

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

Bachelor Thesis



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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*¹:

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

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.

¹Alternatively 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:

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

Analogously:

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

Thus one obtains:

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

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

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

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

Substituting $\epsilon_k := 2t_0 \cos(ka)$ and $\Delta_k := 2\delta \sin(ka)$ the following form of the hopping term can

be derived:

$$\mathcal{H}_{\text{hopp}} = [\epsilon_k + i\Delta_k]c_{k'}^{\dagger(e)}c_{k'}^{(o)} + [\epsilon_k - i\Delta_k]c_{k'}^{\dagger(o)}c_{k'}^{(e)} \quad (1.24)$$

with the eigenvalues $E_k = \pm\sqrt{\epsilon_k^2 + \Delta_k^2}$ and the eigenfunctions

$$\Psi_k^{(c)} = \frac{1}{\sqrt{2}} \left(c_k^{(e)} + \frac{\epsilon_k + i\Delta_k}{|E_k|} c_k^{(o)} \right) \quad (1.25)$$

$$\Psi_k^{(v)} = \frac{1}{\sqrt{2}} \left(c_k^{(e)} - \frac{\epsilon_k + i\Delta_k}{|E_k|} c_k^{(o)} \right) \quad (1.26)$$

corresponding to the valance (v) and conduction (c) band. Hereby the eigenfunctions have to be understood as operating on the completely occupied state, $|(e), (o)\rangle = |1, 1\rangle$. Due to this one can check the orthogonality:

$$\langle \Psi_k^{(v)} | \Psi_k^{(v)} \rangle = \frac{1}{2} \left(c_k^{\dagger(e)} - \frac{\epsilon_k - i\Delta_k}{|E_k|} c_k^{\dagger(o)} \right) \left(c_k^{(e)} - \frac{\epsilon_k + i\Delta_k}{|E_k|} c_k^{(o)} \right) \quad (1.27)$$

$$= 2 \left[c_k^{\dagger(e)} c_k^{(e)} + \frac{(\epsilon_k - i\Delta_k)(\epsilon_k + i\Delta_k)}{|E_k|^2} c_k^{\dagger(o)} c_k^{(o)} \right. \\ \left. - \frac{\epsilon_k - i\Delta_k}{|E_k|} c_k^{\dagger(o)} c_k^{(e)} - \frac{\epsilon_k + i\Delta_k}{|E_k|} c_k^{\dagger(e)} c_k^{(o)} \right] \quad (1.28)$$

$$= \frac{1}{2} \left[c_k^{\dagger(e)} c_k^{(e)} + c_k^{\dagger(o)} c_k^{(o)} \right] \quad (1.29)$$

$$= 1 \quad (1.30)$$

Here the number operator n has the inconvenient definition $n = c^\dagger c$.

Check also the correspondence to the correct eigenvalues:

$$\langle \Psi_k^{(v)} | \mathcal{H}_{\text{hopp}} | \Psi_k^{(v)} \rangle = \left[\frac{1}{\sqrt{2}} \left(c_k^{\dagger(e)} - \frac{\epsilon_k - i\Delta_k}{|E_k|} c_k^{\dagger(o)} \right) \right] \cdot \\ \left[[\epsilon_k + i\Delta_k] c_{k'}^{\dagger(e)} c_{k'}^{(o)} + [\epsilon_k - i\Delta_k] c_{k'}^{\dagger(o)} c_{k'}^{(e)} \right] \cdot \\ \left[\frac{1}{\sqrt{2}} \left(c_k^{(e)} - \frac{\epsilon_k + i\Delta_k}{|E_k|} c_k^{(o)} \right) \right] \quad (1.31)$$

$$= \frac{1}{2} \left[-\frac{(\epsilon_k - i\Delta_k)(\epsilon_k + i\Delta_k)}{|E_k|} - \frac{(\epsilon_k - i\Delta_k)(\epsilon_k + i\Delta_k)}{|E_k|} \right] \quad (1.32)$$

$$= -|E_k| \quad (1.33)$$

$$\langle \Psi_k^{(c)} | \mathcal{H}_{\text{hopp}} | \Psi_k^{(c)} \rangle = |E_k| \quad (1.34)$$

