MANY-PARTICLE APPROACH TO LEAD-MOLECULE INTERACTIONS AND TO THE IMAGE-CHARGE EFFECT

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Päiväys 9.5.2011

Abstrakti

Pro-Gradu tutkielmassani käsittelen kahta erilaista mallia, jotka kuvaavat yksinkertaista molekyyliä pitkän atomiketjun vieressä. Mallit on valittu siten että molemmat ratkaistaan erilaista tekniikkaa käyttäen. Näin minun oli mahdollista oppia aiheesta mahdollisimman paljon. Ensimmäistä malleista ns. kuvavaraus-mallia tutkitaan häiriöteoriaa hyödyntäen, käyttäen Feynmanin diagrammeja. Jälkimmäinen, ns. kahden tilan Fano-malli pystytään ratkaisemaan analyyttisesti käyttäen Greenin funktioiden liikeyhtälöitä.

Vaikkei käyttämääni kuvavaraus mallia pystykään ratkaisemaan analyyttisesti, saamme kuitenkin joitakin ominaisuuksia selvitettyä eksaktisti käyttäen apuna yhden tilan Fano-mallista saatuja tuloksia. Nämä ovat helppoja laskea, heti kun kahden tilan Fano-malli on ratkaistu. Ominaisuudet, jotka selvitin eksaktisti ovat ns. kuvavaraus atomiketjun molekyyliä lähimmällä atomilla. Voimme vertailla erilaisten approksimaatioiden kykyä selvittää tämän kuvavarauksen suuruus. Käy ilmi, että ensimmäisessä häiriöteoria kertaluvussa, ns Hartree-Fock approksimaatiossa emme löydä minkäänlaista molekyylin ja ketjun vuorovaikutuksista nousevaa efektiä. Aivan kuin ketju ja molekyyli eivät "näkisi" toisiaan. Tästä syystä minkäänlaista kuvavaraus efektie ei ole nähtävissä Hartree-Fock approksimaation tasolla. Toisessa kertaluvussa kuvavaraus nousee esiin ja sen arvo on melko lähellä eksaktia riippuen kuitenkin ketjun hyppyparametrin t arvosta.

Käy ilmi, että kuvavaraus-mallissa syntyy ns. spektri piikkejä, jotka ovat merkkejä atomiketjun energiavyön ulkopuolelle syntyneistä tiloista. Nämä tilat syntyvät molekyylin ja ketjun vuorovaikutuksen johdosta. Molekyylin omatessa netto varausta se luo potentiaalin joka, jos vuorovaikutus on tarpeeksi suuri, työntää yhden tilan ulos ketjun energia vyöltä. Pystymme selvittämään käyttäen Hellmann-Feymann teoreemaa, että edellä mainitun spektri piikin siirtymästä vuorovaikutus parametrin suhteen on mahdollista johtaa yhtälö kuvavaraukselle ketjun ensimmäisellä paikalla. Edellä mainitusta eksaktista kuvavarauksesta pystyimme myös selvittämään eksaktit piikin siirtymät, joten pystyimme nyt vertaamaan sekä piikin siirtymää vuorovaikutusparametrin funktiona että kuvavarauksen määrää atomiketjulla.

Myös piikin siirtymät ovat melko hyvin ennustettavissa kuvavaraus mallin toisessa kertaluvussa. Meidän on kuitenkin muistettava, että en ole tehnyt häiriökehitelmää iteroiden loppuun asti, joten tulokset todennäköisesti muuttuisivat jos jatkaisimme iterointia kunnes Greenin funktio konvergoisi. Ongelmat liittyen tällaiseen "ensimmäisen kertaluvun iterointiin" tulevat joissakin tuloksissa esille jolloin kommentoin niitä.

Lopuksi huomaamme, että vaikkei kahden tilan Fano malli sisällä lainkaan vuorovaikutusta molekyylin ja ketjun välillä löydämme silti edellä mainittuja spektri piikkejä. Nämä piikit osoittavat, että tila voi työntyä energia vyöltä ulos myös muista syistä, kuin ulkoisen potentiaalin työntämänä.

Abstract

In this Master's thesis we study two different models describing a molecule next to infinite chain of atoms. The models are chosen such that one can learn two separate ways of approaching the quantum many-particle problem. First of the models, the image-charge model, is studied with the famous Feynman diagram methods. The latter, the two-level Fano model, is solved exactly with the aid of equations of motion for the Green's functions.

From the image-charge model we also deduce exact properties with the aid of calculations from the Fano model. We are able to compare the approximate image-charge to the exact one at the terminal site of the chain. In first order of perturbation theory we do not find any effect of the molecule-chain interactions. However already in the second order "single shot" approximation we find the image-charge effect quite accurately, depending on the chain hopping parameter t.

We find that in the image-charge model one obtains spectral peaks as a signal of the fact that a split-off state has formed in the chain due to the molecule-chain interactions. This split-off state however requires sufficiently strong interaction, between the molecule and chain to be formed. The image-charge at the terminal site turns out to be solvable from the spectral peak shift w.r.t. to the interaction strength between the molecule and the chain. We also solve the exact density at the terminal site of the chain and solve the peak shifts exactly.

The ability of the image-charge model to predict the peak shift can be compared to exact results. It turns out that the peak shifts are also quite well predicted by the model. However, one still has to keep in mind the problems related to the "single shot" approximation, namely the fact that the model seems to work at some preferred hopping parameter t_e, which is also deduced.

Finally we notice that even though in our two-level Fano model there are no interactions, we still obtain spectral peaks giving sign of split-off states in the chain.

Contents

Chapter 1

Introduction

1.1 many-particle quantum theory

In order to tackle the problems of microscopic many-particle systems we need a proper theory to describe many-particle behavior in such systems. We will thus review a quantum version of the statistical mechanics. We will follow the lines of courses ”Quantum mechanics 2” by Kimmo Tuominen, ”many-particle quantum mechanics” by prof. Robert van Leeuwen. Both courses were given in the university of Jyväskylä, the formar at autumn 2008 and the latter at spring 2010. The books that are used are cited when necessary.

1.1.1 Basics

We start by introducing notation, the Dirac notation [3]. The quantum state of a given system is described by

$$|\psi(t)\rangle_n, \tag{1.1}$$

which is a time dependent state vector in n-particle Hilbert space [10]. The subscript n is often dropped for convenience. In Hilbert space we introduce an inner product by

$$\langle\Phi|\Psi\rangle_n = \langle\Psi|\Phi\rangle_n^*, \tag{1.2}$$

which is, in general, a complex number. To measure some physical property of the system we need to project the state $|\psi(t)\rangle_n$ to a proper basis. This is done through inner product

$$\langle\lambda_1 \dots \lambda_n|\psi(t)\rangle_n = \psi(\lambda_1 \dots \lambda_n, t) = z \in C, \tag{1.3}$$

where $|\psi(t)\rangle_n$ is projected to basis $\langle\lambda_1 \dots \lambda_n|$, where $|\lambda_1 \dots \lambda_n\rangle$ are the eigenvectors of the operator $\hat{\Lambda}$. The probability p in measurement of operator Λ to obtain the eigenvalue $\lambda_1 \dots \lambda_n$ is the square of the norm of z [10]

$$\begin{aligned} |\langle\lambda_1 \dots \lambda_n|\psi(t)\rangle_n|^2 &= \langle\lambda_1 \dots \lambda_n|\psi(t)\rangle_n^* \langle\lambda_1 \dots \lambda_n|\psi(t)\rangle_n \\ &= \langle\psi(t)|\lambda_1 \dots \lambda_n\rangle_n \langle\lambda_1 \dots \lambda_n|\psi(t)\rangle_n \\ &= p(\lambda_1 \dots \lambda_n, t) \in R. \end{aligned} \tag{1.4}$$

We now restrict ourselves to the one-particle Hilbert space for a moment. We introduce the operator

$$\int \mathrm{d}\mathbf{x}\ |\mathbf{x}\rangle\langle\mathbf{x}|. \tag{1.5}$$

Here $\mathbf{x}$ represents some continuous variable in Hilbert space, by which we can define basis, with the property $\langle \mathbf{x}|\mathbf{y}\rangle = \delta(\mathbf{x}-\mathbf{y})$. We may deduce the operation of (1.5) through

$$\langle \mathbf{y}|\psi_k\rangle = \langle \mathbf{y}| \int \mathrm{d}\mathbf{x}\ |\mathbf{x}\rangle \overbrace{\langle \mathbf{x}|\psi_k\rangle}^{=\psi_k(\mathbf{x})} = \int \mathrm{d}\mathbf{x}\ \overbrace{\langle \mathbf{y}|\mathbf{x}\rangle}^{\delta(\mathbf{x}-\mathbf{y})}\ \psi_k(\mathbf{x}) = \psi_k(\mathbf{y}). \tag{1.6}$$

Thus we may deduce that operator in Eq. (1.5) is just unity, and any state can be expanded as

$$|\psi_k\rangle = \int \mathrm{d}\mathbf{x}\ \psi_k(\mathbf{x})|\mathbf{x}\rangle. \tag{1.7}$$

A similar operator can be formed for the sub-index of state $|\psi_k\rangle$ as well (now with $\langle k|p\rangle = \delta_{kp}$). However, since $k \in Z$ we have a sum instead of an integral

$$\langle k|\psi(\mathbf{x})\rangle = \langle k| \overbrace{\left(\sum_p |p\rangle\langle p|\right)}^{=1} |\psi(\mathbf{x})\rangle = \sum_p \overbrace{\langle k|p\rangle}^{\delta_{kp}} \overbrace{\langle p|\psi(\mathbf{x})\rangle}^{\psi_p(\mathbf{x})} = \psi_k(\mathbf{x}). \tag{1.8}$$

With (1.5) we may also see that the inner product in (1.2) can be expressed as

$$\langle \Phi|\Psi\rangle = \int \mathrm{d}\mathbf{x}\ \ \langle \Phi|\mathbf{x}\rangle \langle \mathbf{x}|\Psi\rangle = \int \mathrm{d}\mathbf{x}\ \Phi(\mathbf{x})^*\Psi(\mathbf{x}). \tag{1.9}$$

To proceed we introduce the following argument. Particles in quantum mechanics are completely identical and thus we have no way of separating them from each other [4]. This implies some properties to the wave function. Let us say that our many-particle system is in state $\Psi(\mathbf{x}_1, \dots, \mathbf{x}_i, \dots, \mathbf{x}_j, \dots, \mathbf{x}_n)$, where $\mathbf{x}_i = (\mathbf{r}_i, \sigma_i)$ is the space-spin coordinate of the i:th particle. Now, since the particles are indistinguishable, we may change the order of two particles in Ψ and in the measurement we should see a difference. Thus, we gain only a phase, i.e.,

$$\Psi(\mathbf{x}_1, \dots, \mathbf{x}_i, \dots, \mathbf{x}_j, \dots, \mathbf{x}_n) = e^{i\theta}\Psi(\mathbf{x}_1, \dots, \mathbf{x}_j, \dots, \mathbf{x}_i, \dots, \mathbf{x}_n). \tag{1.10}$$

This property must be valid for all pairs i, j. We denote the interchange of particles i and j by P_{ij}. Performing two successive permutations we yield the original state, and thus $P_{ij}^2 = e^{2i\theta} = 1$, i.e., $\theta = \pm\pi/2$. The particles corresponding to $\theta = +(-)\pi/2$ are called bosons (fermions).

All the following derivations are done for fermions. This due to the fact that an electron is a fermion, and we are mainly interested in the behavior of electrons in the system. We will now introduce the machinery of the second quantization to tackle the problem of changing particle number states.

1.1.2 Second quantization

The second quantization deals with a changing particle number. We thus need a proper space to describe states with a different number of particles. The space required is called Fock space [4] and it is a collection of all different particle number Hilbert spaces

$$\mathcal{F} = \{\mathcal{H}_0, \mathcal{H}_1, \mathcal{H}_2, \dots, \mathcal{H}_n, \dots\}. \tag{1.11}$$

Any element of Fock space can be written as

$$|\psi\rangle = \sum_{n=0}^{\infty} c_n|\psi\rangle_n, \tag{1.12}$$

where $|\psi\rangle_n$ is an element of $\mathcal{H}_n$. In Fock space we define the inner product as

$$\langle \Phi|\Psi\rangle = \sum_{n=0}^{\infty} d_n^* c_n \left\langle \Phi|\Psi\right\rangle_n, \tag{1.13}$$

where $\langle\Phi|\Psi\rangle_n$ is just the normal inner product in n-particle Hilbert space. One can see that for n-particle state $|\Psi\rangle = c_n|\Psi\rangle_n$ and for m-particle state $|\Phi\rangle_m = d_m|\Phi\rangle_m$ we have

$$\langle\Phi|\Psi\rangle = \begin{cases} d_m^* c_n \langle\Phi|\Psi\rangle_n, & \text{for } n = m \\ 0, \quad \text{for } n \neq m. \end{cases} \tag{1.14}$$

We define a basis to every Hilbert space by n-particle ket vectors of space-spin coordinates $\mathbf{x}_j = (\mathbf{r}_j, \sigma_j)$ as $|\mathbf{x}_1, \dots, \mathbf{x}_n\rangle \in \mathcal{H}_n$. These basis states satisfy

$$\begin{aligned} \langle\mathbf{x}|\mathbf{y}\rangle &= \delta(\mathbf{x}-\mathbf{y}) \\ \langle\mathbf{x}_1\mathbf{x}_2|\mathbf{y}_1\mathbf{y}_2\rangle &= \delta(\mathbf{x}_1-\mathbf{y}_1)\delta(\mathbf{x}_2-\mathbf{y}_2) - \delta(\mathbf{x}_1-\mathbf{y}_2)\delta(\mathbf{x}_2-\mathbf{y}_1) \\ &\vdots \\ \langle\mathbf{x}_1\dots\mathbf{x}_n|\mathbf{y}_1\dots\mathbf{y}_n\rangle &= \sum_\sigma (-1)^\sigma \prod_{i=1}^n \delta(\mathbf{x}_i - \mathbf{y}_{\sigma(i)}), \end{aligned} \tag{1.15}$$

where $\sigma(i)$ means the permutation of index i and σ is the number of permutation. These relations (1.15) follow directly from the antisymmetry of wave function $\Psi(\mathbf{x}_1\dots\mathbf{x}_n)$ and from the fact that the particles $1, \dots, n$ are identical.

The empty/vacuum state is important and we define it as

$$|0\rangle \in \mathcal{H}_0, \text{ with the property } \langle 0|0\rangle = 1. \tag{1.16}$$

The unit operator in Fock space is the sum of unit operators in different particle number Hilbert spaces. One must, however, be careful with unit operator in more than one particle Hilbert spaces because of the antisymmetry property of the wave function. To see this, consider

$$\begin{aligned} \langle\mathbf{y}_1\dots\mathbf{y}_n|\psi\rangle &= c\int d\mathbf{x}_1\dots d\mathbf{x}_n \langle\mathbf{y}_1\dots\mathbf{y}_n|\mathbf{x}_1\dots\mathbf{x}_n\rangle\langle\mathbf{x}_1\dots\mathbf{x}_n|\psi\rangle \\ &= c\int d\mathbf{x}_1\dots d\mathbf{x}_n \sum_\sigma (-1)^\sigma \prod_{i=1}^n \delta(\mathbf{y}_{\sigma(i)} - \mathbf{x}_i)\langle\mathbf{x}_1\dots\mathbf{x}_n|\psi\rangle \\ &= c\sum_\sigma (-1)^\sigma \langle\mathbf{y}_{\sigma(1)}\dots\mathbf{y}_{\sigma(n)}|\psi\rangle = c\sum_\sigma (-1)^{2\sigma}\langle\mathbf{y}_1\dots\mathbf{y}_n|\psi\rangle \\ &= cn!\langle\mathbf{y}_1\dots\mathbf{y}_n|\psi\rangle, \qquad c = \frac{1}{n!} \end{aligned} \tag{1.17}$$

Here we only used the antisymmetry of wave function and the definition of inner product in n particle Hilbert space. The unit operator in n-particle Hilbert space can be read from Eq. (1.17)

$$1_N = \frac{1}{N!}\int d\mathbf{x}_1\dots d\mathbf{x}_N|\mathbf{x}_1\dots\mathbf{x}_N\rangle\langle\mathbf{x}_1\dots\mathbf{x}_N|. \tag{1.18}$$

The unit operator in Fock space thus becomes

$$1 = |0\rangle\langle 0| + \int d\mathbf{x}\ |\mathbf{x}\rangle\langle\mathbf{x}| + \frac{1}{2!}\int d\mathbf{x}_1 d\mathbf{x}_2\ |\mathbf{x}_1\mathbf{x}_2\rangle\langle\mathbf{x}_1\mathbf{x}_2| + \dots \tag{1.19}$$

We are now ready to generate n-particle basis states from vacuum. This is done through special operators that we will present next.

Creation and annihilation operators

We define the operator $\hat{\psi}^\dagger(\mathbf{x})$ such that it adds particle to space-spin point $\mathbf{x}$, i.e. it maps an object from N particle Hilbert space to $N+1$ particle Hilbert space,

$$\hat{\psi}^\dagger(\mathbf{x})|\mathbf{y}_1\dots\mathbf{y}_n\rangle = |\mathbf{x}\mathbf{y}_1\dots\mathbf{y}_n\rangle. \tag{1.20}$$

moreover, we have

$$\begin{aligned}
&\hat{\psi}^\dagger(\mathbf{x}_1)\ldots\hat{\psi}^\dagger(\mathbf{x}_i)\ldots\hat{\psi}^\dagger(\mathbf{x}_j)\ldots\hat{\psi}^\dagger(\mathbf{x}_n)|0\rangle = |\mathbf{x}_1\ldots\mathbf{x}_i\ldots\mathbf{x}_j\ldots\mathbf{x}_n\rangle \\
= \quad & -|\mathbf{x}_1\ldots\mathbf{x}_j\ldots\mathbf{x}_i\ldots\mathbf{x}_n\rangle = -\hat{\psi}^\dagger(\mathbf{x}_1)\ldots\hat{\psi}^\dagger(\mathbf{x}_j)\ldots\hat{\psi}^\dagger(\mathbf{x}_i)\ldots\hat{\psi}^\dagger(\mathbf{x}_n)|0\rangle,
\end{aligned} \tag{1.21}$$

and this must hold for all pairs i, j. Thus, we conclude that

$$\left\{\hat{\psi}^\dagger(\mathbf{x}), \hat{\psi}^\dagger(\mathbf{y})\right\} = 0, \tag{1.22}$$

where we defined the anticommutator $\{\hat{A}, \hat{B}\} = \hat{A}\hat{B} + \hat{B}\hat{A}$. The anticommutation relations of these operators will determine the fermionic behavior of the system. For bosons we would find, instead of anticommutation relations, the usual commutation relations.

Next we deduce the operation of $(\hat{\psi}^\dagger(\mathbf{x}))^\dagger = \hat{\psi}(\mathbf{x})$. Consider a wave function $\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_n)$. For it we have

$$\begin{aligned}
\Psi(\mathbf{x}_1,\ldots,\mathbf{x}_n) &= \langle\mathbf{x}_1\ldots,\mathbf{x}_n|\Psi\rangle = \langle\Psi|\mathbf{x}_1\ldots,\mathbf{x}_n\rangle^* = \langle\Psi|\hat{\psi}^\dagger(\mathbf{x}_1)\ldots\hat{\psi}^\dagger(\mathbf{x}_n)|0\rangle^* \\
&= \langle 0|\hat{\psi}(\mathbf{x}_n)\ldots\hat{\psi}(\mathbf{x}_1)|\Psi\rangle.
\end{aligned} \tag{1.23}$$

Thus the operation of $\hat{\psi}(\mathbf{x})$ may be read from last line of (1.23)

$$\langle 0|\hat{\psi}(\mathbf{x}_n)\ldots\hat{\psi}(\mathbf{x}_1) = \langle\mathbf{x}_1\ldots\mathbf{x}_n|. \tag{1.24}$$

These bra-vectors must of course be also antisymmetric leading to

$$\left\{\hat{\psi}(\mathbf{x}), \hat{\psi}(\mathbf{y})\right\} = 0. \tag{1.25}$$

Due to a bit lengthy calculations the operation of $\hat{\psi}(\mathbf{x})$ to any ket-vector is derived in Appendix A.1.1. The operation reads

$$\hat{\psi}(\mathbf{y})|\mathbf{x}_1\ldots\mathbf{x}_n\rangle = \sum_i (-1)^{i-1}\delta(\mathbf{y}-\mathbf{x}_i)|\mathbf{x}_1\ldots\mathbf{x}_{i-1}\mathbf{x}_{i+1}\ldots\mathbf{x}_n\rangle. \tag{1.26}$$

The effect of $\hat{\psi}(\mathbf{y})$ is to destroy a particle from the state under operation and thus the name annihilation operator.

