# Calculation of tight binding parameters with density functional theory to describe transport phenomena

Bachelor Thesis

ALBERT-LUDWIGS-
UNIVERSITÄT FREIBURG

Fabian Glatzel

# Contents

# Chapter 1

# Introduction

## 1.1 Theoretical Background

### 1.1.1 Lattice

A solid has typically a periodicity in the placing of its atoms. This property is called *crystal structure*, which can be locally restricted due to occurring crystal defects. Exceptions are the amorphous solids, that behave like very viscous fluids and will not be treated here (see [1, 2]).
Bravais lattice
Points $\vec{R}$ with:

$$\vec{R} = \sum_{i=0}^{N_D} n_i \vec{a}_i \tag{1.1}$$

with linearly independent primitive vectors $\vec{a}_i$, $n_i \in \mathbb{Z}$ and the dimension $N_D$.

*primitive (unit) cell*
Fills complete space without any overlap under all transitions $\vec{R}$

*(conventional) unit cell*
Fills complete space without any overlap under a subset of transitions of $\vec{R}$. Sometimes preferred due to a different symmetry.

*Wigner-Seitz primitive cell*
Primitive cell containing all space closer to a certain lattice point than to all others.

*Reciprocal lattice*

Set of wave vectors $\vec{K}$, so that the plane wave has the periodicity of a given Bravais lattice:

$$\exp\Big(i\vec{K}\cdot\vec{r}\Big) = \exp\Big[i\vec{K}\cdot\Big(\vec{r}+\vec{R}\Big)\Big] \qquad \Leftrightarrow \qquad \vec{K}\cdot\vec{R} = \mathbb{Z}\cdot 2\pi \tag{1.2}$$

Therefore the wave vectors $\vec{K}$ form also a Bravais lattice called the *reciprocal lattice*. The primitive vectors $\vec{b}_i$ of a three dimensional reciprocal lattice can be derived as follows:

$$\vec{b}_i = 2\pi\frac{\vec{a}_{i+1}\times\vec{a}_{i+2}}{\vec{a}_1\cdot(\vec{a}_2\times\vec{a}_3)} \tag{1.3}$$

where the indices have to be understood modulo 3.

*First Brillouine Zone*
Wigner-Seitz cell of reciprocal lattice.

### 1.1.2 Bloch Theorem

According to Bloch's theorem a wave functions $\Psi(\vec{r})$ of a periodic potential, $V\big(\vec{r}+\vec{R}\big) = V\big(\vec{r}\big)$ for all $\vec{R}$ of a Bravais lattice, can be written in the form:

$$\Psi(\vec{r}) = \exp\Big(i\vec{k}\cdot\vec{r}\Big)\cdot u(\vec{r}) \tag{1.4}$$

where $\vec{k}$ is an arbitrary wave vector and $u(\vec{r})$ denotes a $\vec{R}$-periodic function.
Under the assumption, that the boundary condition at the surface should not change the physical properties of the bulk, one assumes the periodic *Born-von Karman boundary condition*[1]:

$$\Psi(\vec{r}+N_i\vec{a}_i) = \Psi(\vec{r}) \tag{1.5}$$

where $N_i$ denotes the number of unit cells in the direction $\vec{a}_i$ of the bulk. Hereby one obtains additional conditions for the wave vector $\vec{k}$, namely:

$$\vec{k} = \sum_{i=1}^{N_D}\frac{m_i}{N_i}\vec{b}_i \qquad\qquad m_i\in\mathbb{Z} \tag{1.6}$$

One considers that the number of states in the first Brillouine zone equals the number of sites $N = \prod_{i=1}^{N_D} N_i$ of the bulk.

[1] Alternatively one can choose the boundary condition for a vanishing wave function on the surface $\Psi\big(\vec{S}\big) = 0$. But the periodic boundary condition has the advantage, that it corresponds with propagating waves, which suits transport phenomena very well, whereas a vanishing boundary condition corresponds with standing waves.

