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

Bachelor Thesis

ALBERT-LUDWIGS-UNIVERSITÄT FREIBURG

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Contents

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:

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

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

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

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.

1.1.3 Finite difference method

The finite difference method is used to solve the Schrödinger equation numerically, whereat the wave function will be evaluated only on discrete positions. For this purpose the Schrödinger

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

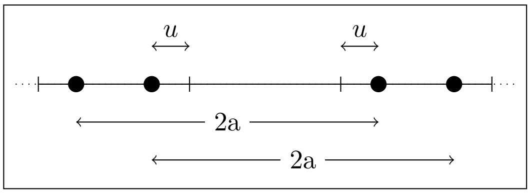


Figure 1.1: Schema: perfectly dimerized molecule

equation has to be transformed into a finite difference equation.

$$\mathcal{H}\Psi = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\Psi = E\Psi \tag{1.7}$$

1.1.4 Polyacetylene Hamiltonian

Hamiltonian for trans-polyacetylene:

$$\mathcal{H} = \underbrace{-2\sum_n t_{n+1,n}\left(c_{n+1}^\dagger c_n + c_n^\dagger c_{n+1}\right)}_{\text{electrone hopping}} + \underbrace{\frac{1}{2}\sum_n \kappa(u_{n+1} - u_n)^2}_{\sigma\text{ bonding energy}} + \underbrace{\frac{1}{2}\sum_n M\dot{u}_n^2}_{\text{kinetic energy}} \tag{1.8}$$

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

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

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

$$\neq -2\sum_n^{N_d}\left[(t_0+\delta)\left(c_{2n+1}^\dagger c_{2n} + c_{2n}^\dagger c_{2n+1}\right) + (t_0-\delta)\left(c_{2n+1}^\dagger c_{2n} + c_{2n}^\dagger c_{2n+1}\right)\right] + 2N\kappa u^2 \tag{1.11}$$

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

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

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

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

$$c_k^{(o)} = \frac{1}{\sqrt{N_d}}\sum_n \exp[-ik(2n+1)a] \cdot c_{2n+1} \tag{1.15}$$

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}:

$$\begin{aligned}
c_{2n_0}(c_k^{(e)}(c_{2n_i})) &= c_{2n} && (1.16)\\
&= \frac{1}{\sqrt{N_d}} \sum_k \exp[ik(2n_0)a] \cdot \frac{1}{\sqrt{N_d}} \sum_n \exp[-ik(2n)a] \cdot c_{2n} && (1.17)\\
&= \frac{1}{N_d} \sum_{k,n} \exp[ika(2n_0 - 2n)] \cdot c_{2n} && (1.18)\\
&= \frac{1}{N_d} \sum_n N_d \delta_{2n_0,2n} c_{2n} && (1.19)\\
&= c_{2n_0} && (1.20)
\end{aligned}$$

Warm up calculation:

$$\begin{aligned}
\sum_n^{N_d} c_{2n+1}^\dagger c_{2n} &= \sum_{n,k,k'} \exp[ika(2n)] \cdot \exp[-ik'a(2n+1)] \cdot \frac{c_{k'}^{\dagger(o)} c_k^{(e)}}{N_d} && (1.21)\\
&= \sum_{n,k,k'} \exp[ia(k-k')(2n)] \cdot \exp(-ik'a) \cdot \frac{c_{k'}^{\dagger(o)} c_k^{(e)}}{N_d} && (1.22)\\
&= \sum_{k,k'} \delta_{k,k'} \cdot \exp(-ik'a) \cdot c_{k'}^{\dagger(o)} c_k^{(e)} && (1.23)\\
&= \sum_{k'} \exp(-ik'a) \cdot c_{k'}^{\dagger(o)} c_{k'}^{(e)} && (1.24)
\end{aligned}$$

Analogously:

$$\begin{aligned}
\sum_n^{N_d} c_{2n}^\dagger c_{2n+1} &= \sum_{k'} \exp(ik'a) \cdot c_{k'}^{\dagger(e)} c_{k'}^{(o)} && (1.25)\\
\sum_n^{N_d} c_{2n}^\dagger c_{2n-1} &= \sum_{k'} \exp(-ik'a) \cdot c_{k'}^{\dagger(e)} c_{k'}^{(o)} && (1.26)\\
\sum_n^{N_d} c_{2n-1}^\dagger c_{2n} &= \sum_{k'} \exp(ik'a) \cdot c_{k'}^{\dagger(o)} c_{k'}^{(e)} && (1.27)
\end{aligned}$$