With Eq. (1.26) we may deduce the operation of anticommutation between $\hat{\psi}^\dagger(\mathbf{y})$ and $\hat{\psi}(\mathbf{x})$. This is done in Appendix A.1.2. Collecting all the anti-commutators we have

$$\left\{\hat{\psi}(\mathbf{x}), \hat{\psi}(\mathbf{y})\right\} = \left\{\hat{\psi}^\dagger(\mathbf{x}), \hat{\psi}^\dagger(\mathbf{y})\right\} = 0, \quad \left\{\hat{\psi}^\dagger(\mathbf{x}), \hat{\psi}(\mathbf{y})\right\} = \delta(\mathbf{x}-\mathbf{y}). \tag{1.27}$$

General basis states

In the previous chapter we have obtained machinery to create and destroy particles in Fock space. However, we have only considered the space-spin basis in our calculations. We would like to have more general bases in order to deal with a wider amount of problems. We introduce these bases next. Consider any basis in one-particle Hilbert space, denote the basis kets as $|n\rangle \in \mathcal{H}$, and require that the basis is orthonormal. Hence,

$$\langle m|n\rangle = \delta_{mn} \tag{1.28}$$

$$\sum_n |n\rangle\langle n| = 1. \tag{1.29}$$

We want to relate these new basis states to the space-spin basis in order to use the relations derived for the field operators $\hat{\psi}^\dagger$ and $\hat{\psi}$. Use Eq. (1.29) to show that

$$\delta(\mathbf{x}-\mathbf{y}) = \langle\mathbf{x}|\mathbf{y}\rangle = \sum_n \langle\mathbf{x}|n\rangle\,\langle n|\mathbf{y}\rangle \equiv \sum_n \varphi_n(\mathbf{x})\varphi_n^*(\mathbf{y}). \tag{1.30}$$

We define new creation and annihilation operators in this new basis through

$$\hat{a}_n^\dagger = \int \mathrm{d}\mathbf{x}\ \varphi_n(\mathbf{x})\hat{\psi}^\dagger(\mathbf{x}) \tag{1.31}$$

$$\hat{a}_n = \int \mathrm{d}\mathbf{x}\ \varphi_n^*(\mathbf{x})\hat{\psi}(\mathbf{x}). \tag{1.32}$$

By using Eq. (1.30) and the definitions (1.31) and (1.32) it is easy to show that

$$\hat{\psi}^\dagger(\mathbf{x}) = \sum_n \varphi_n^*(\mathbf{x})\hat{a}_n^\dagger = \sum_{n=(n',\sigma_{n'})} \varphi_n^*(\mathbf{r})\hat{a}_n^\dagger, \tag{1.33}$$

$$\hat{\psi}(\mathbf{x}) = \sum_n \varphi_n(\mathbf{x})\hat{a}_n = \sum_{n=(n',\sigma_{n'})} \varphi_n(\mathbf{r})\hat{a}_n. \tag{1.34}$$

Moreover, we immediately see from the definitions (1.31) and (1.32) and from the anticommutation relations (1.27) that the new creation and annihilation operators satisfy

$$\{\hat{a}_n, \hat{a}_m\} = \left\{\hat{a}_n^\dagger, \hat{a}_m^\dagger\right\} = 0, \quad \left\{\hat{a}_n^\dagger, \hat{a}_m\right\} = \delta_{nm}. \tag{1.35}$$

We may now define many-particle ket states with these new operators $\hat{a}_n^\dagger$. These become clearly antisymmetric due to the anticommutation of the creation operators. We thus have

$$\hat{a}_{n_1}^\dagger \dots \hat{a}_{n_N}^\dagger|0\rangle = |n_1 \dots n_N\rangle = -P_{ij}|n_1 \dots n_N\rangle, \tag{1.36}$$

where P_{ij} denotes the usual permutation of n_i and n_j. For bra-states we similarly have

$$\langle 0|\hat{a}_{n_N} \dots \hat{a}_{n_1} = \langle n_1 \dots n_N| = -P_{ij}\langle n_1 \dots n_N|. \tag{1.37}$$

However, since the particles are indistinguishable, the states $\langle n_1 \dots n_N|$ and $-P_{ij}\langle n_1 \dots n_N|$ are equivalent. We would thus like to obtain basis of inequivalent configurations of numbers n_i. An obvious one is the configuration $n_1 < n_2 \dots < n_N$. With this ordering one can show using (1.31) and (1.32) that

$$\sum_{n_1<n_2\dots<n_N} |n_1 \dots n_N\rangle\langle n_1 \dots n_N| = 1, \tag{1.38}$$

and further from

$$|m_1 \dots m_N\rangle = \sum_{n_1<n_2\dots<n_N} |n_1 \dots n_N\rangle \langle n_1 \dots n_N|m_1 \dots m_N\rangle, \tag{1.39}$$

that $\langle n_1 \dots n_N|m_1 \dots m_N\rangle = \delta_{n_1 m_1} \dots \delta_{n_N m_N}$. Thus the states $|n_1 \dots n_N\rangle$ form a basis to N particle Hilbert space.

We further want to introduce one important property of this basis. As we already mentioned any N-particle state can be expanded as

$$|\Psi\rangle = \sum_{n_1<n_2\dots<n_N} |n_1 \dots n_N\rangle \langle n_1 \dots n_N|\Psi\rangle \equiv \sum_{n_1<n_2\dots<n_N} c_{n_1\dots n_N}|n_1 \dots n_N\rangle. \tag{1.40}$$

One could thus wonder what would be the expansion for $\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N)$ in the coordinate representation. This requires the calculation of the matrix element $\langle \mathbf{x}_1 \dots \mathbf{x}_N|n_1 \dots n_N\rangle$, see Appendix A.1.3 for details. The result is

$$\langle \mathbf{x}_1 \dots \mathbf{x}_N|n_1 \dots n_N\rangle = \begin{vmatrix} \varphi_{n_1}(\mathbf{x}_1) & \dots & \varphi_{n_1}(\mathbf{x}_N) \\ \vdots & & \vdots \\ \varphi_{n_N}(\mathbf{x}_1) & \dots & \varphi_{n_N}(\mathbf{x}_N) \end{vmatrix} \equiv \Phi_{n_1\dots n_N}(\mathbf{x}_1 \dots \mathbf{x}_N). \tag{1.41}$$

This is the famous Slater determinant [4], which is completely antisymmetric in all indices $n_1 \dots n_N$ and coordinates $\mathbf{x}_1 \dots \mathbf{x}_N$. Using Eqs. (1.41) and (1.40) we may deduce that any N-particle wave function can be expanded in Slater determinants as

$$\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N) = \langle \mathbf{x}_1 \dots \mathbf{x}_N \Psi\rangle = \sum_{n_1<n_2\dots<n_N} c_{n_1\dots n_N}\Phi_{n_1\dots n_N}(\mathbf{x}_1 \dots \mathbf{x}_N), \tag{1.42}$$

where $c_{n_1\dots n_N} = \langle n_1 \dots n_N|\Psi\rangle$.

1.1.3 Hamiltonians in second quantization

The evolution of a non-relativistic quantum mechanical state is governed by Schrödinger equation. We would now like to express this equation in second quantization. The many-particle Schrödinger equation with no electromagnetic fields present reads

$$\begin{aligned}
&\hat{H}\Psi(\mathbf{x}_1 \ldots \mathbf{x}_n, t) \\
= &\left[-\sum_{i=1}^{n} \frac{\hbar^2}{2m_i}\nabla_i^2 + \sum_{i=1}^{n} U(\mathbf{r}_i) + \frac{1}{2}\sum_{i\neq j} V(\mathbf{r}_i, \mathbf{r}_j)\right] \Psi(\mathbf{x}_1 \ldots \mathbf{x}_n, t) \\
= &\, i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{x}_1 \ldots \mathbf{x}_n, t), \qquad (1.43)
\end{aligned}$$

so we have three operators in total to express in terms of field operators $\hat{\psi}$ and $\hat{\psi}^\dagger$. The result, derived in A.1.4, reads

$$\begin{aligned}
\hat{H} &= \int \mathrm{d}\mathbf{x}\; \hat{\psi}^\dagger(\mathbf{x}) \left(\frac{\hbar^2}{2m_i}\nabla^2 + U(\mathbf{r}_i)\right) \hat{\psi}(\mathbf{x}) \\
&+ \frac{1}{2}\int \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}'\; V(\mathbf{r}, \mathbf{r}')\hat{\psi}^\dagger(\mathbf{x})\hat{\psi}^\dagger(\mathbf{x}')\hat{\psi}(\mathbf{x}')\hat{\psi}(\mathbf{x}), \qquad (1.44)
\end{aligned}$$

and in terms of general operators $\hat{a}_i^\dagger$ and $\hat{a}_i$

$$\hat{H} = \sum_{i,j} h_{ij}\hat{a}_i^\dagger\hat{a}_j + \frac{1}{2}\sum_{i,j,k,l} V_{ijkl}\hat{a}_i^\dagger\hat{a}_j^\dagger\hat{a}_k\hat{a}_l, \qquad (1.45)$$

where we defined

$$\begin{aligned}
h_{ij} &= \int \mathrm{d}\mathbf{x}\; \varphi_i^*(\mathbf{x}) \left(\frac{\hbar^2}{2m_i}\nabla^2 + U(\mathbf{r}_i)\right) \varphi_j(\mathbf{x}) \qquad (1.46) \\
V_{ijkl} &= \int \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}'\; V(\mathbf{r}, \mathbf{r}')\varphi_i^*(\mathbf{x})\varphi_j^*(\mathbf{x}')\varphi_k(\mathbf{x}')\varphi_l(\mathbf{x}). \qquad (1.47)
\end{aligned}$$

The operation of (1.44) and (1.45) is defined as

$$(\hat{H}\Psi)(\mathbf{x}_1 \ldots \mathbf{x}_n, t) = \langle \mathbf{x}_1 \ldots \mathbf{x}_n|\hat{H}|\Psi(t)\rangle = \langle \Psi(t)|\hat{H}|\mathbf{x}_1 \ldots \mathbf{x}_n\rangle^*. \qquad (1.48)$$

We will mostly work with the Hamiltonian in general operators, i.e., (1.45). In this form we have reduced the problem of solving a group of differential Eqs. (1.43) into a diagonalization of a matrix. One sees that this is actually the case through the following consideration. Define a basis for our Hilbert space in terms of operators $\hat{a}_{n_1}^\dagger \ldots \hat{a}_{n_N}^\dagger$. The basis states are orthonormal as we have already seen from (1.39) and with all possible combinations, with $n_1 < \cdots < n_N$, they span the whole N-particle Hilbert space uniquely. Denote the basis states as $|i\rangle$. Now we have, for any state in this Hilbert space, the expansion

$$|\Psi\rangle = \sum_{i=1}^{m} c_i|i\rangle, \qquad (1.49)$$

where m is the number of basis states, i.e., the number of configurations in which one can put N particles to the number of sites in use. We now may take the energy eigenstate $|\Psi_k\rangle$ and deduce

$$\begin{aligned}
\hat{H}|\Psi_k\rangle = \sum_{i=1}^{m} c_i^k\hat{H}|i\rangle &= E_k\sum_{i=1}^{m} c_i^k|i\rangle \qquad |\langle j| \\
\sum_{i=1}^{m} c_i^k \overbrace{\langle j|\hat{H}|i\rangle}^{H_{ji}} &= E_k\sum_{i=1}^{m} c_i^k \overbrace{\langle j|i\rangle}^{=\delta_{ij}} \\
\sum_{i=1}^{m} H_{ji}c_i^k &= Ec_j^k. \qquad (1.50)
\end{aligned}$$

Finding the energy eigenstates in terms of the basis $|i\rangle$ thus corresponds to the diagonalization of the matrix H_{ji}. However in general this becomes tricky immediately as the number m increases, and it grows very quickly in terms of possible sites and the particle number.

We may find approximations to the terms h_{ij} and V_{ijkl} in Eqs. (1.46) and (1.47), and this results in Hamiltonians that can be diagonalized even for an infinite number of sites and particles, see for example Appendix A.3.

1.1.4 Evolution of states

As we have already mentioned the evolution of quantum state is governed by the Schrödinger Eq. [3]. We may thus wonder if we know some state at moment t_0 what it will be at time t. For a time-independent Hamiltonian this can be deduced easily from

$$\hat{H}|\Psi(t)\rangle = i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle. \tag{1.51}$$

We immediately notice that for energy eigenstates we have

$$\begin{aligned} & \hat{H}|\psi_k(t)\rangle = i\hbar\frac{\partial}{\partial t}|\psi_k(t)\rangle \qquad |\langle\psi_k(t_0)| \\ \Rightarrow\quad & E_k\,\langle\psi_k(t_0)|\psi_k(t)\rangle - i\hbar\frac{\partial}{\partial t}\,\langle\psi_k(t_0)|\psi_k(t)\rangle = 0 \\ \Rightarrow\quad & \langle\psi_k(t_0)|\psi_k(t)\rangle = e^{-i\frac{E_k}{\hbar}(t-t_0)} \\ \Rightarrow\quad & \langle\psi_k(t_0)|\psi_k(t)\rangle = \langle\psi_k(t_0)|e^{-i\frac{E_k}{\hbar}(t-t_0)}|\psi_k(t_0)\rangle \\ \Rightarrow\quad & \langle\psi_k(t_0)|\psi_k(t)\rangle = \langle\psi_k(t_0)|\hat{U}_k(t,t_0)|\psi_k(t_0)\rangle \end{aligned} \tag{1.52}$$

Thus, we see that $\hat{U}_k(t,t_0)|\psi_k(t_0)\rangle = e^{-i\frac{E_k}{\hbar}(t-t_0)}|\psi_k(t_0)\rangle = |\psi_k(t)\rangle$, where $\hat{U}_k(t,t_0)$ is the time-evolution operator defined by $|\psi_k(t)\rangle = \hat{U}_k(t,t_0)|\psi_k(t_0)\rangle$. We may expand any $|\Psi(t)\rangle$ in energy eigenstates $|\psi_k(t)\rangle$ and obtain

$$\begin{aligned} |\Psi(t)\rangle &= \hat{U}(t,t_0)|\Psi(t_0)\rangle = \sum_k c_k\hat{U}_k(t,t_0)|\psi_k(t_0)\rangle = \sum_k c_k e^{i\frac{E_k}{\hbar}(t-t_0)}|\psi_k(t_0)\rangle \\ &= e^{i\frac{\hat{H}}{\hbar}(t-t_0)}\sum_k c_k|\psi_k(t_0)\rangle = e^{i\frac{\hat{H}}{\hbar}(t-t_0)}|\Psi(t_0)\rangle. \end{aligned} \tag{1.53}$$

We see that the time-evolution operator for any state, with a time-independent Hamiltonian, can be expressed as

$$\hat{U}(t,t_0) = e^{-i\frac{\hat{H}}{\hbar}(t-t_0)}. \tag{1.54}$$

For a time-dependent Hamiltonian we must use the following argument. Any time-dependent Hamiltonian is constant in a "short enough" interval Δ, and thus we may use the operator (1.54) at each of these intervals separately. We obtain for a time-dependent Hamiltonian with the property

$$\hat{H}(t) = \begin{cases} \hat{H}(t_0),\ t\in[t_0,t_1[\\ \hat{H}(t_1),\ t\in[t_1,t_2[\\ \vdots \\ \hat{H}(t_{n-1}),\ t\in[t_{n-1},t_n=t], \end{cases} \tag{1.55}$$

where $t_k = t_0 + k\Delta$, that the evolution operator becomes

$$\begin{aligned} |\Psi(t)\rangle &= \hat{U}(t,t_0)|\Psi(t_0)\rangle = \hat{U}(t,t_{n-1})\ldots\hat{U}(t_1,t_0)|\Psi(t_0)\rangle \\ &= e^{-\frac{i}{\hbar}\hat{H}(t_{n-1})(t_n-t_{n-1})}\ldots e^{-\frac{i}{\hbar}\hat{H}(t_0)(t_1-t_0)}|\Psi(t_0)\rangle \\ &= \mathcal{T}(e^{-\frac{i}{\hbar}\sum_{i=1}^{n}\hat{H}(t_{i-1})(\Delta)})|\Psi(t_0)\rangle, \qquad \Delta\to 0 \\ &\to\ |\Psi(t)\rangle = \mathcal{T}(e^{-\frac{i}{\hbar}\int_{t_0}^{t}\hat{H}(t')\mathrm{d}t'})|\Psi(t_0)\rangle, \end{aligned} \tag{1.56}$$

where we have defined the time-ordered product $\mathcal{T}$ by equation $\mathcal{T}(\hat{O}(t_{\sigma(n)})\dots\hat{O}(t_{\sigma(1)})) = \hat{O}(t_n)\dots\hat{O}(t_1)$, for $t_n > \cdots > t_1$. On the third equality we used the fact that operators commute under time-ordered product, see A.1.5.

We also define the operator propagating backwards in time, i.e., for $t < t_0$. This is evaluated in the same manner as (1.56) but instead of time ordering we must use anti time-ordering defined by $\mathcal{T}_A(\hat{O}(t_{\sigma(n)})\dots\hat{O}(t_{\sigma(1)})) = \hat{O}(t_n)\dots\hat{O}(t_1)$, for $t_n < \cdots < t_1$. Collecting we have

$$\hat{U}(t,t') = \begin{cases} \mathcal{T}(e^{-\frac{i}{\hbar}\int_{t'}^{t}\hat{H}(t)\mathrm{d}t}) & t > t' \\ \mathcal{T}_A(e^{\frac{i}{\hbar}\int_{t'}^{t}\hat{H}(t)\mathrm{d}t}) & t < t'. \end{cases} \tag{1.57}$$

The time orderings $\mathcal{T}$ and $\mathcal{T}_A$ will play an important role in future considerations, especially in the formulation of perturbation theory.

Time-evolution operator for bra-states

To see how the bra-vectors evolve in time we do the following calculation

$$\begin{aligned} 1 &= \langle\Psi(t)|\Psi(t)\rangle = \langle\Psi(t)|\hat{U}(t,t_0)|\Psi(t_0)\rangle \\ &= \langle\Psi(t_0)|\hat{U}^\dagger(t,t_0)|\Psi(t)\rangle^* = \langle\Psi(t_0)|\hat{U}^\dagger(t,t_0)\hat{U}(t,t_0)|\Psi(t_0)\rangle^* \\ &\Rightarrow \hat{U}^\dagger(t,t_0)\hat{U}(t,t_0) = 1, \end{aligned} \tag{1.58}$$

but definitely we must have $\hat{U}(t_0,t)\hat{U}(t,t_0) = 1$ and thus we see $\hat{U}^\dagger(t,t_0) = \hat{U}(t_0,t)$, and further

$$\langle\Psi(t)| = \langle\Psi(t_0)|\hat{U}(t_0,t). \tag{1.59}$$

1.1.5 Different pictures

Before proceeding we further introduce two different viewpoints on quantum mechanics. These are namely the Schrödinger and Heisenberg pictures [3]. Up to this point our states have evolved in time and the operators have just operated at each time point. We have operated in the Schrödinger picture. We can, however, consider also different viewpoint, the Heisenberg picture, where operators evolve and states remain unchanged. This is most easily done by considering the expectation value of some operator $\hat{O}(t)$ in the Schrödinger picture

$$\begin{aligned} \left\langle\hat{O}(t)\right\rangle &= \langle\Psi(t)|\hat{O}(t)|\Psi(t)\rangle = \langle\Psi(t_0)|\hat{U}(t_0,t)\hat{O}(t)\hat{U}(t,t_0)|\Psi(t_0)\rangle \\ &\equiv \langle\Psi(t_0)|\hat{O}_H(t)|\Psi(t_0)\rangle, \end{aligned} \tag{1.60}$$

where we have defined the operator $\hat{O}(t)$ in the Schrödinger picture as the operator

$$\hat{O}_H(t) = \hat{U}(t_0,t)\hat{O}(t)\hat{U}(t,t_0) \tag{1.61}$$

in the Heisenberg picture.

There is also the interaction picture where both the states and operators evolve in time, but as we do not need it in this thesis it is not presented.

1.1.6 Equations of motion for operators

We may calculate the equations of motion for operators in the Heisenberg picture [1]. These turn out to be handy as we will need the equations of motion for $\hat{\psi}_H$ and $\hat{\psi}_H^\dagger$ in the future. We start by noticing that for the time-evolution operator $\hat{U}$ we have simple differential equations which can be seen considering the obvious fact

$$\hat{U}(t_3, t_1) = \hat{U}(t_3, t_2)\hat{U}(t_2, t_1). \tag{1.62}$$

Now for $t_3 = t_2 + \Delta$ we may immediately write

$$\begin{aligned} \hat{U}(t_3, t_1) &= e^{-\frac{i}{\hbar}\hat{H}(z_2)\Delta}\hat{U}(t_2, t_1) \approx (1 - \frac{i}{\hbar}\hat{H}(z_2)\Delta + \mathcal{O}(\Delta^2))\hat{U}(t_2, t_1) \\ \Rightarrow &\quad \frac{\hat{U}(t_2 + \Delta, t_1) - \hat{U}(t_2, t_1)}{\Delta} = -\frac{i}{\hbar}\hat{H}(t_2)\hat{U}(t_2, t_1) \\ \Rightarrow &\quad i\hbar\partial_t\hat{U}(t, t_0) = \hat{H}(t)\hat{U}(t, t_0) \end{aligned} \tag{1.63}$$

Moreover, for the latter time coordinate we similarly find

$$i\hbar\partial_{t_0}\hat{U}(t, t_0) = -\hat{U}(t, t_0)\hat{H}(t_0). \tag{1.64}$$

Now consider Heisenberg operators. As in Eq. (1.61), taking the time derivative, and using Eqs. (1.63) and (1.64) we obtain

$$\begin{aligned} i\hbar\partial_t\hat{O}_H(t) &= i\hbar\partial_t\hat{U}(t_0, t)\hat{O}(t)\hat{U}(t, t_0) + i\hbar\hat{U}(t_0, t)\partial_t\hat{O}(t)\hat{U}(t, t_0) + i\hbar\hat{U}(t_0, t)\hat{O}(t)\partial_t\hat{U}(t, t_0) \\ &= -\hat{U}(t_0, t)\hat{H}(t)\overbrace{\hat{U}(t, t_0)\hat{U}(t_0, t)}^{=1}\hat{O}(t)\hat{U}(t, t_0) + i\hbar\hat{U}(t_0, t)\partial_t\hat{O}(t)\hat{U}(t, t_0) \\ &+ \hat{U}(t_0, t)\hat{O}(t)\hat{U}(t, t_0)\hat{U}(t_0, t)\hat{H}(t)\hat{U}(t, t_0) \\ &= \left[\hat{O}_H(t), \hat{H}_H(t)\right] + i\hbar(\partial_t\hat{O})_H(t). \end{aligned} \tag{1.65}$$

Then the equation of motion for a Heisenberg operator becomes

$$\partial_t\hat{O}_H(t) = -\frac{i}{\hbar}\left[\hat{O}_H(t), \hat{H}_H(t)\right] + (\partial_t\hat{O})_H(t). \tag{1.66}$$

Equations of motion for field operators

From Eq. (1.66) we may deduce the equations of motion for the $\hat{\psi}_H$ and $\hat{\psi}_H^\dagger$, which will be useful later. To proceed we notice that one can write

$$\left[\hat{O}_H(t), \hat{H}_H(t)\right] = \hat{U}(t_0, t)\left[\hat{O}(t), \hat{H}(t)\right]\hat{U}(t, t_0) \tag{1.67}$$

and thus it is sufficient to calculate the commutator in the Schrödinger picture. For a Hamiltonian of the form (1.44) we may deduce, using the anticommutation relations (1.27), that the equations of motion for field operators become

$$i\hbar\partial_t\hat{\psi}_H(\mathbf{x}t) = \left(-\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r})\right)\hat{\psi}_H(\mathbf{x}t) + \int \mathrm{d}\mathbf{x}'\ V(\mathbf{r}, \mathbf{r}')\hat{\psi}_H^\dagger(\mathbf{x}'t)\hat{\psi}_H(\mathbf{x}'t)\hat{\psi}_H(\mathbf{x}t) \tag{1.68}$$

$$-i\hbar\partial_t\hat{\psi}_H^\dagger(\mathbf{x}t) = \left(-\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r})\right)\hat{\psi}_H^\dagger(\mathbf{x}t) + \int \mathrm{d}\mathbf{x}'\ V(\mathbf{r}, \mathbf{r}')\hat{\psi}_H^\dagger(\mathbf{x}t)\hat{\psi}_H^\dagger(\mathbf{x}'t)\hat{\psi}_H(\mathbf{x}'t). \tag{1.69}$$

1.2 Quantum statistical mechanics

The presentation in this section follows the lines of courses "Many-particle quantum mechanics" and "Statistical physics" given by profs. Robert van Leeuwen and Jussi Timonen, respectively. We have put the Boltzmann constant $k_b = 1$.

