutter^{147,148} pseudo-potential using the PBE functional to describe the sulfur $1s^2$ state. We use the atom package as supplied in the CP2K simulation software.¹²²

The pseudo-potential is optimised by a simultaneous minimisation of the difference between the all-electron and pseudo wave-functions beyond $R > 1.85 a_0$, as well as of the eigenvalues and the node-positions of the wave-functions. We consider for the optimisation only the wave-functions of the occupied $2s^2$, $2p^6$, $3s^2$, $3p^4$, and the unoccupied $3d^0$ states. We found good results using a pseudo-potential with a maximum angular moment of 2. The $1s^2$ -sulfur pseudo-potential parameters are shown in table 6.2. We refer to the original publications on the Goedecker, Teter, and Hutter pseudo-potentials^{147,148} for a definition of the parameters. We confirm the validity of the sulfur model by comparing the sulfur pseudo wave-functions to the all-electron wave-functions, see figure 6.5.

We are able to use the previously fitted SVP pair-potentials (appendix A.5) since the core electrons will have little effect on the chemical bonding. We shall pragmatically refer to this model as All-Electron (AE). We benchmark the AE-GTB model in comparison with PBE-DFT with the cc-pVTZ basis set by computing the energies of the P3HT reference monomer and dimer core-states, see figure 6.6.

Overall we find a favourable agreement between AE-GTB and PBE-DFT. Tight binding generally overestimates the energies by a few eV. This can be attributed to an underestimation of the Kohn-Sham potential due to the lack of crystal-field and three-centre

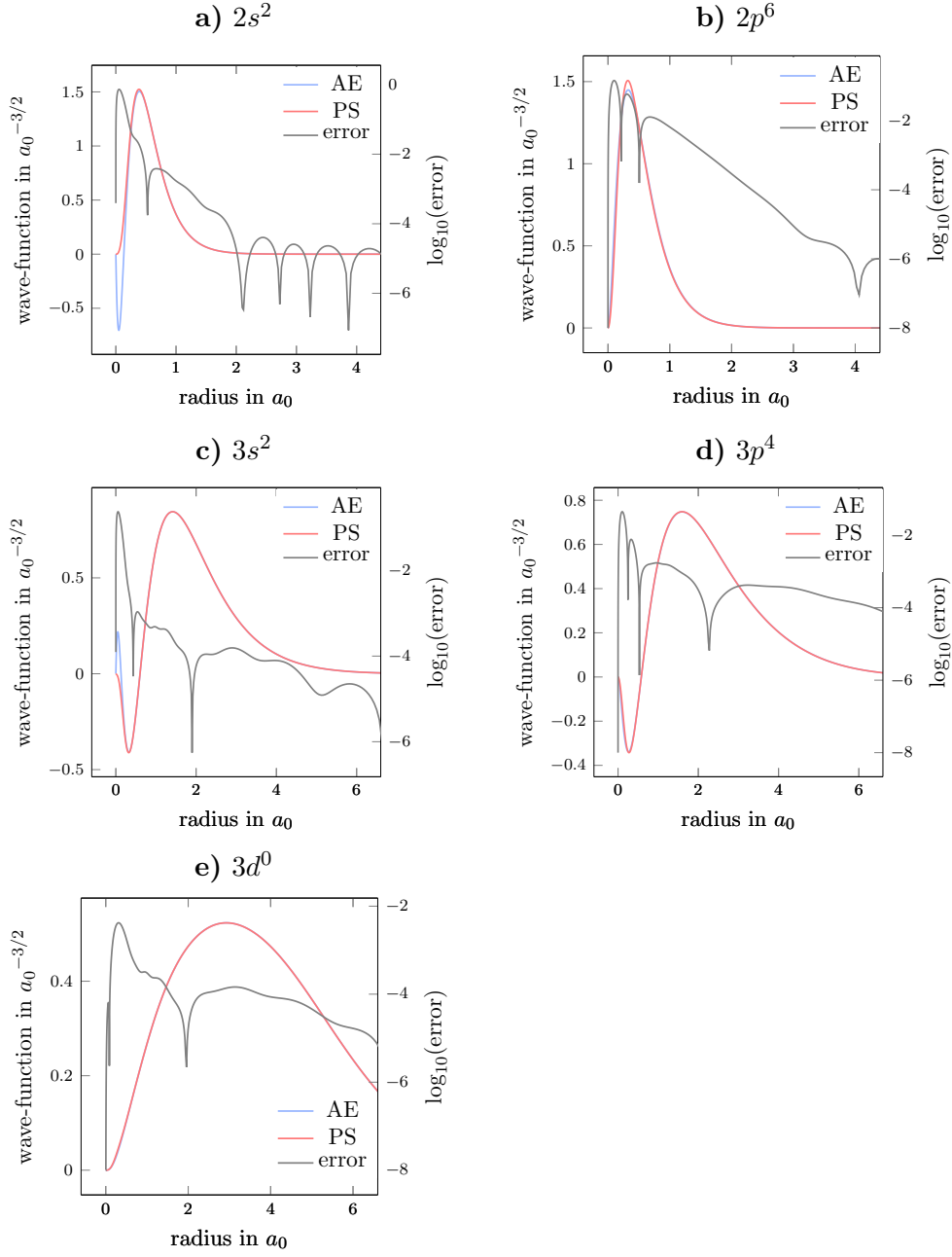


FIGURE 6.5: All-electron and pseudo radial wave-functions for the $1s^2$ sulfur pseudo-potential. The absolute difference between the wave-functions is displayed on a separate logarithmic axis.

contributions.

Table 6.1: Basis set size of the single-electron-valence (SVP) and the all-electron (AE) basis set for the elements H, C, and S in the Gaussian tight binding model.

species	SVP basis configuration	AE basis configuration
H	$1s^1 2p^0$	$1s^1 2p^0$
C	$2s^2 2p^2 3d^0$	$1s^2 2s^2 2p^2 3d^0$
S	$3s^2 3p^4 3d^0$	$2s^2 2p^6 3s^2 3p^4 3d^0$

Table 6.2: Non-relativistic Goedecker, Teter, and Hutter pseudo-potential for the sulfur $1s^2$ state using the PBE functional. Sulfur in this model is treated as having an effective charge of $Z_{eff} = 14$. We use atomic units, values not shown are zero.

r_{loc}	C_1	C_2
r_0	$h_{1,1}^0$	
r_1		$h_{2,2}^0$
0.184771577	-53.834434237	7.993577240
0.118065797	64.690446937	
0.228198051		0.615023294

6.2.2.3 Pump pulse: excited states of P3HT monomer and dimer

As outlined in section 6.2.1, we need to find the lowest excited states of the P3HT monomer and dimer to define the pump-pulse frequency. For this purpose we apply an external field of the shape

$$\vec{E}_{ext}(t) = E_0 \hat{e}_k e^{-(t-t_0)^2/2\sigma^2}, \quad (6.15)$$

where $k = x, y$, or z , $t_0 = 0.15$ fs, $\sigma = 0.03$ fs, and $E_0 = 0.001 E_h/ea_0$, see figure 6.7. The width is chosen such that only excitations with energies below 50 eV are pumped. We are basically measuring the UV-VIS response.

We use the SVP-GTB model as the core states are not involved at the UV-VIS energy range. The propagation is run for 60 fs with a time-step of $\delta t = 0.002$ fs and with unitary projection being applied after every step. We sample the dipole moment starting from 0.5 fs to remove the noise associated with the initial driving of the system by the field. A Hann window is applied from 0.5 fs to 60 fs to smooth out the numerical noise caused by the finite duration of the signal. The energy resolution in the frequency domain is $\Delta E = 2\pi\hbar/59.5$ fs = 0.07 eV, but is practically slightly worse as the Hann window has a broadening effect in the frequency domain. No convolution is applied here.

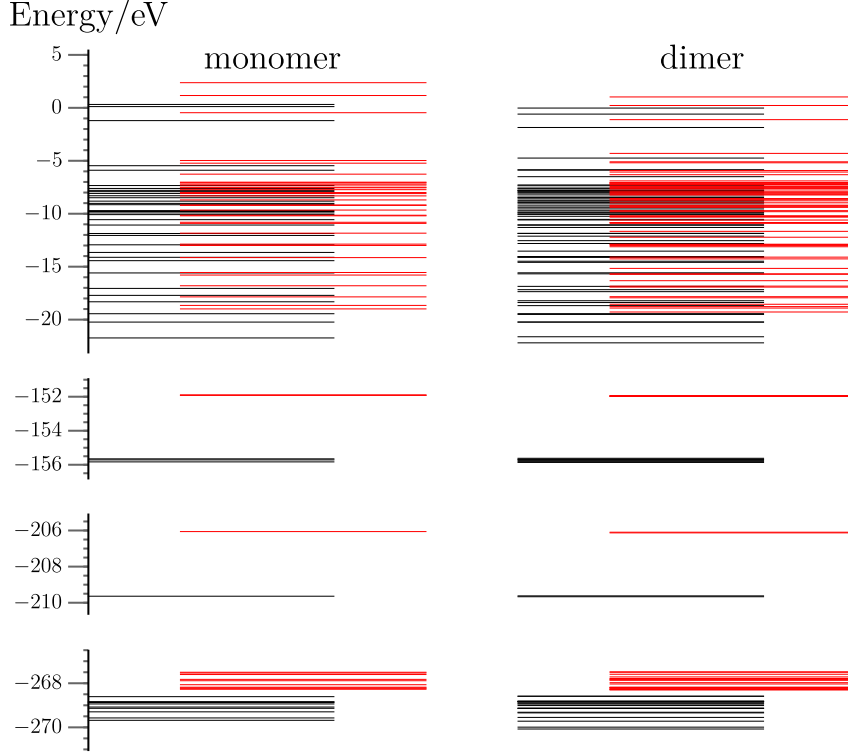


FIGURE 6.6: Kohn-Sham molecular orbital states for the P3HT monomer and dimer in AE-GTB (red) and all-electron PBE-DFT with the cc-pVTZ basis set (black) on the absolute energy scale. Core and valence states are drawn in, including the LUMO, LUMO+1, and LUMO+2.

The directionally averaged dipole-moment cross-sections are obtained following the procedure described in section 5.3. The lowest lying excitation is found at (5.17 ± 0.07) eV for the monomer and at (3.79 ± 0.07) eV for the dimer. Linear-response PBE-DFT with the cc-pVTZ basis set predicts the lowest excitation energies as 5.40 eV and 3.94 eV respectively for the monomer and dimer, and is therefore in good agreement. Photo-absorption experiments on crystalline P3HT in a thin film find a value of 2.2 eV,¹⁴⁹ which follows our trend of longer chains yielding lower excitation energies. We refer to figure 6.8 for a plot of the absorption cross-sections.

Finally we choose the functional form of our pump-pulse using a cosine envelope:

$$\vec{E}_{pump}(t) = E_0 \hat{e}_k \cdot \begin{cases} \sin(\omega t) \cos(\pi t/T + \pi/2) & 0 \leq t \leq T \\ 0 & \text{otherwise} \end{cases} \quad (6.16)$$

where $\hbar\omega$ is equal to the lowest excitation energy, $E_0 = 0.0005 E_h/ea_0$, and $T = 10$ fs, see figure 6.9. We note that the signal is broad enough to resonantly excite the two lowest

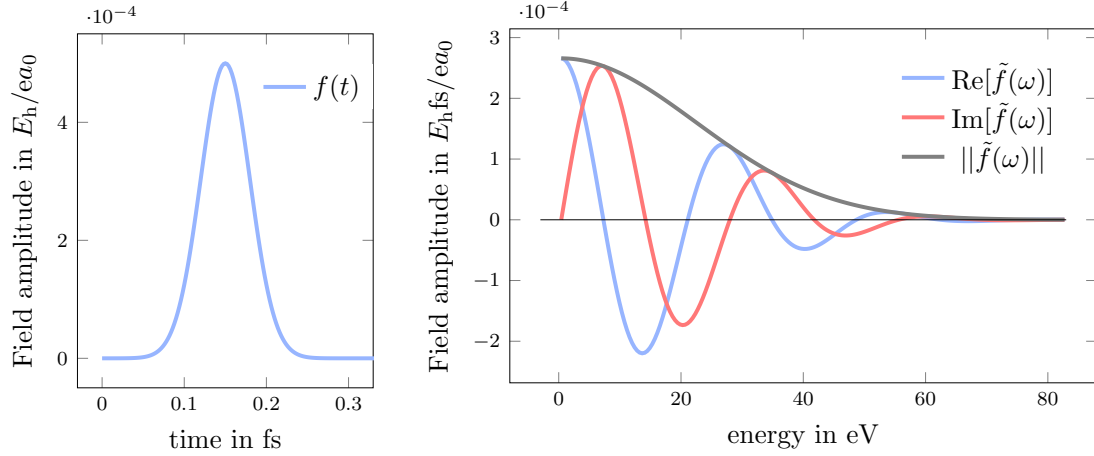


FIGURE 6.7: UV-VIS signal amplitude in the time domain $f(t)$ (left) and in the frequency domain $\tilde{f}(\omega)$ as found by Fourier transform (right). This pulse is used to find the low-lying excited states of the P3HT fragments.

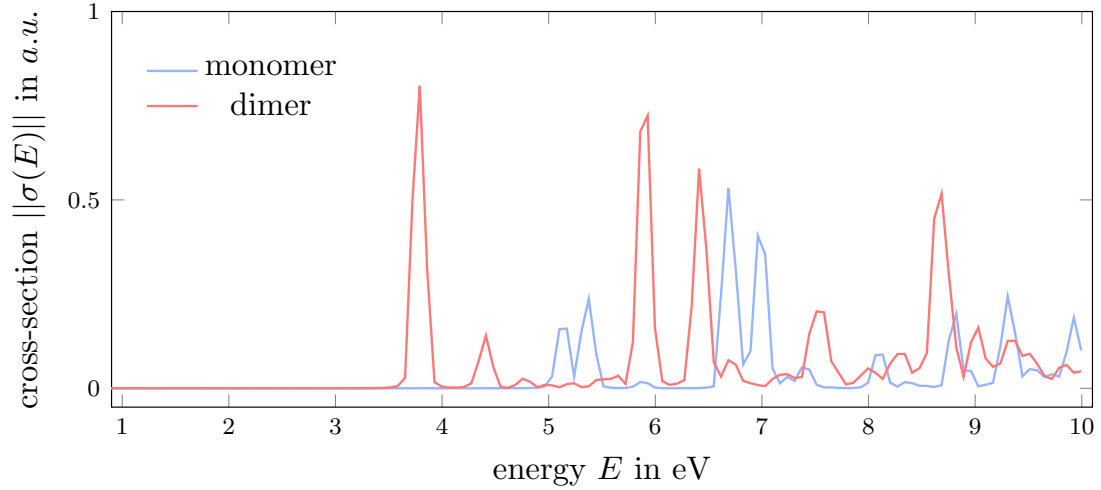


FIGURE 6.8: Absorption cross-sections of the P3HT monomer and dimer following excitation with a narrow UV-VIS pulse.

lying excited states, as they are fairly close in energy, see figure 6.8. The duration is chosen as a compromise between simulation time and spectral width of the signal.