### 1.1.3 Polyacetylene Hamiltonian

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$$\mathcal{H} = \underbrace{-2\sum_n t_{n+1,n}\left(c_{n+1}^\dagger c_n + c_n^\dagger c_{n+1}\right)}_{\text{electrone hopping}} + \underbrace{\frac{1}{2}\sum_n \kappa(u_{n+1}-u_n)^2}_{\sigma\text{ bonding energy}} + \underbrace{\frac{1}{2}\sum_n M\dot{u}_n^2}_{\text{kinetic energy}} \tag{1.7}$$

Born-Oppenheimer and $u_n = (-1)^n u$, $\alpha = {}^{\partial t}/_{\partial u}$, $\delta = 2\alpha u$:

$$\mathcal{H} = -2\sum_n [t_0 + (-1)^n\delta]\cdot\left(c_{n+1}^\dagger c_n + c_n^\dagger c_{n+1}\right) + 2N\kappa u^2 \tag{1.8}$$

$$= -2\sum_n^{N_d}\left[(t_0+\delta)\left(c_{2n+1}^\dagger c_{2n} + c_{2n}^\dagger c_{2n+1}\right) + (t_0-\delta)\left(c_{2n+2}^\dagger c_{2n+1} + c_{2n+1}^\dagger c_{2n+2}\right)\right] + 2N\kappa u^2 \tag{1.9}$$

$$\stackrel{?}{=} -2\sum_n^{N_d}\left[(t_0+\delta)\left(c_{2n+1}^\dagger c_{2n} + c_{2n}^\dagger c_{2n+1}\right) + (t_0-\delta)\left(c_{2n+1}^\dagger c_{2n} + c_{2n}^\dagger c_{2n+1}\right)\right] + 2N\kappa u^2 \tag{1.10}$$

Calculate creation and annihilation operator in k-space (symmetric normation factors):

$$c_{2n} = \frac{1}{\sqrt{N_d}}\sum_k \exp[ik(2n)a]\cdot c_k^{(e)} \tag{1.11}$$

$$c_{2n+1} = \frac{1}{\sqrt{N_d}}\sum_k \exp[ik(2n+1)a]\cdot c_k^{(o)} \tag{1.12}$$

$$c_k^{(e)} = \frac{1}{\sqrt{N_d}}\sum_n \exp[-ik(2n)a]\cdot c_{2n} \tag{1.13}$$

$$c_k^{(o)} = \frac{1}{\sqrt{N_d}}\sum_n \exp[-ik(2n+1)a]\cdot c_{2n+1} \tag{1.14}$$

Remember: operators $c_{2n(+1)}$ operate on double unit cell length $\rightarrow$ halve Brillouin zone $\left(-\frac{\pi}{2a}, \frac{\pi}{2a}\right]$
boundary condition: $\exp[2ik(n+N_d)a] = 1 \rightarrow N_d$ allowed kpts in Brillouin zone
Check for $c_{2n}$:

$$c_{2n_0}(c_k^{(e)}(c_{2n_i})) = c_{2n} \tag{1.15}$$

$$= \frac{1}{\sqrt{N_d}}\sum_k \exp[ik(2n_0)a]\cdot\frac{1}{\sqrt{N_d}}\sum_n \exp[-ik(2n)a]\cdot c_{2n} \tag{1.16}$$

$$= \frac{1}{N_d}\sum_{k,n}\exp[ika(2n_0-2n)]\cdot c_{2n} \tag{1.17}$$

$$= \frac{1}{N_d}\sum_n N_d\delta_{2n_0,2n}c_{2n} \tag{1.18}$$

$$= c_{2n_0} \tag{1.19}$$

Warm up calculation:

$$\begin{aligned}\sum_{n}^{N_d} c^\dagger_{2n+1}c_{2n} &= \sum_{n,k,k'} \exp[ika(2n)]\cdot\exp[-ik'a(2n+1)]\cdot\frac{c^{(e)}_k c^{\dagger(o)}_{k'}}{N_d}\\ &= \sum_{n,k,k'} \exp[ia(k-k')(2n)]\cdot\exp(-ik'a)\cdot\frac{c^{(e)}_k c^{\dagger(o)}_{k'}}{N_d}\\ &= \sum_{k,k'}\delta_{k,k'}\cdot\exp(-ik'a)\cdot c^{(e)}_k c^{\dagger(o)}_{k'}\\ &= \sum_{k'}\exp(-ik'a)\cdot c^{(e)}_{k'}c^{\dagger(o)}_{k'}\end{aligned}$$