As we are dealing with many-particle systems, and by many we mean 10^{23}, and we are having the system in contact with the environment, it is necessary to introduce quantum statistics. Our system is considered to be weakly coupled to its environment. This gives rise to interesting phenomena. However, we have to start the journey from the middle and just state that the expectation value of an operator for a system in thermal equilibrium with environment becomes [1]

$$\left\langle \hat{A} \right\rangle = \sum_n p_n \langle n|\hat{A}|n\rangle, \tag{1.70}$$

where p_n is the time average of the actual, fluctuating probability $w_n(t)$,

$$p_n = \frac{1}{\Delta} \int_{T_0}^{T_0+\Delta} w_n(t)\ \mathrm{d}t. \tag{1.71}$$

However, we have another way of finding p_n, that is, we prepare a large number M of identical systems and measure each separately. We find out that M_n of the systems are in state $|n\rangle$. Thus, the probability p_n can be expressed as

$$p_n = \frac{M_n}{M}. \tag{1.72}$$

This is called the ensemble average. We assume that the time average and ensemble average are equal; this is called the ergodic theorem [13].

We now consider a system that is perturbed at time t_0 by some possibly time-dependent potential $\hat{V}(t)$. We observe the evolution of the probabilities p_n. We start by expanding an evolved state in terms of the states at t_0

$$\hat{U}(t,t_0)|n,t_0\rangle = |n,t\rangle = \sum_m |m,t_0\rangle \left\langle m,t_0|n,t\right\rangle. \tag{1.73}$$

The probability of finding the state $|m,t_0\rangle$ is given by

$$p_{m,n}(t) = |\left\langle m,t_0|n,t\right\rangle|^2. \tag{1.74}$$

Thus, to find the probability of the state $|m,t_0\rangle$ we must multiply $p_{m,n}(t)$ with the probability that the system was initially at $|n,t_0\rangle$, that is, p_n. Moreover, we sum over all possible initial states, since obviously the system can evolve to $|m,t_0\rangle$ from any initial state. We then obtain

$$\begin{aligned} p_m(t) &= \sum_n |\left\langle m,t_0|n,t\right\rangle|^2 p_n \\ &= \sum_n \left\langle m,t_0|n,t\right\rangle p_n \left\langle n,t|m,t_0\right\rangle \\ &= \langle m,t_0|\hat{p}(t)|m,t_0\rangle. \end{aligned} \tag{1.75}$$

Thus we see that the time dependent density matrix is given by

$$\hat{p}(t) = \sum_n p_n |n,t\rangle\langle n,t|. \tag{1.76}$$

The time dependent expectation value of an operator $\hat{A}$ is now given by

$$\begin{aligned} \left\langle \hat{A} \right\rangle(t) &= \sum_n p_n \langle n,t|\hat{A}|n,t\rangle \\ &= \sum_n p_n \langle n,t_0|\hat{U}(t_0,t)\hat{A}\hat{U}(t,t_0)|n,t_0\rangle \qquad (1.77) \\ &= \sum_{n,k} \left\langle \psi_k|n,t_0\right\rangle p_n \langle n,t_0|\hat{A}_H(t)|\psi_k\rangle \\ &= \sum_k \langle \psi_k|\hat{p}(t_0)\hat{A}_H(t)|\psi_k\rangle \\ &= \mathrm{Tr}\left[\hat{p}(t_0)\hat{A}_H(t)\right]. \end{aligned} \tag{1.78}$$

Here we defined $\sum_k \langle\psi_k|\hat{O}|\psi_k\rangle = \mathrm{Tr}[\hat{O}]$, where $|\psi_k\rangle$ is any complete set of basis functions.

We are left to determine the explicit form of $\hat{p}$. We introduce again a large number (M) of systems now weakly coupled. We insist that the energy and the particle number are conserved in our hypersystem containing all M subsystems. In the measurement we find M_r systems in state $|r\rangle$. Thus the total energy and particle number become, respectively

$$E = \sum_{r=1}^{n} M_r E_r, \tag{1.79}$$

$$N = \sum_{r=1}^{n} M_r N_r. \tag{1.80}$$

We calculate the degeneracy Ω of an energy level E, that is, in how many independent ways one can have the same energy E of the whole system. This becomes clearly

$$\Omega_E = \frac{M!}{M_1! \dots M_n!}. \tag{1.81}$$

As the numbers $M_1, \dots, M_n$ are very large it is convenient to use the Stirling formula [2] to approximate the degeneracy. With the approximation

$$\ln N! \simeq N \ln N - N, \tag{1.82}$$

we may write $\ln \Omega_E$ using Eq. (1.81) as

$$\begin{aligned}\ln \Omega_E &= \ln M! - \ln \prod_{r=1}^{n} M_r! = \ln M! - \sum_{r=1}^{n} \ln M_r! \\ &= M \ln M - M - \sum_{r=1}^{n} M_r \ln M_r - M_r \\ &= -\sum_{r=1}^{n} M_r (\ln M_r - \ln M) \\ &= -M \sum_{r=1}^{n} p_r \ln p_r \equiv MS, \end{aligned} \tag{1.83}$$

where $p_r = M_r/M$, and we have used the well known formulas for the logarithm and the obvious fact that $\sum_{r=1}^{n} M_r = M$. We further defined

$$S = -\sum_{r=1}^{n} p_r \ln p_r, \tag{1.84}$$

which is a quantity called entropy and it represents the amount of disorder in the ensemble. The most likely state for the hypersystem with constrains (1.79), (1.80) and $\sum_{r=1}^{n} M_r = M$ is the one that maximizes the degeneracy and thus the entropy. With the method of Lagrange multipliers [2] we may write

$$-M \sum_{r=1}^{n} p_r \ln p_r + \alpha \sum_{r=1}^{n} M_r E_r + \beta \sum_{r=1}^{n} M_r N_r + \gamma \sum_{r=1}^{n} M_r = \text{maximal}. \tag{1.85}$$

Dividing (1.85) by the number of systems we find

$$-\sum_{r=1}^{n} p_r \ln p_r + \alpha \sum_{r=1}^{n} p_r E_r + \beta \sum_{r=1}^{n} p_r N_r + \gamma \sum_{r=1}^{n} p_r = \text{maximal}, \tag{1.86}$$

where we implicitly required

$$\sum_{r=1}^{n} p_r = 1. \tag{1.87}$$

We search the extremum of (1.86) by the usual method of differentiating w.r.t. p_r and requiring the derivative to be zero. This yields

$$p_r = \frac{1}{e^{\gamma+1}} e^{-\beta E_r - \alpha N_r}. \tag{1.88}$$

From Eqs. (1.87) and (1.88) we find immediately

$$\begin{aligned} 1 &= \frac{1}{e^{\gamma+1}} \sum_{r=1}^{n} e^{-\beta E_r - \alpha N_r} \\ \Rightarrow e^{\gamma+1} &= \sum_{r=1}^{n} e^{-\beta E_r - \alpha N_r} \equiv \mathcal{Z} \end{aligned} \tag{1.89}$$

and thus

$$p_r = \frac{1}{\mathcal{Z}} e^{-\beta E_r - \alpha N_r}, \tag{1.90}$$

where parameters $\alpha(E,N)$ and $\beta(E,N)$ are functions of the energy and particle number. Next we will determine the form of these parameters. Consider Eq. (1.84). With Eq. (1.90) we have

$$\begin{aligned} S &= -\sum_{r=1}^{n} p_r \ln p_r = -\sum_{r=1}^{n} p_r \ln \frac{1}{\mathcal{Z}} e^{-\beta E_r - \alpha N_r} \\ &= -\sum_{r=1}^{n} p_r \left(-\beta E_r - \alpha N_r - \ln \mathcal{Z}\right) \\ &= \beta E + \alpha N + \ln \mathcal{Z}. \end{aligned} \tag{1.91}$$

Now differentiating

$$\frac{\partial S}{\partial E} = \beta + E \frac{\partial S}{\partial E} \beta + N \frac{\partial \alpha}{\partial E} + \frac{\partial \ln \mathcal{Z}}{\partial E}, \tag{1.92}$$

where

$$\begin{aligned} \frac{\partial \ln \mathcal{Z}}{\partial E} &= \frac{\partial \beta}{\partial E} \frac{\partial \ln \mathcal{Z}}{\partial \beta} + \frac{\partial \alpha}{\partial E} \frac{\partial \ln \mathcal{Z}}{\partial \alpha} \\ &= \frac{\partial \beta}{\partial E} \left(\frac{\partial}{\partial \beta} \ln \left[\sum_{r=1}^{n} e^{-\beta E_r - \alpha N_r} \right] \right) + \frac{\partial \alpha}{\partial E} \left(\frac{\partial}{\partial \alpha} \ln \left[\sum_{r=1}^{n} e^{-\beta E_r - \alpha N_r} \right] \right) \\ &= \frac{\partial \beta}{\partial E} \left(\sum_{r=1}^{n} \frac{-E_r}{\mathcal{Z}} e^{-\beta E_r - \alpha N_r} \right) + \frac{\partial \alpha}{\partial E} \left(\sum_{r=1}^{n} \frac{-N_r}{\mathcal{Z}} e^{-\beta E_r - \alpha N_r} \right) \\ &\overset{(1.90)}{=} -\frac{\partial \beta}{\partial E} \sum_{r=1}^{n} E_r p_r - \frac{\partial \alpha}{\partial E} \sum_{r=1}^{n} N_r p_r = -\frac{\partial \beta}{\partial E} E - \frac{\partial \alpha}{\partial E} N, \end{aligned} \tag{1.93}$$

we obtain

$$\frac{\partial S}{\partial E} = \beta. \tag{1.94}$$

Similarly we find

$$\frac{\partial S}{\partial N} = \alpha. \tag{1.95}$$

We next define

$$\beta = \frac{\partial S}{\partial E} \equiv \frac{1}{T}, \qquad \frac{\partial S}{\partial N} \equiv -\frac{\mu}{T}. \tag{1.96}$$

Although we just defined Eqs. (1.96) they can be motivated by considering two systems that can exchange energy and particles, see A.2. With (1.96) we may write (1.90) as

$$p_r = \frac{1}{\mathcal{Z}} e^{-\beta(E_r - \mu N_r)}, \tag{1.97}$$

and for the density matrix we have

$$\hat{\rho} = \sum_{r=1}^{n} p_r |r\rangle\langle r| = \sum_{r=1}^{n} \frac{1}{\mathcal{Z}} e^{-\beta(E_r - \mu N_r)} |r\rangle\langle r| = \frac{1}{\mathcal{Z}} e^{-\beta(\hat{H} - \mu\hat{N})} \overbrace{\sum_{r=1}^{n} |r\rangle\langle r|}^{=1} . \tag{1.98}$$

Moreover,

$$\mathcal{Z} = \sum_{r=1}^{n} e^{-\beta E_r - \alpha N_r} = \sum_{k} \langle \psi_k | e^{-\beta\hat{H} - \alpha\hat{N}} | \psi_k \rangle = \mathrm{Tr}\left[e^{-\beta\hat{H} - \alpha\hat{N}} \right], \tag{1.99}$$

which can be seen by inserting $|\psi_k\rangle = \sum_{r=1}^{n} c_r^k |r\rangle$ and using the unitary of matrix $[c]$. Now using Eqs. (1.98) and (1.99) we may finally deduce

$$\hat{\rho} = \frac{e^{-\beta(\hat{H} - \mu\hat{N})}}{\mathrm{Tr}\left[e^{-\beta\hat{H} - \alpha\hat{N}} \right]}, \tag{1.100}$$

and, moreover, inserting Eq. (1.100) into Eq. (1.77) we get

$$\left\langle \hat{A} \right\rangle (t) = \frac{\mathrm{Tr}\left\{ e^{-\beta(\hat{H} - \mu\hat{N})} \hat{A}_H(t) \right\}}{\mathrm{Tr}\left\{ e^{-\beta(\hat{H} - \mu\hat{N})} \right\}}. \tag{1.101}$$

1.3 Contours

In this section we will introduce the concept of imaginary time in order to extend the time contour to temperatures as well. The formalism was first introduced by Matsubara and the contour used is called the Keldysh contour. We again follow the line of lectures "Many-particle quantum mechanics" given by prof. Robert van Leeuwen.

Examining the structure of Eq. (1.101) we see that it contains the time propagation to time t, then operating at this point by operator $\hat{A}$ then time propagation back to time t_0 and some exponent of the Hamiltonian. We now make a somewhat wild trick and write the exponent as

$$e^{-\beta(\hat{H} - \mu\hat{N})} \equiv e^{-\beta\hat{H}_{eq}} = e^{-\frac{i}{\hbar}\hat{H}_{eq}(t_0 - i\beta\hbar - t_0)}, \tag{1.102}$$

comparing (1.102) to (1.54) we may write

$$e^{-\beta(\hat{H} - \mu\hat{N})} = \hat{U}(t_0 - i\beta\hbar, t_0), \tag{1.103}$$

with the evolution Hamiltonian being $\hat{H}_{eq}$. We now define the Hamiltonian to be of the form

$$\hat{H}(t) = \begin{cases} \hat{H} - \mu\hat{N} \equiv \hat{H}_{eq}, & t \in [t_0, t_0 - i\beta\hbar] \\ \hat{H}(t), & \mathrm{Im}\ t = 0, \end{cases} \tag{1.104}$$

or equivalently

$$\hat{H}(t) = \hat{H}(t) - \theta_\beta(t)\mu\hat{N}, \tag{1.105}$$

where

$$\theta_\beta(t) = \begin{cases} 1, & t \in [t_0, t_0 - i\beta\hbar] \\ 0, & \mathrm{Im}\ t = 0 \end{cases} . \tag{1.106}$$

Now with Eq. (1.104) we can write Eq. (1.101) in a form

$$\left\langle \hat{A} \right\rangle (t) = \frac{\mathrm{Tr}\left\{ \hat{U}(t_0 - i\beta\hbar, t_0)\hat{U}(t_0, t)\hat{A}(t)\hat{U}(t, t_0) \right\}}{\mathrm{Tr}\left\{ \hat{U}(t_0 - i\beta\hbar, t_0) \right\}}. \tag{1.107}$$

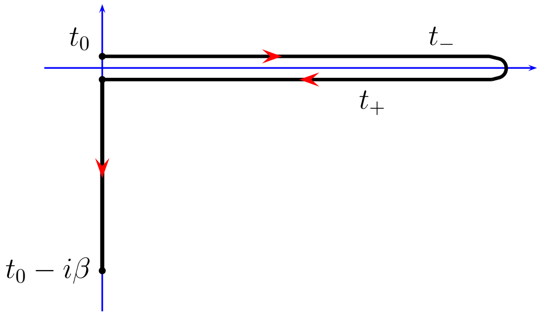


Figure 1.1: Keldysh contour

The contour on which we calculate the expectation value is illustrated in Fig. 1.1.

We now emphasize the fact that our time parameter has become complex and change the notation from t to z. As we look at the forms of the time-evolution operators in Eq. (1.57) we see that we are having both anti-time-ordering and time-ordering inside Eq. (1.101). We get rid of this by introducing time-ordering on our complex contour γ. For fermionic operators the time-ordering on contour γ becomes

$$\mathcal{T}_\gamma(\hat{A}(z_1)\dots\hat{A}(z_n)) = \sum_\sigma (-1)^\sigma \theta(z_{\sigma(1)},\dots,z_{\sigma(n)})\hat{A}(z_{\sigma(1)})\dots\hat{A}(z_{\sigma(n)}), \tag{1.108}$$

where

$$\theta(z_1,\dots,z_n) = \theta(z_1,z_2)\theta(z_2,z_3)\dots\theta(z_{n-1},z_n) \tag{1.109}$$

and the fact that we have $(-1)^\sigma$ comes from the fact that we want managable equations of motion for fermionic the operators. This will be satisfied if we let the operators anti-commute under this time-ordering.

With Eq. (1.108) we may write the time-evolution operators on contour. The time-evolution on contour is governed by the operator

$$\hat{U}(z_2,z_1) = \mathcal{T}_\gamma\left(e^{-\frac{i}{\hbar}\int_\gamma \mathrm{d}z \hat{H}(z)}\right), \quad z_1 < z_2. \tag{1.110}$$

The product of operators under the trace in (1.107) can now be written as

$$\hat{U}(z_f,z_i)\hat{U}(z_i,z')\hat{A}(z')\hat{U}(z',z_i) = \mathcal{T}_\gamma\left(e^{-\frac{i}{\hbar}\int_\gamma \mathrm{d}z\ \hat{H}(z)}\hat{A}(z')\right), \tag{1.111}$$

where $\hat{H}(z)$ is given by Eq. (1.104) and the form of the contour γ is presented in Fig. 1.1. We emphasize that the operator $\hat{A}$ must operate at the instant $z' = t$ by writing the time argument explicitly. The expectation value of any operator on this contour is given now by

$$\left\langle \hat{A} \right\rangle(t) = \frac{\mathrm{Tr}\left\{\mathcal{T}_\gamma\left(e^{-\frac{i}{\hbar}\int_\gamma \mathrm{d}z\ \hat{H}(z)}\hat{A}(z')\right)\right\}}{\mathrm{Tr}\left\{e^{-\frac{i}{\hbar}\int_\gamma \mathrm{d}z\ \hat{H}(z)}\right\}}, \tag{1.112}$$

where on the denominator we used the fact

$$\hat{U}(t_0 - i\beta\hbar, t_0)\overbrace{\hat{U}(t_0,t)\hat{U}(t,t_0)}^{=1} = e^{-\frac{i}{\hbar}\int_\gamma \mathrm{d}z\ \hat{H}(z)}. \tag{1.113}$$

1.3.1 Equations of motion for field operators on contour

On contour we have equations of motion for the Heisenberg operators. On contour the Heisenberg operators are defined as

$$\hat{O}_H(z) = \hat{U}(z_i,z)\hat{O}(z)\hat{U}(z,z_i). \tag{1.114}$$

The equation of motion can be derived similarly as in Chapter 1.1.6, by considering first the differential operators for the complex time-evolution operator on contour and then differentiating a general Heisenberg operator on the contour. The equation of motion becomes

$$\partial_z \hat{O}_H(z) = -\frac{i}{\hbar}\left[\hat{O}_H(z), \hat{H}_H(z)\right] + (\partial_z \hat{O})_H(z). \tag{1.115}$$

And for the Heisenberg field operators on contour defined as in (1.114) we find

$$i\hbar\partial_z\hat{\psi}_H(\mathbf{x}z) = \left(-\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r}) - \mu\theta_\beta(z)\right)\hat{\psi}_H(\mathbf{x}t) + \int \mathrm{d}\mathbf{x}'\ V(\mathbf{r},\mathbf{r}')\hat{\psi}^\dagger_H(\mathbf{x}'z)\hat{\psi}_H(\mathbf{x}'z)\hat{\psi}_H(\mathbf{x}z) \tag{1.116}$$

$$-i\hbar\partial_z\hat{\psi}^\dagger_H(\mathbf{x}z) = \left(-\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r}) - \mu\theta_\beta(z)\right)\hat{\psi}^\dagger_H(\mathbf{x}z) + \int \mathrm{d}\mathbf{x}'\ V(\mathbf{r},\mathbf{r}')\hat{\psi}^\dagger_H(\mathbf{x}z)\hat{\psi}^\dagger_H(\mathbf{x}'z)\hat{\psi}_H(\mathbf{x}'z), \tag{1.117}$$

where the contour step function θ_β is due to the fact that the Hamiltonian changes on the vertical track of contour to $\hat{H} - \mu\hat{N}$ as defined in (1.105).