6.2.2.4 Chirped probe pulse

The probe pulse is required to span a bandwidth of 50 eV to 300 eV to sample core-excitations without interfering with low-lying excitations. We apply a chirped probe-pulse

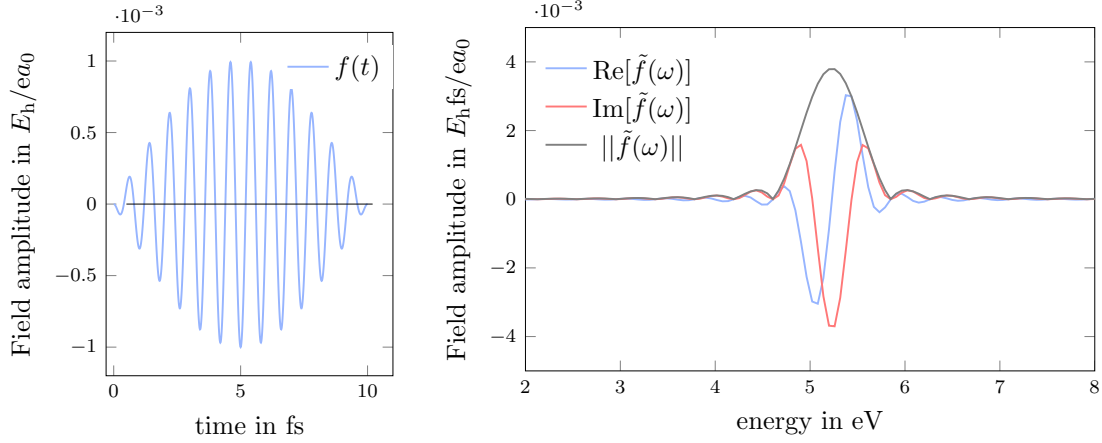


FIGURE 6.9: Pump pulse amplitude for the P3HT monomer in the time domain $f(t)$ (left) and in the frequency domain $\tilde{f}(\omega)$ as found by Fourier transform (right). This pulse is used to excite the lowest lying excitation of the P3HT monomer.

in the shape:

$$\vec{E}_{probe}(t) = E_0 \hat{e}_k \cdot \begin{cases} \sin(\omega_C(t)t) \cos^2(\pi t/T + \pi/2) & 0 \leq t \leq T \\ 0 & \text{otherwise} \end{cases} \quad (6.17)$$

where $\omega_C(t)$ is the time-dependent chirp-frequency given by

$$\omega_C(t) = (\omega_F - \omega_S) \frac{t}{T} + \omega_S, \quad (6.18)$$

with ω_S being the initial frequency and ω_F being the final frequency of the chirped pulse, and T the total duration of the probe-pulse. We found a squared cosine envelope to be more effective than a normal cosine at screening low energy components in frequency. The duration of the signal is chosen as a compromise between two effects: a shorter pulse allows probing of the electron density over a shorter snapshot in time with more temporal resolution, however it inversely also carries a larger Fourier amplitude at lower energies, thereby interfering with the excitation dynamics of the valence electrons. We settled for a duration of $T = 0.3$ fs, a field amplitude of $E_0 = 0.001 E_h/ea_0$, and for chirp frequencies of $\hbar\omega_S = 100$ eV and $\hbar\omega_F = 250$ eV, see figure 6.10 for a plot of the signal.

6.2.2.5 XUV reference absorption spectrum

Before proceeding with the pump-probe simulations it is reasonable to first generate a reference XUV absorption spectrum. We apply the probe-pulse to sample the transitions of the core-electrons into the ensemble of the unoccupied molecular states, holding the ionic positions fixed. The pulse is polarised along the $\hat{e}_z$ -direction to maximise the response from

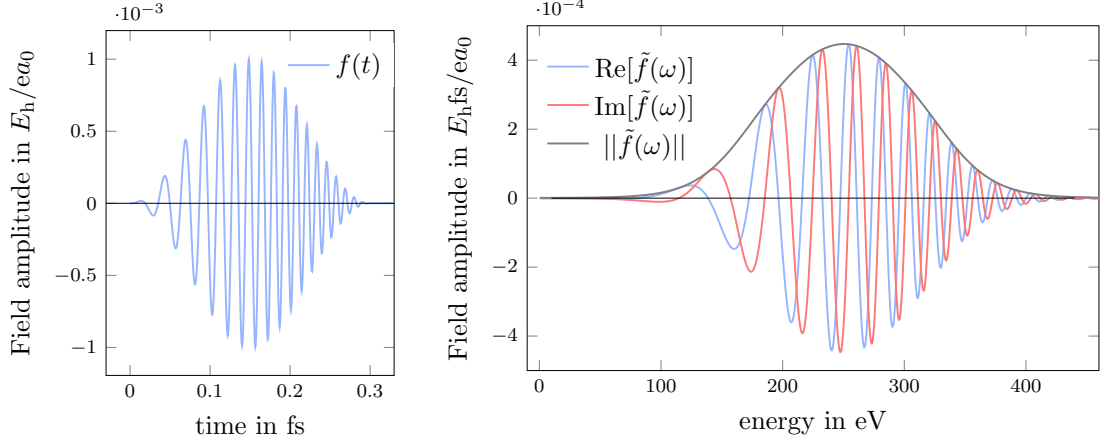


FIGURE 6.10: Chirped XUV signal amplitude in the time domain $f(t)$ (left) and in the frequency domain $\tilde{f}(\omega)$ as found by Fourier transform (right).

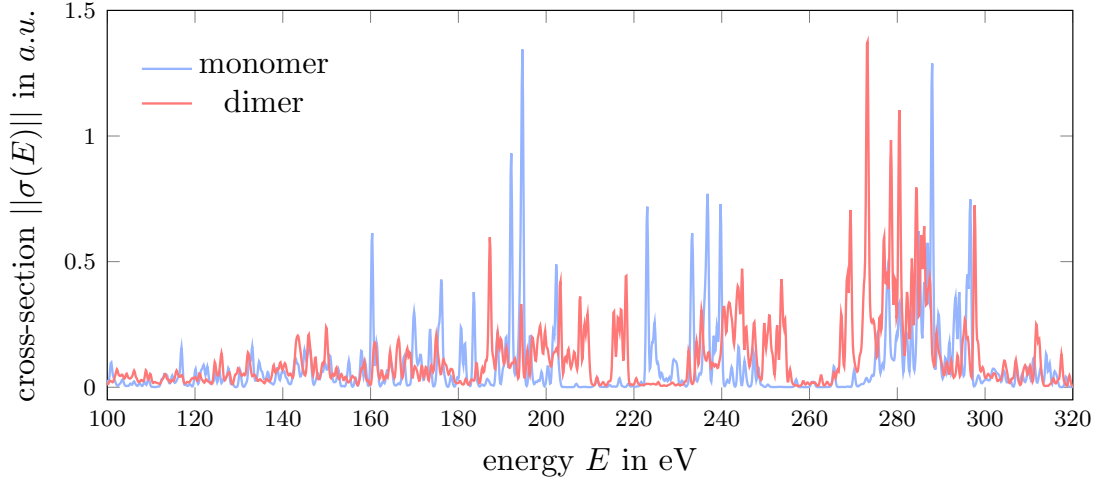


FIGURE 6.11: Absorption cross-sections of the P3HT monomer and dimer following excitation with a chirped XUV pulse.

the hexyl chains. We note that the inclusion of the core states requires a smaller time-step to keep the numerical integration stable. The propagation is run for 30 fs with a time-step of $\delta t = 0.0005$ fs and the unitary projection applied after every step. Again the dipole moment is sampled from 0.5 fs on, with a Hann window applied from 0.5 fs to 30 fs. The energy resolution of the Fourier transformed signal follows as $\Delta E = 2\pi\hbar/29.5 \text{ fs} = 0.14 \text{ eV}$. We further apply a Gaussian convolution with a full-width-half-maximum of 0.5 eV to smooth out experimentally inaccessible features. We refer to figure 6.11 for a plot of the cross-sections.

6.2.2.6 Force extrapolation

The Madelung and multipole moment matrices depend on the pairwise interionic distances, and therefore need to be rebuilt after every update. While the electronic core states oscillate rapidly, the ionic coordinates change comparatively slowly. The construction of the moment matrices and their derivatives is by far the most costly step in Ehrenfest Gaussian tight binding. We can save a lot of computational effort by extrapolating these slowly-changing matrices over several steps. A simple linear extrapolation scheme is implemented in PLATO, which we shall briefly outline and test in the following.

Let the ionic coordinates at time $t = t_n$ be $\{\vec{R}_I^n\}$. We construct the Madelung matrix $B_{Ilm,Jl'm'}(\vec{R}_{IJ}^n)$ and multipole matrix $M_{I\alpha J\beta}^{lm}(\vec{R}_{IJ}^n)$, as well as their derivatives $\vec{\nabla}_{R_{IJ}^n} B_{Ilm,Jl'm'}(\vec{R}_{IJ}^n)$ and $\vec{\nabla}_{R_{IJ}^n} M_{I\alpha J\beta}^{lm}(\vec{R}_{IJ}^n)$, where $\vec{R}_{IJ}^n = \vec{R}_I^n - \vec{R}_J^n$. The matrices are implicitly time-dependent through the ionic coordinates.

Next, let the ionic coordinates at a later point in time $t_m > t_n$ be $\{\vec{R}_I^m\}$. We extrapolate the electrostatic matrices by series expansion with respect to the coordinate change $\vec{R}_{IJ}^m - \vec{R}_{IJ}^n$ at the point $\vec{R}_{IJ}^n$ up to linear order:

$$B_{Ilm,Jl'm'}(\vec{R}_{IJ}^m) \approx B_{Ilm,Jl'm'}(\vec{R}_{IJ}^n) + \vec{\nabla}_{R_{IJ}^n} B_{Ilm,Jl'm'}(\vec{R}_{IJ}^n) \cdot (\vec{R}_{IJ}^m - \vec{R}_{IJ}^n)$$

$$M_{I\alpha J\beta}^{lm}(\vec{R}_{IJ}^m) \begin{cases} = M_{I\alpha J\beta}^{00}(\vec{R}_{IJ}^m) & l = 0 \\ \approx M_{I\alpha J\beta}^{lm}(\vec{R}_{IJ}^n) + \vec{\nabla}_{R_{IJ}^n} M_{I\alpha J\beta}^{lm}(\vec{R}_{IJ}^n) \cdot (\vec{R}_{IJ}^m - \vec{R}_{IJ}^n) & l > 0 \end{cases} \quad (6.19)$$

Note that we compute the monopole moments and their derivatives exactly at every step to ensure charge conservation. The monopole terms are very efficiently computed from the Slater-Koster table, and therefore do not take considerable computational effort.

This extrapolation is applied over multiple steps while keeping the previously constructed matrices and the ionic coordinates at $t = t_n$ as reference values for the extrapolation. After a given number of extrapolation steps are reached, the matrices are rebuilt fully and, alongside with the ionic coordinates, redefined as a new reference point.

The use of analytic gradients for the extrapolation has the benefit of ensuring energy conservation, as the matrices underlying the force and energy calculations are consistently extrapolated. We consider the matrix gradients as constant over the extrapolation time, leading to discontinuous forces; however this seems to have only a negligible effect on the benchmarks taken here. One can also envision a second-order extrapolation scheme based on the finite-difference derivatives of the matrix gradients. This would lead to piecewise continuous forces, but would also require the additional storage of the previous step's gradients.

Next we benchmark the extrapolation scheme for various extrapolation lengths. We propagate a P3HT monomer with moving ions at $T = 300$ K under the influence of the

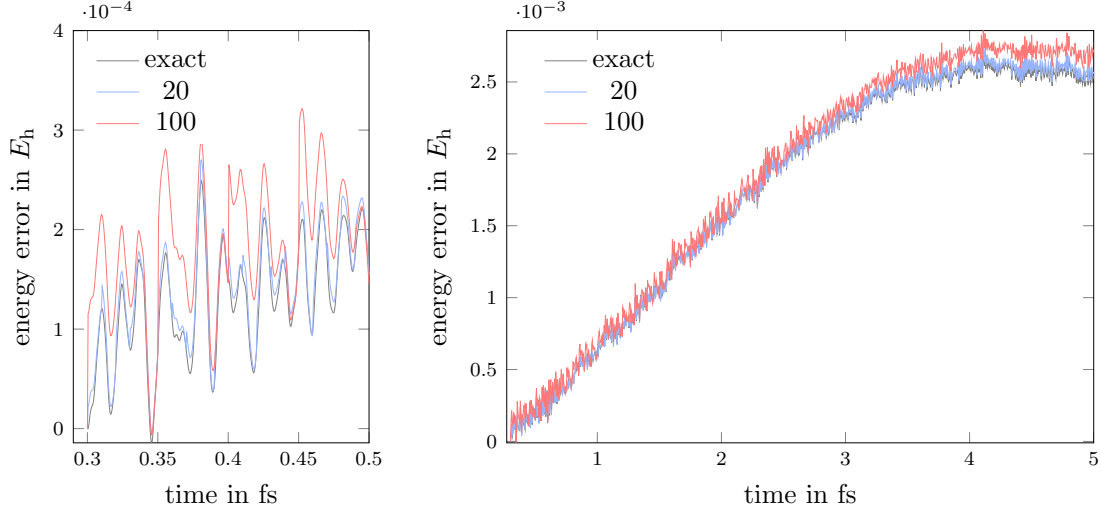


FIGURE 6.12: Right: energy conservation of the extrapolated Ehrenfest dynamics scheme for a XUV-pumped P3HT monomer. The simulation was repeated for 20, 100, and no extrapolation steps (exact). Left: plot over shorter time of the same simulation.

broad-band XUV pulse, using a time-step of $\delta t = 0.0005$ fs. The energy conservation is monitored after 0.3 fs, just after the XUV pulse subsides, see figure 6.12. We found excellent energy conservation using up to 100 extrapolation steps, which corresponds to a recomputation of the matrices every 0.05 fs. The extrapolation scheme speeds up the simulation benchmarked here by a factor of 2.5 for 10 extrapolation steps, up to a factor of 4 for 100 extrapolation steps. The computational benefit of using so many extrapolation steps has diminishing returns, given that the electronic structure calculation starts to dominate the computational expenses. We therefore choose a more conservative value of 20 extrapolation steps for our subsequent pump-probe simulations.

6.2.2.7 Pump-probe simulation setup

Let us define the pump-probe field $\vec{E}_{pp}(t, \tau)$ as:

$$\vec{E}_{pp}(t, \tau) = \vec{E}_{pump}(t) + \vec{E}_{probe}(t - \tau), \quad (6.20)$$

where τ is the time-delay between the onset of the pump-pulse and the onset of the probe-pulse. In all cases we apply the field polarised along the $\hat{e}_z$ -direction to maximise the response of the hexyl chains.

We ran a series of P3HT monomer and dimer simulations for 30 fs with a time-step of $\delta t = 0.0005$ fs, applying the unitary projection after every step. We run simulations for a delay time τ ranging from 1 fs to 21 fs in steps of $\delta \tau = 0.1$ fs. This leads to a spectral

bin-width of 0.14 eV, however we note that this value is a bit misleading. The probe-signals act only between the time interval of $t \in [\tau, 30 \text{ fs})$, and are therefore more poorly resolved as the delay-time increases. For the extreme case of $\tau = 21 \text{ fs}$ the resolution is only 0.46 eV, which causes the spectra to smear out. Every series of pump-probe simulations is ran under three distinct scenarios:

- a) Fixed correlated.** The ionic coordinates are held fixed at a common fragment reference geometry, and only the electronic structure is propagated in time. This scenario is expected to show the effect of the pump-probe fields on the electron dynamics most clearly.
- b) Free correlated.** The initial ionic coordinates and velocities are taken from a common snapshot of a Born-Oppenheimer simulation of the crystalline system at room temperature, as outlined in section 6.2.2.1. The same initial conditions are used for every separate pump-probe simulation. This scenario is ran to investigate the effects of moving ions on the spectra.
- c) Free uncorrelated.** Same as **b)**, however every separate pump-probe simulation uses different, uncorrelated initial geometries and velocities. This simulation setup attempts to mimic the experimental reality, in which there is a substantial amount of time between every pump-probe experiment. We expect the effects of the pump-probe field to be less visible in the spectra due as the eigenstates of the molecule vary considerably with geometry.

This results in a total number of 200 simulations with fixed ions, and 400 simulations including forces each for the monomer and dimer pump-probe setups. A monomer simulation with fixed ions takes about 2 hours on a single core, while a monomer simulation including forces takes about 4 hours. Similarly, a dimer simulation with fixed ions takes about 9 hours, while a dimer simulation including forces takes about 14 hours. The simulations therefore required roughly 10000 CPU hours. This is in stark contrast to grid-based density-functional theory, where a single monomer calculation with fixed ions already requires about a thousand CPU hours for similar accuracy.

6.2.2.8 Discussion

We shall in the following present the results of the different pump-probe scenarios for the sulfur L-series and the carbon K-series of the P3HT monomer. Only the monomer spectra are discussed here for clarity, while the dimer spectra are shown in the appendix A.6.

Scenario a) Fixed correlated. The spectra around the sulfur L-series (figure 6.13) and carbon K-series (figure 6.14) visibly display time-delay-dependent oscillations in the cross-section. We can link these to the probe-pulse accessing the lower-lying excited states. Consider for instance the K-series peak at 290 eV. We measure an oscillation period of about 2.2 fs, corresponding to an energy difference of 1.9 eV. Considering the absorption spectrum of the monomer, see figure 6.8, we can make the educated guess that this corresponds to a transition between the lowest-lying and second-lowest-lying excited states. Similarly, the peak at 296 eV has an oscillation period of about 0.6 fs, which is consistent to an energy difference of 6.9 eV, equal to the transition between ground-state and the second-lowest-lying excited state.

We can furthermore see a hint that new transition channels have opened in the carbon K-series, note the red arrows in figure 6.14. This confirms our basic hypothesis that the pump-pulse would partially deplete the previously fully occupied molecular orbitals, allowing the probe-pulse to excite core-electrons into these new channels (section 6.2.1). The peak indicated by the central red arrow has an oscillation period of 0.8 fs, corresponding to an energy difference of 5.2 eV, which is consistent with the energy of the lowest-lying excited state.