Hence it is shown explicitly, that the energies of the valence band are decreased by $-|E_k|$ and the energies of the conduction band are increased by $|E_k|$. Using this the ground state energy

can be derived as follows (completely occupied valence, empty conduction band):

$$E_0(u) = -2 \sum_k |E_k| + 2N\kappa u^2 \quad (1.35)$$

$$= -2 \sum_k \sqrt{\epsilon_k^2 + \Delta_k^2} + 2N\kappa u^2 \quad (1.36)$$

$$= -2 \sum_k \sqrt{[2t_0 \cos(ka)]^2 + [2\delta \sin(ka)]^2} + 2N\kappa u^2 \quad (1.37)$$

$$(1.38)$$

In the limit of $N \rightarrow \infty$ the sum becomes an integral:

$$E_0(u) = \frac{-N}{\pi} \int_{-\pi/2a}^{\pi/2a} dk \sqrt{[2t_0 \cos(ka)]^2 + [2\delta \sin(ka)]^2} + 2N\kappa u^2 \quad (1.39)$$

$$= \frac{-4Nt_0}{\pi} \int_0^{\pi/2} d\theta \sqrt{1 - \left(1 - \frac{\delta}{t_0}\right) \sin^2(\theta)} + 2N\kappa u^2 \quad (1.40)$$

To calculate energy in manually charged state (cdft), use the states:

$$\Psi_k^{(v)} = \sqrt{\frac{1}{2} - q} c_k^{(e)} - \sqrt{\frac{1}{2} + q} \frac{\epsilon_k + i\Delta_k}{|E_k|} c_k^{(o)} \quad (1.41)$$

One obtains the energies:

$$\begin{aligned} \langle \Psi_k^{(v)} | \mathcal{H}_{\text{hopp}} | \Psi_k^{(v)} \rangle &= \left[\sqrt{\frac{1}{2} - q} c_k^{\dagger(e)} - \sqrt{\frac{1}{2} + q} \frac{\epsilon_k - i\Delta_k}{|E_k|} c_k^{\dagger(o)} \right] \cdot \\ &\quad \left[[\epsilon_k + i\Delta_k] c_{k'}^{\dagger(e)} c_{k'}^{(o)} + [\epsilon_k - i\Delta_k] c_{k'}^{\dagger(o)} c_{k'}^{(e)} \right] \cdot \\ &\quad \left[\sqrt{\frac{1}{2} - q} c_k^{(e)} - \sqrt{\frac{1}{2} + q} \frac{\epsilon_k + i\Delta_k}{|E_k|} c_k^{(o)} \right] \end{aligned} \quad (1.42)$$

$$\begin{aligned} &= -\sqrt{\frac{1}{2} - q} c_k^{\dagger(e)} [\epsilon_k - i\Delta_k] c_{k'}^{\dagger(o)} c_{k'}^{(e)} \sqrt{\frac{1}{2} + q} \frac{\epsilon_k + i\Delta_k}{|E_k|} c_k^{(o)} \\ &\quad - \sqrt{\frac{1}{2} + q} \frac{\epsilon_k - i\Delta_k}{|E_k|} c_k^{\dagger(o)} [\epsilon_k + i\Delta_k] c_{k'}^{\dagger(e)} c_{k'}^{(o)} \sqrt{\frac{1}{2} - q} c_k^{(e)} \end{aligned} \quad (1.43)$$

$$\begin{aligned} &= -\sqrt{\frac{1}{2} + q} \sqrt{\frac{1}{2} - q} \left[\frac{(\epsilon_k - i\Delta_k)(\epsilon_k + i\Delta_k)}{|E_k|} + \frac{(\epsilon_k - i\Delta_k)(\epsilon_k + i\Delta_k)}{|E_k|} \right] \end{aligned} \quad (1.44)$$

$$= -\sqrt{\frac{1}{4} - q^2} |E_k| \quad (1.45)$$

1.2 Other Preparations

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Bibliography

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