Thus one obtains:

$$
\begin{aligned}
\mathcal{H} = -2\sum_{n}^{N_d}\Big[(t_0+\delta)\Big(c^\dagger_{2n+1}c_{2n} + c^\dagger_{2n}c_{2n+1}\Big) + (t_0-\delta)\Big(c^\dagger_{2n+2}c_{2n+1} + c^\dagger_{2n+1}c_{2n+2}\Big)\Big] + 2N\kappa u^2 \quad (1.28)\\
= -2\sum_{k'}\Big[(t_0+\delta)\Big(\exp(-ik'a)\cdot c^{\dagger(o)}_{k'}c^{(e)}_{k'} + \exp(ik'a)\cdot c^{\dagger(e)}_{k'}c^{(o)}_{k'}\Big) + \\
(t_0-\delta)\Big(\exp(-ik'a)\cdot c^{\dagger(e)}_{k'}c^{(o)}_{k'} + \exp(ik'a)\cdot c^{\dagger(o)}_{k'}c^{(e)}_{k'}\Big)\Big] + 2N\kappa u^2 \quad (1.29)\\
= -2\sum_{k'}\Big\{[2t_0\cos(k'a) + 2i\delta\sin(k'a)]c^{\dagger(e)}_{k'}c^{(o)}_{k'} + \\
[2t_0\cos(k'a) - 2i\delta\sin(k'a)]c^{\dagger(o)}_{k'}c^{(e)}_{k'}\Big\} + 2N\kappa u^2 \quad (1.30)\\
\neq -2\sum_{k'}\Big\{[-2t_0\cos(k'a) + 2i\delta\sin(k'a)]c^{\dagger(e)}_{k'}c^{(o)}_{k'} + \\
[-2t_0\cos(k'a) - 2i\delta\sin(k'a)]c^{\dagger(o)}_{k'}c^{(e)}_{k'}\Big\} + 2N\kappa u^2 \quad (1.31)
\end{aligned}
$$

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

$$
\mathcal{H}_{\text{hopp},k} = [\epsilon_k + i\Delta_k]c^{\dagger(e)}_k c^{(o)}_k + [\epsilon_k - i\Delta_k]c^{\dagger(o)}_k c^{(e)}_k \quad (1.32)
$$

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

$$
\begin{aligned}
\Psi^{(c)}_k &= \frac{1}{\sqrt{2}}\left(c^{\dagger(e)}_k + \frac{\epsilon_k - i\Delta_k}{|E_k|}c^{\dagger(o)}_k\right) \quad (1.33)\\
\Psi^{(v)}_k &= \frac{1}{\sqrt{2}}\left(c^{\dagger(e)}_k - \frac{\epsilon_k - i\Delta_k}{|E_k|}c^{\dagger(o)}_k\right) \quad (1.34)
\end{aligned}
$$

corresponding to the valance (v) and conduction (c) band. Hereby the eigenfunctions have to be understood as operating on the vacuum state, $|(e),(o)\rangle = |0,0\rangle$. Due to this one can check the orthogonality and normalization, for example:

$$
\begin{aligned}
\left\langle \Psi^{(v)}_k \middle| \Psi^{(v)}_k \right\rangle &= \frac{1}{2}\left(c^{(e)}_k - \frac{\epsilon_k + i\Delta_k}{|E_k|}c^{(o)}_k\right)\left(c^{\dagger(e)}_k - \frac{\epsilon_k - i\Delta_k}{|E_k|}c^{\dagger(o)}_k\right) \quad (1.35)\\
&= \frac{1}{2}\Bigg[c^{(e)}_k c^{\dagger(e)}_k + \frac{(\epsilon_k - i\Delta_k)(\epsilon_k + i\Delta_k)}{|E_k|^2}c^{(o)}_k c^{\dagger(o)}_k \\
&\qquad - \frac{\epsilon_k + i\Delta_k}{|E_k|}c^{(o)}_k c^{\dagger(e)}_k - \frac{\epsilon_k - i\Delta_k}{|E_k|}c^{(e)}_k c^{\dagger(o)}_k\Bigg] \quad (1.36)\\
&= \frac{1}{2}\left[c^{(e)}_k c^{\dagger(e)}_k + c^{(o)}_k c^{\dagger(o)}_k\right] \quad (1.37)\\
&= 1 \quad (1.38)
\end{aligned}
$$