Scenario b) Free correlated. The spectra around the sulfur L-series (figure 6.15) and carbon K-series (figure 6.16) now carry a considerably amount of noise. This is somewhat surprising, as we previously did not expect the mere introduction of moving ions to decorrelate the spectra to such an extent. We can still barely make out oscillations in the cross-section peak amplitudes, but most interestingly we can see several resonance peaks shifting over energy-scales of ≈ 10 eV and time-scales of ≈ 5 fs, see the ridges marked by the red lines in figure 6.16. While a more thorough analysis would attempt to correlate these with changes in the atomic charges and molecular structure, we again make an educated guess that these shifts are caused by carbon-hydrogen oscillations. The marked peaks at the 280 eV – 290 eV energy range seem to return to their original positions over a period of $T \approx 10$ fs. This corresponds to a vibrational frequency of $1/\lambda \approx 3000 \text{ cm}^{-1}$, which is commonly associated with carbon-hydrogen bonds, see figure A.3. Using similar reasoning, we may also expect peak-shifts corresponding to oscillations in carbon-carbon bonds to be visible in the spectrum. Carbon-carbon bonds have a wavenumber of $1/\lambda \approx 1500 \text{ cm}^{-1}$, which corresponds to an oscillation period of $T = \lambda/c \approx 22$ fs, however no very clear signatures are found in the spectra presented here. The marked peaks at the 260 eV – 270 eV energy range could correspond to half such a period, but the evidence is somewhat lacking.

Based on this interpretation we can now attempt to explain why so much noise is

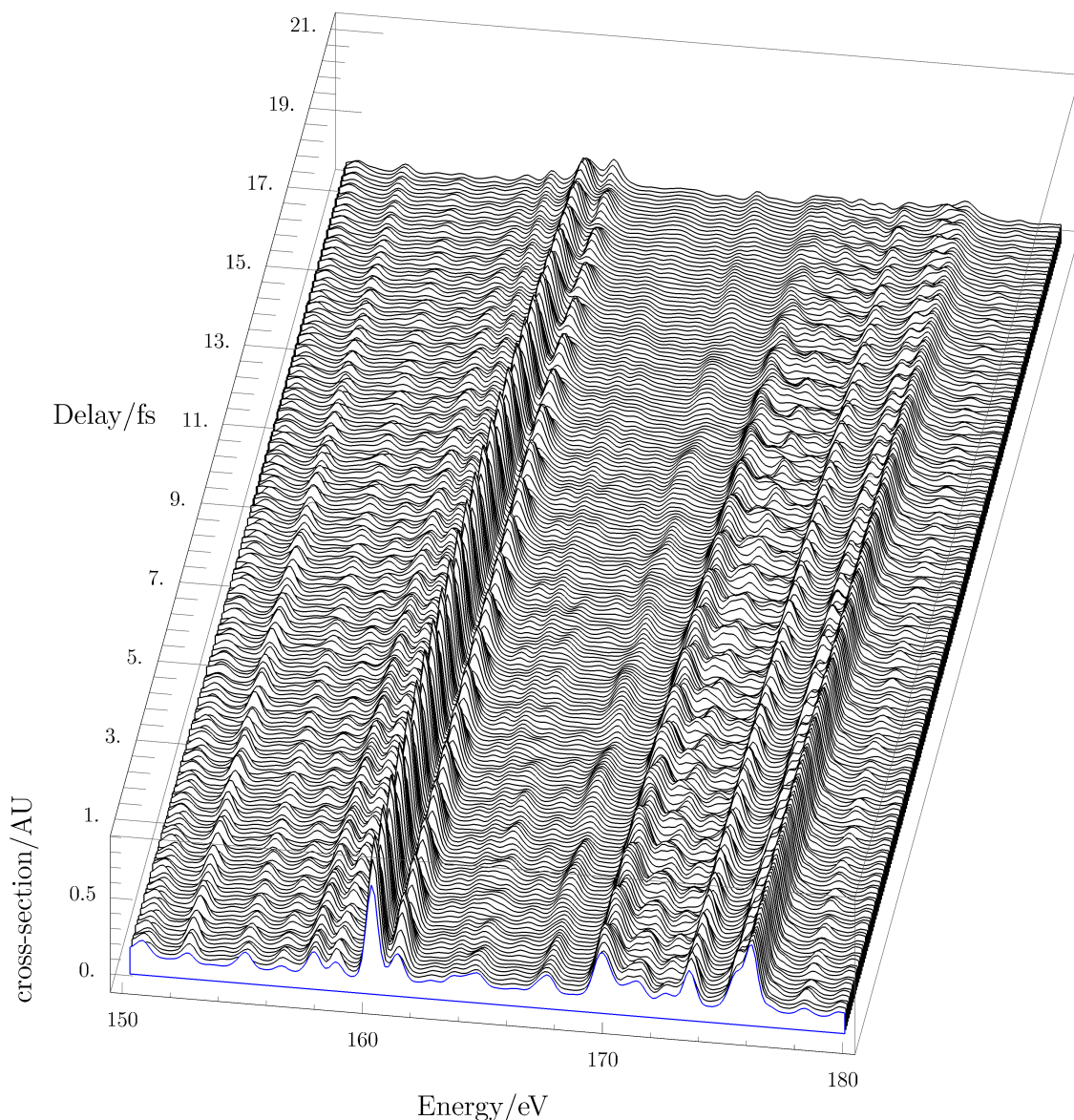


FIGURE 6.13: Sulfur L-series spectrum for the P3HT monomer over various pump-probe delay times. The ions are held fixed. The un-pumped reference spectrum is shown as the first spectrum in blue colour.

observed in the signal. From our fixed-ions scenario we have already established that the cross-section amplitudes are dependent on the time-delay. Allowing our ions to move now introduces further modulations to the spectra on the time-scale associated with the characteristic vibrational motion of the chemical bonds. In the linear-combination of atomic-orbitals picture we understand that each molecular orbital carries different contributions from each atomic orbital: changes in the bond-lengths will therefore affect each molecular orbital to a different degree. The electronic structure is subsequently very

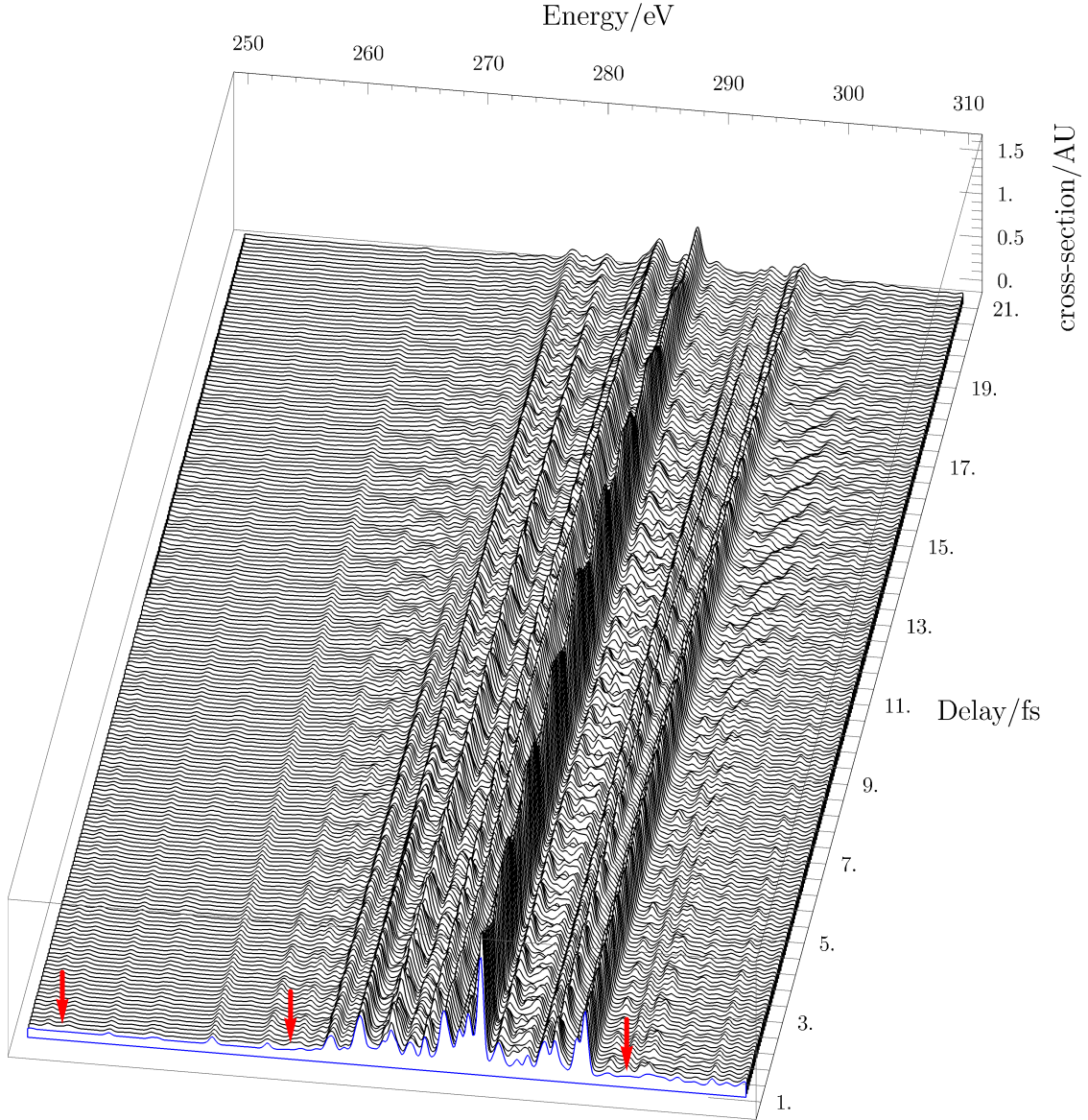


FIGURE 6.14: Carbon K-series spectrum for the P3HT monomer over various pump-probe delay times. The ions are held fixed. The un-pumped reference spectrum is shown as the first spectrum in blue colour. The arrows in red indicate the appearance of new resonances following excitation by the pump-pulse.

sensitive with respect to geometrical changes, which manifests itself in the apparent chaos we see particularly during the first 10 fs as the pump-pulse acts.

Scenario c) Free uncorrelated. Based on the previous findings it is no surprise that we see here a completely uncorrelated and noisy spectrum. We refer to the appendix A.6 for the figures.

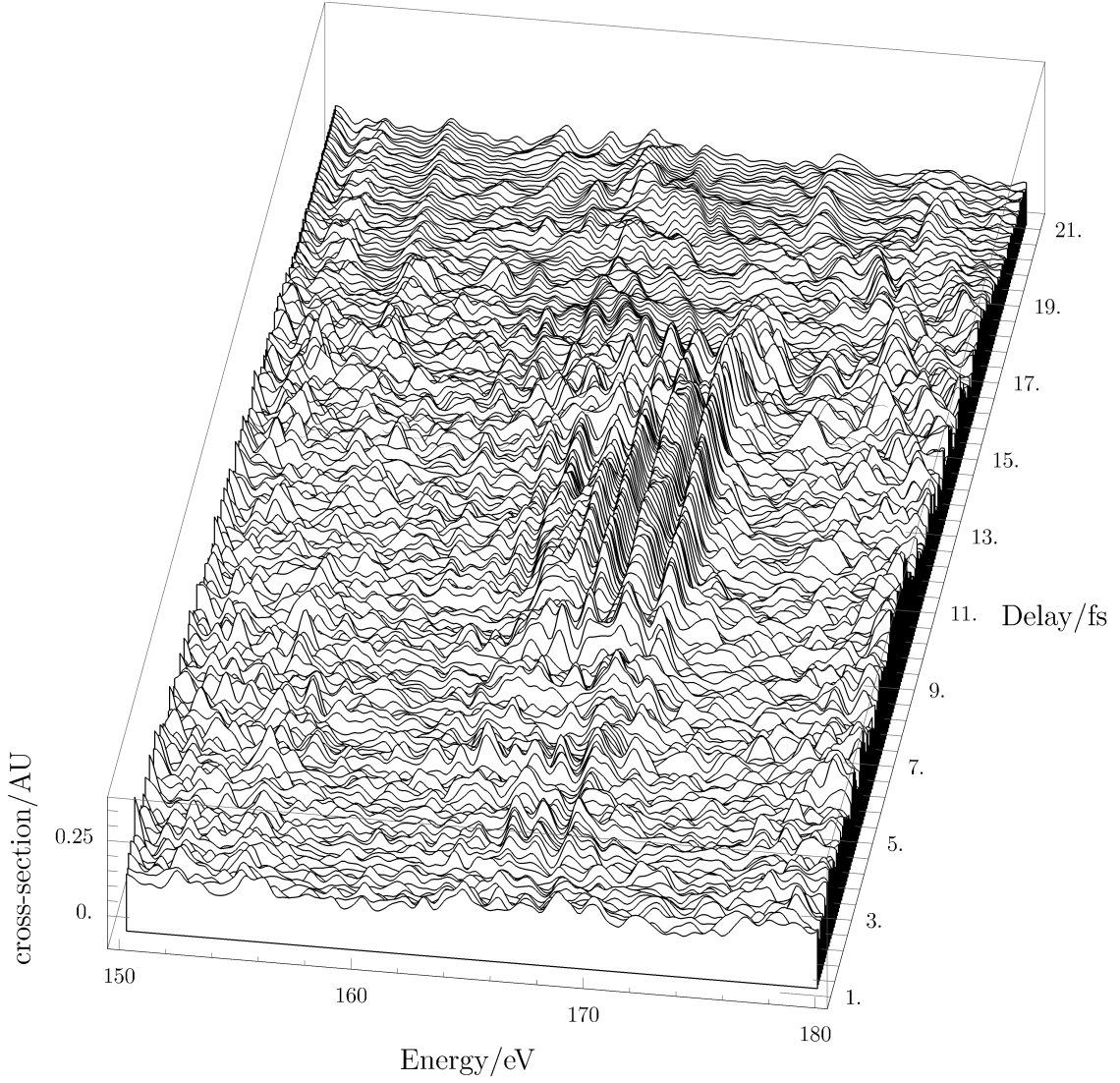


FIGURE 6.15: Sulfur L-series spectrum for the P3HT monomer over various pump-probe delay times. The initial ion positions and velocities for each simulation are taken from the same molecular dynamics snapshot of a P3HT crystal simulation at 300 K.

6.2.3 Conclusion

We ran an extensive amount of pump-probe simulations to investigate to which extent coherent features remain visible over various delay times. Simulations with fixed ions allowed most clearly the identification of excited states dynamics, as we found oscillations in the cross-section peak amplitudes consistent with the excited states energy differences. Simulations with moving ions on one hand allowed us a tentative estimate of the vibrational dynamics of the system, but on the other hand deteriorated the overall clarity of the excitation dynamics.