Analogously:

$$\begin{aligned}\sum_{n}^{N_d} c^\dagger_{2n}c_{2n+1} &= \sum_{k'}\exp(ik'a)\cdot c^{\dagger(e)}_{k'}c^{(o)}_{k'}\\ \sum_{n}^{N_d} c^\dagger_{2n+2}c_{2n+1} &= \sum_{n}^{N_d} c^\dagger_{2n}c_{2n-1}\\ &= \sum_{k'}\exp(-ik'a)\cdot c^{\dagger(e)}_{k'}c^{(o)}_{k'}\\ \sum_{n}^{N_d} c^\dagger_{2n+1}c_{2n+2} &= \sum_{k'}\exp(ik'a)\cdot c^{(e)}_{k'}c^{\dagger(o)}_{k'}\end{aligned}$$

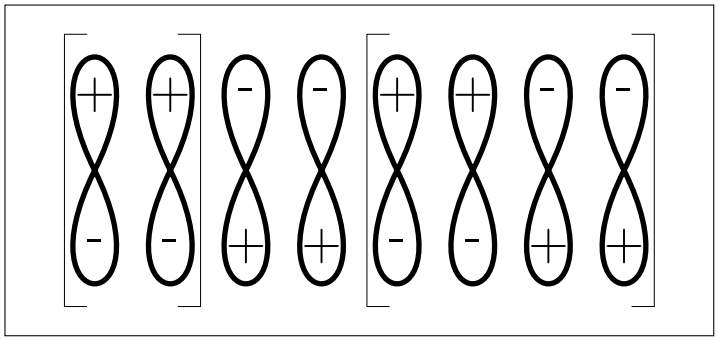
Thus one obtains:

$$\mathcal{H} = -2\sum_{n}^{N_d}\Big[(t_0+\delta)\Big(c^\dagger_{2n+1}c_{2n}+c^\dagger_{2n}c_{2n+1}\Big)+(t_0-\delta)\Big(c^\dagger_{2n+2}c_{2n+1}+c^\dagger_{2n+1}c_{2n+2}\Big)\Big]+2N\kappa u^2 \tag{1.20}$$

$$\begin{aligned}&= -2\sum_{k'}\Big[(t_0+\delta)\Big(\exp(-ik'a)\cdot c^{(e)}_{k'}c^{\dagger(o)}_{k'}+\exp(ik'a)\cdot c^{\dagger(e)}_{k'}c^{(o)}_{k'}\Big)+\\ &\qquad (t_0-\delta)\Big(\exp(-ik'a)\cdot c^{\dagger(e)}_{k'}c^{(o)}_{k'}+\exp(ik'a)\cdot c^{(e)}_{k'}c^{\dagger(o)}_{k'}\Big)\Big]+2N\kappa u^2\end{aligned} \tag{1.21}$$

$$\begin{aligned}&= -2\sum_{k'}\Big\{[2t_0\cos(k'a)+2i\delta\sin(k'a)]c^{\dagger(e)}_{k'}c^{(o)}_{k'}+\\ &\qquad [2t_0\cos(k'a)-2i\delta\sin(k'a)]c^{(e)}_{k'}c^{\dagger(o)}_{k'}\Big\}+2N\kappa u^2\end{aligned} \tag{1.22}$$

$$\begin{aligned}&\neq -2\sum_{k'}\Big\{[-2t_0\cos(k'a)+2i\delta\sin(k'a)]c^{\dagger(e)}_{k'}c^{(o)}_{k'}+\\ &\qquad [-2t_0\cos(k'a)-2i\delta\sin(k'a)]c^{(e)}_{k'}c^{\dagger(o)}_{k'}\Big\}+2N\kappa u^2\end{aligned} \tag{1.23}$$



## 1.2 Other Preparations

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# Bibliography

[1] Ashcroft, N.W. ; Mermin, N.D.: *Solid State Physics*. Holt, Rinehart and Winston, 1976 (HRW international editions). https://books.google.de/books?id=1C9HAQAAIAAJ. – ISBN 9780030839931

[2] Gerthsen, K. ; Vogel, H.: *Physik*. Springer Berlin Heidelberg, 2013 (DUV Sozialwissenschaft). https://books.google.de/books?id=SbjPBgAAQBAJ. – ISBN 9783642878398