Check also the correspondence to the correct eigenvalues:

$$\begin{aligned}
\left\langle \Psi_k^{(v)} \middle| \mathcal{H}_{\mathrm{hopp},k} \middle| \Psi_k^{(v)} \right\rangle &= \left[\frac{1}{\sqrt{2}}\left(c_k^{(e)} - \frac{\epsilon_k + i\Delta_k}{|E_k|} c_k^{(o)}\right)\right] \cdot \\
&\quad \left[[\epsilon_k + i\Delta_k] c_k^{\dagger(e)} c_k^{(o)} + [\epsilon_k - i\Delta_k] c_k^{\dagger(o)} c_k^{(e)}\right] \cdot \\
&\quad \left[\frac{1}{\sqrt{2}}\left(c_k^{\dagger(e)} - \frac{\epsilon_k - i\Delta_k}{|E_k|} c_k^{\dagger(o)}\right)\right] && (1.39) \\
&= \frac{1}{2}\left[-\frac{(\epsilon_k - i\Delta_k)(\epsilon_k + i\Delta_k)}{|E_k|} - \frac{(\epsilon_k - i\Delta_k)(\epsilon_k + i\Delta_k)}{|E_k|}\right] && (1.40) \\
&= -|E_k| && (1.41) \\
\left\langle \Psi_k^{(c)} \middle| \mathcal{H}_{\mathrm{hopp},k} \middle| \Psi_k^{(c)} \right\rangle &= |E_k| && (1.42)
\end{aligned}$$

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):

$$\begin{aligned}
E_0(u) &= -2\sum_k |E_k| + 2N\kappa u^2 && (1.43) \\
&= -2\sum_k \sqrt{\epsilon_k^2 + \Delta_k^2} + 2N\kappa u^2 && (1.44) \\
&= -2\sum_k \sqrt{[2t_0\cos(ka)]^2 + [2\delta\sin(ka)]^2} + 2N\kappa u^2 && (1.45) \\
& && (1.46)
\end{aligned}$$

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

$$\begin{aligned}
E_0(u) &= \frac{-N}{\pi} \int_{-\pi/2a}^{\pi/2a} \mathrm{d}k\, \sqrt{[2t_0\cos(ka)]^2 + [2\delta\sin(ka)]^2} + 2N\kappa u^2 && (1.47) \\
&= \frac{-4Nt_0}{\pi} \underbrace{\int_0^{\pi/2} \mathrm{d}\theta\, \sqrt{1 - \left(1 - \frac{\delta}{t_0}\right)\sin^2(\theta)}}_{=:I(\delta/t_0)} + 2N\kappa u^2 && (1.48)
\end{aligned}$$

For small δ/t_0 the integral can be approximated as follows:

$$I\left(\frac{\delta}{t_0}\right) \approx 1 + \frac{1}{2}\left[\ln\left(\frac{4|t_0|}{|\delta|}\right) - \frac{1}{2}\right]\frac{\delta^2}{t_0^2} \qquad (1.49)$$

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

$$\Psi_k^{(v)}(q) = \sqrt{\frac{1}{2} - \frac{q}{2}}\, c_k^{\dagger(e)} - \sqrt{\frac{1}{2} + \frac{q}{2}}\, \frac{\epsilon_k - i\Delta_k}{|E_k|} c_k^{\dagger(o)} \tag{1.50}$$

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

$$\begin{aligned}
\left|\left\langle c_k^{\dagger(e)} | \Psi_k^{(v)}(q) \right\rangle\right|^2 &= \left| c_k^{(e)} \left(\sqrt{\frac{1}{2} - \frac{q}{2}}\, c_k^{\dagger(e)} - \sqrt{\frac{1}{2} + \frac{q}{2}}\, \frac{\epsilon_k - i\Delta_k}{|E_k|} c_k^{\dagger(o)} \right) \right|^2 && (1.51)\\
&= \frac{1-q}{2} && (1.52)
\end{aligned}$$