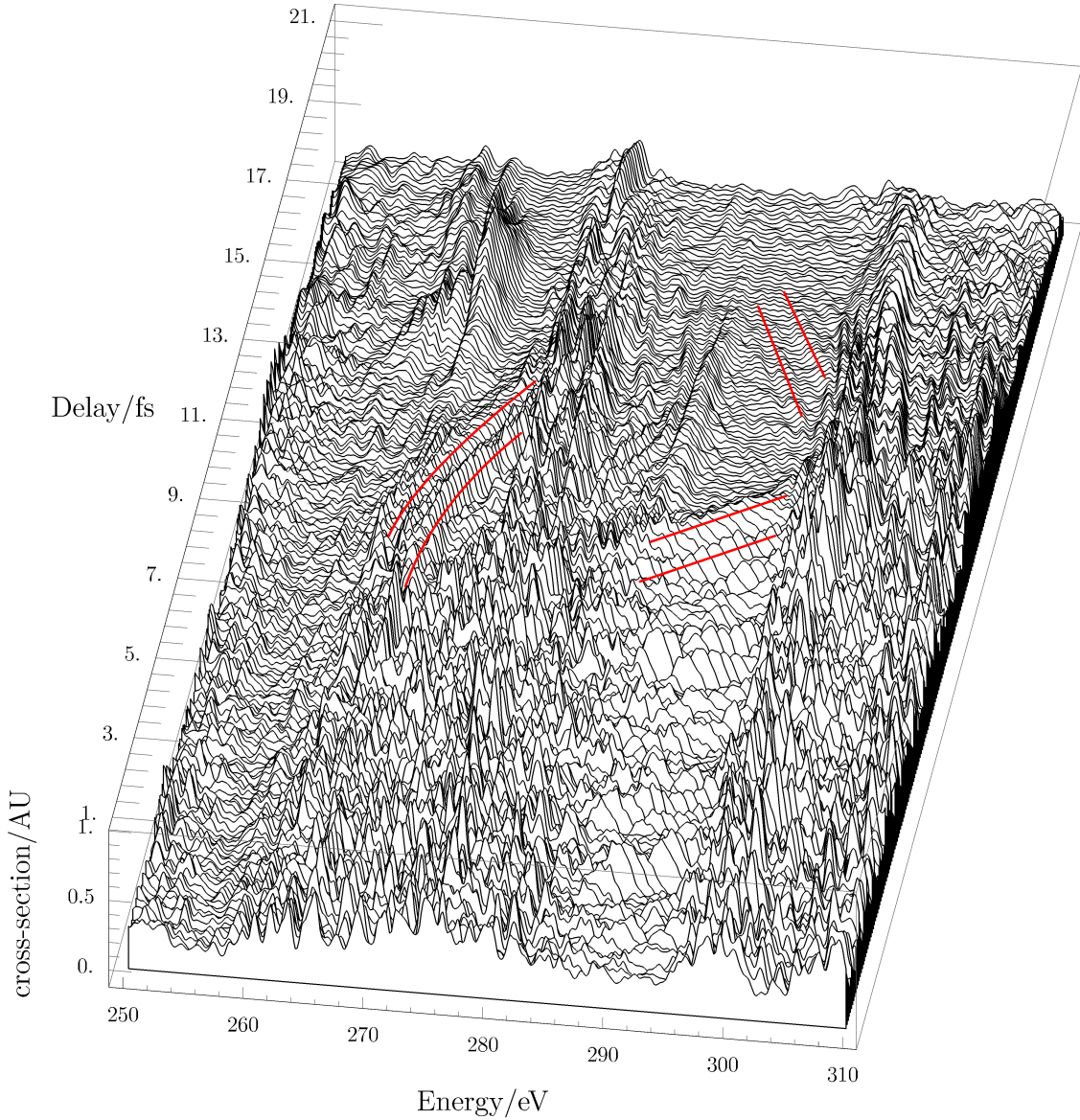


FIGURE 6.16: Carbon K-series spectrum for the P3HT monomer over various pump-probe delay times. The initial ion positions and velocities for each simulation are taken from the same molecular dynamics snapshot of a P3HT crystal simulation at 300 K. The red lines indicate delay-time-dependent energy shifts in the resonances.

Our fully uncorrelated simulations however did not yield the expected results, we could not extract any information on the electronic or ionic dynamics. This raises the need to make a point regarding the representability of the samples chosen: while in an experimental setup the ionic coordinates between each pump-probe run would certainly be uncorrelated, the absorption spectrum of a rather a large ensemble of polymer strands would be measured. Our simulations found that the peak positions in the spectra are

extremely variable. However, the simple fact that absorption spectra of dilute molecular gas clearly show peaks, albeit broad, suggests that certain spectral features must become apparent through ensemble averaging.

Some of the spectral features may well be unphysical too, given that atomically-localised basis set representations are known to give rise to artificial peaks in the continuum regime beyond the absorption edge. Inclusion of plane-wave states may well reduce the severity of these unphysical artefacts, thereby allowing the peaks associated with bound-bound transitions to stand out better.

It would be an interesting project to investigate whether the neglect of periodicity led us to leave out any important correlations. A periodic system is more constrained in its degrees of freedom compared to a molecular fragment, as the ionic motion is limited by the neighbouring polymer strands. We may also see the emergence of long-range correlation, seeing as currents would be able to flow across periodic cell. This would however require the extension of Gaussian tight-binding either by the current-density-functional theory formalism to enable a treatment of electric fields in periodic boundary conditions, or at least by implementation of 2D-periodic boundary conditions for slab simulations.

6.3 Summary

We have implemented a basic description of non-adiabatic dynamics into the Gaussian tight binding model in the form of Ehrenfest dynamics excluding the ionic velocity-dependent force contributions. The method was benchmarked and found to conserve energy well, while the total momentum drift remains small to a satisfying degree. We formulated an all-electron tight-binding model with the exception of the sulfur $1s^2$ -state, and used this model to study the P3HT monomer and dimer in a transient core absorption spectroscopy setup over various time-delays. We were able to identify signatures corresponding to excitation dynamics very clearly, and saw signatures that could be attributed to ionic dynamics less clearly. These findings show that approximate electronic structure methods in principle allow the direct simulation of pump-probe experiments due their sheer efficiency. There is however more work to be done in understanding how these methods can be applied to simulate setups that are more representable of the experiment.

We have outlined a semi-empirical electronic-structure method that is capable of computing the optical properties of molecules with accuracy comparable to density-functional theory, albeit at a fraction of the cost. The Gaussian tight binding (GTB) method expands the density functional tight binding method by a more generalised description of self-consistency, while staying true to the underlying two-centre tight binding approximations. Importantly, we found in chapter 4 that a higher-order self-consistent description only offers significant improvements if combined with the inclusion of polarisation orbitals.

We emphasise that GTB strikes a highly effective balance between accuracy and computational speed. We found the method to reach the precision of PBE-DFT, while only being a factor of 4-8 slower than conventional minimal basis-set tight binding*. This enabled us to produce an enormous volume of simulation data on the example of transient core pump-probe spectroscopy of thiophene. These preliminary simulations demonstrated effectively that transient core spectroscopy is well capable of resolving the excitation and vibrational dynamics of a molecular system. However, the link between the optical response of a single molecule and that of a periodic ensemble of polymers strands requires further investigation. This motivates the implementation of GTB in a linear-scaling tight binding code, so that larger systems of interest can be investigated.

Nevertheless, it is important to remember that Gaussian tight binding as an approximate Kohn-Sham theory also inherits the flaws of density-functional theory. In chapter 4 we demonstrated that the polarisability of extended conjugated systems is severely and

*This is mostly caused by the choice of a larger basis set. The exact factor depends on the scaling of the computational algorithm, e.g. solving the eigensystem scales as $\mathcal{O}(N_{basis}^3)$, while time-propagation roughly scales as $\mathcal{O}(N_{basis}^2)$.

systematically overestimated. Furthermore, considering core-spectroscopy, the energies of the core transitions are off by several tens of electronvolts. These flaws can partly be attributed to the self-interaction error inherent to local and semi-local exchange-correlation functionals, though a more accurate description of core-states certainly also needs to respect the relativistic nature of the core-electrons. On the flip side, one may apply the techniques originally developed to improve the density-functional theory accuracy similarly to tight binding, for instance by adding long-range or self-interaction corrections, or by inclusion of exact-exchange. The challenge again lies in formulating a framework that does not significantly increase the computational load of standard two-centre tight binding.

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A.1 Variational principle

Kato¹⁵⁰ showed in 1951 that any Hamiltonian with interacting many-body Coulomb potentials is an essentially self-adjoint operator on the Hilbert space. The Sturm-Liouville theorem as a consequence states that the Hamiltonian has real eigenvalues $\varepsilon^{(n)}$ with a corresponding complete orthogonal set of eigenfunctions $|\psi^{(n)}\rangle$. Any self-adjoint operator on $\mathcal{H}$ is called an observable. Suppose now that we want to find the state with the lowest energy $\varepsilon^{(0)}$, the so-called ground-state $|\psi^{(0)}\rangle$ of $\hat{H}$. Let us start with a guess for the wave-function that is close, but not quite at the ground-state:

$$|\Psi\rangle = |\psi^{(0)}\rangle + |\delta\psi\rangle = |\psi^{(0)}\rangle + \sum_{n=1}^{\infty} c^{(n)} |\psi^{(n)}\rangle. \quad (\text{A.1})$$

The variation $|\delta\psi\rangle$ here is expressed in the complete set of eigenfunctions with the expansion coefficients $c^{(n)} \in \mathbb{C}$. The energy of the system is given as:

$$E = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\langle \psi_0 + \sum_{n=1}^{\infty} c^{(n)} \psi^{(n)} | \hat{H} | \psi_0 + \sum_{n=1}^{\infty} c^{(n)} \psi^{(n)} \rangle}{\langle \psi_0 + \sum_{n=1}^{\infty} c^{(n)} \psi^{(n)} | \psi_0 + \sum_{n=1}^{\infty} c^{(n)} \psi^{(n)} \rangle}, \quad (\text{A.2})$$

using $\hat{H} |\psi^{(n)}\rangle = \varepsilon^{(n)} |\psi^{(n)}\rangle$ this simplifies to:

$$E = \varepsilon^{(0)} + \sum_{n=1}^{\infty} |c^{(n)}|^2 (\varepsilon^{(n)} - \varepsilon^{(0)}) + \mathcal{O}(|c^{(n)}|^4). \quad (\text{A.3})$$

This expression leads to two important conclusions. For one, $\varepsilon^{(n)} > \varepsilon^{(0)}$ for all $n > 0$, hence $E > \varepsilon^{(0)}$. The total energy is bound from below by the ground-state energy, which

yields the lowest energy of all antisymmetric states in the Hilbert space $\mathcal{H}$ for a given Hamiltonian $\hat{H}$:

$$\forall_{\substack{\Psi \in \mathcal{H} \\ \Psi \neq \Psi_0}} E[\Psi_0] = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle < \langle \Psi | \hat{H} | \Psi \rangle. \quad (\text{A.4})$$

Furthermore the deviation of the total energy to $\varepsilon^{(0)}$ is quadratic in $c^{(n)}$; small deviations in the trial state from the ground-state therefore lead to even smaller errors.

A.2 Proof of the Hohenberg-Kohn theorem

The Hohenberg-Kohn theorems presented in section 2.2.1 are proven below.

Theorem 1. Let $G : v_{ext}(\vec{r}) \rightarrow \rho_0(\vec{r})$ be the map from the one-particle potential $v_{ext}(\vec{r})$ to the ground-state density $\rho_0(\vec{r}) = \langle \Psi_0 | \hat{n} | \Psi_0 \rangle$. The map G is invertible up to an additive constant v_0 in $v_{ext}(\vec{r})$.

Proof. We shall here follow Hohenberg and Kohn's proof by reduction to absurdity. Consider the same ground-state density $\rho_0(\vec{r})$ to follow from the ground-state solutions $|\Psi_0^{(1)}\rangle$ and $|\Psi_0^{(2)}\rangle$ to the time-independent Schrödinger equations

$$\begin{aligned} E^{(1)} |\Psi_0^{(1)}\rangle &= \hat{H}^{(1)} |\Psi_0^{(1)}\rangle = (\hat{F} + \hat{V}_{ext}^{(1)}) |\Psi_0^{(1)}\rangle \\ E^{(2)} |\Psi_0^{(2)}\rangle &= \hat{H}^{(2)} |\Psi_0^{(2)}\rangle = (\hat{F} + \hat{V}_{ext}^{(2)}) |\Psi_0^{(2)}\rangle \end{aligned} \quad (\text{A.5})$$

where $\hat{V}_{ext}^{(1)} \neq \hat{V}_{ext}^{(2)}$ and hence $|\Psi_0^{(1)}\rangle \neq |\Psi_0^{(2)}\rangle$. Following the variational principle (A.4), we also know that $|\Psi^{(1)}\rangle$ cannot be the ground-state for $\hat{H}^{(2)}$ and vice versa:

$$\begin{aligned} E^{(1)} &= \langle \Psi_0^{(1)} | \hat{H}^{(1)} | \Psi_0^{(1)} \rangle < \langle \Psi_0^{(2)} | \hat{H}^{(1)} | \Psi_0^{(2)} \rangle \\ E^{(2)} &= \langle \Psi_0^{(2)} | \hat{H}^{(2)} | \Psi_0^{(2)} \rangle < \langle \Psi_0^{(1)} | \hat{H}^{(2)} | \Psi_0^{(1)} \rangle. \end{aligned} \quad (\text{A.6})$$

The two equations above are next expanded:

$$\begin{aligned} E^{(1)} &< \langle \Psi_0^{(2)} | \hat{H}^{(1)} | \Psi_0^{(2)} \rangle = \langle \Psi_0^{(2)} | \hat{H}^{(2)} | \Psi_0^{(2)} \rangle + \langle \Psi_0^{(2)} | \hat{V}_{ext}^{(1)} - \hat{V}_{ext}^{(2)} | \Psi_0^{(2)} \rangle \\ E^{(2)} &< \langle \Psi_0^{(1)} | \hat{H}^{(2)} | \Psi_0^{(1)} \rangle = \langle \Psi_0^{(1)} | \hat{H}^{(1)} | \Psi_0^{(1)} \rangle + \langle \Psi_0^{(1)} | \hat{V}_{ext}^{(2)} - \hat{V}_{ext}^{(1)} | \Psi_0^{(1)} \rangle. \end{aligned} \quad (\text{A.7})$$

We have previously derived that the external field energies are functionals of the density following Eq. (2.25). The hypothesis also states that wave-functions $|\Psi^{(1)}\rangle$ and $|\Psi^{(2)}\rangle$ yield the same density ρ_0 , hence it follows:

$$\begin{aligned} E^{(1)} &< \langle \Psi_0^{(2)} | \hat{H}^{(2)} | \Psi_0^{(2)} \rangle + \int \rho_0(\vec{r}) \left(v_{ext}^{(1)}(\vec{r}) - v_{ext}^{(2)}(\vec{r}) \right) d^3r \\ E^{(2)} &< \langle \Psi_0^{(1)} | \hat{H}^{(1)} | \Psi_0^{(1)} \rangle + \int \rho_0(\vec{r}) \left(v_{ext}^{(2)}(\vec{r}) - v_{ext}^{(1)}(\vec{r}) \right) d^3r. \end{aligned} \quad (\text{A.8})$$

Summing the equation above yields

$$E^{(1)} + E^{(2)} < E^{(1)} + E^{(2)}, \quad (\text{A.9})$$

which is an absurd contradiction.

Theorem 2. Let $\mathcal{V}$ be the space of all v -representable electron densities* and E_0 the ground-state energy of N electrons in the external potential $v(\vec{r})$. Then it follows from the variational principle, see section A.1, that:

$$\forall_{\rho \in \mathcal{V}} E_v[\rho] \geq E_0, \quad (\text{A.10})$$

where $E_v[\rho]$ is defined by Eq. (2.32).

Proof. Following theorem 1, the trial density ρ defines an external potential $v_\rho(\vec{r})$ and trial wave-function $|\Psi\rangle$ for the variational principle:

$$E_v[\rho] = \int \rho(\vec{r}) v_\rho(\vec{r}) d^3r + F[\rho] \geq E_0. \quad (\text{A.11})$$

A.3 Transposed multipole moments

We have outlined the construction of the multipole moment matrix elements $M_{I\alpha J\beta}^{lm}$ in section 3.5.2. The expressions for the self-consistent energy and force however also require the transposed matrix elements $M_{J\beta I\alpha}^{lm}$. We will here present the symmetry relations that transform the $M_{I\alpha J\beta}^{lm}$ elements into their transposed counterparts $M_{J\beta I\alpha}^{lm}$. Note that we follow the PLATO convention here, that is $\vec{r} = (x, y, z)^T$, and the harmonics are defined as $lm = \{00, 11, 12, 10, 24, 22, 21, 23, 20\}$ compared to table 2.1.

Let us first recall the definition of the multipole moment integral (3.11):

$$M_{I\alpha J\beta}^{lm} = \int \phi_{I\alpha}(\vec{r}_I) K_{lm}(\vec{r}_I) \phi_{J\beta}(\vec{r}_J) d^3r, \quad (\text{A.12})$$

where $\vec{r}_K = \vec{r} - \vec{R}_K$, with the transposed integral given as:

$$M_{J\beta I\alpha}^{lm} = \int \phi_{I\alpha}(\vec{r}_I) K_{lm}(\vec{r}_J) \phi_{J\beta}(\vec{r}_J) d^3r. \quad (\text{A.13})$$

We therefore merely need to apply the substitution $(\vec{r} - \vec{R}_I) = (\vec{r} - \vec{R}_J) - (\vec{R}_I - \vec{R}_J)$ to the argument of the harmonic function $K_{lm}(\vec{r}_I)$, and expand the resulting expressions.

*Not all densities are v -representable,³⁴ however this condition can be relaxed by the Levi-construction,³⁵ where instead the ground-state electron density is defined as the lowest-energy density from the ensemble of all densities with an identical number of electrons N .

