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

Bachelor Thesis

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# 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.

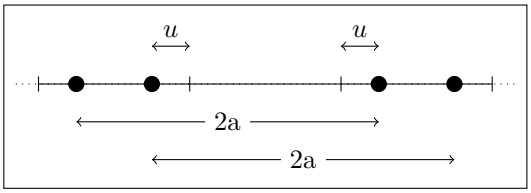



Figure 1.1: Schema: perfectly dimerized molecule

### 1.1.3 Polyacetylene Hamiltonian

Hamiltonian for trans-polyacetylene:

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

Born-Oppenheimer and $u_n = (-1)^n u$, $\alpha = {}^{\partial t}/_{\partial u}$, $\delta = 2\alpha u$ (see fig. 1.1):

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

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

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

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:

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

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:

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

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

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

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

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

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

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

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

$$\Psi^{(v)}_k = \frac{1}{\sqrt{2}}\left(c^{(e)}_k - \frac{\epsilon_k + i\Delta_k}{|E_k|}c^{(o)}_k\right) \tag{1.26}$$

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:

$$\left\langle \Psi^{(v)}_k \middle| \Psi^{(v)}_k \right\rangle = \frac{1}{2}\left(c^{\dagger(e)}_k - \frac{\epsilon_k - i\Delta_k}{|E_k|}c^{\dagger(o)}_k\right)\left(c^{(e)}_k - \frac{\epsilon_k + i\Delta_k}{|E_k|}c^{(o)}_k\right) \tag{1.27}$$

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

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

$$= 1 \tag{1.30}$$

Here the number operator $n$ has the inconvenient definition $n = c^\dagger c$.
Check also the correspondence to the correct eigenvalues:

$$\begin{aligned}
\left\langle \Psi_k^{(v)} \middle| \mathcal{H}_{\text{hopp}} \middle| \Psi_k^{(v)} \right\rangle &= \left[ \frac{1}{\sqrt{2}} \left( c_k^{\dagger(e)} - \frac{\epsilon_k - i\Delta_k}{|E_k|} c_k^{\dagger(o)} \right) \right] \cdot \\
&\quad \left[ [\epsilon_k + i\Delta_k] c_{k'}^{\dagger(e)} c_{k'}^{(o)} + [\epsilon_k - i\Delta_k] c_{k'}^{\dagger(o)} c_{k'}^{(e)} \right] \cdot \\
&\quad \left[ \frac{1}{\sqrt{2}} \left( c_k^{(e)} - \frac{\epsilon_k + i\Delta_k}{|E_k|} c_k^{(o)} \right) \right] && (1.31) \\
&= \frac{1}{2} \left[ - \frac{(\epsilon_k - i\Delta_k)(\epsilon_k + i\Delta_k)}{|E_k|} - \frac{(\epsilon_k - i\Delta_k)(\epsilon_k + i\Delta_k)}{|E_k|} \right] && (1.32) \\
&= -|E_k| && (1.33) \\
\left\langle \Psi_k^{(c)} \middle| \mathcal{H}_{\text{hopp}} \middle| \Psi_k^{(c)} \right\rangle &= |E_k| && (1.34)
\end{aligned}$$

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):

$$\begin{aligned}
E_0(u) &= -2 \sum_k |E_k| + 2N\kappa u^2 && (1.35) \\
&= -2 \sum_k \sqrt{\epsilon_k^2 + \Delta_k^2} + 2N\kappa u^2 && (1.36) \\
&= -2 \sum_k \sqrt{[2t_0 \cos(ka)]^2 + [2\delta \sin(ka)]^2} + 2N\kappa u^2 && (1.37) \\
& && (1.38)
\end{aligned}$$

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

$$\begin{aligned}
E_0(u) &= \frac{-N}{\pi} \int_{-\pi/2a}^{\pi/2a} \mathrm{d}k \, \sqrt{[2t_0 \cos(ka)]^2 + [2\delta \sin(ka)]^2} + 2N\kappa u^2 && (1.39) \\
&= \frac{-4Nt_0}{\pi} \underbrace{\int_0^{\pi/2} \mathrm{d}\theta \, \sqrt{1 - \left(1 - \frac{\delta}{t_0}\right) \sin^2(\theta)}}_{=: I(\delta/t_0)} + 2N\kappa u^2 && (1.40)
\end{aligned}$$