1.3.2 Perturbation theory on contour

We could now wonder if we make a small perturbation to Hamiltonian (1.104)

$$\hat{H}'(z) = \hat{H}(z) + \delta\hat{V}(z), \tag{1.118}$$

how our expectation value in Eq. (1.112) changes. This is quite quickly seen just by expanding in $\delta\hat{V}$. We write

$$\left\langle \hat{A}\right\rangle(t) = \frac{\mathrm{Tr}\left\{\mathcal{T}_\gamma\left(e^{-\frac{i}{\hbar}\int_\gamma \mathrm{d}z\ \hat{H}(z)+\delta\hat{V}(z)}\hat{A}(z')\right)\right\}}{\mathrm{Tr}\left\{e^{-\frac{i}{\hbar}\int_\gamma \mathrm{d}z\ \hat{H}(z)+\delta\hat{V}(z)}\right\}}, \tag{1.119}$$

so now the numerator can be expanded as follows

$$\begin{aligned}
&-i\mathrm{Tr}\left\{\mathcal{T}_\gamma\left(e^{-\frac{i}{\hbar}\int_\gamma \mathrm{d}z\hat{H}(\mathbf{z})}e^{-\frac{i}{\hbar}\int_\gamma \mathrm{d}z\delta\hat{V}(z)}\hat{A}(z')\right)\right\} \\
=\ & -i\sum_{k=0}^{\infty}\frac{1}{k!}\left(\frac{-i}{\hbar}\right)^k\int_\gamma \mathrm{d}z_1\ldots\int_\gamma \mathrm{d}z_k\ \mathrm{Tr}\left\{\mathcal{T}_\gamma\left(e^{-\frac{i}{\hbar}\int_\gamma \mathrm{d}z\hat{H}(\mathbf{z})}\delta\hat{V}(z_1)\ldots\delta\hat{V}(z_k)\hat{A}(z')\right)\right\} \\
=\ & -i\sum_{k=0}^{\infty}\frac{1}{k!}\left(\frac{-i}{\hbar}\right)^k\int_\gamma \mathrm{d}z_1\ldots\int_\gamma \mathrm{d}z_k\ \mathrm{Tr}\left\{\hat{U}(z_f,z_i)\mathcal{T}_\gamma\left(\delta\hat{V}_H(z_1)\ldots\delta\hat{V}_H(z_k)\hat{A}(z')\right)\right\},
\end{aligned} \tag{1.120}$$

where we used

$$\begin{aligned}
&\mathcal{T}_\gamma\left(e^{-\frac{i}{\hbar}\int_\gamma \mathrm{d}z\hat{H}(\mathbf{z})}\hat{O}_1(z_1)\ldots\hat{O}_k(z_k)\right) \\
=\ & \mathcal{T}_\gamma\left(\hat{U}(z_f,z_i)\hat{U}(z_i,z_1)\hat{O}_1(z_1)\hat{U}(z_1,z_i)\hat{U}(z_i,z_2)\hat{O}_2(z_2)\hat{U}(z_2,z_i)\ldots\hat{U}(z_i,z_k)\hat{O}_k(z_k)\hat{U}(z_k,z_i)\right) \\
=\ & \mathcal{T}_\gamma\left(\hat{U}(z_f,z_i)\hat{O}_{H,1}(z_1)\hat{O}_{H,2}(z_2)\ldots\hat{O}_{H,k}(z_k)\right) \\
=\ & \hat{U}(z_f,z_i)\mathcal{T}_\gamma\left(\hat{O}_{H,1}(z_1)\ldots\hat{O}_{H,k}(z_k)\right).
\end{aligned} \tag{1.121}$$

Similar expansion can be carried out for the denominator yielding

$$\begin{aligned}
&\mathrm{Tr}\left\{e^{-\frac{i}{\hbar}\int_\gamma \mathrm{d}z\hat{H}'(\mathbf{z})}\right\} \\
=\ & \sum_{k=0}^{\infty}\frac{1}{k!}\left(\frac{-i}{\hbar}\right)^k\int_\gamma \mathrm{d}z_1\ldots\int_\gamma \mathrm{d}z_k\ \mathrm{Tr}\left\{\hat{U}(z_f,z_i)\mathcal{T}_\gamma\left(\delta\hat{V}_H(z_1)\ldots\delta\hat{V}_H(z_k)\right)\right\}.
\end{aligned} \tag{1.122}$$

Now both the numerator and denominator can be divided by $\hat{U}(z_f, z_i)$ and by defining

$$\begin{aligned}\left\langle \hat{A}_H(z) \right\rangle_0 &= \mathrm{Tr}\left\{ \hat{\rho}_0 \hat{A}_H(z) \right\} &(1.123)\\ \hat{\rho}_0 &= \frac{e^{\beta \hat{H}_{0,eq}}}{\mathrm{Tr} e^{\beta \hat{H}_{0,eq}}}, \qquad \hat{H}_{0,eq} = \hat{H}(z) - \mu \hat{N} &(1.124)\end{aligned}$$

we obtain

$$\left\langle \hat{A} \right\rangle (z') = -i \frac{\sum_{k=0}^{\infty} \frac{1}{k!} \left(\frac{-i}{\hbar}\right)^k \int_\gamma \mathrm{d}z_1 \ldots \int_\gamma \mathrm{d}z_k \ \left\langle \mathcal{T}_\gamma \left(\delta \hat{V}_H(z_1) \ldots \delta \hat{V}_H(z_k) \hat{A}(z') \right) \right\rangle_0}{\sum_{k=0}^{\infty} \frac{1}{k!} \left(\frac{-i}{\hbar}\right)^k \int_\gamma \mathrm{d}z_1 \ldots \int_\gamma \mathrm{d}z_k \ \left\langle \mathcal{T}_\gamma \left(\delta \hat{V}_H(z_1) \ldots \delta \hat{V}_H(z_k) \right) \right\rangle_0}. \tag{1.125}$$

We next assume that the perturbation is of the form of the two-particle interaction, see Eq. (1.44) lower line. In the Heisenberg picture the operators $\delta \hat{V}$ become

$$\hat{V}_H(z_j) = \frac{1}{2} \int \mathrm{d}\mathbf{x}_j \int \mathrm{d}\mathbf{x}'_j \ V(\mathbf{r}_j, \mathbf{r}'_j) \hat{\psi}^\dagger_H(\mathbf{x}_j z_j) \hat{\psi}^\dagger_H(\mathbf{x}'_j z'_j) \hat{\psi}_H(\mathbf{x}'_j z'_j) \hat{\psi}_H(\mathbf{x}_j z_j). \tag{1.126}$$

Since we are about to set these two particle interactions in Eq. (1.126) inside time ordering it is essential to keep track of the proper ordering of the operators. We do this as follows. First, we write (1.126) as

$$\begin{aligned}\hat{V}_H(z_j) &= \lim_{z''_j \to z^+_j} \frac{1}{2} \int \mathrm{d}z'_j \int \mathrm{d}\mathbf{x}_j \int \mathrm{d}\mathbf{x}'_j \ \delta(z^+_j, z'_j) V(\mathbf{r}_j, \mathbf{r}'_j) \\ &\times \ \mathcal{T}_\gamma \left(\hat{\psi}^\dagger_H(\mathbf{x}_j z''_j) \hat{\psi}^\dagger_H(\mathbf{x}'_j z'^+_j) \hat{\psi}_H(\mathbf{x}'_j z_j) \hat{\psi}_H(\mathbf{x}_j z_j) \right), &(1.127)\end{aligned}$$

where the limit $\lim_{z''_j \to z^+_j}$ is to be taken after the integration over z'_j. We invent a short hand notation for the terms in Eqs. (1.125) and (1.127). Namely, we write

$$\begin{aligned}(\mathbf{x}_j z_j) &= j, &(1.128)\\ \delta(z^+_j, z'_j) V(\mathbf{r}_j, \mathbf{r}'_j) &= v(j^+, j'), &(1.129)\\ \int \mathrm{d}z_j \mathrm{d}x_j &= \int \mathrm{d}j, &(1.130)\\ z''_j &\to z^+_j. &(1.131)\end{aligned}$$

Now we may write the $\langle\rangle_0$ term in numerator of (1.125) as

$$\begin{aligned}&\left\langle \mathcal{T}_\gamma \left(\delta \hat{V}_H(z_1) \ldots \delta \hat{V}_H(z_k) \hat{A}(z') \right) \right\rangle_0 \\ = \ &\left(\frac{1}{2}\right)^k \int \mathrm{d}\mathbf{x}_1 \ldots \mathbf{x}_k \int \mathrm{d}1' \ldots \mathrm{d}k' \ v(1^+, 1') \ldots v(k^+, k') \\ \times \ &\left\langle \mathcal{T}_\gamma \left(\hat{\psi}^\dagger_H(1'') \hat{\psi}^\dagger_H(1'^+) \hat{\psi}_H(1') \hat{\psi}_H(1) \ldots \hat{\psi}^\dagger_H(k'') \hat{\psi}^\dagger_H(k'^+) \hat{\psi}_H(k') \hat{\psi}_H(k) \hat{A}(z') \right) \right\rangle_0. \quad (1.132)\end{aligned}$$

Here we did not write the limits $\lim_{z''_j \to z^+_j}$ explicitly visible, but they are taken normally after the integration. Now we just reorder the terms inside the time ordering, and permute all creation operators to the right and annihilation operators to the left. Performing the same procedure in the denominator as well leads to an expression for the perturbed expectation value,

$$\begin{aligned}
&\left\langle \hat{A} \right\rangle (z') \\
=\;& \left[\sum_{k=0}^{\infty} \frac{1}{k!} \left(\frac{-i}{2\hbar} \right)^k \int_\gamma \mathrm{d}1\mathrm{d}1' \dots \mathrm{d}k\mathrm{d}k' v(1^+, 1') \dots v(k^+, k') \right. \\
&\left. \times \left\langle \mathcal{T}_\gamma \left(\hat{\psi}_H(1')\hat{\psi}_H(1) \dots \hat{\psi}_H(k')\hat{\psi}_H(k)\hat{\psi}_H^\dagger(k'^+)\hat{\psi}_H^\dagger(k'') \dots \hat{\psi}_H^\dagger(1'^+)\hat{\psi}_H^\dagger(1'')\hat{A}(z') \right) \right\rangle_0 \right] \\
\times\;& \left[\sum_{k=0}^{\infty} \frac{1}{k!} \left(\frac{-i}{2\hbar} \right)^k \int_\gamma \mathrm{d}1\mathrm{d}1' \dots \mathrm{d}k\mathrm{d}k' \; v(1^+, 1') \dots v(k^+, k') \right. \\
&\left. \times \left\langle \mathcal{T}_\gamma \left(\hat{\psi}_H(1')\hat{\psi}_H(1) \dots \hat{\psi}_H(k')\hat{\psi}_H(k)\hat{\psi}_H^\dagger(k'^+)\hat{\psi}_H^\dagger(k'') \dots \hat{\psi}_H^\dagger(1'^+)\hat{\psi}_H^\dagger(1'') \right) \right\rangle_0 \right]^{-1} .
\end{aligned} \tag{1.133}$$

This expression will be motivation for us to introduce Green's functions. We will also use it in development of the perturbation theory for Green's functions.

Chapter 2

Green's Functions

We introduce the concept of Green's function and derive properties for it. Again most of the derivations are based on the lectures "Many-particle quantum mechanics" given by prof. Robert van Leeuwen. Also Refs. [1] and [4] were used.

2.1 Definition

From Eq. (1.133) one immediately deduces the general structure of the expectation value of $\hat{A}$. The easiest operators that one can plug into (1.133) are of the form

$$\begin{align} \hat{A} &= \hat{\psi}^{\dagger}_{H}(\mathbf{x}z)\hat{\psi}_{H}(\mathbf{x}'z'), \tag{2.1}\\ \hat{A} &= \hat{\psi}_{H}(\mathbf{x}'z')\hat{\psi}^{\dagger}_{H}(\mathbf{x}z). \tag{2.2}\\ & \tag{2.3} \end{align}$$

For operators containing different number of creation and annihilation operators we obtain zero expectation value due to the fact that one would calculate an inner product between states in different particle number Hilbert spaces, yielding zero as in (1.14). We could thus consider expectation values of the form

$$\begin{align} G^{>}(\mathbf{x}z;\mathbf{x}'z') &= i\left\langle \hat{\psi}^{\dagger}_{H}(\mathbf{x}z)\hat{\psi}_{H}(\mathbf{x}'z')\right\rangle, \tag{2.4}\\ G^{<}(\mathbf{x}z;\mathbf{x}'z') &= i\left\langle \hat{\psi}_{H}(\mathbf{x}'z')\hat{\psi}^{\dagger}_{H}(\mathbf{x}z)\right\rangle. \tag{2.5}\\ & \tag{2.6} \end{align}$$

Here we actually already defined the greater and lesser Green's functions, respectively. However it turns out to be convenient to combine Eqs. (2.4) and (2.5) into

$$\begin{align} G(\mathbf{x}z,\mathbf{x}'z') &= -i\left\langle \mathcal{T}_{\gamma}\left(\hat{\psi}_{H}(\mathbf{x}t)\hat{\psi}^{\dagger}_{H}(\mathbf{x}'t)\right)\right\rangle \tag{2.7}\\ &= \theta(z'-z)G^{<}(\mathbf{x}z;\mathbf{x}'z') - \theta(z-z')G^{>}(\mathbf{x}z;\mathbf{x}'z'), \notag \end{align}$$

since for this object, which we will from now on call the single-particle Green's function on the contour γ, we can derive a equation of motion (see Chapter 2.2) unlike for the two components separately.

We can, of course, plug also an arbitrary number of field operators as long as there are equally many annihilation and creation operators. This leads us to the definition of the many-particle Green's function on the contour γ.

2.1.1 n-particle Green's function

For $2n$ field operators we write the n-particle Green's function as

$$\begin{aligned}
& G_n(1\ldots n;1'\ldots n') \\
= \quad & (-i)^n \left\langle \hat{\psi}(1)\ldots\hat{\psi}(n)\hat{\psi}^\dagger(n')\ldots\hat{\psi}^\dagger(1) \right\rangle \\
\overset{(1.112)}{=} \quad & (-i)^n \frac{\mathrm{Tr}\left\{\mathcal{T}_\gamma\left(e^{-\frac{i}{\hbar}\int_\gamma \mathrm{d}z\hat{H}(\mathbf{z})}\hat{\psi}(1)\ldots\hat{\psi}(n)\hat{\psi}^\dagger(n')\ldots\hat{\psi}^\dagger(1')\right)\right\}}{\mathrm{Tr}\left\{e^{-\frac{i}{\hbar}\int_\gamma \mathrm{d}z\hat{H}(\mathbf{z})}\right\}} \\
\overset{(1.121)}{=} \quad & (-i)^n \mathrm{Tr}\left\{\hat{\rho}\mathcal{T}_\gamma\left(\hat{\psi}_H(1)\ldots\hat{\psi}_H(n)\hat{\psi}_H^\dagger(n')\ldots\hat{\psi}_H^\dagger(1')\right)\right\},
\end{aligned} \tag{2.8}$$

where we used the short-hand notation given in Eq. (1.128). Moreover, we wrote

$$\hat{\rho} = \frac{\hat{U}(z_f,z_i)}{\mathrm{Tr}\left\{e^{-\beta\hat{H}_{eq}}\right\}} = \frac{e^{-\beta\hat{H}_{eq}}}{\mathrm{Tr}\left\{e^{-\beta\hat{H}_{eq}}\right\}}. \tag{2.9}$$

For a non-interacting system, the n-particle Green's function becomes

$$\begin{aligned}
G_{0,n}(1\ldots n;1'\ldots n') &= (-i)^n \mathrm{Tr}\left\{\hat{\rho}_0\mathcal{T}_\gamma\left(\hat{\psi}_H(1)\ldots\hat{\psi}_H(n)\hat{\psi}_H^\dagger(n')\ldots\hat{\psi}_H^\dagger(1')\right)\right\} \\
&= (-i)^n \left\langle \mathcal{T}_\gamma\left(\hat{\psi}_H(1)\ldots\hat{\psi}_H(n)\hat{\psi}_H^\dagger(n')\ldots\hat{\psi}_H^\dagger(1')\right)\right\rangle_0 ,
\end{aligned} \tag{2.10}$$

where $\hat{\rho}_0$ is the same as in (1.124). Next we will consider the equations of motion for Green's functions.

2.2 Equations of motion for Green's functions

The equations of motion for single-particle Green's function on contour are easy to deduce once we know the equations of motion for field operators on this contour (1.116), (1.117), and the derivative of the step function. We start by taking the time derivative from the single-particle Green's function defined in (2.7)

$$\begin{aligned}
\partial_z G(\mathbf{x}z,\mathbf{x}'z') &= -i\partial_z \left\langle \mathcal{T}(\hat{\psi}_H(\mathbf{x}z)\hat{\psi}_H^\dagger(\mathbf{x}'z'))\right\rangle \\
&= -i\partial_z \left[\theta(z-z')\left\langle\hat{\psi}_H(\mathbf{x}z)\hat{\psi}_H^\dagger(\mathbf{x}'z')\right\rangle - \theta(z'-z)\left\langle\hat{\psi}_H^\dagger(\mathbf{x}'z')\hat{\psi}_H(\mathbf{x}z)\right\rangle\right] \\
&= -i\Big[\delta(z-z')\left\langle\hat{\psi}_H(\mathbf{x}z)\hat{\psi}_H^\dagger(\mathbf{x}'z')\right\rangle + \theta(z-z')\left\langle\partial_z\hat{\psi}_H(\mathbf{x}z)\hat{\psi}_H^\dagger(\mathbf{x}'z')\right\rangle \\
&\quad +\delta(z'-z)\left\langle\hat{\psi}_H^\dagger(\mathbf{x}'z')\hat{\psi}_H(\mathbf{x}z)\right\rangle - \theta(z'-z)\left\langle\hat{\psi}_H^\dagger(\mathbf{x}'z')\partial_z\hat{\psi}_H(\mathbf{x}z)\right\rangle\Big]. \qquad (2.11)
\end{aligned} \tag{2.12}$$

Here we used the well known relation

$$\partial_z\theta(z-z') = \delta(z-z'). \tag{2.13}$$

We use the equation of motion in Eq. (1.116) for a field operator to proceed as

$$
\begin{aligned}
& i\partial_z G(\mathbf{x}z,\mathbf{x}'z') \\
= \;& \delta(z-z')\left\langle \hat{\psi}_H(\mathbf{x}z)\hat{\psi}^\dagger_H(\mathbf{x}'z')\right\rangle - \theta(z-z')\frac{i}{\hbar}\Big\langle\Big(\hat{h}(\mathbf{r}z)\hat{\psi}_H(\mathbf{x}z) \\
& + \int \mathrm{d}\mathbf{x}''\ V(\mathbf{r},\mathbf{r}'')\hat{\psi}^\dagger_H(\mathbf{x}''z)\hat{\psi}_H(\mathbf{x}''z)\hat{\psi}_H(\mathbf{x}z)\Big)\hat{\psi}^\dagger_H(\mathbf{x}'z')\Big\rangle \\
& + \delta(z'-z)\left\langle \hat{\psi}^\dagger_H(\mathbf{x}'z')\hat{\psi}_H(\mathbf{x}z)\right\rangle + \theta(z'-z)\frac{i}{\hbar}\Big\langle\hat{\psi}^\dagger_H(\mathbf{x}'z')\Big(\hat{h}(\mathbf{r}z)\hat{\psi}_H(\mathbf{x}z) \\
& + \int \mathrm{d}\mathbf{x}''\ V(\mathbf{r},\mathbf{r}'')\hat{\psi}^\dagger_H(\mathbf{x}''z)\hat{\psi}_H(\mathbf{x}''z)\hat{\psi}_H(\mathbf{x}z)\Big)\Big\rangle \\
= \;& \delta(z-z')\delta(\mathbf{x}-\mathbf{x}') - \frac{i}{\hbar}\hat{h}(\mathbf{r}z)\Big\langle\mathcal{T}_\gamma\left(\hat{\psi}_H(\mathbf{x}z)\hat{\psi}^\dagger_H(\mathbf{x}'z')\right)\Big\rangle \\
& + \frac{i}{\hbar}\int \mathrm{d}\mathbf{x}''\mathrm{d}\mathbf{z}''\ \delta(z''-z^+)V(\mathbf{r},\mathbf{r}'')\Big[\theta(z'-z)\Big\langle\hat{\psi}^\dagger_H(\mathbf{x}'z')\hat{\psi}^\dagger_H(\mathbf{x}''z'')\hat{\psi}_H(\mathbf{x}''z'')\hat{\psi}_H(\mathbf{x}z)\Big\rangle \\
& - \theta(z-z')\Big\langle\hat{\psi}^\dagger_H(\mathbf{x}''z'')\hat{\psi}_H(\mathbf{x}''z'')\hat{\psi}_H(\mathbf{x}z)\hat{\psi}^\dagger_H(\mathbf{x}'z')\Big\rangle\Big] \\
= \;& \delta(z-z')\delta(\mathbf{x}-\mathbf{x}') + \frac{1}{\hbar}\hat{h}(\mathbf{r}z)G(\mathbf{x}z;\mathbf{x}'z') \\
& - \frac{i}{\hbar}\int \mathrm{d}\mathbf{x}''\mathrm{d}\mathbf{z}''\ v(\mathbf{r}^+,\mathbf{r}'')G(\mathbf{x}z,\mathbf{x}''z'';\mathbf{x}'z',\mathbf{x}''z''^+), \qquad (2.14)
\end{aligned}
$$

where we used the definition of the two-particle Green's function given in Eq. (2.8) and the anticommutation relation of equal time field operators. moreover, we wrote $\delta(z''-z^+)V(\mathbf{r},\mathbf{r}'') = v(\mathbf{r}^+,\mathbf{r}'')$. With a similar calculation we obtain a result for the time derivative w.r.t the latter time-coordinate as well. The equations then become

$$
\begin{aligned}
& \left[i\hbar\partial_z - \hat{h}(\mathbf{r}z)\right] G(\mathbf{x}z,\mathbf{x}'z') \\
= \;& \hbar\delta(z-z')\delta(\mathbf{x}-\mathbf{x}') - i\int \mathrm{d}\mathbf{x}''\mathrm{d}\mathbf{z}''\ v(\mathbf{r}^+,\mathbf{r}'')G(\mathbf{x}z,\mathbf{x}''z'';\mathbf{x}'z',\mathbf{x}''z''^+), \qquad (2.15) \\
& \left[-i\hbar\partial_{z'} - \hat{h}(\mathbf{r}'z')\right] G(\mathbf{x}z,\mathbf{x}'z') \\
= \;& \hbar\delta(z-z')\delta(\mathbf{x}-\mathbf{x}') - i\int \mathrm{d}\mathbf{x}''\mathrm{d}\mathbf{z}''\ v(\mathbf{r},\mathbf{r}''^+)G(\mathbf{x}z,\mathbf{x}''z'';\mathbf{x}'z',\mathbf{x}''z''^+). \qquad (2.16)
\end{aligned}
$$

We notice that the single-particle and two particle Green's functions are connected. This will turn out to be very useful. The remaining task is to determine the equations of motion for the n-particle Green's function.