Defining $\vec{R}_{IJ} = \vec{R}_I - \vec{R}_J$ and similarly $x_{IJ} = x_I - x_J$ etc., we arrive at the following transformation rules up to quadrupole order:

$l = 0$:

$$M_{J\beta I\alpha}^{00} = M_{I\alpha J\beta}^{00} \quad (\text{A.14})$$

$l = 1$:

$$M_{J\beta I\alpha}^{1m} = M_{I\alpha J\beta}^{1m} + (\vec{R}_{IJ})_m M_{I\alpha J\beta}^{00} \quad (\text{A.15})$$

$l = 2$:

$$\begin{aligned} M_{J\beta I\alpha}^{20} &= M_{I\alpha J\beta}^{20} + \sqrt{3} (y_{IJ} M_{I\alpha J\beta}^{10} + x_{IJ} M_{I\alpha J\beta}^{11} + x_{IJ} y_{IJ} M_{I\alpha J\beta}^{00}) \\ M_{J\beta I\alpha}^{21} &= M_{I\alpha J\beta}^{21} + \sqrt{3} (z_{IJ} M_{I\alpha J\beta}^{11} + y_{IJ} M_{I\alpha J\beta}^{12} + y_{IJ} z_{IJ} M_{I\alpha J\beta}^{00}) \\ M_{J\beta I\alpha}^{22} &= M_{I\alpha J\beta}^{22} + \sqrt{3} (x_{IJ} M_{I\alpha J\beta}^{12} + z_{IJ} M_{I\alpha J\beta}^{10} + z_{IJ} x_{IJ} M_{I\alpha J\beta}^{00}) \\ M_{J\beta I\alpha}^{23} &= M_{I\alpha J\beta}^{23} + \sqrt{3} (x_{IJ} M_{I\alpha J\beta}^{10} - y_{IJ} M_{I\alpha J\beta}^{11} + \frac{1}{2}(x_{IJ}^2 - y_{IJ}^2) M_{I\alpha J\beta}^{00}) \\ M_{J\beta I\alpha}^{24} &= M_{I\alpha J\beta}^{24} + 2z_{IJ} M_{I\alpha J\beta}^{12} - x_{IJ} M_{I\alpha J\beta}^{10} - y_{IJ} M_{I\alpha J\beta}^{11} \\ &\quad + (z_{IJ}^2 - \frac{1}{2}(x_{IJ}^2 + y_{IJ}^2)) M_{I\alpha J\beta}^{00} \end{aligned} \quad (\text{A.16})$$

The transformation rules shown above seem to follow a recursive relation involving derivatives of the harmonic functions. I believe this is not by chance and could possibly be generalised rigorously using the multipole recursion schemes from Quantum Chemistry, see Helgaker.⁸⁹ The derivatives of the transposed matrix elements are easily found by differentiating the expressions presented above:

$l = 0$:

$$\vec{\nabla}_{R_{JI}} M_{J\beta I\alpha}^{00} = -\vec{\nabla}_{R_{IJ}} M_{I\alpha J\beta}^{00} \quad (\text{A.17})$$

$l = 1$:

$$\partial_{(R_{JI})_n} M_{J\beta I\alpha}^{1m} = -\partial_{(R_{IJ})_n} M_{I\alpha J\beta}^{1m} - \delta_{nm} M_{I\alpha J\beta}^{00} - (\vec{R}_{IJ})_m \partial_{(R_{IJ})_n} M_{I\alpha J\beta}^{00} \quad (\text{A.18})$$

$l = 2$:

$$\begin{aligned} \partial_{x_{JI}} M_{J\beta I\alpha}^{20} &= -M_x^{20} - \sqrt{3} (y M_x^{10} + M^{11} + x M_x^{11} + y M^{00} + x y M_x^{00}) \\ \partial_{y_{JI}} M_{J\beta I\alpha}^{20} &= -M_y^{20} - \sqrt{3} (M^{10} + y M_y^{10} + x M_y^{11} + x M^{00} + x y M_y^{00}) \\ \partial_{z_{JI}} M_{J\beta I\alpha}^{20} &= -M_z^{20} - \sqrt{3} (y M_z^{10} + x M_z^{11} + x y M_z^{00}) \\ \partial_{x_{JI}} M_{J\beta I\alpha}^{21} &= -M_x^{21} - \sqrt{3} (z M_x^{11} + y M_x^{12} + y z M_x^{00}) \\ \partial_{y_{JI}} M_{J\beta I\alpha}^{21} &= -M_y^{21} - \sqrt{3} (z M_y^{11} + M^{12} + y M_y^{12} + z M^{00} + y z M_y^{00}) \\ \partial_{z_{JI}} M_{J\beta I\alpha}^{21} &= -M_z^{21} - \sqrt{3} (M^{11} + z M_z^{11} + y M_z^{12} + y M^{00} + y z M_z^{00}) \end{aligned}$$

$$\begin{aligned}
\partial_{x_{JI}} M_{J\beta I\alpha}^{22} &= -M_x^{22} - \sqrt{3} (zM_x^{10} + M^{12} + xM_x^{12} + zM^{00} + xzM_x^{00}) \\
\partial_{y_{JI}} M_{J\beta I\alpha}^{22} &= -M_y^{22} - \sqrt{3} (zM_y^{10} + xM_y^{12} + xzM_y^{00}) \\
\partial_{z_{JI}} M_{J\beta I\alpha}^{22} &= -M_z^{22} - \sqrt{3} (M^{10} + zM_z^{10} + xM_z^{12} + xM^{00} + xzM_z^{00}) \\
\partial_{x_{JI}} M_{J\beta I\alpha}^{23} &= -M_x^{23} - \sqrt{3} (M^{10} + xM_x^{10} - yM_x^{11} + xM^{00} + \frac{1}{2}(x^2 - y^2)M_x^{00}) \\
\partial_{y_{JI}} M_{J\beta I\alpha}^{23} &= -M_y^{23} - \sqrt{3} (xM_y^{10} - M^{11} - yM_y^{11} - yM^{00} + \frac{1}{2}(x^2 - y^2)M_y^{00}) \\
\partial_{z_{JI}} M_{J\beta I\alpha}^{23} &= -M_z^{23} - \sqrt{3} (M_z^{10} - yM_z^{11} + \frac{1}{2}(x^2 - y^2)M_z^{00}) \\
\partial_{x_{JI}} M_{J\beta I\alpha}^{24} &= -M_x^{24} - 2zM_x^{12} + M^{10} + xM_x^{10} + yM_x^{11} + xM^{00} - (z^2 - \frac{1}{2}(x^2 + y^2))M_x^{00} \\
\partial_{y_{JI}} M_{J\beta I\alpha}^{24} &= -M_y^{24} - 2zM_y^{12} + xM_y^{10} + M^{11} + yM_y^{11} + yM^{00} - (z^2 - \frac{1}{2}(x^2 + y^2))M_y^{00} \\
\partial_{z_{JI}} M_{J\beta I\alpha}^{24} &= -M_z^{24} - 2M^{12} - 2zM_z^{12} + xM_z^{10} + yM_z^{11} - 2zM^{00} - (z^2 - \frac{1}{2}(x^2 + y^2))M_z^{00}
\end{aligned} \tag{A.19}$$

We have here in Eq. (A.19) used the notation: $\partial_{x_{IJ}} M_{I\alpha J\beta}^{lm} \equiv M_x^{lm}$ and $x_{IJ} \equiv x$, and equivalent for y and z .

A.4 Multipole integral tables

Table A.3: Excerpt of numerically and analytically evaluated multipole moments for a pair of atoms. The error is only given to 10^{-10} precision. A carbon atom is placed at $\vec{R}_I = (0, 0, 0)$, and an oxygen atom placed at $\vec{R}_J = (3, 1, 2)$. We employ the frozen core approximation, using a single-zeta polarisable valence basis set. See 4.1.1 for more details on the basis set. The indices l_α, m_α refer to the carbon ($2s^2, 2p^2, 3d^0$) $\leftrightarrow l_\alpha = (0, 1, 2)$ orbitals, while the indices l_β, m_β refer to the oxygen ($2s^2, 2p^4, 3d^0$) $\leftrightarrow l_\beta = (0, 1, 2)$ orbitals. The indices l_γ, m_γ refer to the order of the multipole expansion.

l_α	m_α	l_β	m_β	l_γ	m_γ	analytical	numerical	error
0	0	0	0	0	0	0.100 217 994 5	0.100 217 994 3	$-2. \times 10^{-10}$
0	0	0	0	1	0	0.117 097 809 9	0.117 097 809 7	$-2. \times 10^{-10}$
0	0	0	0	1	1	0.058 548 904 93	0.058 548 904 85	0
0	0	0	0	1	2	0.175 646 714 8	0.175 646 713 5	-1.3×10^{-9}
0	0	0	0	2	0	-0.035 532 344 03	-0.035 532 339 97	4.1×10^{-9}
0	0	0	0	2	1	0.123 087 650 3	0.123 087 650 2	$-1. \times 10^{-10}$
0	0	0	0	2	2	0.369 262 951	0.369 262 948 8	-2.2×10^{-9}
0	0	0	0	2	3	-0.246 175 300 7	-0.246 175 293 1	7.6×10^{-9}
0	0	0	0	2	4	0.184 631 475 5	0.184 631 474 4	-1.1×10^{-9}
0	0	1	0	0	0	-0.086 446 489 06	-0.086 446 488 9	1.6×10^{-10}
...								
2	4	0	0	0	0	0.128 175 332 9	0.128 175 332	$-9. \times 10^{-10}$
2	0	0	0	1	0	0.091 271 348 8	0.091 271 350 87	2.1×10^{-9}
2	0	0	0	1	1	-0.046 888 069 45	-0.046 888 067 7	1.7×10^{-9}
2	0	0	0	1	2	-0.140 664 208 3	-0.140 664 183 1	2.5×10^{-8}

Continued on next page

l_α	m_α	l_β	m_β	l_γ	m_γ	analytical	numerical	error
2	1	0	0	1	0	0.164 594 249	0.164 594 248 6	$-4. \times 10^{-10}$
2	1	0	0	1	1	0.162 425 037 1	0.162 425 036 8	$-3. \times 10^{-10}$
2	1	0	0	1	2	0.166 763 460 8	0.166 763 459 9	$-9. \times 10^{-10}$
2	2	0	0	1	0	0.493 782 746 9	0.493 782 743 2	-3.7×10^{-9}
2	2	0	0	1	1	0.166 763 460 8	0.166 763 459 9	$-9. \times 10^{-10}$
2	2	0	0	1	2	0.607 127 599 3	0.607 127 586 4	-1.3×10^{-8}
2	3	0	0	1	0	-0.222 351 281 1	-0.222 351 274 8	6.3×10^{-9}
2	3	0	0	1	1	-0.057 757 032 13	-0.057 757 029 14	$3. \times 10^{-9}$
2	3	0	0	1	2	-0.493 782 746 9	-0.493 782 701 5	4.5×10^{-8}
2	4	0	0	1	0	0.166 763 460 8	0.166 763 459 9	$-9. \times 10^{-10}$
2	4	0	0	1	1	0.243 637 555 7	0.243 637 553 7	$-2. \times 10^{-9}$
2	4	0	0	1	2	0.303 563 799 6	0.303 563 793 2	-6.4×10^{-9}
2	0	0	0	2	0	0.629 653 833 2	0.629 653 738 1	-9.5×10^{-8}
2	0	0	0	2	1	0.026 613 069 69	0.026 613 071 57	1.9×10^{-9}
2	0	0	0	2	2	0.079 839 209 08	0.079 839 246 24	3.7×10^{-8}
...								
2	4	2	2	2	0	-0.256 110 060 8	-0.256 110 497 3	-4.4×10^{-7}
2	4	2	2	2	1	-0.062 136 533 93	-0.062 136 521 81	1.2×10^{-8}
2	4	2	2	2	2	-0.038 017 751 87	-0.038 017 722 12	$3. \times 10^{-8}$
2	4	2	2	2	3	0.188 144 026 1	0.188 143 335 8	-6.9×10^{-7}
2	4	2	2	2	4	0.715 126 518	0.715 126 977 9	4.6×10^{-7}
2	4	2	3	2	0	0.070 166 864 92	0.070 166 025 59	-8.4×10^{-7}
2	4	2	3	2	1	0.325 424 568 7	0.325 424 676 6	1.1×10^{-7}
2	4	2	3	2	2	-0.482 180 848 8	-0.482 180 452 5	$4. \times 10^{-7}$
2	4	2	3	2	3	0.373 413 191 4	0.373 411 772 9	-1.4×10^{-6}
2	4	2	3	2	4	0.776 021 475 9	0.776 022 291 7	8.2×10^{-7}
2	4	2	4	2	0	0.164 423 507 7	0.164 424 013 3	5.1×10^{-7}
2	4	2	4	2	1	-0.103 584 721 5	-0.103 584 734 7	-1.3×10^{-8}
2	4	2	4	2	2	-0.456 257 889 2	-0.456 258 127 1	-2.4×10^{-7}
2	4	2	4	2	3	-0.384 062 592 3	-0.384 061 771 5	8.2×10^{-7}
2	4	2	4	2	4	-0.225 435 425 3	-0.225 435 531 1	-1.1×10^{-7}

A.5 Pair-potentials for hydrogen-carbon-sulfur

The pair-potentials within the two-centre tight binding approximations are simply dependent on the ionic coordinates, taking in geometry data and returning an energy. There are two major steps involved in the fitting process. First, the pair-potentials need to be fitted to reproduce the properties of a given fitting set. The fitting set contains data on energies and forces from one or more systems over a selection of geometries. Second, the pair-potentials are also required to reproduce the energies and forces of geometries that have not been explicitly included in the fitting set. This is to avoid over-fitting and to ensure that the pair-potentials are transferable to other systems.

Table A.1: Net angular momenta $l_\alpha + l_\gamma$ and l_β for the primitive Cartesian overlap integrals corresponding to a primitive multipole moment matrix element of two orbitals with angular momentum l_α and l_β . The multipole moment is taken to order l_γ .

multipole harmonic indices			overlap harmonic indices	
l_α	l_β	l_γ	$l_\alpha + l_\gamma$	l_β
Monopole order				
0	0	0	0	0
1	0	0	1	0
0	1	0	0	1
1	1	0	1	1
2	0	0	2	0
0	2	0	0	2
2	1	0	2	1
1	2	0	1	2
2	2	0	2	2
Dipole order				
0	0	1	1	0
1	0	1	2	0
0	1	1	1	1
1	1	1	2	1
2	0	1	3	0
0	2	1	1	2
2	1	1	3	1
1	2	1	2	2
2	2	1	3	2
Quadrupole order				
0	0	2	2	0
1	0	2	3	0
0	1	2	2	1
1	1	2	3	1
2	0	2	4	0
0	2	2	2	2
2	1	2	4	1
1	2	2	3	2
2	2	2	4	2

A.5.1 Density functional theory reference systems

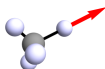
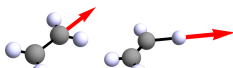
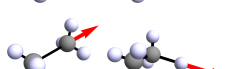
The SVP-GTB model can be considered an approximate density-functional theory using the Perdew-Becke-Ernzerhof⁹¹ (PBE) exchange-correlation functional. While functionals including exact-exchange such as B3LYP¹³² find molecular vibrational frequencies in better agreement with experiments, for this project we see more value in deriving a theory that is consistent to PBE-DFT using the cc-pVTZ basis set in the ORCA software.

Table A.2: List of unique primitive Cartesian integrals $S_{IJ}(\alpha, \beta)|_{000}^{tuv}$ for given net angular momentum: $l_\alpha + l_\gamma$. The entry $zxyy$ for example stands for $S_{IJ}(\alpha, \beta)|_{000}^{121}$. We look up integrals for $l_\beta > 0$ in the angular momentum column corresponding to $l_\alpha + l_\beta + l_\gamma$, treating the last l_β characters as powers for $t'u'v'$. For instance, $zxxx|yy$ corresponds to $S_{IJ}(\alpha, \beta)|_{020}^{301}$.