For small $\delta/t_0$ the integral can be approximated as follows:

$$I\left(\frac{\delta}{t_0}\right) \approx 1 + \frac{1}{2} \left[ \ln\left( \left| \frac{4t_0}{\delta} \right| \right) - \frac{1}{2} \right] \frac{\delta^2}{t_0^2} \qquad (1.41)$$

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

$$\Psi_k^{(v)}(q) = \sqrt{\frac{1}{2} - \frac{q}{2}}\, c_k^{(e)} - \sqrt{\frac{1}{2} + \frac{q}{2}} \frac{\epsilon_k + i\Delta_k}{|E_k|} c_k^{(o)} \tag{1.42}$$

To test for the correct properties one calculates $\left|\left\langle c^{(*)} | \Psi_k^{(v)}(q) \right\rangle\right|^2$, for example:

$$\left|\left\langle c^{(e)} | \Psi_k^{(v)}(q) \right\rangle\right|^2 = \left| c^{\dagger(e)} \left( \sqrt{\frac{1}{2} - \frac{q}{2}}\, c_k^{(e)} - \sqrt{\frac{1}{2} + \frac{q}{2}} \frac{\epsilon_k + i\Delta_k}{|E_k|} c_k^{(o)} \right) \right|^2 \tag{1.43}$$

$$= \frac{1-q}{2} \tag{1.44}$$

Because of the two different spin orientations of the electron an additional factor 2 has to be taken into account to get the correct number of valence electrons at the even/odd positions. The number of valence electrons is given by $1 \pm q$. The energies for this states are given by:

$$\begin{aligned} \left\langle \Psi_k^{(v)}(q) \middle| \mathcal{H}_{\text{hopp}} \middle| \Psi_k^{(v)}(q) \right\rangle = & \left[ \sqrt{\frac{1-q}{2}}\, c_k^{\dagger(e)} - \sqrt{\frac{1+q}{2}} \frac{\epsilon_k - i\Delta_k}{|E_k|} c_k^{\dagger(o)} \right] \cdot \\ & \left[ [\epsilon_k + i\Delta_k] c_{k'}^{\dagger(e)} c_{k'}^{(o)} + [\epsilon_k - i\Delta_k] c_{k'}^{\dagger(o)} c_{k'}^{(e)} \right] \cdot \\ & \left[ \sqrt{\frac{1-q}{2}}\, c_k^{(e)} - \sqrt{\frac{1+q}{2}} \frac{\epsilon_k + i\Delta_k}{|E_k|} c_k^{(o)} \right] \end{aligned} \tag{1.45}$$

$$\begin{aligned} = & -\sqrt{\frac{1-q}{2}}\, c_k^{\dagger(e)} [\epsilon_k - i\Delta_k] c_{k'}^{\dagger(o)} c_{k'}^{(e)} \sqrt{\frac{1+q}{2}} \frac{\epsilon_k + i\Delta_k}{|E_k|} c_k^{(o)} \\ & - \sqrt{\frac{1+q}{2}} \frac{\epsilon_k - i\Delta_k}{|E_k|} c_k^{\dagger(o)} [\epsilon_k + i\Delta_k] c_{k'}^{\dagger(e)} c_{k'}^{(o)} \sqrt{\frac{1-q}{2}}\, c_k^{(e)} \end{aligned} \tag{1.46}$$

$$= -\sqrt{\frac{1+q}{2}} \sqrt{\frac{1-q}{2}} \left[ \frac{(\epsilon_k - i\Delta_k)(\epsilon_k + i\Delta_k)}{|E_k|} + \frac{(\epsilon_k - i\Delta_k)(\epsilon_k + i\Delta_k)}{|E_k|} \right] \tag{1.47}$$

$$= -\sqrt{1-q^2}\, |E_k| \tag{1.48}$$

Therefore the expected ground state energy as function of the transfered charge for a negligible small phonon coupling constant $\delta$ has the form:

$$E_0(q,u) = -\frac{4Nt_0}{\pi} \sqrt{1-q^2} + 2N\kappa u^2 \tag{1.49}$$

Fit this function with simulation results for small q, see fig. 1.2. Optimized fit coefficient:

$$t_0 = 9,4\,\text{eV} \qquad \text{from fit} \tag{1.50}$$

$$t_0 = 2.5\,\text{eV} \qquad \text{Glen paper} \tag{1.51}$$

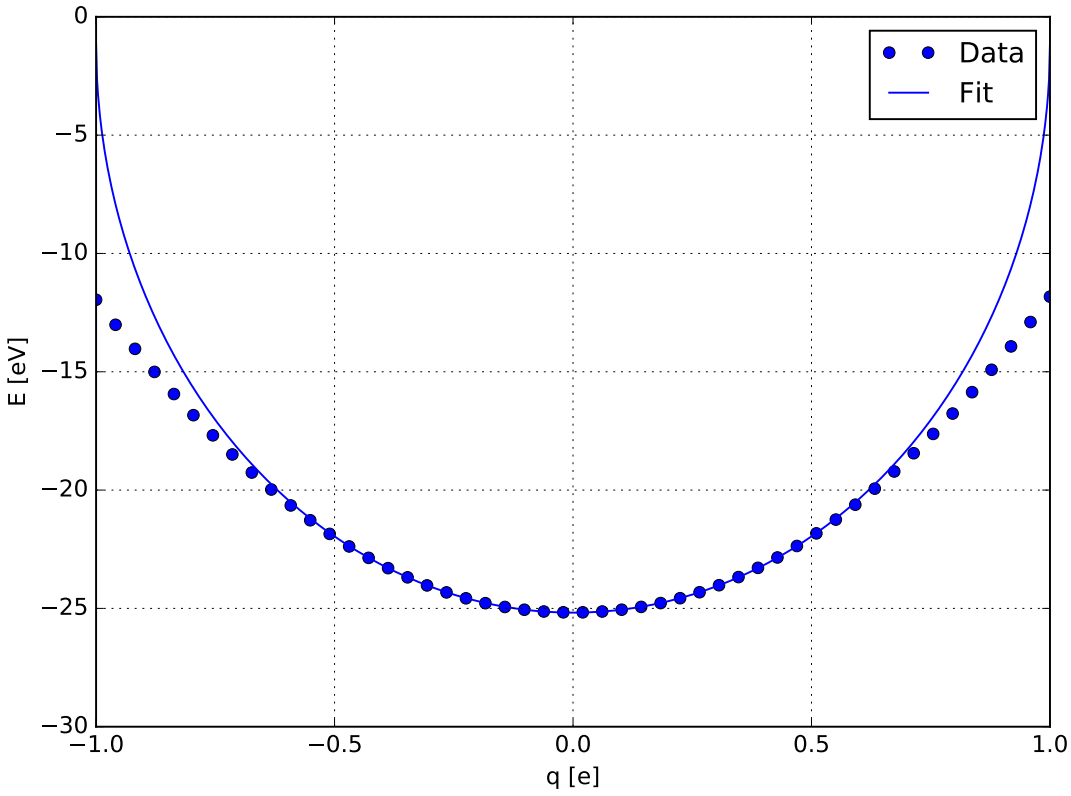



Figure 1.2: Unit cell energy as function of the manually shiftet charge for many k-points

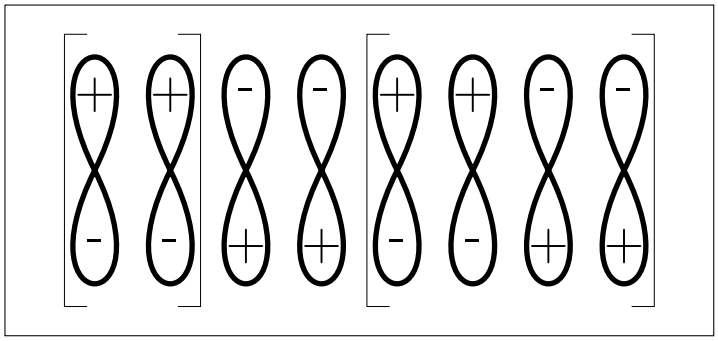
Probably this assumption is wrong:

$$\Psi_k^{(v)}(q) = \sqrt{\frac{1-q}{2}}\, c_k^{(e)} - \sqrt{\frac{1+q}{2}}\, \frac{\epsilon_k + i\Delta_k}{|E_k|} c_k^{(o)} \tag{1.52}$$

and should rather be formulated in a more general way:

$$\Psi_k^{(v)}(q) = \sqrt{\frac{1-q_k}{2}}\, c_k^{(e)} - \sqrt{\frac{1+q_k}{2}}\, \frac{\epsilon_k + i\Delta_k}{|E_k|} c_k^{(o)} \tag{1.53}$$

$$\Rightarrow \left\langle \Psi_k^{(v)}(q) \middle| \mathcal{H}_{\text{hopp}} \middle| \Psi_k^{(v)}(q) \right\rangle = -\sqrt{1-q_k^2}\,|E_k| \tag{1.54}$$



## 1.2 Other Preparations

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# Bibliography

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