2.2.1 Equations of motion for n-particle Green's function on temperature contour

The equations of motion for the n-particle Green's function on the temperature contour γ, the so-called Martin-Schwinger hierarchy Eqs. [6], read

$$
\begin{aligned}
& \left[i\hbar\partial_{z_k} - (\hat{h}(k) - \mu\theta_\beta(z_k))\right] G_n(1\ldots n;1'\ldots n) \\
= \;& \sum_{j=1'}^{n'}(-1)^{k+j}\hbar\delta(k,j')G_{n-1}(1\ldots \overset{\sqcap}{k}\ldots n;1'\ldots \overset{\sqcap}{j'}\ldots n') \\
& - i\int \mathrm{d}(n+1)v(k^+,n+1)G_{n+1}(1\ldots n+1;1'\ldots n'\ n+1^+),
\end{aligned}
\qquad (2.17)
$$

$$\begin{aligned}
&\left[-i\hbar\partial_{z'_k} - (\hat{h}(k') - \mu\theta_\beta(z'_k))\right] G_n(1\dots n; 1'\dots n) \\
= \;& \sum_{j=1'}^{n'} (-1)^{k+j}\hbar\delta(j,k') G_{n-1}(1\dots \overset{\sqcap}{j} \dots n; 1'\dots \overset{\sqcap}{k'} \dots n') \\
&-i\int \mathrm{d}(n+1) v(k', n+1^+) G_{n+1}(1\dots n+1; 1'\dots n'\; n+1),
\end{aligned} \tag{2.18}$$

where we use the short notations defined in Eqs. (1.128) to (1.130), the contour step function Eq. (1.109), and

$$\begin{aligned}
\delta(k,j) &= \delta(\mathbf{x}_k - \mathbf{x}_j)\delta(z_k, z_j) \\
(1\dots \overset{\sqcap}{j} \dots n) &= (1\dots j-1\; j+1\dots n).
\end{aligned} \tag{2.19}$$

Here as before we see that the n-particle Green's function is connected to the $n+1$ and $n-1$ particle Green's functions. These will be useful when developing perturbation theory for Green's function. By these equations we will prove the so-called Wick's theorem.

2.3 Perturbative expansion

Let us write the Hamiltonian in the form

$$\hat{H}'_\lambda(z) = \hat{H}(z) + \hat{V}. \tag{2.20}$$

We write the one-particle Green's function as

$$G(\mathbf{x}z, \mathbf{x}'z') = -i\left\langle \mathcal{T}_\gamma\left(\hat{\psi}(\mathbf{x}z)\hat{\psi}^\dagger(\mathbf{x}'z')\right)\right\rangle \tag{2.21}$$

We use the already introduced expansion (1.133) for Eq. (2.21). Now we may compare the expressions under integration to the many-particle non-interacting Green's function in Eq. (2.10)

$$-\,i\left\langle \mathcal{T}_\gamma\left(\hat{\psi}_H(\mathbf{x}z)\hat{\psi}_H(1')\hat{\psi}_H(1)\dots\hat{\psi}_H(k')\hat{\psi}_H(k)\hat{\psi}^\dagger_H(k'^+)\hat{\psi}^\dagger_H(k'')\dots\hat{\psi}^\dagger_H(1'^+)\hat{\psi}^\dagger_H(1'')\hat{\psi}^\dagger_H(\mathbf{x}'z')\right)\right\rangle_0$$

$$G_{n,0}(1\dots n; 1'\dots n') = (-i)^n\left\langle \hat{\psi}_H(1)\dots\hat{\psi}_H(n)\hat{\psi}_H(n')\dots\hat{\psi}_H(1')\right\rangle_0,$$

from which we see that

$$\begin{aligned}
&-i\left\langle \mathcal{T}_\gamma\left(\hat{\psi}_H(\mathbf{x}z)\hat{\psi}_H(1')\hat{\psi}_H(1)\dots\hat{\psi}_H(k')\hat{\psi}_H(k)\hat{\psi}^\dagger_H(k'^+)\hat{\psi}^\dagger_H(k'')\dots\hat{\psi}^\dagger_H(1'^+)\hat{\psi}^\dagger_H(1'')\hat{\psi}^\dagger_H(\mathbf{x}'z')\right)\right\rangle_0 \\
= \;& \underbrace{(-i)(-i)^{2k+1}}_{=(-1)^k} G_{2k+1,0}(\mathbf{x}z, 1, 1', \dots, k, k'; \mathbf{x}'z', 1'', 1'^+, \dots, k'', k'^+).
\end{aligned} \tag{2.22}$$

We deduce that the numerator of (1.133) for $\hat{A}(z) = -i\mathcal{T}(\hat{\psi}(\mathbf{x}z)\hat{\psi}^\dagger(\mathbf{x}'z'))$ becomes

$$\begin{aligned}
= \;& \sum_{k=0}^{\infty}\frac{1}{k!}\left(\frac{i}{2\hbar}\right)^k \int_\gamma \mathrm{d}1\dots\int_\gamma \mathrm{d}k \int_\gamma \mathrm{d}1'\dots\int_\gamma \mathrm{d}k'\; v(1^+,1')\dots v(k^+,k') \\
\times \;& G_{2k+1,0}(\mathbf{x}z, 1, 1', \dots, k, k'; \mathbf{x}'z', 1'', 1'^+, \dots, k'', k'^+).
\end{aligned} \tag{2.23}$$

We may perform a similar derivation on the denominator and obtain a solution for the single-particle Green's function in terms of non-interacting many-particle Green's functions

$$\begin{aligned}
&G(\mathbf{x}t, \mathbf{x}'t') \\
= \;& \frac{\sum_{k=0}^{\infty}\frac{1}{k!}\left(\frac{i}{2\hbar}\right)^k \int_\gamma \mathrm{d}1\mathrm{d}1'\dots\mathrm{d}k\mathrm{d}k'\; v_{11'}\dots v_{kk'} G_{2k+1,0}(\mathbf{x}z, 1, 1', \dots, k, k'; \mathbf{x}'z', 1'', 1'^+, \dots, k'', k'^+)}{\sum_{k=0}^{\infty}\frac{1}{k!}\left(\frac{i}{2\hbar}\right)^k \int_\gamma \mathrm{d}1\mathrm{d}1'\dots\mathrm{d}k\mathrm{d}k'\; v_{11'}\dots v_{kk'} G_{2k,0}(1, 1', \dots, k, k'; 1'', 1'^+, \dots, k'', k'^+)},
\end{aligned} \tag{2.24}$$

where we further introduced the short notation $v(j^+, j') = v_{jj'}$. We will proceed to derive an expression for the non-interacting many-particle Green's function in terms of non interacting single-particle Green's functions. The result is called Wick's theorem and it is essential the perturbation theory.

2.3.1 Wick's theorem

From the Martin-Schwinger hierarchy equations on contour, Eqs. (2.17) and (2.18), we may deduce that for a non-interacting system the equations of motion for n-particle Green's function become

$$\begin{aligned} & \left[i\hbar\partial_{z_k} - (\hat{h}(k) - \mu\theta_\beta(z_k))\right] G_{n,0}(1\ldots n; 1'\ldots n) \\ = & \sum_{j=1'}^{n'} (-1)^{k+j} \hbar\delta(k, j') G_{n-1,0}(1\ldots \overset{\sqcap}{k} \ldots n; 1' \ldots \overset{\sqcap}{j'} \ldots n'), \end{aligned} \tag{2.25}$$

$$\begin{aligned} & \left[-i\hbar\partial_{z'_k} - (\hat{h}(k') - \mu\theta_\beta(z'_k))\right] G_{n,0}(1\ldots n; 1'\ldots n) \\ = & \sum_{j=1'}^{n'} (-1)^{k+j} \hbar\delta(j, k') G_{n-1,0}(1\ldots \overset{\sqcap}{j} \ldots n; 1' \ldots \overset{\sqcap}{k'} \ldots n'). \end{aligned} \tag{2.26}$$

For the single-particle non-interacting Green's function the similar expressions are

$$\left[i\hbar\partial_{z_1} - (\hat{h}(1) - \mu\theta_\beta(z_1))\right] G_0(1, 1') = \hbar\delta(1, 1') \tag{2.27}$$

$$\left[-i\hbar\partial_{z_2} - (\hat{h}(2) - \mu\theta_\beta(z_2))\right] G_0(1, 1') = \hbar\delta(1, 1'). \tag{2.28}$$

Now we notice the connection with the expansion of a determinant in Eqs. (2.25) and (2.26). If we consider $G_{n-1,0}(1\ldots k-1\ k+1\ldots n; 1'\ldots j'-1\ j'+1\ldots n')$ in (2.25) as a sub-determinant we may check if the solution is of the form

$$G_{n,0}(1\ldots n; 1'\ldots n') = \begin{vmatrix} G_0(1,1') & \ldots & G_0(1,n') \\ \vdots & & \vdots \\ G_0(n,1') & \ldots & G_0(n,n') \end{vmatrix} \tag{2.29}$$

This is indeed the case and it can be quickly checked, by expanding the determinant into n sub determinants and operating by $(i\hbar\partial_{z_k} - (\hat{h}(k) - \mu\theta_\beta(z_k)))$ from the left, leading to

$$\begin{aligned} & G_{n,0}(1\ldots n; 1'\ldots n') \\ = & \sum_{j=1}^{n} (-1)^{k+j} G_0(k, j') G_{n-1,0}(1\ldots \overset{\sqcap}{k} \ldots n; 1' \ldots \overset{\sqcap}{j'} \ldots n') \\ \Rightarrow & \left[i\hbar\partial_{z_k} - (\hat{h}(k) - \mu\theta_\beta(z_k))\right] G_{n,0}(1\ldots n; 1'\ldots n') \\ = & \hbar \sum_{j=1}^{n} (-1)^{k+j} \delta(k, j') G_{n-1,0}(1\ldots \overset{\sqcap}{k} \ldots n; 1' \ldots \overset{\sqcap}{j'} \ldots n'), \end{aligned} \tag{2.30}$$

which agrees exactly with Eq. (2.25). Operating by $\left[-i\hbar\partial_{z'_k} - (\hat{h}(k') - \mu\theta_\beta(z'_k))\right]$ on (2.29) we obtain (2.26) as we should. Thus we conclude that the non-interacting many-particle Green's function can be written in terms of non-interacting single-particle Green's functions as

$$G_{n,0}(1\ldots n; 1'\ldots n') = \sum_\sigma (-1)^\sigma G_0(1, \sigma(1'))\ldots G_0(n, \sigma(n')) \tag{2.31}$$

2.3.2 Diagrammatics

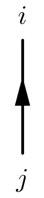
With the aid of Wick's theorem [Eqs. (2.29) and (2.31)] the perturbative expansion for the single-particle Green's function (2.24) can finally be written as

$$G(\mathbf{x}t,\mathbf{x}'t') = \frac{\sum_{k=0}^{\infty}\frac{1}{k!}\left(\frac{i}{2\hbar}\right)^k\int_\gamma \mathrm{d}1\mathrm{d}1'\ldots\mathrm{d}k\mathrm{d}k'\; v_{11'}\ldots v_{kk'}\begin{vmatrix} G_0(\mathbf{x}z,\mathbf{x}'z') & G_0(\mathbf{x}z,1'') & \ldots & G_0(\mathbf{x}z,k'^{+}) \\ G_0(1,\mathbf{x}'z') & G_0(1,1'') & \ldots & G_0(1,k'^{+}) \\ \vdots & & & \vdots \\ G_0(k',\mathbf{x}'z') & G_0(k',1'') & \ldots & G_0(k',k'^{+}) \end{vmatrix}}{\sum_{k=0}^{\infty}\frac{1}{k!}\left(\frac{i}{2\hbar}\right)^k\int_\gamma \mathrm{d}1\mathrm{d}1'\ldots\mathrm{d}k\mathrm{d}k'\; v_{11'}\ldots v_{kk'}\begin{vmatrix} G_0(1,1'') & G_0(1,1'^{+}) & \ldots & G_0(1,k'^{+}) \\ G_0(1',1'') & G_0(1',1'^{+}) & \ldots & G_0(1',k'^{+}) \\ \vdots & & & \vdots \\ G_0(k',1'') & G_0(k',1'^{+}) & \ldots & G_0(k',k'^{+}) \end{vmatrix}}. \tag{2.32}$$

We have now completely defined the expansion for the interacting single-particle Green's function. However, the formula (2.32) is somewhat horrendous to deal with. Hence we further introduce the celebrated Feynman diagrams [10] by which the task of calculating $G(\mathbf{x}t,\mathbf{x}'t')$ is greatly reduced.

The pictorial representation for Eq. (2.32) may be written immediately as one defines

$G_0(i,j) \quad =$



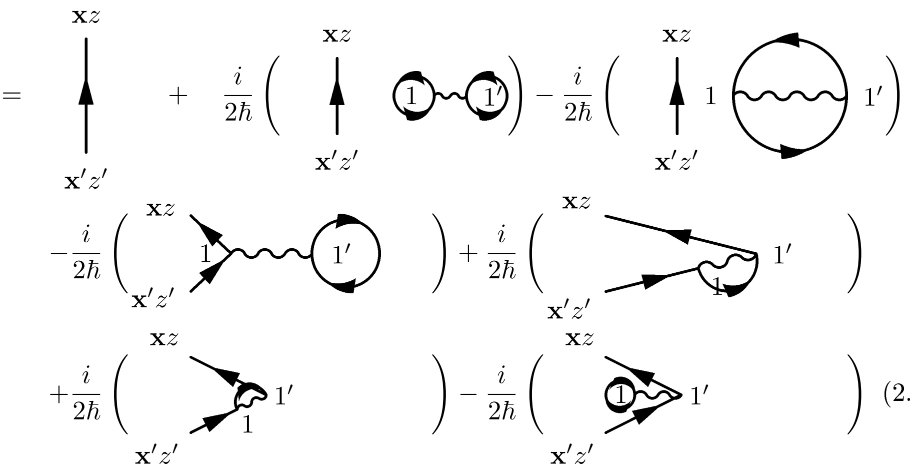
$v_{ij} \quad =$

(2.33)

Note that here we let time flow from bottom to top. Now any term in the numerator/denominator of (2.32) may be written pictorially if we demand that there is an integration over every vertex.

For example, in the numerator there are the first-order terms

$$
\begin{aligned}
G(\mathbf{x}t,\mathbf{x}'t') &\approx G_0(\mathbf{x}z,\mathbf{x}'z') + \frac{i}{2\hbar}\int_\gamma \mathrm{d}1\mathrm{d}1'\; v_{11'} \begin{vmatrix} G_0(\mathbf{x}z,\mathbf{x}'z') & G_0(\mathbf{x}z,1'') & G_0(\mathbf{x}z,1'^{+}) \\ G_0(1,\mathbf{x}'z') & G_0(1,1'') & G_0(1,1'^{+}) \\ G_0(1',\mathbf{x}'z') & G_0(1',1'') & G_0(1',1'^{+}) \end{vmatrix} \\
&= G_0(\mathbf{x}z,\mathbf{x}'z') + \frac{i}{2\hbar}G_0(\mathbf{x}z,\mathbf{x}'z')\int_\gamma \mathrm{d}1\mathrm{d}1'\; v_{11'} \begin{vmatrix} G_0(1,1'') & G_0(1,1'^{+}) \\ G_0(1',1'') & G_0(1',1'^{+}) \end{vmatrix} \\
&\quad -\frac{i}{2\hbar}\int_\gamma \mathrm{d}1\mathrm{d}1'\; v_{11'}G_0(\mathbf{x}z,1'') \begin{vmatrix} G_0(1,\mathbf{x}'z') & G_0(1,1'^{+}) \\ G_0(1',\mathbf{x}'z') & G_0(1',1'^{+}) \end{vmatrix} \\
&\quad +\frac{i}{2\hbar}\int_\gamma \mathrm{d}1\mathrm{d}1'\; v_{11'}G_0(\mathbf{x}z,1'^{+}) \begin{vmatrix} G_0(1,\mathbf{x}'z') & G_0(1,1'') \\ G_0(1',\mathbf{x}'z') & G_0(1',1'') \end{vmatrix}
\end{aligned}
$$



(2.34)

(2.35)

As before time is taken to run from bottom to top. Thus all the interaction vertices are horizontal and for the Green's functions containing the same beginning and endpoint we have to see from the equal time limit in which direction the loop is to be closed.

Similar expansion may be done for the denominator of (2.32). It turns out that the denominator contains only closed and connected diagrams. By closed and connected we mean that every part of the diagram is connected to the rest by an interaction or Green's function line, and that there are no "loose" lines hanging around as above in the last four diagrams.

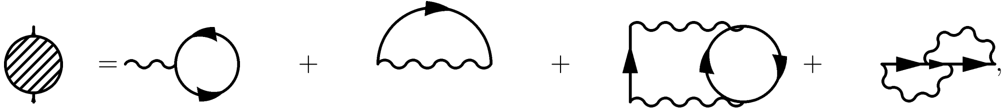
One can prove that all the disconnected diagrams in the numerator are exactly canceled by the denominator in Eq. (2.32), see [9]. Moreover, considering the topology of the diagrams it becomes clear that all topologically equivalent diagrams attain the same numerical value, since one can always rename the interaction variables to attain similar figures from diagrams with the same topology [9]. It is thus sufficient to consider only all connected and topologically inequivalent diagrams. The factor due to topologically equivalent diagrams turns out to be $2^k k!$, where k is the number of interaction lines, i.e., the order of the diagram. With these results Eq. (2.32) may be written as

$$G(\mathbf{x}t,\mathbf{x}'t')$$

$$= \sum_{k=0}^{\infty}\left(\frac{i}{\hbar}\right)^{k}\int_{\gamma}\mathrm{d}1\mathrm{d}1'\ldots\mathrm{d}k\mathrm{d}k'\; v_{11'}\ldots v_{kk'}\left.\begin{vmatrix} G_0(\mathbf{x}z,\mathbf{x}'z') & G_0(\mathbf{x}z,1'') & \ldots & G_0(\mathbf{x}z,k'^{+}) \\ G_0(1,\mathbf{x}'z') & G_0(1,1'') & \ldots & G_0(1,k'^{+}) \\ \vdots & & & \vdots \\ G_0(k',\mathbf{x}'z') & G_0(k',1'') & \ldots & G_0(k',k'^{+}) \end{vmatrix}\right|_{\substack{\text{conn.}\\ \text{top. inequiv.}}} . \tag{2.36}$$

Self-energy

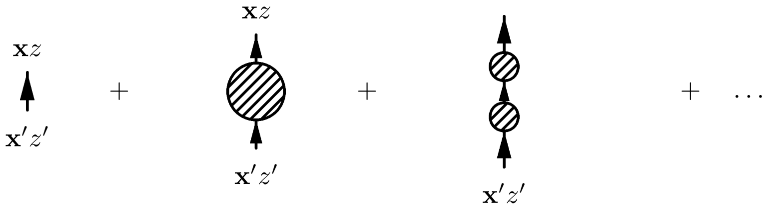
One can reduce the amount of diagrams to be calculated even further by introducing the concept of self-energy. As we start to expand Eq. (2.36) one quickly notices that there is class of "sub-diagrams" in every order that seem to appear in the same form in higher order diagrams as well. We call these diagrams irreducible diagrams, since they are defined by the property that one cannot cut such a diagram into two pieces by cutting a single Green's function line. In the second order these irreducible diagrams become



(2.37)

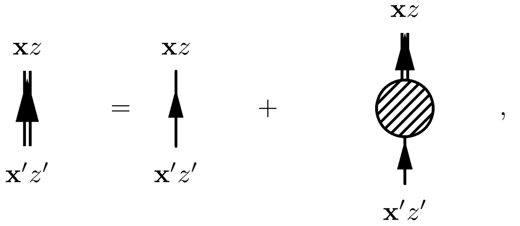
where we already gave the symbol "shaded blob" to the collection to these diagrams. It turns out that one can get great a reduction in the number of diagrams if one considers these self-energy diagrams. The Green's function may be written, with the aid of all self-energy diagrams, as

$G(\mathbf{x}z,\mathbf{x}'z') =$



(2.38)

or equivalently



(2.39)

where we see that a repeated insertion of the left-hand side to the right-hand side in Eq. (2.39) generates Eq. (2.38). The equation in Eq. (2.39) is called the Dyson equation [4] and it can be written explicitly as

$$G(\mathbf{x}z,\mathbf{x}'z') = G_0(\mathbf{x}z,\mathbf{x}'z') + \int_{\gamma}\mathrm{d}1\mathrm{d}1' G_0(\mathbf{x}z,1)\;\Sigma(1,1')G(1',\mathbf{x}'z'), \tag{2.40}$$

where $\Sigma(1,1')$ contains all irreducible diagrams. Note that this equation should be solved self-consistently, i.e., we first put some approximation for the Green's function into the equation and after solving for the Green's function we put these solutions back into the Dyson equation. This is done as long as the Green's function converges. Since we are working most of the time in general bases we need the form of Dyson Eq. (2.40) in general bases. This is derived in Appendix A.6.

Physically the self-energy describes the energy arising from the interactions between the system and the particle under consideration [7]. For example, when one brings a particle in to the system it starts to interact with the other particles in the system. These interactions then modify the system and the modified system interacts back to the particle. The self-energy modifies the ”single-particle” energy in such a way that it then contains also the effect of the particle-system interactions. The self-energy thus contains all the information about the interactions in the system; this is already seen in the diagrammatic structure, since all the interaction lines are included in the self-energy diagrams.

It should now be plausible that one can do perturbation theory of the Green’s function by drawing diagrams and calculating the resulting integrals. We only need to have proper rules by which we construct the mathematical description of each diagram. The rules can be deduced for example from Eq. (2.36) by drawing the diagrams and observing the corresponding term in the expansion.