#	$l_\alpha + l_\gamma$ angular momentum in $\vec{r}_I$						
	0	1	2	3	4	5	6
1	1	z	zz	zzz	zzzz	zzzzz	zzzzzz
2		x	zx	zzx	zzzx	zzzzx	zzzzzx
3		y	zy	zzy	zzzy	zzzzzy	zzzzzy
4			xx	zxx	zzxx	zzzxx	zzzzxx
5			xy	zxy	zzxy	zzzxy	zzzzxy
6			yy	zyy	zzyy	zzzyy	zzzzyy
7				xxx	zxxx	zzxxx	zzzxxx
8				xyy	zxyy	zzxyy	zzzxyy
9				yyy	zyyy	zzyyy	zzzyyy
10					xxx	zxxx	zzxxx
11					xyy	zxyy	zzxyy
12					yyy	zyyy	zzyyy
13					xxxx	zxxxx	zzxxxx
14					xxxy	zxxxy	zzxxxy
15					xxyy	zxyyy	zzxyyy
16					xyyy	zyyyy	zzyyyy
17					yyyy	zyyyy	zzyyyy
18						xxxxx	zxxxxx
19						xxxxy	zxxxxy
20						xxxxy	zxxxxy
21						xxxyy	zxxxyy
22						xyyyy	zxyyyy
23						yyyyy	zyyyyy
24							xxxxxx
25							xxxxxy
26							xxxxyy
27							xxxxyy
28							xxxyyy
29							xyyyyy
30							yyyyyy

We follow a simple strategy for generating reference data: given a selection of molecules containing hydrogen, carbon, and sulfur, we select a molecular fragment and displace it along the vector connecting the fragment to the rest of the molecule. The total energy is computed along the path, yielding binding energy curves. We note here that these are not

Table A.4: Reference molecules and their respective fragments for the generation of DFT fragmentation energy curves. Displacement vectors are shown as red arrows.

formula	name	fragments
H ₂	hydrogen dimer	
C ₂	carbon dimer	
S ₂	sulfur dimer	
CH	carbon-hydrogen dimer	
CS	carbon-sulfur dimer	
HS	hydrogen-sulfur dimer	
CH ₄	methane	
C ₂ H ₄	ethylene	
C ₂ H ₆	ethane	
H ₂ S	hydrogen sulfide	
CS ₂	carbon disulfide	
CH ₄ S	methanethiol	
CH ₂ S	thioformaldehyde	

the truly physical fragmentation energy curves, as that would require us to also consider the geometric relaxation as the fragment detaches, for instance by using path-relaxation algorithms such as the nudged-elastic-band method,¹⁵¹ or the art-relaxation-technique.¹⁵²

Previously we have shown that the static- and time-dependent electronic structure of GTB agrees well with DFT. Given these findings we are confident that a selection of small molecules will be sufficient to deliver transferable pair-potentials. The list of reference systems and their respective molecular fragments are shown in table A.4.

A.5.2 Definition of the fitting error

We know that the total energy of a system in the ground-state depends parametrically on the ionic coordinates $\{\vec{R}_I\}$:

$$E^{TB}[\{\vec{R}_I\}] = E_{ele}^{TB}[\{\vec{R}_I\}] + \sum_{\substack{IJ \\ I \neq J}} U_{rep}^{IJ}(R_{IJ}) + U_0. \quad (\text{A.20})$$

Assuming the energy difference between tight binding and density functional theory to be accounted for by the energy contribution from the pair-potential, we define the energy difference between DFT and TB for a given set of ionic coordinates $\chi = \{\vec{R}_I\}$:

$$\Delta E[\chi] = E^{DFT}[\chi] - E^{TB}[\chi] \quad (\text{A.21})$$

Let us now define $\text{Geom}(\kappa)$ as the set of geometries $\{\chi_\kappa\}$ contained in a given reference data set κ . This could for instance be a fragmentation curve. We now define the fitting error $err(\kappa)$ associated with a data set as the variance of the energy differences over every data point:

$$err(\kappa) = \text{Var}(\{\Delta E[\chi_\kappa] \mid \chi_\kappa \in \text{Geom}(\kappa)\}). \quad (\text{A.22})$$

We use here the variance to eliminate the effect of any constant energy shift, such as U_0 in equation (A.20). After all, constant offsets in energy do not contribute to forces; we merely need to reproduce the correct relative ordering of the energies in the reference data, their absolute values are irrelevant. Similarly the total fitting error follows as:

$$Err = \sum_{\kappa} f_{\kappa} \cdot err(\kappa), \quad (\text{A.23})$$

where f_{κ} is a weighting factor to enable scaling the errors of certain data sets differently. This can be useful if curves with vastly different energy scales are compared, e.g. volume-energy curves versus defect formation energies in metals. One could for instance rescale the errors by the energy variance of the respective data set, as a simple measure for the energy deviation:

$$f_{\kappa} \sim \text{Var}(\{E^{DFT}[\chi_\kappa] \mid \chi_\kappa \in \text{Geom}(\kappa)\}). \quad (\text{A.24})$$

For the fragmentation curves considered in this work we found $f_{\kappa} = 1$ to be sufficient, as the energy scales associated with molecular fragmentation are of comparable magnitude.

A.5.3 Gaussian Monte-Carlo fitting scheme

We are left to find the functional form of the pair-potentials $\{U^{IJ}(R)\}$ such that the total fitting error Err is minimised. Previous work on fitting tight binding models

has led to the development of a wide variety of fitting schemes, distinguished by their parametrisation of the pair-potentials, for instance by analytic functions, splines, or data points, as well by their choice of the optimisation algorithm, from steepest descent, to evolutionary algorithms.^{153,154} We shall here present our own approach, designed to grant the optimiser flexibility in changing the shape of the pair-potentials while requiring little user input.

A.5.3.1 Functional form of the pair-potential

Let $U_{spline}(R)$ be a pair-potential defined by the cubic spline interpolation of a set of points $\{r_i, U_i\}$. We choose the grid-spacing as $\delta r = r_{i+1} - r_i = 0.01 a_0$. We further impose the restriction that $U(R)$ needs to be continuously differentiable to second order. Furthermore, we impose that $U(R_C) = U'(R_C) = U''(R_C) = 0$ for a given cut-off radius R_C . This is to ensure that the forces are continuous and smooth at all points, and that the pair-potential is indeed of limited range. This condition is enforced by attaching a polynomial tail of fifth degree $P_5(R)$ to $U_{spline}(R)$ from R_0 to R_C , such that:

$$\begin{aligned} P_5(R_0) &= U(R_0), & P'_5(R_0) &= U'(R_0), & P''_5(R_0) &= U''(R_0) \\ P_5(R_C) &= 0, & P'_5(R_C) &= 0, & P''_5(R_C) &= 0. \end{aligned} \quad (\text{A.25})$$

The pair-potential $U(R)$ is then given by:

$$U(R) = \begin{cases} U_{spline}(R) & R < R_0 \\ P_5(R) & R_0 \leq R < R_C \\ 0 & R \geq R_C. \end{cases} \quad (\text{A.26})$$

A.5.3.2 Gaussian Monte-Carlo algorithm

Let us start with an initial choice of $\{r_i, U_i\}$ such that TB energy curves reproduce the DFT energy curves for the homo- and hetero-atomic dimers. We smooth the initial pair-potentials by convolution with a Gaussian to remove discontinuities and narrow features. Polynomial tails are attached for the values given in table A.5. We compute the initial fitting error Err as defined in section A.5.2.

We use a Monte-Carlo based approach in updating our initial guess for the pair-potentials. First a random pair-potential is selected from the pool $\{U^{IJ}(R)\}$. Next we generate two random variables from a uniform distribution $Q_i \in [0, 1]$. The shape of the pair-potential is updated by applying a Gaussian shift at every point:

$$U'_i = U_i + \omega a(1 - 2Q_1)e^{-c(r_i - 1.2R_0Q_2)^2}, \quad (\text{A.27})$$

Table A.5: Polynomial tail attachment radii R_0 and truncation radii R_C for carbon-hydrogen-sulfur pair-potentials of the SVP-GTB model.

R_0/a_0				R_C/a_0			
	C	H	S		C	H	S
C	3.4	2.8	4.5	C	4.4	4.0	5.0
H		2.0	3.0	H		2.5	3.6
S			4.8	S			5.5

where a is the Gaussian amplitude, c is the inverse quadratic width, R_0 is the polynomial tail attachment point for the given pair-potential, and ω is a general scaling factor to tune the convergence behaviour of the Monte-Carlo update. Note that the inverse width c is directly linked to the transferability of the fit; the risk of overfitting is reduced by choosing wider Gaussians, as the Monte-Carlo algorithm becomes unable to resolve narrow features. The full updated pair-potential is subsequently constructed by attaching a new polynomial tail after equation (A.26). We note that the update Gaussian is centred around $1.2R_0Q_2$, allowing it to be placed behind the polynomial tail attachment point at R_0 . This gives the update step a small probability to affect the height and slope of the polynomial tail attachment point.

The total error Err is recomputed after each update step. A step is only accepted if it lowers the error, corresponding to a zero temperature Monte-Carlo step. The updates are repeated until the total error Err does not measurably change despite an acceptance rate of above several percent.

A.5.3.3 Fitting results

Our values of choice are $a = 0.01 E_h$, $c = 3 a_0^{-2}$, with ω starting initially at 1, going down to 0.001 as the fitting proceeds. We also gave geometries in our data set up to three times more weight if the fragment was displaced within a range of $\pm 0.8a_0$ with respect to the equilibrium bond length, as that range is associated with the dynamics of bonded systems. The Gaussian tight binding level of theory was chosen as SVP-GTB with dipole order multipoles.

In practice we found a few tens of thousands of steps sufficient to converge the fit. The fitting process took a few minutes. We present the initial and final dimer pair-potentials in figure A.1, as well as their first and second order derivatives to demonstrate their smoothness. We left the pair-potentials for hydrogen-hydrogen and sulfur-sulfur

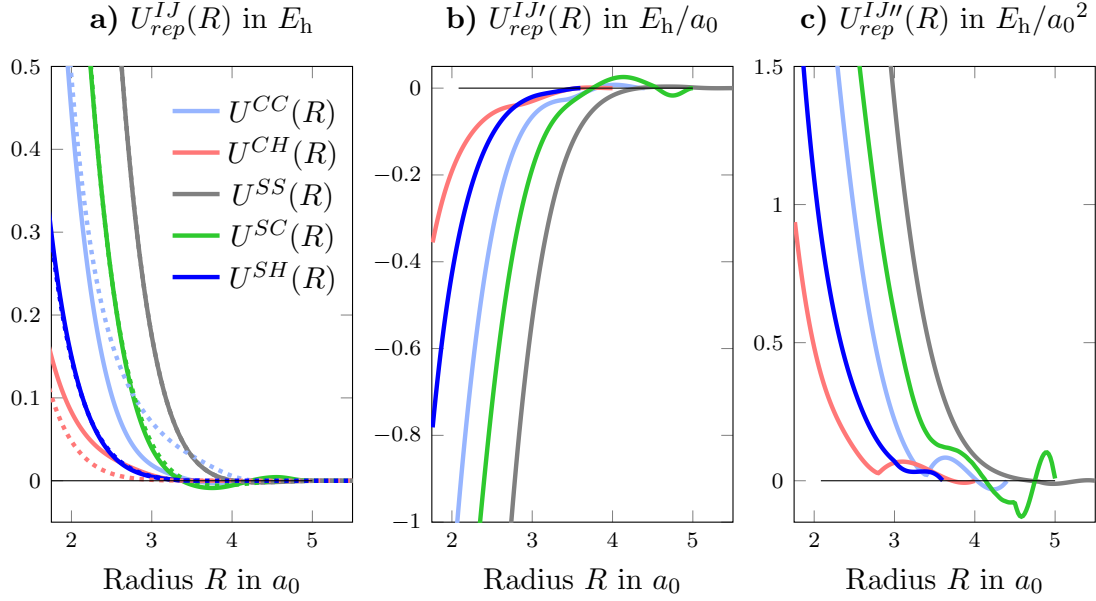


FIGURE A.1: Pair-potentials for carbon, hydrogen, and sulfur in the SVP-GTB model. Plot **a)** shows the original dimer pair-potentials (dotted) and the optimised pair-potentials (solid). Plots **b)** and **c)** show the first and second order derivatives. The pair-potentials for hydrogen-hydrogen and sulfur-sulfur were not optimised in the fit.

unchanged. Any improvements they could bring to the fit would be at the detriment of the dimer behaviour, which we considered more important.

A.5.4 Geometry and vibrational frequency benchmarks

The extensive benchmarking of the GTB tight binding forces lies beyond the scope of this project, however we shall confirm the quality of the pair-potentials on a small sample of test systems.

We relax the geometry of several molecules containing carbon, hydrogen, and sulfur in SVP-GTB-1 and PBE-DFT using the cc-pVTZ basis set, see figure A.2. The bond-lengths between carbon and hydrogen are reproduced by GTB in excellent agreement with DFT. Compounds containing sulfur are less described with less accuracy, but still sufficiently well for our purposes.

The PBE-DFT vibrational frequencies are computed using analytical second-order derivatives. While the SVP-GTB-1 method has access to second-order derivatives of the Slater-Koster tables, we have yet to implement the second-order derivatives of the self-consistent multipole energies. We instead construct the Hessian matrix in terms of the force derivatives $H_{I\mu J\nu} = \partial_{R_{I\mu}} \partial_{R_{J\nu}} E^{TB} = -\partial_{R_{I\mu}} F_{J\nu}^{TB}$. The force derivatives are found using the mid-point finite-differences scheme, where each atom is displaced by a finite

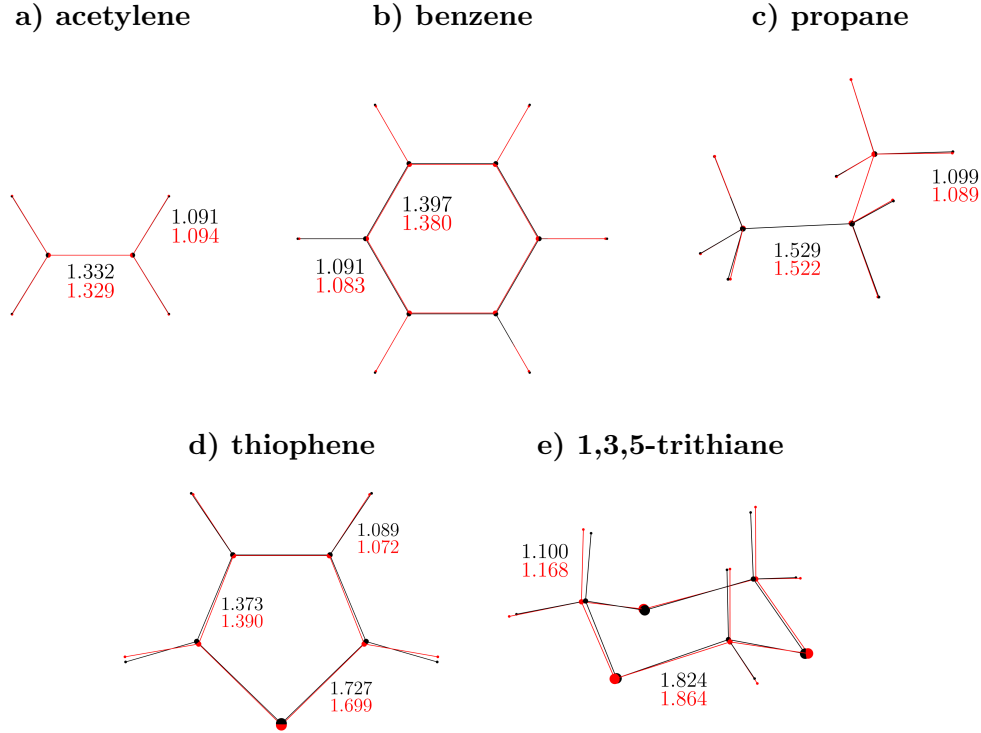


FIGURE A.2: Relaxed molecular geometries, using PBE-DFT in the cc-pVTZ basis set (black) and SVP-GTB-1 (red). The numbers refer to select bond-lengths in Å. Atoms are drawn as spheres, their species distinguished by the radius $R_S > R_C > R_H$.

shift of $\Delta = 0.001 a_0$ in the x , y , and z -directions. The eigenfrequencies are subsequently retrieved by diagonalisation of the Hessian matrix. The vibrational frequencies are shown in figure A.3.

While the SVP-GTB pair-potentials are found to be sufficiently accurate for our purposes, there is certainly room for improvement in the model. The vibrations associated with carbon-carbon bonds at 3000 cm^{-1} show larger errors in the range of up to 10 %. The sulfur-carbon vibrations of the sulfur-containing molecule 1,3,5-trithiane in particular are very poorly described. Looking at figure A.1 we can see that the second-order derivative of the sulfur-carbon pair-potential show irregularities around the $3.5 a_0$ bond-length. This suggests that our fitting data needs better sampling of sulfur-carbon bonds. These results could also be improved by explicitly including vibrational frequencies into the fitting process, or by directly fitting forces instead of binding energies, as is done in the force-matching method.



FIGURE A.3: Vibrational frequencies for a set of molecules in PBE-DFT (black) and SVP-GTB (red). The lines around 3000 cm^{-1} correspond to carbon-hydrogen bond vibrations, while the ones below correspond to carbon-carbon and carbon sulfur-bond vibrations.

