

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

Bachelor Thesis



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# Contents

<b>1</b>	<b>Introduction</b>	<b>1</b>
1.1	Theoretical Background . . . . .	1
1.1.1	Lattice . . . . .	1
1.1.2	Bloch Theorem . . . . .	2
1.1.3	Polyacetylene Hamiltonian . . . . .	3
1.2	Other Preparations . . . . .	5



# 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:

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

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:

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

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:

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

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,  $V(\vec{r} + \vec{R}) = V(\vec{r})$  for all  $\vec{R}$  of a Bravais lattice, can be written in the form:

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

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*<sup>1</sup>:

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

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:

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

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.

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<sup>1</sup>Alternatively one can choose the boundary condition for a vanishing wave function on the surface  $\Psi(\vec{S}) = 0$ . 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

paper...

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

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

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

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

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

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

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

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

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

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

Remember: operators  $c_{2n(+1)}$  operate on double unit cell length  $\rightarrow$  halve Brillouin zone  $(-\frac{\pi}{2a}, \frac{\pi}{2a}]$

boundary condition:  $\exp[2ik(n + N_d)a] = 1 \rightarrow N_d$  allowed kpts in Brillouin zone

Check for  $c_{2n}$ :

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

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

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

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

$$= c_{2n_0} \quad (1.19)$$

Warm up calculation:

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

Analogously:

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

Thus one obtains:

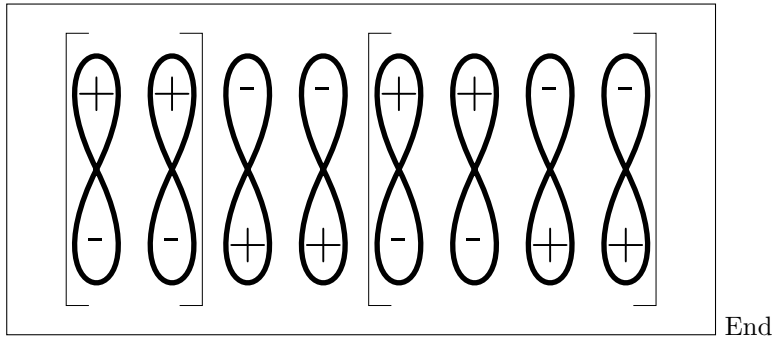
$$\mathcal{H} = -2 \sum_n^{N_d} \left[ (t_0 + \delta) \left( c_{2n+1}^\dagger c_{2n} + c_{2n}^\dagger c_{2n+1} \right) + (t_0 - \delta) \left( c_{2n+2}^\dagger c_{2n+1} + c_{2n+1}^\dagger c_{2n+2} \right) \right] + 2N\kappa u^2 \quad (1.20)$$

$$\begin{aligned}
&= -2 \sum_{k'} \left[ (t_0 + \delta) \left( \exp(-ik'a) \cdot c_{k'}^{(e)} c_{k'}^{\dagger(o)} + \exp(ik'a) \cdot c_{k'}^{\dagger(e)} c_{k'}^{(o)} \right) + \right. \\
&\quad \left. (t_0 - \delta) \left( \exp(-ik'a) \cdot c_{k'}^{\dagger(e)} c_{k'}^{(o)} + \exp(ik'a) \cdot c_{k'}^{(e)} c_{k'}^{\dagger(o)} \right) \right] + 2N\kappa u^2 \quad (1.21)
\end{aligned}$$

$$\begin{aligned}
&= -2 \sum_{k'} \left\{ [2t_0 \cos(k'a) + 2i\delta \sin(k'a)] c_{k'}^{\dagger(e)} c_{k'}^{(o)} + \right. \\
&\quad \left. [2t_0 \cos(k'a) - 2i\delta \sin(k'a)] c_{k'}^{(e)} c_{k'}^{\dagger(o)} \right\} + 2N\kappa u^2 \quad (1.22)
\end{aligned}$$

$$\begin{aligned}
&\neq -2 \sum_{k'} \left\{ [-2t_0 \cos(k'a) + 2i\delta \sin(k'a)] c_{k'}^{\dagger(e)} c_{k'}^{(o)} + \right. \\
&\quad \left. [-2t_0 \cos(k'a) - 2i\delta \sin(k'a)] c_{k'}^{(e)} c_{k'}^{\dagger(o)} \right\} + 2N\kappa u^2 \quad (1.23)
\end{aligned}$$





## 1.2 Other Preparations



# List of Figures



# List of Tables



# Bibliography

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