Similarly for the self-energy one can deduce diagrammatic rules and then by using Dyson equation we again attain the Green’s function. The diagrammatic rules are called Feynman rules and they are a handy tool when expanding Green’s functions. Before introducing the Feynman rules we will make some remarks about the systems that we are going to study in order to reduce the complexity even more.

2.3.3 Zero-temperature formalism

We have now a powerful machinery to solve the Green’s function on the Keldysh contour γ. In the discussions to come we however have $T = 0$, i.e., we are working at the zero temperature limit. We would now like to see how the Green’s functions and self-energies transform as we take the limit $T \to 0$.

The expectation value of any operator is written in (1.112). Assume that the energy levels are non-degenerate. Then we may write (1.112) as

$$\left\langle \hat{A} \right\rangle (t) = \frac{\mathrm{Tr}\left\{ \mathcal{T}_\gamma \left(e^{-\beta \hat{H}_{eq}} \hat{A}_H(t) \right) \right\}}{\mathrm{Tr}\left\{ e^{-\beta \hat{H}_{eq}} \right\}} = \frac{\sum_k e^{-\beta(E_k - \mu N_k)} \langle \psi_k | \hat{A}_H(t) | \psi_k \rangle}{\sum_k e^{-\beta(E_k - \mu N_k)}}. \tag{2.41}$$

Let us then define μ such that $E_0 < \mu < E_1 < E_2 < \ldots$, moreover, $N_k \in \{0, 1\}$ and for zero temperature we definitely have the ground state occupied. Then as $\beta \to \infty$ we see in the denominator of Eq. (2.41) that

$$\sum_k e^{-\beta(E_k - \mu N_k)} = e^{-\beta(E_0 - \mu)} + \sum_{k=1} e^{-\beta(\overbrace{E_k - \mu N_k}^{>0})} \overset{\beta \to \infty}{\to} e^{\beta |E_0 - \mu|}. \tag{2.42}$$

Now we see that to obtain a non-zero expectation value, the only term that survives from the sum in the nominator of Eq. (2.41) is

$$\left\langle \hat{A} \right\rangle (t) \to \frac{e^{\beta|E_0 - \mu|}}{e^{\beta|E_0 - \mu|}} \langle \psi_0 | \hat{A}_H(t) | \psi_0 \rangle + \frac{\sum_{k=1} \overbrace{e^{-\beta(E_k - \mu N_k)}}^{\to 0} \langle \psi_k | \hat{A}_H(t) | \psi_k \rangle}{\underbrace{e^{\beta|E_0 - \mu|}}_{\to \infty}} = \langle \psi_0 | \hat{A}_H(t) | \psi_0 \rangle. \tag{2.43}$$

Thus, for example, the Green’s function in zero temperature attains the form

$$G_{0,n}(1 \ldots n; 1' \ldots n') = (-i)^n \langle \psi_0 | \hat{\psi}(1) \ldots \hat{\psi}(n) \hat{\psi}^\dagger(n') \ldots \hat{\psi}^\dagger(1) | \psi_0 \rangle. \tag{2.44}$$

To obtain the zero-temperature limit the changes to be made in our formalism introduced are just to replace all Green’s functions with these zero-temperature Green’s functions. We will work with in the zero-temperature limit from now on.

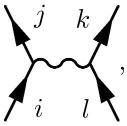
2.3.4 Frequency space

Another simplification that we can make, again knowing what is ahead, is to Fourier transform our equations. This can easily be carried out for time independent Hamiltonians. We notice that for the time-independent Hamiltonian all the equations are only functions of $t - t'$. We denote this difference by τ and perform the Fourier transform [2]. One can find the Fourier transforms of the single-particle non-interacting Green's function and the Green's function in tight-bindin chain respectively in Appendices A.4.1 and A.4.2.

One can do the derivations for frequency space as well [4], and actually this does not even turn out to be too difficult. However, to save space I will just give the Feynman rules in frequency space to be used as a tool to calculate different properties of our systems through the self-energy diagrams.

Feynman rules in frequency space

The Feynman rules in general bases and in zero-temperature frequency space for self-energy Σ are listed in the following [4]

1. Draw all topologically inequivalent irreducible connected diagrams.
2. Assign indices, frequency, and direction to all Green's function lines. Conserve the frequency at each vertex and integrate and sum over all internal vertexes.
3. Multiply all diagrams with prefactor $(-1)^l(\frac{i}{\hbar})^n$, where l is the number of closed fermion loops and n is the order of diagram, i.e., the number of interaction lines.
4. When a Green's function line ($G_{ij}(\omega)$) closes itself or is closed by the same interaction line insert a factor $e^{i\omega\eta}$ ($\eta \to 0$).
5. Every non-interacting Green's function is represented by $G_{ij}(\omega) = \frac{\delta_{ij}}{\omega-(\xi_i-U_{ext})+i\mathrm{sgn}(\xi_i)\eta}$.
6. For every vertex 

, assign V_{iklj}.

2.4 Properties of Green's functions

So far we have not given any better reason for calculating the Green's function than the one that it is almost the easiest operator for which to solve the expectation value, see Sec. 2.1. However, it turns out that one can deduce many properties of the system through the Green's function, for example the total energy and many more. [4, 1].

In the following we will introduce only a couple of properties that are easily seen from the Green's function of the system.

2.4.1 Density

The particle density is probably the most obvious thing that one can immediately deduce from the Green's function. The expectation value of density at $\mathbf{x}$ may be written as $iG(\mathbf{x}z^+, \mathbf{x}z)$. We may also expand the Green's function in general bases as for example in (A.5.1). Now we may for example deduce that

$$\int \mathrm{d}\mathbf{x}\; G(\mathbf{x}z^+, \mathbf{x}z) = \sum_{k,k',\sigma} \int \mathrm{d}\mathbf{r}\; \phi_k(\mathbf{r})\phi^*_{k'}(\mathbf{r}) G_{kk'}(z^+, z') = \sum_{k,k'} \delta_{kk'} G_{kk'}(z^+, z') = N, \tag{2.45}$$

where N is the number of particles in the system.

2.4.2 Spectral function

Starting from the definition of Green's function (2.7) one can proceed as in Appendix A.4.1 and A.4.2 to obtain the Fourier transformed Green's function

$$G(\mathbf{x}, \mathbf{x}', \omega) = \sum_j \frac{g_j(\mathbf{x}) g^*_j(\mathbf{x}')}{\omega - (E^{N+1}_j - E_0) + i\eta} + \frac{f_j(\mathbf{x}) f^*_j(\mathbf{x}')}{\omega - (E^{N-1}_j - E_0) - i\eta}, \tag{2.46}$$

where $g_j(\mathbf{x}) = \langle \psi_0 | \hat{\psi}(\mathbf{x}) | \psi^{N+1}_j \rangle$ and $f_j(\mathbf{x}) = \langle \psi^{N-1}_j | \hat{\psi}(\mathbf{x}) | \psi_0 \rangle$. Now there exists μ such that

$$E_0 - E^{N-1}_s < \mu < E^{N+1}_s - E_0. \tag{2.47}$$

Define

$$\begin{aligned} \epsilon_s &= \begin{cases} E^{N+1}_s - E_0, & \epsilon_s > \mu \\ E_0 - E^{N-1}_s, & \epsilon_s < \mu \end{cases} \\ \varphi_s(\mathbf{x}) &= \begin{cases} g_s(\mathbf{x}), & \epsilon_s > \mu \\ f_s(\mathbf{x}), & \epsilon_s < \mu. \end{cases} \end{aligned} \tag{2.48}$$

Now one can write

$$\begin{aligned} G(\mathbf{x}, \mathbf{x}', \omega) &= \sum_{\substack{s \\ \epsilon_s > \mu}} \frac{\varphi_s(\mathbf{x})\varphi^*_s(\mathbf{x}')}{\omega - \epsilon_s + i\eta} + \sum_{\substack{s \\ \epsilon_s < \mu}} \frac{\varphi_s(\mathbf{x})\varphi^*_s(\mathbf{x}')}{\omega - \epsilon_s - i\eta} \\ &= \sum_s \frac{\varphi_s(\mathbf{x})\varphi^*_s(\mathbf{x}')}{\omega - \epsilon_s + i\eta\,\mathrm{sgn}(\epsilon_s - \mu)} \\ &= \int \mathrm{d}\nu\; \frac{\sum_s \delta(\nu - \epsilon_s)\varphi_s(\mathbf{x})\varphi^*_s(\mathbf{x}')}{\omega - \nu + i\eta\,\mathrm{sgn}(\nu - \mu)} \\ &= \int \mathrm{d}\nu\; \frac{A(\mathbf{x}, \mathbf{x}', \nu)}{\omega - \nu + i\eta\,\mathrm{sgn}(\nu - \mu)}, \end{aligned} \tag{2.49}$$

where we defined the spectral function

$$A(\mathbf{x}, \mathbf{x}', \nu) = \sum_s \delta(\nu - \epsilon_s)\varphi_s(\mathbf{x})\varphi^*_s(\mathbf{x}'). \tag{2.50}$$

One immediately notices that the spectral function is peaked at the addition and removal energies of the system. It could thus describe, for example, the photoelectric spectrum of the system.

Multiplying by the complex conjugate of the denominator in (2.49) we obtain

$$\int \mathrm{d}\nu\; \frac{A(\mathbf{x}, \mathbf{x}', \nu)}{\omega - \nu + i\eta\,\mathrm{sgn}(\nu - \mu)} = \mathcal{P} \int \mathrm{d}\nu\; \frac{A(\mathbf{x}, \mathbf{x}', \nu)}{\omega - \nu} - i\pi\,\mathrm{sgn}(\nu - \mu)\delta(\omega - \nu) A(\mathbf{x}, \mathbf{x}', \nu). \tag{2.51}$$

Thus we get

$$\begin{aligned} \mathrm{Im}G(\mathbf{x}, \mathbf{x}', \omega) &= -\pi\,\mathrm{sgn}(\nu - \mu)\delta(\omega - \nu) A(\mathbf{x}, \mathbf{x}', \nu) \\ &= -\pi\,\mathrm{sgn}(\nu - \mu)\delta(\omega - \nu) \sum_s \delta(\nu - \epsilon_s)\varphi_s(\mathbf{x})\varphi^*_s(\mathbf{x}') \\ &= -\pi\,\mathrm{sgn}(\omega - \mu) \sum_s \delta(\omega - \epsilon_s)\varphi_s(\mathbf{x})\varphi^*_s(\mathbf{x}') \end{aligned} \tag{2.52}$$

Comparing (2.52) with (2.50) one may deduce

$$A(\mathbf{x},\mathbf{x}',\omega) = \frac{1}{\pi}\mathrm{sgn}(\mu-\omega)\mathrm{Im}G(\mathbf{x},\mathbf{x}',\omega). \tag{2.53}$$

The considerations above may be simplified even more by introducing the retarded Green's function

$$G^R(\mathbf{x},\mathbf{x}',\omega) = \sum_s \frac{\varphi_s(\mathbf{x})\varphi_s^*(\mathbf{x}')}{\omega-\epsilon_s+i\eta}, \tag{2.54}$$

where $\varphi_s(\mathbf{x})$ and ϵ_s are as in (2.48). By similar considerations as above we find

$$A(\mathbf{x},\mathbf{x}',\omega) = -\frac{1}{\pi}\mathrm{Im}G^R(\mathbf{x},\mathbf{x}',\omega). \tag{2.55}$$

The spectral function can, as usual, be expressed in general bases. This is easily obtained by expanding the field operators in Eq. (2.50). Using the expansions Eqs. (1.33) and (1.34) we may write

$$A(\mathbf{x},\mathbf{x}',\nu) = \sum_{k,l}\phi_k(\mathbf{x})\phi_l(\mathbf{x}')\left[\sum_{s,\epsilon_s<\mu}\delta(\nu-\epsilon_s)f_{sk}f_{sl}^* + \sum_{s,\epsilon_s>\mu}\delta(\nu-\epsilon_s)g_{sk}g_{sl}^*\right], \tag{2.56}$$

from which we see

$$A_{kl}(\nu) = \sum_{s,\epsilon_s<\mu}\delta(\nu-\epsilon_s)f_{sk}f_{sl}^* + \sum_{s,\epsilon_s>\mu}\delta(\nu-\epsilon_s)g_{sk}g_{sl}^*, \tag{2.57}$$

where

$$f_{sk} = \langle\psi_s^{N-1}|\hat{a}_k|\psi_0\rangle \tag{2.58}$$
$$g_{sk} = \langle\psi_0|\hat{a}_k|\psi_s^{N+1}\rangle. \tag{2.59}$$

Expanding the retarted Green's function Eq. (2.54) similarly we immediately find in accordance with Eq. (2.55) that

$$A_{ij}(\omega) = -\frac{1}{\pi}\mathrm{Im}G_{ij}^R(\omega). \tag{2.60}$$

From Eq. (2.57) we may find a way to calculate the density at a given site. Consider Eq. (2.57), now at zero temperature so that all states up to the chemical potential are occupied. Now, integrating over ν from $-\infty$ to μ we immediately find

$$\int_{-\infty}^{\mu}\mathrm{d}\nu\ A_{ii}(\nu) = \sum_s f_{si}f_{si}^* = \sum_s\langle\psi_0|\hat{a}_i^\dagger|\psi_s^{N-1}\rangle\langle\psi_s^{N-1}|\hat{a}_i|\psi_0\rangle = \langle\psi_0|\hat{n}_i|\psi_0\rangle = n_i. \tag{2.61}$$

Hence, at zero temperature one may find the density at a given site from the spectral function at that given site.

Chapter 3

Applications

The presented Green's function methods are applied to two systems. Both systems consisted of a two-level system (="molecule") coupled to the first site of infinite tight-binding chain introduced in Appendix A.3. The Hamiltonians have different interactions and hoppings between the two-level system and the chain. For now on we will put $\hbar = 1$.

In both cases we are mainly interested in the spectral functions (chapter 2.4.2) at the molecule and we are deducing properties out of these spectral functions. We also calculate the self energies (chapter 2.3.2) for these two levels. In the end we try to deduce the features of the Hamiltonian that are responsible for the particular behavior.

The first of the models is treated with perturbation theory (Chapter 2.3) and we study the effects of different Feynman diagrams on the energy levels and image-charge effect as well as the self-energies and the spectral functions. The system is quite similar to the one introduced in [11] with the difference that we do not have hoppings between the molecule and the lead.

The latter of the models is the famous Fano model, now with two levels coupled to the first site of the chain. As in the usual Fano model we do not have any two-body interactions and hence we are able to solve the model exactly. In the following we will present and treat both systems separately.

3.1 Interacting model

Our aim in this chapter is to introduce a model used to describe some simple (=two-level) molecule next to an infinite tight-binding chain. We use the perturbation theory method to find out the approximate self-energy for the system. With this self-energy we calculate the approximate Green's function and further the approximate spectral peaks for the molecular energy levels. In the end we also compare results of the different approximations for the spectral peak shift to an exact shift calculated by the Hellman-Feynman theorem [10].

Schematically the system can be presented as in Fig. 3.1.

As mentioned above the Hamiltonian for this model is similar to the one introduced in [11]. We write the Hamiltonian as

$$\hat{H} = \hat{H}_{\mathrm{TB}} + \hat{H}_{\mathrm{MOL}} + \hat{U}_{\mathrm{MOL}} + \hat{V}, \tag{3.1}$$

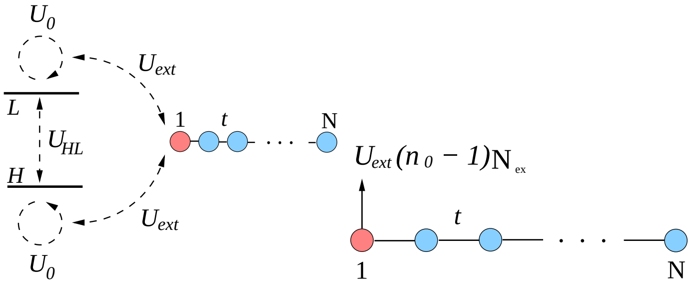


Figure 3.1: Left: Molecule and chain system schematically. Right: Bare chain system

where

$$\begin{aligned}\hat{H}_{TB} &= t\sum_{\langle i,j\rangle}\hat{a}_i^\dagger\hat{a}_j\\ \hat{H}_{\mathrm{MOL}} &= \hat{n}_H\xi_H+\hat{n}_L\xi_L\\ \hat{U}_{\mathrm{MOL}} &= U_0(\hat{n}_{H\uparrow}\hat{n}_{H\downarrow}+\hat{n}_{L\uparrow}\hat{n}_{L\downarrow})+U_{HL}\hat{n}_H\hat{n}_L\\ \hat{V} &= U_{ext}(\hat{n}_1-1)(\hat{N}-2).\end{aligned}\tag{3.2}$$

Here the operators $\hat{a}_i^\dagger$ ($\hat{a}_i$) create (annihilate) electrons to the i:th site of the chain; note that i is a double index $i=(i,\sigma)$ corresponding to site and spin. The density operators $\hat{n}_{H/L}$ in $\hat{H}_{\mathrm{MOL}}$ (and elsewhere) are defined as $\hat{n}_{H/L}=\hat{n}_{H/L\uparrow}+\hat{n}_{H/L\downarrow}=\hat{a}_{H/L\uparrow}^\dagger\hat{a}_{H/L\uparrow}+\hat{a}_{H/L\downarrow}^\dagger\hat{a}_{H/L\downarrow}$, where $\hat{a}_H$ refers to the HOMO (highest occupied molecular orbital) site of the two-level system and $\hat{a}_L^\dagger$ refers to LUMO (lowest unoccupied molecular orbital). For $\hat{U}_{\mathrm{MOL}}$ we have two terms corresponding to the repulsion between electrons at the same site (U_0) and between the levels (U_{HL}). Finally the interaction between the TB chain and the molecule is introduced in $\hat{V}$ with the strength U_{EXT}. The $\hat{n}_1-1$ and $\hat{N}-2$ represent the excess charge on the terminal site of the chain and on the molecule, respectively, $\hat{N}$ being $\hat{n}_H+\hat{n}_L$.

In the limit $N\to\infty$ the Hamiltonian in Eq. (3.1) cannot be solved exactly which leads to a treatment in Feynman diagrams. To use the Feynman diagram methods we need the components of the Green's function in the chain and the molecule. They are derived in A.4; note that we are working in the frequency space in order to have an easy access to the energies of the system. Moreover, to have a clear picture of the situation we have to rearrange the terms in Hamiltonian in Eq. (3.1) to obtain

$$\begin{aligned}\hat{H} &= t\sum_{\langle i,j\rangle}\hat{a}_i^\dagger\hat{a}_j+(\hat{n}_H-U_{ext})\xi_H+(\hat{n}_L-U_{ext})\xi_L\\ &\quad -2U_{ext}\hat{n}_1+\hat{U}_{\mathrm{MOL}}+U_{ext}\hat{N}\hat{n}_1.\end{aligned}\tag{3.3}$$

We have subtracted the term $2U_{ext}$ since it is just a constant factor and thus does not affect the properties of the Hamiltonian. Note also that we will treat the first line of (3.3) as the unperturbed Hamiltonian and the second line as the perturbation.

The components of the Green's function in the molecule and in the chain are calculated in A.4 and they become, respectively

$$\begin{aligned}G_{ij}(\omega) &= \frac{\delta_{ij}}{\omega-(\xi_i-U_{ext})+i\mathrm{sgn}(\xi_i)\eta},\qquad i,j\in\{H,L\}\\ G_{ij}^{\mathrm{TB}}(\omega) &= \delta_{\sigma_i\sigma_j}\frac{2}{N+1}\sum_{k=1}^{N}\frac{\sin\left(\frac{\pi k}{N+1}i\right)\sin\left(\frac{\pi k}{N+1}j\right)}{\omega-2t\cos\left(\frac{\pi k}{N+1}\right)+i\mathrm{sgn}(t\cos\left(\frac{\pi k}{N+1}\right)\eta},\end{aligned}\tag{3.4}$$

where in the former expression we have included the interaction energies $-\hat{n}_{H/L}U_{ext}$ into the Green's function to simplify the calculations. Note also that, as before, the indices contain also the spin index, i.e., $i = (i, \sigma)$.

From the general structure of the Hamiltonians in the second quantization (1.45) we can deduce that the factors V_{ijkl} are in our model of the form $V_{ijkl} = V_{ij}\delta_{il}\delta_{jk}$, and the whole structure of the two-body interactions is confined in the matrix

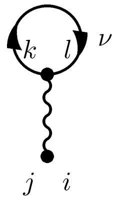
$$V_{ij} = \begin{pmatrix} V_0 & V_{HL} & V_{H1} \\ V_{LH} & V_{LL} & V_{L1} \\ V_{1H} & V_{1L} & V_{11} \end{pmatrix} = \begin{pmatrix} U_0 & U_{HL} & U_{ext} \\ U_{HL} & U_0 & U_{ext} \\ U_{ext} & U_{ext} & 0 \end{pmatrix}. \tag{3.5}$$

Note that all the elements that are not presented explicitly are zero. Finally we have everything needed to do perturbation theory for the self-energy of this system. We start with the Hartree-Fock approximation.