A.5.5 Summary

We have outlined a fitting procedure for tight binding pair-potentials. The procedure is applied to the SVP-GTB model. We find the model to deliver accurate geometries in comparison to PBE-DFT, while specifically the vibrational properties of the sulfur-carbon bond have room for improvement.

A.6 Pump-probe simulations

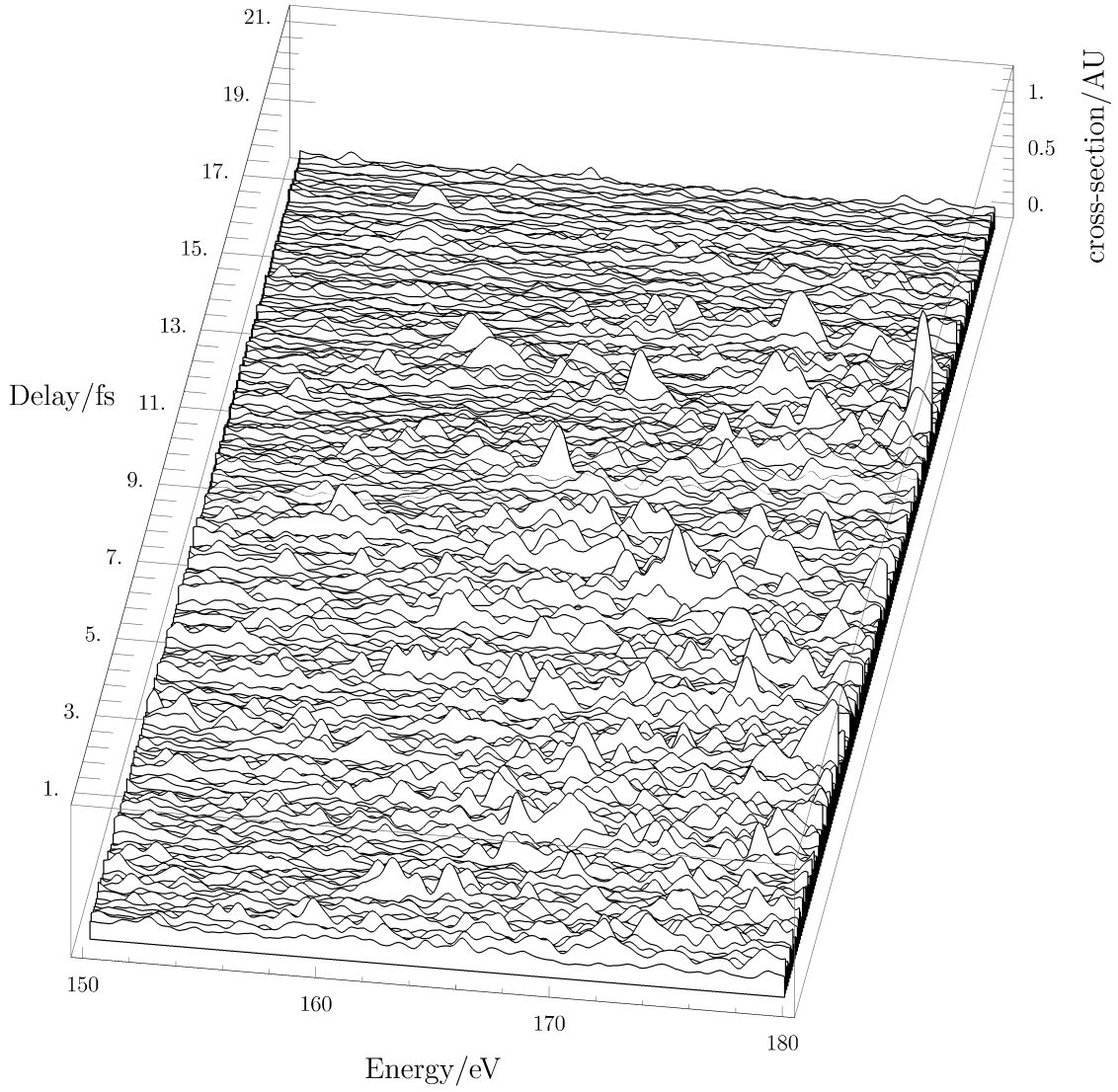


FIGURE A.4: Sulfur L-series spectrum for the P3HT monomer over various pump-probe delay times. The initial ion positions and velocities for each simulation are taken from a different molecular dynamics snapshot of a P3HT crystal simulation at 300 K.

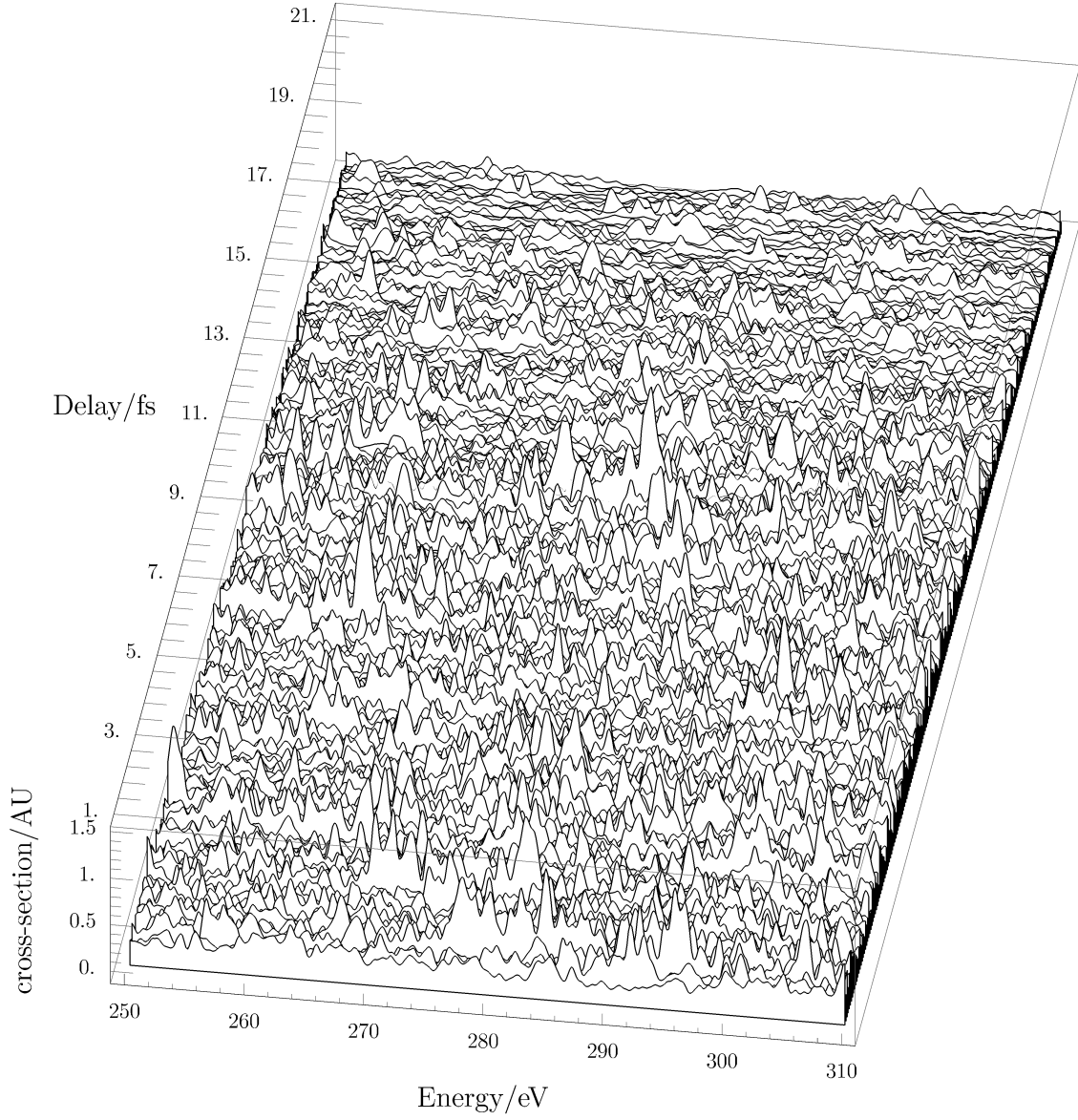


FIGURE A.5: Carbon K-series spectrum for the P3HT monomer over various pump-probe delay times. The initial ion positions and velocities for each simulation are taken from a different molecular dynamics snapshot of a P3HT crystal simulation at 300 K.

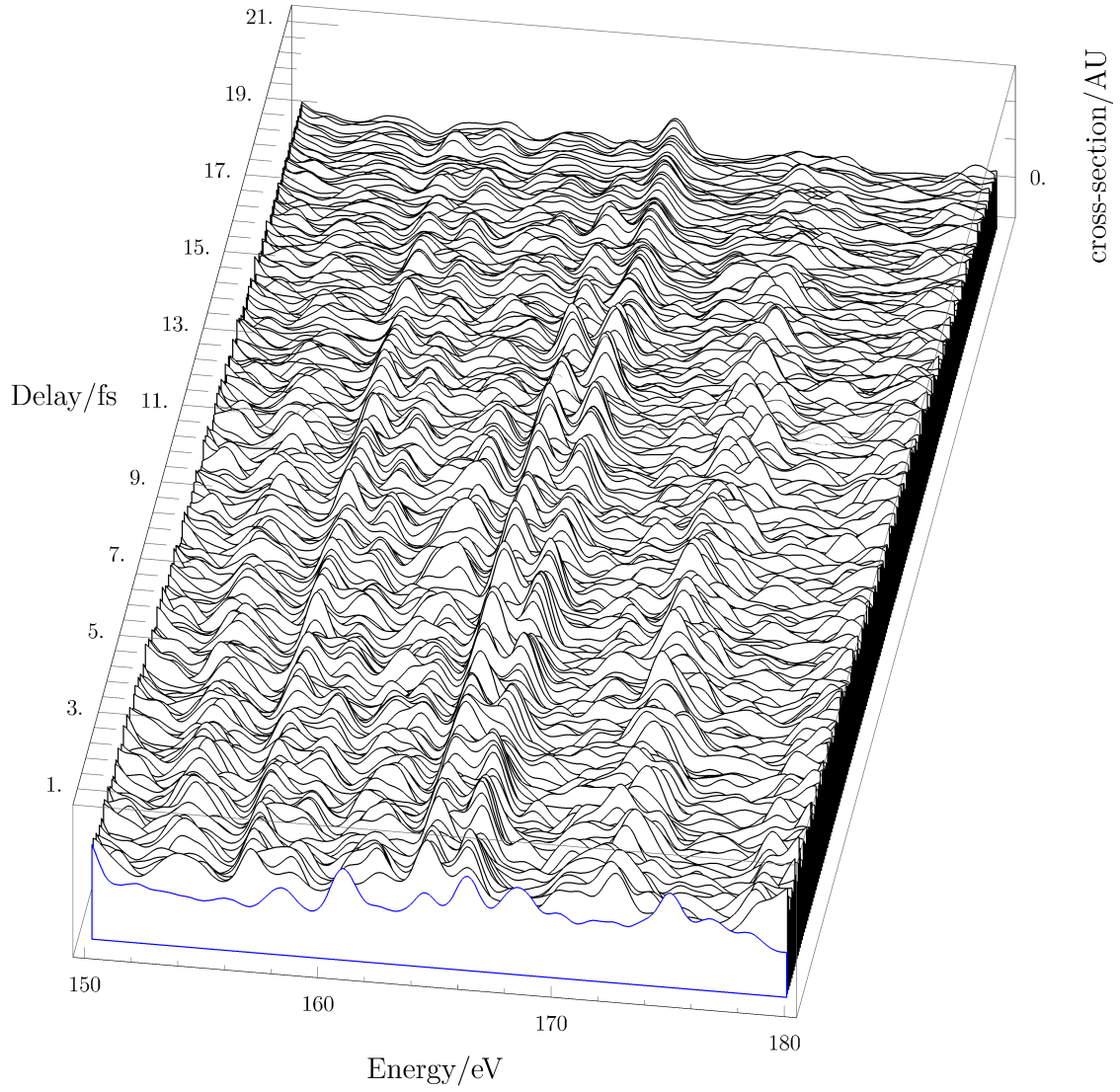


FIGURE A.6: Sulfur L-series spectrum for the P3HT dimer over various pump-probe delay times. The ions are held fixed. The un-pumped reference spectrum is shown as the first spectrum in blue colour.

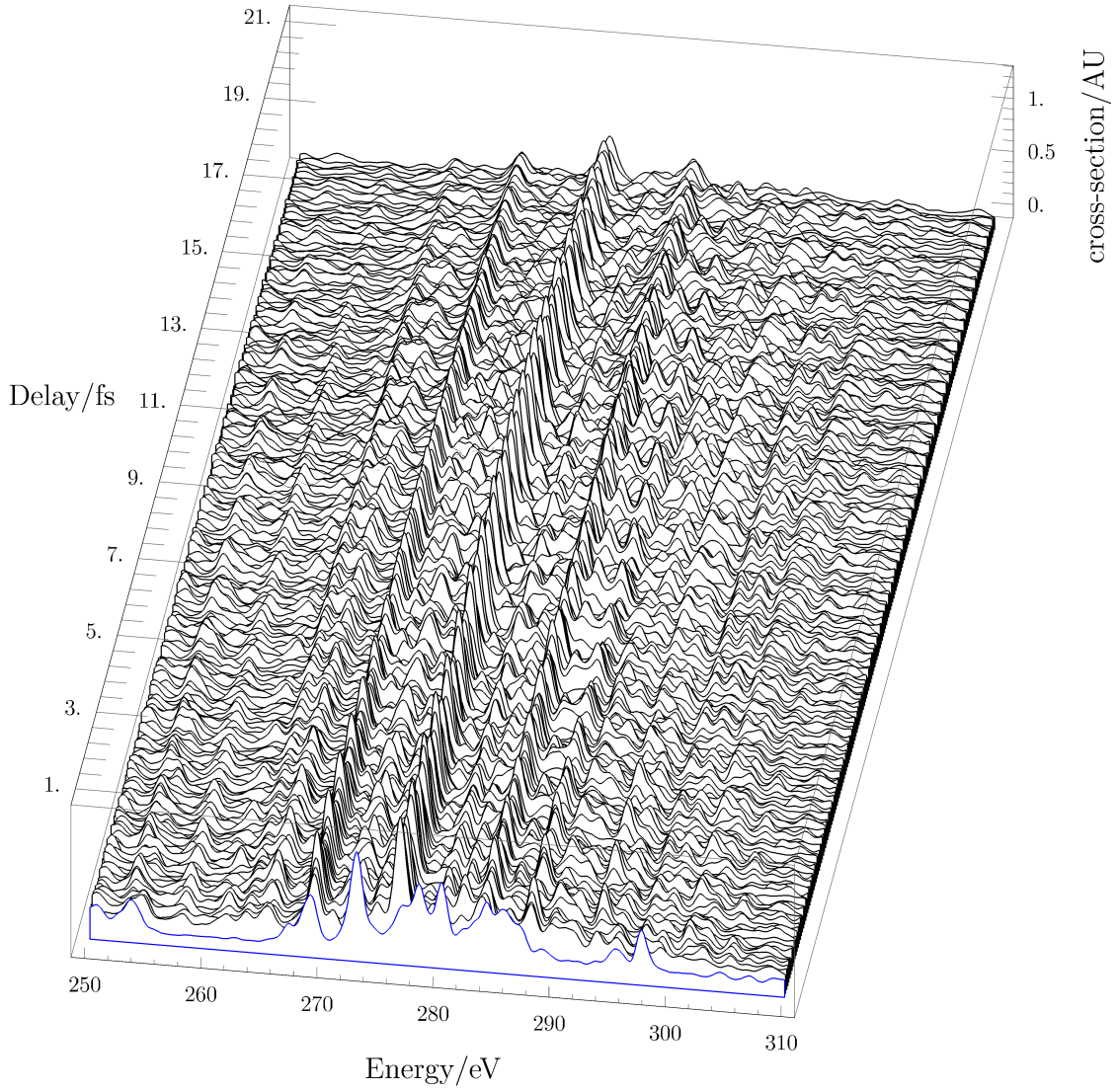


FIGURE A.7: Carbon K-series spectrum for the P3HT dimer over various pump-probe delay times. The ions are held fixed. The un-pumped reference spectrum is shown as the first spectrum in blue colour.