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. Therefore the number of valence electrons is given by $1 \pm q$. The energies for this states are given by:

$$\begin{aligned}
\left\langle \Psi_k^{(v)}(q) \middle| \mathcal{H}_{\mathrm{hopp},k} \middle| \Psi_k^{(v)}(q) \right\rangle &= \left[\sqrt{\frac{1-q}{2}}\, c_k^{(e)} - \sqrt{\frac{1+q}{2}}\, \frac{\epsilon_k + i\Delta_k}{|E_k|} c_k^{(o)} \right] \cdot \\
&\quad \left[[\epsilon_k + i\Delta_k] c_k^{\dagger(e)} c_k^{(o)} + [\epsilon_k - i\Delta_k] c_k^{\dagger(o)} c_k^{(e)} \right] \cdot \\
&\quad \left[\sqrt{\frac{1-q}{2}}\, c_k^{\dagger(e)} - \sqrt{\frac{1+q}{2}}\, \frac{\epsilon_k - i\Delta_k}{|E_k|} c_k^{\dagger(o)} \right] && (1.53)\\
&= -\sqrt{\frac{1-q}{2}}\, c_k^{(e)} [\epsilon_k + i\Delta_k] c_k^{\dagger(e)} c_k^{(o)} \sqrt{\frac{1+q}{2}}\, \frac{\epsilon_k - i\Delta_k}{|E_k|} c_k^{\dagger(o)} \\
&\quad - \sqrt{\frac{1+q}{2}}\, \frac{\epsilon_k + i\Delta_k}{|E_k|} c_k^{(o)} [\epsilon_k - i\Delta_k] c_k^{\dagger(o)} c_k^{(e)} \sqrt{\frac{1-q}{2}}\, c_k^{\dagger(e)} && (1.54)\\
&= -\sqrt{\frac{1+q}{2}} \sqrt{\frac{1-q}{2}} \left[\frac{(\epsilon_k - i\Delta_k)(\epsilon_k + i\Delta_k)}{|E_k|} + \frac{(\epsilon_k - i\Delta_k)(\epsilon_k + i\Delta_k)}{|E_k|} \right] && (1.55)\\
&= -\sqrt{1-q^2}\, |E_k| && (1.56)
\end{aligned}$$

For this reason the expected ground state energy as a function of the transferred charge in respect of a negligible small phonon coupling constant δ has the form:

$$E_0(q,u) = -\frac{4Nt_0}{\pi} \sqrt{1-q^2} + 2N\kappa u^2 \tag{1.57}$$

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

$$\begin{aligned}
t_0 &= 9,4\,\mathrm{eV} && \text{from fit} && (1.58)\\
t_0 &= 2.5\,\mathrm{eV} && \text{Glen paper} && (1.59)
\end{aligned}$$