3.1.1 Hartree-Fock

In the Hartree-Fock method we draw the two first Feynman diagrams, namely the tadpole and exchange diagrams. We also have to include the one-body term $-2U_{ext}\delta_{j0}$. We use the Feynman rules in frequency space introduced in Sec. 2.3.4 to obtain the equations for the self-energy. The self-energy in the Hartree-Fock level becomes

$$\Sigma_{ij}(\omega) =$$



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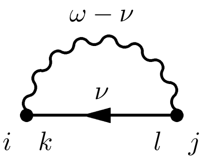


$- 2U_{ext}\delta_{1i}\delta_{1j}$

$$\begin{aligned}
&= -i\sum_{k,l} V_{iklj} \int \frac{\mathrm{d}\nu}{2\pi}\, G^0_{lk}(\nu)e^{i\nu\eta} + i\sum_{k,l} V_{iljk} \int \frac{\mathrm{d}\nu}{2\pi}\, G^0_{kl}(\nu)e^{i\nu\eta} - 2U_{ext}\delta_{1i}\delta_{1j} \\
&= -i\delta_{ij}\sum_{k,l} V_{ik}\delta_{kl} \int \frac{\mathrm{d}\nu}{2\pi}\, G^0_{lk}(\nu)e^{i\nu\eta} + i\sum_{k,l} V_{il}\delta_{lj}\delta_{ik} \int \frac{\mathrm{d}\nu}{2\pi}\, \delta_{\sigma_k\sigma_l}G^0_{kl}(\nu)e^{i\nu\eta} - 2U_{ext}\delta_{1i}\delta_{1j} \\
&= -i\delta_{ij}\sum_{k=(k,\sigma_k)} V_{ik} \int \frac{\mathrm{d}\nu}{2\pi}\, G^0_{kk}(\nu)e^{i\nu\eta} + i\delta_{\sigma_i\sigma_j}V_{ij} \int \frac{\mathrm{d}\nu}{2\pi}\, G^0_{ij}(\nu)e^{i\nu\eta} - 2U_{ext}\delta_{1i}\delta_{1j},
\end{aligned} \tag{3.6}$$

where on the second line the $\delta_{\sigma_k\sigma_l}$ arise from the Green's function.

The different components of the self-energy can now be calculated from Eq. (3.6) just by inserting the desired indices. For example, Σ_{HH} becomes

$$\begin{aligned}
\Sigma_{HH}(\omega) &= -i2\sum_k V_{Hi}\int \frac{\mathrm{d}\nu}{2\pi}\, G^0_{ii}(\nu)e^{i\nu\eta} + iV_{HH}\int \frac{\mathrm{d}\nu}{2\pi}\, G^0_{HH}(\nu)e^{i\nu\eta} \\
&= -i2\int \frac{\mathrm{d}\nu}{2\pi}\, \left(V_{HH}G^0_{HH}(\nu) + V_{HL}G^0_{LL}(\nu) + V_{H1}G^0_{11}(\nu)\right)e^{i\nu\eta} \\
&\quad +iV_{HH}\int \frac{\mathrm{d}\nu}{2\pi}\, G^0_{HH}(\nu)e^{i\nu\eta} \\
&= -i2\int \frac{\mathrm{d}\nu}{2\pi}\, \frac{U_0 e^{i\nu\eta}}{\nu-(\xi_H-U_{ext})-i\eta} + \frac{U_{HL}e^{i\nu\eta}}{\nu-(\xi_L-U_{ext})+i\eta} \\
&\quad -i2\int \frac{\mathrm{d}\nu}{2\pi}\, U_{ext}e^{i\nu\eta}\frac{2}{N+1}\sum_{k=1}^{N}\frac{\sin\left(\frac{\pi k}{N+1}1\right)\sin\left(\frac{\pi k}{N+1}1\right)}{\nu-2t\cos\left(\frac{\pi k}{N+1}\right)+i\mathrm{sgn}\left(t\cos\left(\frac{\pi k}{N+1}\right)\right)\eta} \\
&\quad +i\int \frac{\mathrm{d}\nu}{2\pi}\, \frac{U_0 e^{i\nu\eta}}{\nu-(\xi_H-U_{ext})-i\eta}. \qquad (3.7)
\end{aligned}$$

We perform the integrals by using Cauchy's residue theorem, see Appendix A.8. The factor $e^{i\nu\eta}$ forces the integration loop to be closed in the upper half plane [2] which we have to take into account. The first two and the last integrals are easy to compute and they give altogether U_0.

With the third integral we must be careful with the summation limits due to the sign factor in the denominator. To get a non-zero contribution we must have $\mathrm{sgn}\left(t\cos\left(\frac{\pi k}{N+1}\right)\right) = -1$ due to the fact that the loop must be closed in the UHP. This leads to limits for summation index k. These limits become

$$\begin{aligned}
&\mathrm{sgn}\ \left(t\cos\left(\frac{\pi k}{N+1}\right)\right) = -1, \qquad t<0 \\
\Rightarrow\quad &\cos\left(\frac{\pi k}{N+1}\right) > 0 \Leftrightarrow -\frac{\pi}{2} < \frac{k\pi}{N+1} < \frac{\pi}{2} \\
\Rightarrow\quad &k \in \{1,\ldots,\frac{1}{2}(N+1)\}. \qquad (3.8)
\end{aligned}$$

Note that we are using half filling in the molecule as well as in the chain, i.e., all the states with energy below zero are occupied. Now all the terms in the sum give under integration just $i\sin^2\left(\frac{\pi k}{N+1}\right)$ and we are left with

$$\Sigma_{HH}(\omega) = U_0 + \frac{4U_{ext}}{N+1}\sum_{k=1}^{\frac{1}{2}(N+1)}\sin^2\left(\frac{\pi k}{N+1}\right). \qquad (3.9)$$

In the limit $N\to\infty$ the summation can be turned into an integral with $x = \pi k/(N+1)$ resulting

$$\begin{aligned}
\Sigma_{HH}(\omega) &= U_0 + \frac{4U_{ext}}{N+1}\frac{N+1}{\pi}\int_0^{\frac{1}{2}\pi}\mathrm{d}x\ \sin^2(x) \\
&= U_0 + \frac{4}{U_{ext}}\pi\frac{\pi}{4} = U_0 + U_{ext}. \qquad (3.10)
\end{aligned}$$

All the components of the self-energy matrix are calculated similarly. For the Σ_{11} component we have the additional one-body term $-2U_{ext}$ which exactly cancels with the rest of the terms. In the Hartree-Fock level the part of the self-energy matrix that we are interested in becomes

$$\Sigma^{HF}(\omega) = \begin{pmatrix} \Sigma_{HH} & \Sigma_{HL} & \Sigma_{H1} \\ \Sigma_{LH} & \Sigma_{LL} & \Sigma_{L1} \\ \Sigma_{1H} & \Sigma_{1L} & \Sigma_{11} \end{pmatrix} = \begin{pmatrix} U_0+U_{ext} & 0 & 0 \\ 0 & 2U_{HL}+U_{ext} & 0 \\ 0 & 0 & 0 \end{pmatrix}. \qquad (3.11)$$

From the Dyson equation Eq. (A.6.5) it is now easy to calculate the Green's function. We do this, as above, only for the $G_{HH}(\omega)$ component,

$$G \;=\; (G_0^{-1} - \Sigma)^{-1}. \tag{3.12}$$

Now, since G_0 (3.4) is block-diagonal for H and L components, and Σ^{HF} (3.11) is diagonal, the matrix inversions are easy to make for G_{ij} with $i, j \in \{H, L\}$, yielding

$$\begin{aligned} G_{ij}^{HF}(\omega) &= \frac{\delta_{ij}}{G_{0,ij}^{-1}(\omega) - \Sigma_{ij}^{HF}(\omega)} = \frac{\delta_{ij}}{\omega - \xi_i + U_{ext} - U_{ext} - U_i + i\text{sgn}(\xi_i)\eta} \\ &= \frac{\delta_{ij}}{\omega - \omega_i + i\text{sgn}(\xi_i)\eta}, \qquad i, j \in \{H, L\}, \end{aligned} \tag{3.13}$$

where

$$\omega_i = \xi_i + 2U_{HL}\delta_{iL} + U_0\delta_{iH}. \tag{3.14}$$

For the terminal site one must be more careful due to the fact that the tight-binding part of the Green's function matrix is not diagonal. However, since the self-energy matrix is zero for the chain, we are having the inversion of the inversion of the Green's function in the chain, i.e., no effect on the Green's function in the chain. Thus, we have

$$\begin{aligned} G_{ij}^{HF}(\omega) &= (G_{0,ij}^{TB^{-1}}(\omega) - \Sigma_{ij}^{HF}(\omega))^{-1} \qquad i, j \in \{1, \ldots, \infty\} \\ &= (G_{0,ij}^{TB^{-1}}(\omega))^{-1} = G_{0,ij}^{TB}(\omega). \end{aligned} \tag{3.15}$$

Collecting the results the Green's function in the Hartree-Fock level becomes

$$G^{HF}(\omega) = \begin{pmatrix} G_{MOL}^{HF}(\omega) & 0 \\ 0 & G_{TB}^{HF}(\omega) \end{pmatrix}$$

$$= \begin{pmatrix} \frac{1}{\omega-(\xi_H+U_0)-i\eta} & 0 & 0 & 0 \\ 0 & \frac{1}{\omega-(\xi_L+2U_{HL})+i\eta} & 0 & 0 \\ 0 & 0 & \frac{2}{N+1}\sum_{k=1}^{N} \frac{\sin\left(\frac{\pi k}{N+1}\right)\sin\left(\frac{\pi k}{N+1}\right)}{\omega-2t\cos\left(\frac{\pi k}{N+1}\right)+i\text{sgn}(t\cos\left(\frac{\pi k}{N+1}\right)\eta} & \cdots \\ 0 & 0 & \vdots & \ddots \end{pmatrix}. \tag{3.16}$$

Note the block structure that is preserved due to a similar block structure in the self-energy.

One can immediately make some observations on this Green's function. The absence of U_{ext} in G^{HF} suggests that on the Hartree-Fock level the molecule and chain do not "see" each other. To have some effect of interactions between these two systems we need to go beyond the Hartree-Fock level. Thus, we will next go to the second order and see what it will give.

3.1.2 Bubble

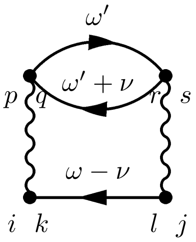
Now that we have obtained the Hartree-Fock Green's function and noticed that it does not give any new information compared to the finite-chain case [12] we would like to go beyond this approximation. The natural step is to take the next two diagrams, now in the second order, into account. These are the bubble and the exchange diagrams.

We will use the Hartree-Fock Green's function in the diagrams. The obvious reason for this is that the HF Green's functions should be already a bit closer to the exact Green's function and thus one should get more accurate results. The approximation is named as HFB. We draw, again, the diagrams for the self-energy using Feynman rules.

The interesting thing here is that the exchange diagram gives zero contribution. This is due to the fact that there are now Green's function lines between the chain and the molecule. Moreover, all the exchange diagrams inside the molecule give zero.

The bubble diagram, however, is non-zero and it becomes

$$\Sigma^B_{ij}(\omega) \quad = $$



$$= \quad \delta_{\sigma_i \sigma_j} 2 \sum_{p,s} V_{ip} V_{sj} \int \frac{\mathrm{d}\nu}{2\pi} \frac{\mathrm{d}\omega'}{2\pi} \, G^{HF}_{ij}(\omega - \nu) G^{HF}_{ps}(\omega' + \nu) G^{HF}_{sp}(\omega'). \tag{3.17}$$

The intermediate steps are similar as in Eq. (3.6); one just keeps in mind that $V_{ijkl} = V_{ij}\delta_{il}\delta_{jk}$ and that the indices contain also the spin index. We have for the the self-energy in the molecule

$$\Sigma^B_{HH/LL}(\omega) = 2U^2_{ext} \int \frac{\mathrm{d}\nu}{2\pi} \frac{\mathrm{d}\omega'}{2\pi} \, G^{HF}_{HH/LL}(\omega - \nu) G^{HF}_{11}(\omega' + \nu) G^{HF}_{11}(\omega'). \tag{3.18}$$

All the other terms of the sum give zero under integration due to the property introduced in A.8. The $\Sigma^B_{11}(\omega)$ is clearly zero due to $V_{11} = 0$. Note also that the self-energy has the same block structure as the Green's functions. Next we insert the Hartree-Fock Green's function and find

$$\begin{aligned}
\Sigma^B_{HH/LL}(\omega) &= 2U^2_{ext} \int \frac{\mathrm{d}\nu}{2\pi} \frac{\mathrm{d}\omega'}{2\pi} \frac{1}{\omega - \nu - \xi_{H/L} \mp i\eta} \left(\frac{2}{N+1} \right)^2 \\
&\times \sum_{i,j=1}^{N} \frac{\sin\left(\frac{\pi i}{N+1}\right)}{\omega' + \nu - \epsilon_i + i\mathrm{sgn}(\epsilon_i)\eta} \frac{\sin\left(\frac{\pi j}{N+1}\right)}{\omega' - \epsilon_j + i\mathrm{sgn}(\epsilon_j)\eta} \\
&= 2U^2_{ext} \int \frac{\mathrm{d}\nu}{2\pi} \frac{1}{\omega - \nu - \xi_{H/L} \mp i\eta} \left(\frac{2}{N+1} \right)^2 \\
&\times \sum_{i,j=1}^{N} \sin\left(\frac{\pi i}{N+1}\right) \sin\left(\frac{\pi j}{N+1}\right) \\
&\times \int \frac{\mathrm{d}\omega'}{2\pi} \frac{1}{\omega' + \nu - \epsilon_i + i\mathrm{sgn}(\epsilon_i)\eta} \frac{1}{\omega' - \epsilon_j + i\mathrm{sgn}(\epsilon_j)\eta}.
\end{aligned} \tag{3.19}$$

The integral on last line is exactly of the form introduced in A.8.8. Thus, to yield a non-zero contribution we must have $\mathrm{sgn}(\epsilon_i) \neq \mathrm{sgn}(\epsilon_j)$. From this we obtain two options (for $t < 0$):

$$t \cos\left(\frac{\pi i}{N+1}\right) < 0 < t \cos\left(\frac{\pi j}{N+1}\right) \quad \Rightarrow \quad i < \frac{1}{2}(N+1) < j \tag{3.20}$$

$$t \cos\left(\frac{\pi j}{N+1}\right) < 0 < t \cos\left(\frac{\pi i}{N+1}\right) \quad \Rightarrow \quad j < \frac{1}{2}(N+1) < i. \tag{3.21}$$

These two options turn out to correspond to the HOMO and LUMO components of the self-energy. This is due to the fact that in the last integration we have to, once again, take into account the property A.8.8. Now for the option in Eq. (3.20) we get from Eq. (3.19)

$$\begin{aligned}\Sigma^B_{HH}(\omega) &= 2U^2_{ext}\int\frac{\mathrm{d}\nu}{2\pi}\,\frac{1}{\omega-\nu-\xi_H-i\eta}\left(\frac{2}{N+1}\right)^2 \\ &\times \sum_{i=1}^{\frac{1}{2}(N+1)}\ \sum_{j=\frac{1}{2}(N+1)}^{N} i\frac{\sin^2\left(\frac{\pi i}{N+1}\right)\sin^2\left(\frac{\pi j}{N+1}\right)}{\epsilon_i-\epsilon_j-\nu+i\eta}, \end{aligned}\tag{3.22}$$

where only the Σ_{HH} component will yield a non-zero contribution due to the placement of the poles under integration. With the option in Eq. (3.21) we obtain the self-energy component for the LUMO level. This becomes

$$\begin{aligned}\Sigma^B_{LL}(\omega) &= 2U^2_{ext}\int\frac{\mathrm{d}\nu}{2\pi}\,\frac{1}{\omega-\nu-\xi_L+i\eta}\left(\frac{2}{N+1}\right)^2 \\ &\times \sum_{j=1}^{\frac{1}{2}(N+1)}\ \sum_{i=\frac{1}{2}(N+1)}^{N} i\frac{\sin^2\left(\frac{\pi i}{N+1}\right)\sin^2\left(\frac{\pi j}{N+1}\right)}{\epsilon_j-\epsilon_i+\nu+i\eta}. \end{aligned}\tag{3.23}$$

We continue by calculating the HOMO self-energy component explicitly. The LUMO component follows the same tracks and only the results are introduced. We start from Eq. (3.22) by first performing the remaining integral over ν,

$$\begin{aligned}\Sigma^B_{HH}(\omega) &= 2U^2_{ext}\left(\frac{2}{N+1}\right)^2\sum_{i=1}^{\frac{1}{2}(N+1)}\ \sum_{j=\frac{1}{2}(N+1)}^{N}\sin^2\left(\frac{\pi i}{N+1}\right)\sin^2\left(\frac{\pi j}{N+1}\right) \\ &\times \int\frac{\mathrm{d}\nu}{2\pi}\,\frac{1}{\omega-\nu-\xi_H-i\eta}\,\frac{-i}{-\epsilon_i+\epsilon_j+\nu-i\eta} \\ &= 2U^2_{ext}\left(\frac{2}{N+1}\right)^2\sum_{i=1}^{\frac{1}{2}(N+1)}\ \sum_{j=\frac{1}{2}(N+1)}^{N}\frac{\sin^2\left(\frac{\pi i}{N+1}\right)\sin^2\left(\frac{\pi j}{N+1}\right)}{\omega-\epsilon_i+\epsilon_j-\xi_H-i\eta}. \end{aligned}\tag{3.24}$$

We proceed by taking the limit $N\to\infty$ in order to transform the sums over i and j into integrals. In this way we hope to be able to calculate the self-energy further. We introduce the following variables

$$\frac{\pi i}{N+1} = x,\qquad \mathrm{d}i=\frac{N+1}{\pi}\mathrm{d}x \tag{3.25}$$

$$\frac{\pi j}{N+1} = y,\qquad \mathrm{d}j=\frac{N+1}{\pi}\mathrm{d}y. \tag{3.26}$$

With these x and y and letting N go to infinity Eq. (3.24) may be written as

$$\Sigma^B_{HH}(\omega)=2U^2_{ext}\left(\frac{2}{\pi}\right)^2\int_{\frac{\pi}{2}}^{\pi}\mathrm{d}y\int_0^{\frac{\pi}{2}}\mathrm{d}x\frac{\sin^2(x)\sin^2(y)}{\omega-2t(\cos(x)-\cos(y))-\xi_H-i\eta}. \tag{3.27}$$

As one can notice this is a quite demanding integral to calculate by hand. We have also seen the connection between the imaginary and real parts of the self-energy through the Kramer-Kronig relations. We will now take the advantage of this knowledge and calculate the imaginary component using the result derived in A.9. The imaginary component becomes

$$\begin{aligned}\mathrm{Im}\Sigma^B_{HH}(\omega) &= 2U^2_{ext}\left(\frac{2}{\pi}\right)^2\pi\int_{\frac{\pi}{2}}^{\pi}\mathrm{d}y\int_0^{\frac{\pi}{2}}\mathrm{d}x\sin^2(x)\sin^2(y) \\ &\times \delta(\omega-2t(\cos(x)-\cos(y))-\xi_H). \end{aligned}\tag{3.28}$$

We perform a change of variables through

$$\begin{aligned} 2t\cos(x) &= u, \qquad -2t\sin(x)\mathrm{d}x = \mathrm{d}u, \qquad \sqrt{1-\left(\frac{u}{2t}\right)^2} = \sin(x) \\ 2t\cos(y) &= v, \qquad -2t\sin(y)\mathrm{d}y = \mathrm{d}v, \qquad \sqrt{1-\left(\frac{v}{2t}\right)^2} = \sin(y), \end{aligned} \tag{3.29}$$

to obtain

$$\begin{aligned} \mathrm{Im}\Sigma^B_{HH}(\omega) &= 2U^2_{ext}\left(\frac{2}{\pi}\right)^2 \pi \int_0^{-2t} \frac{\mathrm{d}v}{-2t} \int_{2t}^0 \frac{\mathrm{d}u}{-2t} \sqrt{1-\left(\frac{u}{2t}\right)^2}\sqrt{1-\left(\frac{v}{2t}\right)^2} \\ &\times \ \delta(\omega - u + v - \xi_H). \end{aligned} \tag{3.30}$$

Next when performing the integral over u one must be careful to use the delta function only if it has zero within the integration limits of u, i.e., within $[2t, 0]$. This can be done by introducing step functions which have the property $\theta(x) = 0 \ \forall \ x < 0$ and $\theta(x) = 1 \ \forall \ x > 0$. With the aid of these step functions the integration limits in (3.30) can be extended to infinity resulting in

$$\begin{aligned} \mathrm{Im}\Sigma^B_{HH}(\omega) &= 2U^2_{ext}\frac{1}{\pi t^2} \int_0^{-2t} \mathrm{d}v \int_{-\infty}^{\infty} \mathrm{d}u \ \sqrt{1-\left(\frac{u}{2t}\right)^2}\sqrt{1-\left(\frac{v}{2t}\right)^2} \\ &\times \ \delta(\omega - u + v - \xi_H)\theta(-u)\theta(u-2t) \\ &= 2U^2_{ext}\frac{1}{\pi t^2} \int_0^{-2t} \mathrm{d}v \sqrt{1-\left(\frac{\omega + v - \xi_H}{2t}\right)^2}\sqrt{1-\left(\frac{v}{2t}\right)^2} \\ &\times \ \theta(\xi_H - \omega - v)\theta(\omega + v - \xi_H - 2t). \end{aligned} \tag{3.31}$$

Similar steps by which we arrived from Eqs. (3.22) to (3.31) may be carried out for the LUMO component starting from Eq. (3.23). The result is very similar to Eq. (3.31), i.e.,

$$\begin{aligned} \mathrm{Im}\Sigma^B_{LL}(\omega) &= -2U^2_{ext}\frac{1}{\pi t^2} \int_{-\infty}^{\infty} \mathrm{d}v \ \sqrt{1-\left(\frac{v + \xi_L - \omega}{2t}\right)^2}\sqrt{1-\left(\frac{v}{2t}\right)^2} \\ &\times \ \theta(\omega - \xi_L - v)\theta(v + \xi_L - \omega - 2t). \end{aligned} \tag{3.32}$$

This is as far as we get by analytical calculations for the imaginary part of the self-energy. The integral in Eq. (3.31) is tedious to calculate by hand, but easy to perform numerically. I have written a FORTRAN code that calculates the imaginary part of the self-energy exactly. However, before introducing the code we still have some things to consider.