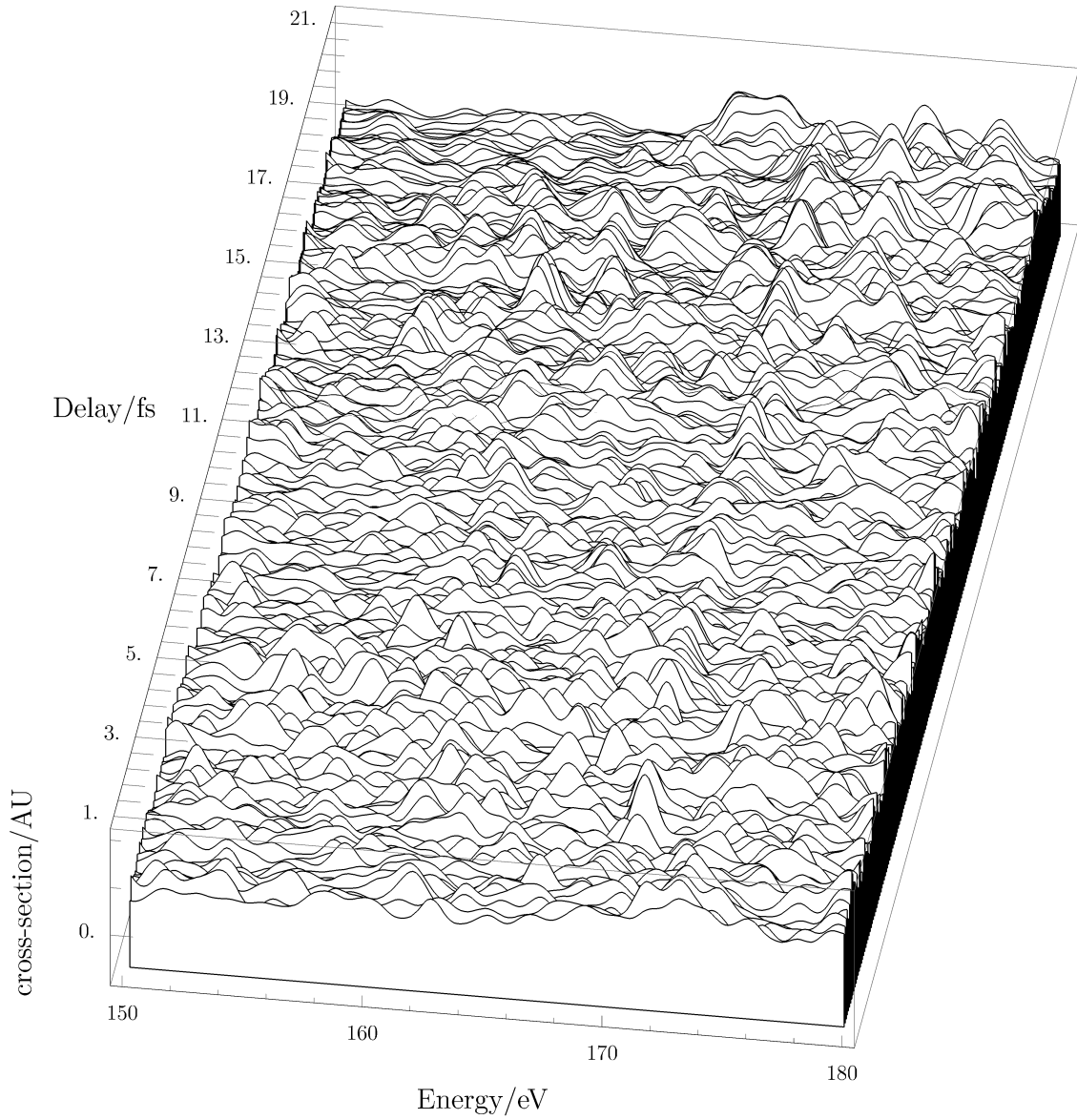


FIGURE A.8: Sulfur L-series spectrum for the P3HT dimer over various pump-probe delay times. The initial ion positions and velocities for each simulation are taken from the same molecular dynamics snapshot of a P3HT crystal simulation at 300 K.

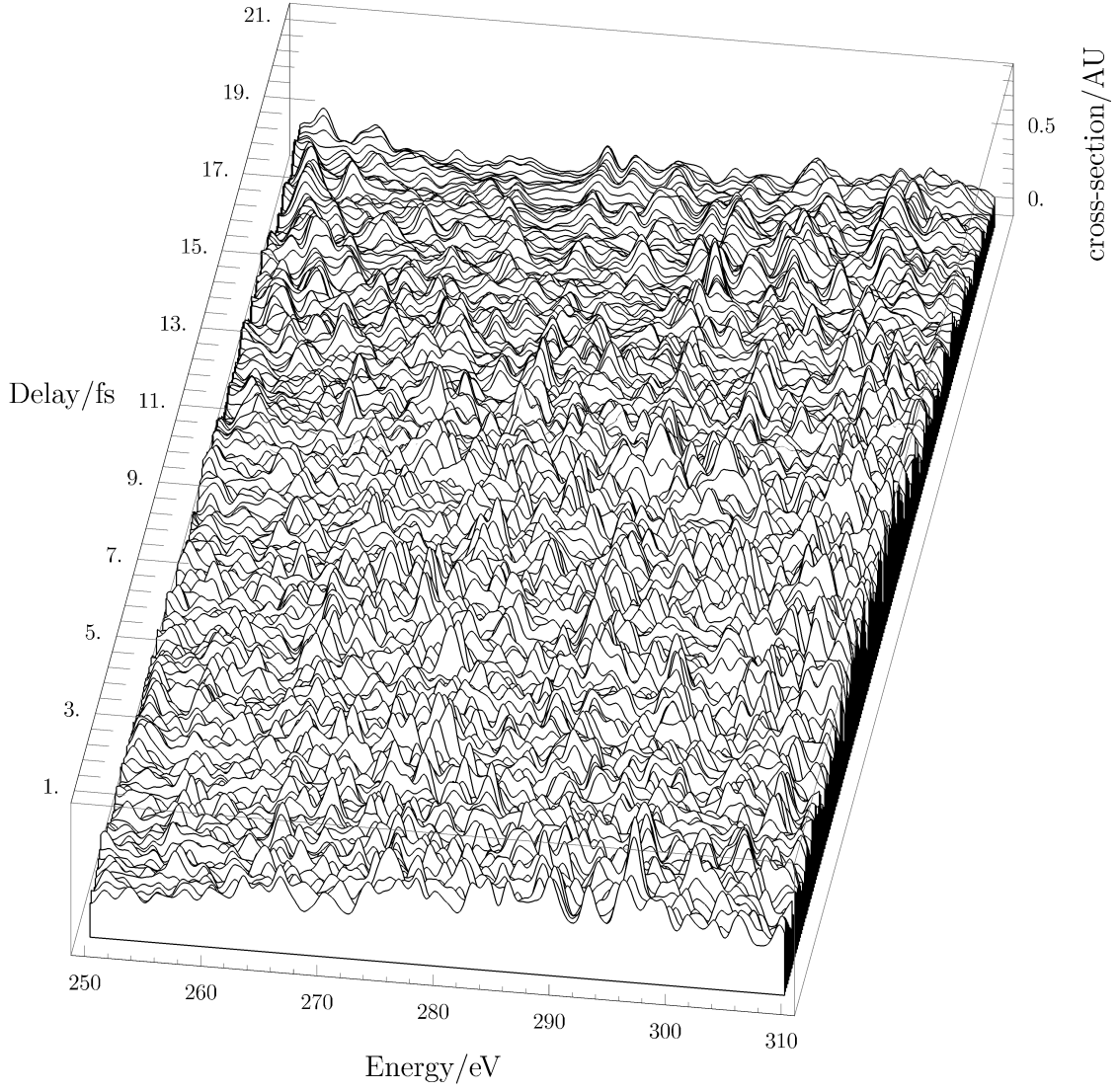


FIGURE A.9: Carbon K-series spectrum for the P3HT dimer over various pump-probe delay times. The initial ion positions and velocities for each simulation are taken from the same molecular dynamics snapshot of a P3HT crystal simulation at 300 K.

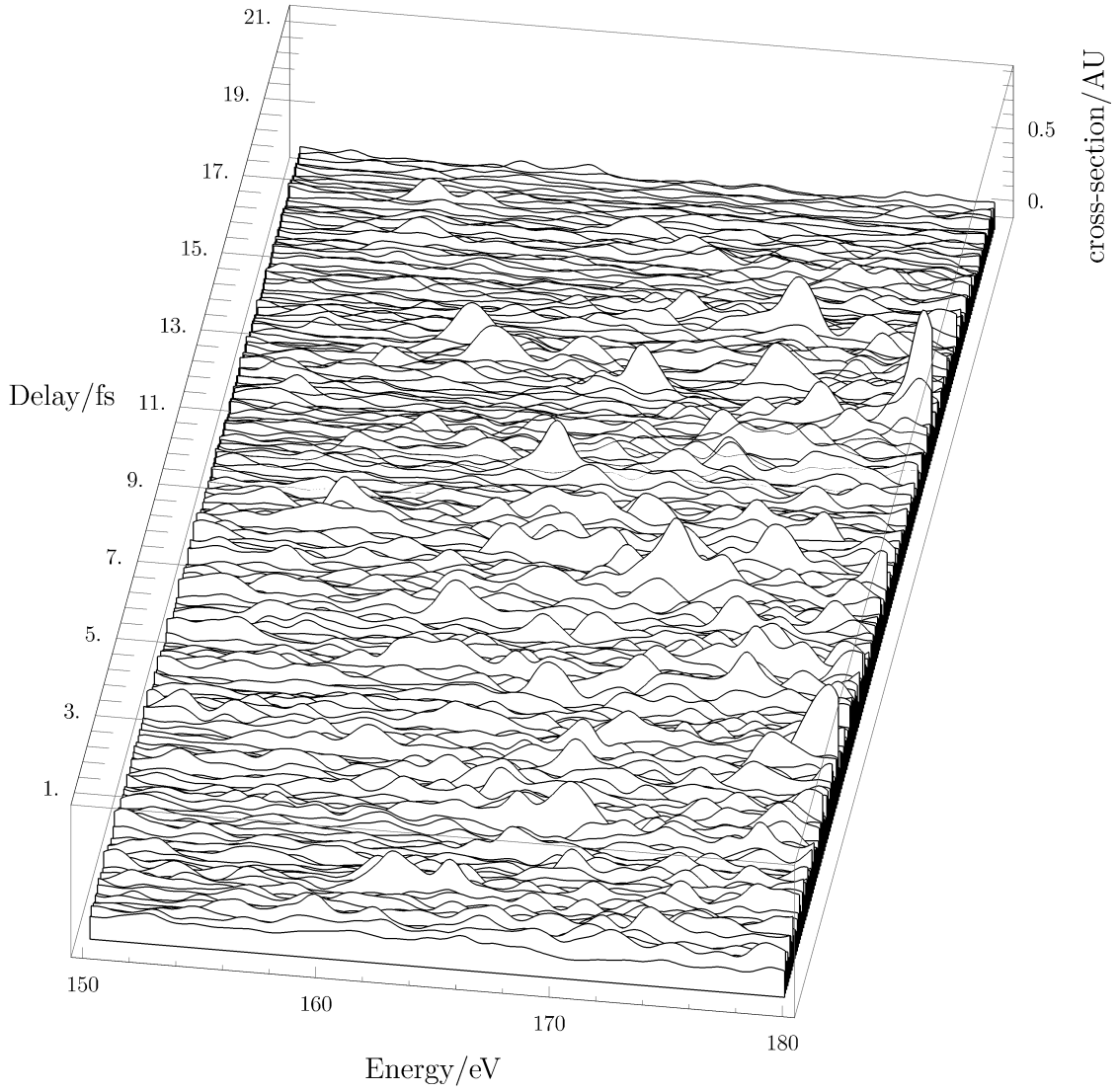


FIGURE A.10: Sulfur L-series spectrum for the P3HT dimer over various pump-probe delay times. The initial ion positions and velocities for each simulation are taken from a different molecular dynamics snapshot of a P3HT crystal simulation at 300 K.

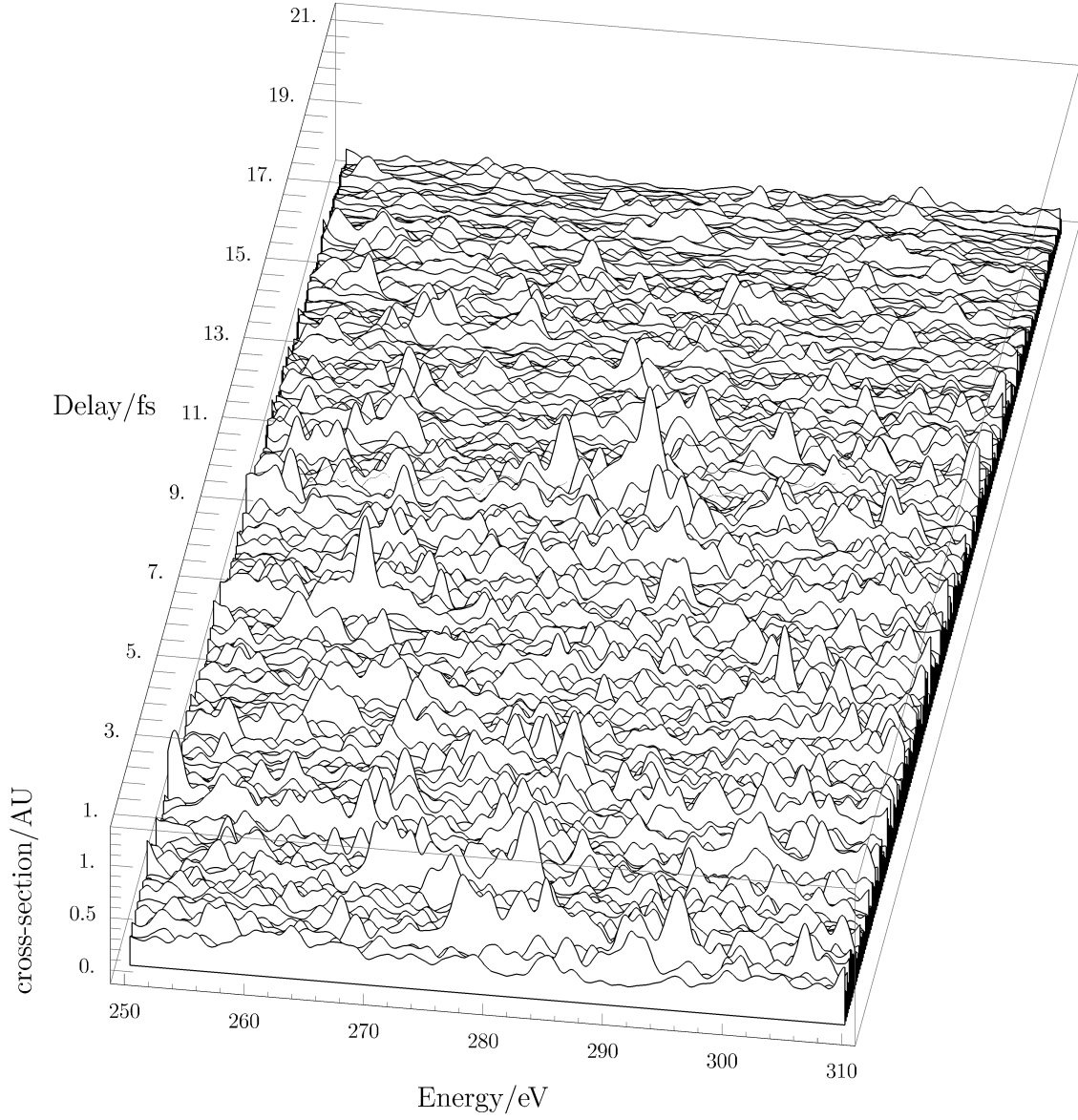


FIGURE A.11: Carbon K-series spectrum for the P3HT dimer over various pump-probe delay times. The initial ion positions and velocities for each simulation are taken from a different molecular dynamics snapshot of a P3HT crystal simulation at 300 K.

A.7 Scripts

We offer here four independent scripts, written and tested with MATHEMATICA version 10. All scripts are available for download on Zenodo under the DOI: 10.5281/zenodo.242307.

1. **klm.nb** constructs the real cubic harmonics from the spherical harmonics $Y_l^m(\theta, \phi)$ up to arbitrary order. The real cubic harmonics are further expressed in terms of the Cartesian coordinate system.
2. **ddskt.nb** defines the Slater-Koster matrix elements up to d - d orbitals, and computes the first and second order derivatives, as well as their limits for $R \rightarrow 0$.
3. **madelung.nb** computes the analytical expressions for the primitive Cartesian-Gaussian electrostatic integrals, or Madelung integrals, and their derivatives.
4. **electrostatic.nb** computes numerically the electrostatic integrals, or Madelung integrals.