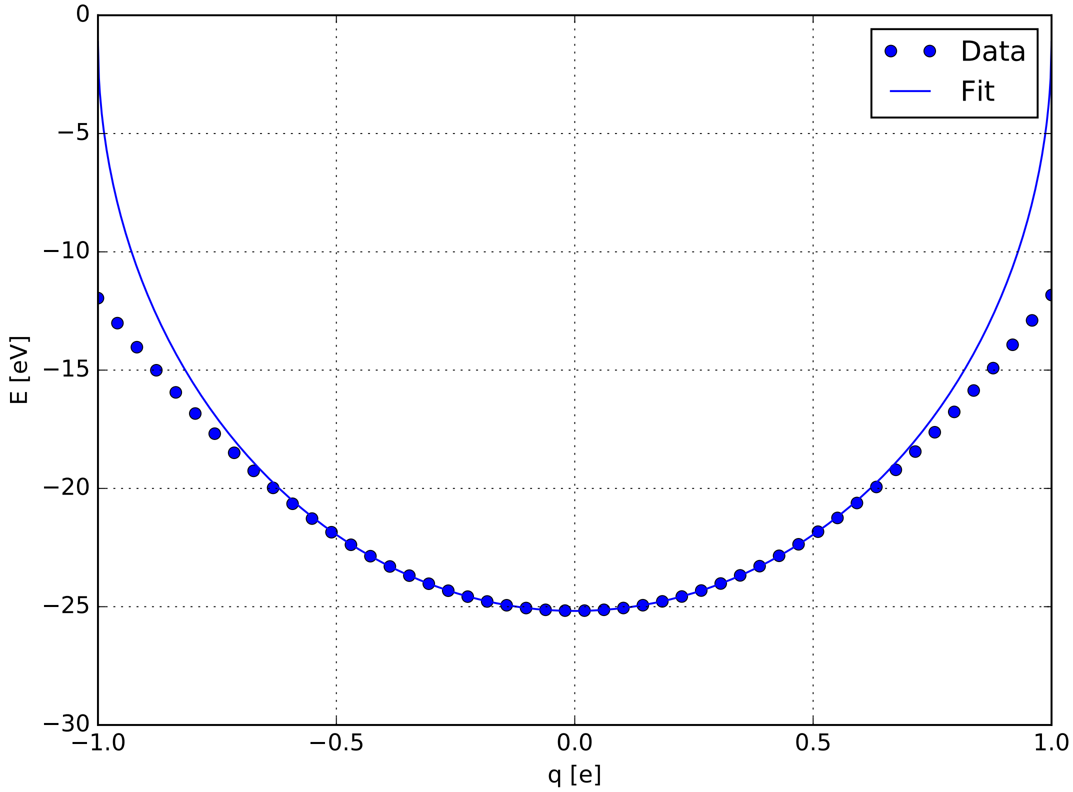


Figure 1.2: Unit cell energy as function of the manually shiftet charge for many k-points

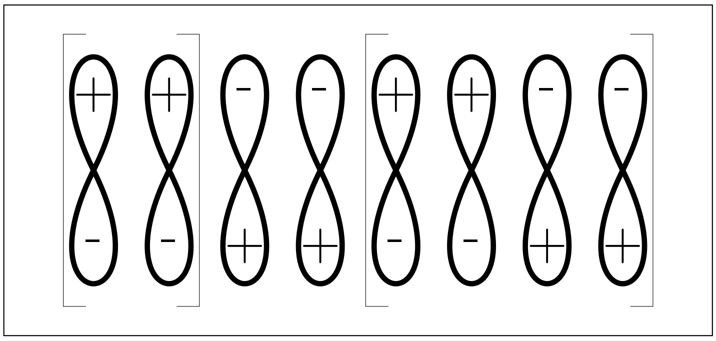
Probably this assumption is wrong:

$$\Psi_k^{(v)}(q) = \sqrt{\frac{1-q}{2}}\, c_k^{\dagger(e)} - \sqrt{\frac{1+q}{2}}\, \frac{\epsilon_k - i\Delta_k}{|E_k|} c_k^{\dagger(o)} \tag{1.60}$$

and should rather be formulated in a more general way:

$$\Psi_k^{(v)}(q_k) = \sqrt{\frac{1-q_k}{2}}\, c_k^{\dagger(e)} - \sqrt{\frac{1+q_k}{2}}\, \frac{\epsilon_k - i\Delta_k}{|E_k|} c_k^{\dagger(o)} \tag{1.61}$$

$$\Rightarrow \quad \left\langle \Psi_k^{(v)}(q_k) \middle| \mathcal{H}_{\text{hopp},k} \middle| \Psi_k^{(v)}(q_k) \right\rangle = -\sqrt{1-q_k^2}\, |E_k| \tag{1.62}$$



Due to the external potential the Hamiltonian can be written in the following form:

$$\mathcal{H} = \begin{pmatrix} -V & \epsilon_k + i\Delta_k \\ \epsilon_k - i\Delta_k & V \end{pmatrix} \tag{1.63}$$

With the eigenvalues $E_k = \pm\sqrt{V^2 + \epsilon_k^2 + \Delta_k^2}$ and the eigenstates[2]:

$$\vec{\Psi}_k(V) = \left[2\left(E_k^2 \mp V|E_k|\right)\right]^{-1/2} \begin{pmatrix} -V \pm \sqrt{V^2 + \epsilon_k^2 + \Delta_k^2} \\ \epsilon_k - i\Delta_k \end{pmatrix} \tag{1.64}$$

For $V = 0$ this matches the previous result. With this states one can easily calculate the number of valence electrons at the even/odd positions, for example:

$$q_k = \vec{\Psi}_k^{*\top} \cdot \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \cdot \vec{\Psi}_k \tag{1.65}$$

$$= \left[2\left(E_k^2 \mp V|E_k|\right)\right]^{-1} \cdot \left(-V \pm |E_k|\right)^2 \tag{1.66}$$

$$= \frac{\left(-V \pm |E_k|\right)^2}{2(E_k^2 \mp V|E_k|)} \tag{1.67}$$

1.2 Other Preparations

[2]the valence state corresponds with the lower signs

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Bibliography

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