Now that we have an expression for the $\mathrm{Im}\Sigma^B_{HH/LL}(\omega)$ we may calculate the real part through a principal value integral as derived in A.9. For $\Sigma^B_{HH(LL)}(\omega)$ the pole is in UHP (LHP) so we use Eq. (A.9.1) (A.9.4) to yield the real part. The equation for HOMO and LUMO, respectively, becomes

$$\mathrm{Re}\Sigma^B_{HH}(\omega) = \frac{1}{\pi}P\int \mathrm{d}\nu \ \frac{\mathrm{Im}\Sigma^B_{HH}(\omega)}{\omega - \nu}, \tag{3.33}$$

$$\mathrm{Re}\Sigma^B_{LL}(\omega) = -\frac{1}{\pi}P\int \mathrm{d}\nu \frac{\mathrm{Im}\Sigma^B_{LL}(\omega)}{\omega - \nu}. \tag{3.34}$$

We do not have an analytical form for $\Sigma^B_{HH/LL}(\omega)$ and thus the principal value integrals are impossible to calculate analytically. The real parts must also be calculated with a computer program. I used a method called the Hilbert transform [14] to obtain the real parts out of the imaginary parts. The self energies are presented in the results chapter.

Now that we have the self-energy it is neat to solve the Green's function. This is done through the Dyson equation as before in the Hartree-Fock case. The self-energy has the same block structure as the Green's function leading to a treatment of the molecule and chain separately. Since there is no change to the chain part even at this level, and even if there were, it would be difficult to calculate (inversion of an infinite-dimensional matrix) we will focus on the effects on the molecular levels.

The Green's function in the molecular orbitals becomes

$$\begin{aligned} G_{HH/LL}(\omega) &= (G_0^{-1}(\omega) - \Sigma(\omega))_{ij}^{-1} \\ &= \frac{\delta_{ij}}{\omega - \xi_i' - \mathrm{Re}\Sigma_{ij}(\omega) - i[\mathrm{Im}\Sigma_{ij}(\omega) \mp \eta]} \\ &= \delta_{ij}\frac{\omega - \xi_i' - \mathrm{Re}\Sigma_{ij}(\omega)}{[\omega - \xi_i' - \mathrm{Re}\Sigma_{ij}(\omega)]^2 + [\mathrm{Im}\Sigma_{ij}(\omega) \mp \eta]^2} \\ &+ i\delta_{ij}\frac{\mathrm{Im}\Sigma_{ij}(\omega) \pm \eta}{[\omega - \xi_i' - \mathrm{Re}\Sigma_{ij}(\omega)]^2 + [\mathrm{Im}\Sigma_{ij}(\omega) \mp \eta]^2}, \end{aligned} \tag{3.35}$$

where $\xi_i' = \xi_i + U_{ext}$. One can now plug different self-energy approximations in the above equation Eq. (3.35) to obtain the corresponding Green's functions in these approximations. The fact that we wrote the imaginary and real parts of G separately is due to spectral functions that can be read from the imaginary part of Green's functions as presented in Sec. 2.4.2. The spectral function for this model ($\mu = 0$) thus reads

$$A_{HH/LL}(\omega) = -\frac{1}{\pi}\mathrm{sgn}(\omega)\delta_{ij}\begin{cases} \frac{\mathrm{Im}\Sigma_{ij}(\omega)}{[\omega-\xi_i'-\mathrm{Re}\Sigma_{ij}(\omega)]^2+(\mathrm{Im}\Sigma_{ij}(\omega))^2}, & \mathrm{Im}\Sigma_{ii} \neq 0 \\ \pm\delta(\omega - \xi_i' - \mathrm{Re}\Sigma_{ij}(\omega)), & \mathrm{Im}\Sigma_{ii} = 0. \end{cases} \tag{3.36}$$

Here we have demanded that the HOMO level is inside the Fermi sphere and the LUMO level outside of the Fermi sphere. We have to be careful with the different parameters to really obtain such a situation. Let us now see how we can find the form of ξ_H and ξ_L. We define the fully occupied HOMO level as our ground state in the molecule. Then all the rest of the molecular states should be higher in energy. The conditions read

$$U_0 + 2\xi_H < \xi_L \tag{3.37}$$

$$U_0 + 2\xi_H < \xi_H \tag{3.38}$$

$$U_0 + 2\xi_H < U_{HL} + \xi_L + \xi_H \tag{3.39}$$

$$U_0 + 2\xi_H < 2\xi_H + U_0 + \xi_L + 2U_{HL} \tag{3.40}$$

$$U_0 + 2\xi_H < 2\xi_H + 2U_0 + 2\xi_L + 4U_{HL}. \tag{3.41}$$

Now with U_0 and U_{HL} positive we may deduce from Eqs. (3.38), (3.39) and (3.40), that

$$\xi_H < -U_0 \tag{3.42}$$

$$\overbrace{\xi_H - \xi_L}^{-\Delta} < U_{HL} - U_0 \tag{3.43}$$

$$\xi_H > -2U_{HL} - \Delta, \tag{3.44}$$

leading to

$$-2U_{HL} - \Delta < \xi_H < -U_0. \tag{3.45}$$

Now,

$$-2U_{HL} - \Delta \overset{(3.43)}{<} -2U_{HL} + U_{HL} - U_0 < U_0, \tag{3.46}$$

and, moreover, from Eq. (3.46) we get

$$\xi_H < -U_{HL} - \frac{1}{2}\Delta + \frac{1}{2}U_0 < -U_0, \tag{3.47}$$

$$-U_{HL} - \frac{1}{2}\Delta - \frac{1}{2}U_0 > U_0 - 2U_{HL} - \Delta > -2U_{HL} - \Delta > \xi_H. \tag{3.48}$$

We see that a natural definition with conditions (3.37) to (3.41) for the ξ_H becomes

$$-U_{HL} - \frac{1}{2}\Delta + \frac{1}{2}U_0 = \xi_H. \tag{3.49}$$

3.1.3 Connection between the density and the peak shift

As we have now derived some results for the model at hand it is time to see what we can deduce out of them. The most interesting thing is the image-charge effect, i.e., the fact that when we have $N \neq 2$ the molecule can polarize the chain, i.e., the charge at terminal site of the chain should depend on U_{ext}. This turns out to be the case at least in the higher order approximation.

Let us use the Hellman-Feynman theorem to deduce from Hamiltonian in Eq. (3.1) that

$$\langle \Psi_0 | \frac{\partial \hat{H}}{\partial U_{ext}} | \Psi_0 \rangle = (n_0 - 1)(N - 2) = \frac{\partial E_0}{\partial U_{ext}}. \tag{3.50}$$

The connection to the spectral function becomes evident by considering the HOMO and LUMO levels separately. Let us have $N = 3$, i.e., there is now also one electron at the LUMO level. Then we may write

$$n_0 - 1 = \frac{\partial E_0^{N+1}}{\partial U_{ext}} = \frac{\partial (E_0^{N+1} - E_0^N)}{\partial U_{ext}} \equiv \frac{\partial A_{L,peak}}{\partial U_{ext}}, \tag{3.51}$$

where we used the fact that E_0^N is independent of U_{ext}. We see that the density at the terminal site of the chain is related to the derivative of the peak shift w.r.t. U_{ext}. The peak shift can be deduced from the spectral function and hence we have a direct measure of the density.

For the HOMO level similar equation to Eq. (3.51) reads

$$1 - n_0 = \frac{\partial A_{H,peak}}{\partial U_{ext}}. \tag{3.52}$$

From Eqs. (3.51) and (3.52) one may also deduce the peak position if the density and the peak position for $U_{ext} = 0$ are known:

$$\begin{aligned} \int_0^{U_{ext}} \mathrm{d}A_{L,peak} &= A_{L,peak}(U_{ext}) - 2U_{HL} - \xi_L = \int_0^{U_{ext}} n_0 - 1 \ \mathrm{d}U, & (3.53) \\ \int_0^{U_{ext}} \mathrm{d}A_{H,peak} &= A_{H,peak}(U_{ext}) - U_0 - \xi_H = \int_0^{U_{ext}} 1 - n_0 \ \mathrm{d}U. & (3.54) \end{aligned}$$

The density at the terminal site may be calculated for HOMO and LUMO levels exactly. Hence we are able to compare the exact peak shifts to those produced by our approximation.

3.1.4 Chain with impurity

We now choose a different point of view into this model. As we do not have any hoppings between the molecule and the chain, we may safely regard the molecule-chain interactions as a potential of the form $U_{ext}(\hat{n}_0 - 1)(\hat{N} - 2)$ at the first site of the chain, see Fig. 3.1. As $\hat{N}$ is the number of electrons in the molecule it is an integer and thus we may write Hamiltonian for the bare chain part as

$$\hat{H} = U_{ext}(\hat{n}_0 - 1)N_{ex} + t \sum_{\langle i,j \rangle} \hat{a}_i^\dagger \hat{a}_j, \tag{3.55}$$

where we defined $\hat{N} - 2 = N_{ex}$ as the excess charge of the molecule. This model may now be solved by introducing new operators

$$\begin{aligned} (\hat{a}_1^\dagger, \hat{a}_1, \hat{a}_2^\dagger, \hat{a}_2, \ldots, \hat{a}_n^\dagger, \hat{a}_n) &\rightarrow (\hat{b}^\dagger, \hat{b}, \hat{c}_1^\dagger, \hat{c}_1, \ldots, \hat{c}_{n-1}^\dagger, \hat{c}_{n-1}) \\ \Rightarrow \hat{H} &= U_{ext}(\hat{b}^\dagger \hat{b} - 1)N_{ex} + t \sum_{\langle i,j \rangle} \hat{c}_i^\dagger \hat{c}_j + t(\hat{b}^\dagger \hat{c}_1 + \hat{c}_1^\dagger \hat{b}). \qquad (3.56) \end{aligned}$$

The chain part may be diagonalized, A.3.9, yielding

$$\hat{H} = U_{ext} N_{ex} \hat{b}^\dagger \hat{b} + \sum_k \epsilon_k \hat{c}_k^\dagger \hat{c}_k + \sum_k A_k (\hat{b}^\dagger \hat{c}_k + \hat{c}_k^\dagger \hat{b}), \tag{3.57}$$

where we dropped the constant $U_{ext}N_{ex}$, and, moreover,

$$\begin{aligned} \epsilon_k &= 2t \cos\left(\frac{\pi k}{n+1}\right) \\ A_k &= t\sqrt{\frac{2}{n+1}} \sin\left(\frac{\pi k}{n+1}\right). \end{aligned} \tag{3.58}$$

One may now notice the block structure of the Hamiltonian and the Green's function. We solve the Green's function at the first site (i.e., the one with impurity) from the equations of motion in Eq. (A.5). We do not do the calculations explicitly since they are almost identical to those of Eqs. (3.72) to (3.86) with the minor change that here we have only one Fano level. And the Dyson equation becomes trivial with only one element in the block matrix. The result for the retarded Green's function at the first site is given by

$$G^R(\omega) = \frac{1}{\omega - U_{ext} N_{ex} - \Sigma^R_{EM} + i\eta}, \tag{3.59}$$

where

$$\Sigma^R_{EM}(\omega) = -\mathrm{sgn}(t) \frac{1}{2} \begin{cases} \omega + \sqrt{\omega^2 - 4t^2}, & \omega < -|2t| \\ \omega + i\mathrm{sgn}(t)\sqrt{4t^2 - \omega^2}, & \omega \in [2t, -2t] \\ \omega - \sqrt{\omega^2 - 4t^2}, & \omega > |2t|. \end{cases} \tag{3.60}$$

The reason why we want the exact Green's function at the first site of the chain is due to the fact that we want to study the image-charge at this site w.r.t. U_{ext}. We may now, using the Hellman-Feynman theorem, calculate the approximate image-charge at the terminal site through the spectral function Eqs. (3.51), (3.52) and compare this result with the exact density (2.61) which now becomes

$$n_0 = \int_{-\infty}^{0} \mathrm{d}\omega \; A_{00}(\omega) = -\frac{1}{\pi} \int_{-\infty}^{0} \mathrm{d}\omega \; \mathrm{Im} G^R(\omega), \tag{3.61}$$

where $\mathrm{Im}G^R(\omega)$ can be solved from (3.59) becoming

$$\mathrm{Im}G^R(\omega) = \begin{cases} \frac{\mathrm{Im}\Sigma^R(\omega)}{(\omega - U_{ext}N_{ex} - \mathrm{Re}\Sigma^R(\omega))^2 + \mathrm{Im}\Sigma^R(\omega)^2}, & \omega \in [2t, -2t] \\ \frac{-\pi}{|\omega - U_{ext}N_{ex} - \mathrm{Re}\Sigma^R(\omega)|_{|\omega = a}}, & \omega \notin [2t, -2t], \end{cases} \tag{3.62}$$

where a is chosen such that

$$a - U_{ext}N_{ex} - \mathrm{Re}\Sigma^R(a) = 0. \tag{3.63}$$

Note that here $N_{ex} = 1 \;\; (-1)$ corresponds to LUMO (HOMO) case, i.e., one electron added (removed) to (from) the molecule.

One may notice a property of the density just by considering the Hamiltonian in Eq. (3.55). We may write

$$\hat{H} = t\left(\frac{U_{ext}}{t}(\hat{n}_0 - 1)N_{ex} + \sum_{\langle i,j \rangle} \hat{a}_i^\dagger \hat{a}_j\right). \tag{3.64}$$

We may deduce that the state functions can be only functions of U_{ext}/t and hence all operators which do not contain U_{ext} or t obtain eigenvalues which are functions of U_{ext}/t. Particularly the density

$$n_i(U_{ext}/t) = \langle \psi_0(U_{ext}/t) | \hat{n}_i | \psi_0(U_{ext}/t) \rangle \tag{3.65}$$

is a function of U_{ext}/t only. This can be also calculated explicitly. We notice that the density for the LUMO/HOMO state with $t < 0$ becomes

$$\begin{aligned} n_0 &= -\frac{1}{\pi}\int_{-\infty}^{0} \mathrm{d}\omega \, \frac{-\sqrt{4t^2-\omega^2}}{(\frac{\omega}{2} \pm U_{ext})^2 + 4t^2 - \omega^2} = -\frac{1}{t^2\pi}\int_{-\infty}^{0} \mathrm{d}\omega \, \frac{-2|t|\sqrt{-\left(\frac{\omega}{2t}\right)^2}}{\pm\frac{\omega}{t^2}U_{ext} + \left(\frac{U_{ext}}{t}\right)^2 + 4 - 3\left(\frac{\omega}{2t}\right)^2} \\ &\overset{\frac{\omega}{2t}=x}{=} \frac{1}{t^2\pi}\int_{0}^{\infty} \mathrm{d}x \, \frac{4|t|^2\sqrt{1-x^2}}{\pm 2x\frac{U_{ext}}{t} + \left(\frac{U_{ext}}{t}\right)^2 + 4 - 3x^2}. \end{aligned} \tag{3.66}$$

We immediately notice that the density at the terminal site is a function only of U_{ext}/t. This will be demostrated in the results chapter.

3.2 Fano Model

As mentioned earlier we also considered a different model for the molecule-chain system. This was the two-sited Fano model. The Fano model is widely studied [5] and it can give nice insights into the properties of particles on surfaces. For the usual Fano model one couples only one state to a continuum of states. Here we couple two states to continuum and see if we could deduce some features of this molecule-chain system through this model.

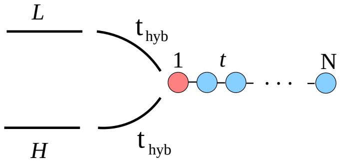


Figure 3.2: Fano model for two sites schematically

The Hamiltonian for the two-site Fano model is defined as

$$\hat{H} = \hat{H}_{mol} + \hat{H}_{ch} + \hat{V} = \sum_{k=1}^{2} \xi_k \hat{b}_k^\dagger \hat{b}_k + \sum_{\langle ij \rangle} t_{ij} \hat{a}_i^\dagger \hat{a}_j + \sum_{k=1}^{2} t_{hyb} \left[\hat{b}_k^\dagger \hat{a}_1 + \hat{a}_1^\dagger \hat{b}_k\right]. \tag{3.67}$$

Now, we make a transformation to operators that diagonalize the chain part:

$$\begin{aligned} \hat{b}^\dagger &\rightarrow \hat{b}^\dagger \\ \hat{b} &\rightarrow \hat{b} \\ \hat{a}_j^\dagger &\rightarrow \sum_k c_k^{j*} \hat{c}_k^\dagger \\ \hat{a}_j &\rightarrow \sum_k c_k^j \hat{c}_k. \end{aligned}$$

We obtain

$$\hat{H} = \hat{H}_{mol} + \hat{H}_{ch} + \hat{V} = \sum_{k=1}^{2} \xi_k \hat{b}_k^\dagger \hat{b}_k + \sum_k \epsilon_k \hat{c}_k^\dagger \hat{c}_k + \sum_j \sum_{k=1}^{2} A_j \left[\hat{b}_k^\dagger \hat{c}_j + \hat{c}_j^\dagger \hat{b}_k\right], \tag{3.68}$$

where

$$A_j = t_{hyb} c_j^1. \tag{3.69}$$

We can solve the Green's function for the molecule directly from the equations of motion for Green's functions. The equations of motion for the single-particle Green's function become (see Appendix A.5)

$$\begin{aligned} \left[i\hbar\partial_z - h(z)\right] G(z,z') &= \hbar\delta(z-z') && (3.70) \\ G(z,z') \left[h(z) - i\hbar\overleftarrow{\partial}_z\right] &= \hbar\delta(z-z'). && (3.71) \end{aligned}$$

To solve the Green's function matrix we start by making a of couple observations of the structure of the different matrices in Eqs. (3.70) and (3.71). First note that the Hamiltonian matrix in energy basis becomes

$$H = \begin{pmatrix} \xi_1 & 0 & A_1 & A_2 & \dots \\ 0 & \xi_2 & A_1 & A_2 & \\ A_1 & A_1 & \epsilon_1 & 0 & \\ A_2 & A_2 & 0 & \epsilon_2 & \dots \\ \vdots & & & & \ddots \end{pmatrix} = \begin{pmatrix} H_{mol} & H_{mc} \\ H_{cm} & H_{ch} \end{pmatrix}. \tag{3.72}$$

Also the single-particle Green's function matrix has the same block structure in energy basis,

$$G = \begin{pmatrix} G_{mol} & G_{mc} \\ G_{cm} & G_{ch} \end{pmatrix}. \tag{3.73}$$

Using now the equation of motion in Eq. (3.70) we find

$$i\hbar\partial_z \begin{pmatrix} G_{mol} & G_{mc} \\ G_{cm} & G_{ch} \end{pmatrix} - \begin{pmatrix} H_{mol} & H_{mc} \\ H_{cm} & H_{ch} \end{pmatrix}\begin{pmatrix} G_{mol} & G_{mc} \\ G_{cm} & G_{ch} \end{pmatrix} = \hbar\delta(z-z')\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \tag{3.74}$$

As we are interested mainly in the molecule part of the Green's function it is sufficient to consider only the equations

$$\begin{aligned} i\hbar\partial_z G_{cm} - H_{cm}G_{mol} - H_{ch}G_{cm} &= 0 && (3.75) \\ i\hbar\partial_z G_{mol} - H_{mol}G_{mol} - H_{mc}G_{cm} &= \delta(z-z'). && (3.76) \end{aligned}$$

The first Eq. (3.75) may be solved by

$$G_{cm}(z,z') = \int \mathrm{d}z_1\ g_{ch}(z,z_1)H_{cm}G_{mol}(z_1,z'), \tag{3.77}$$

where $g_{ch}(z,z_1)$ is the single-particle Green's function in the chain and thus a solution for

$$\left[i\hbar\partial_z - H_{ch}\right] g_{ch}(z,z_1) = \delta(z-z'). \tag{3.78}$$

Plugging the solution (3.77) into (3.76) we obtain

$$\left[i\hbar\partial_z - H_{mol}\right] G_{mol}(z,z') = \delta(z-z') + \int \mathrm{d}z_1\ \Sigma_{EM}(z,z_1)G_{mol}(z_1,z'), \tag{3.79}$$

where we defined the embedding self-energy

$$\Sigma_{EM}(z,z_1) = H_{mc}g_{ch}(z,z_1)H_{cm}. \tag{3.80}$$

The fact that we call the quantity to be integrated with the Green's function self-energy follows immediately if one operates with $i\hbar\partial_t - \hat{H}$ from left to Eq. (2.40). Then one obtains a equivalent equation to Eq. (3.79).

To proceed we now take the zero-temperature limit and use the fact that our Hamiltonian is time independent. We see that every quantity is a function of $z - z'$ and thus we may Fourier transform to frequency space. The Fourier transform of the non-interacting Green's function is calculated in A.4.1. As our tight-binding chain is diagonalized in Eq. (3.68) we may use the form of Eq. (A.4.9) for the Green's function in the chain and thus the embedding self-energy is easily calculated from

Eq. (3.80)

$$\begin{aligned}
&\Sigma_{EM}(\omega) \\
=\;& \begin{pmatrix} A_1 & A_2 & \dots A_N \\ A_1 & A_2 & \dots A_N \end{pmatrix} \begin{pmatrix} \frac{1}{\omega-\epsilon_1+i\eta\mathrm{sgn}(\epsilon_i)} & & & \\ & \frac{1}{\omega-\epsilon_2+i\eta\mathrm{sgn}(\epsilon_2)} & \emptyset & \\ & \emptyset & \ddots & \\ & & & \frac{1}{\omega-\epsilon_N+i\eta\mathrm{sgn}(\epsilon_N)} \end{pmatrix} \begin{pmatrix} A_1 & A_1 \\ A_2 & A_2 \\ \vdots & \vdots \\ A_N & A_N \end{pmatrix} \\
=\;& \sum_{k=1}^{N} \frac{A_k^2}{\omega-\epsilon_k+i\eta\mathrm{sgn}(\epsilon_k)} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \equiv \Sigma(\omega) \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}, \qquad (3.81)
\end{aligned}$$

where we may write $\Sigma(\omega)$ explicitly as

$$\Sigma(\omega) = t_{hyb}^2 \sum_{k=1}^{N} \frac{\frac{2}{N+1}\sin^2\left(\frac{\pi k}{N+1}\right)}{\omega - 2t\cos\left(\frac{\pi k}{N+1}\right) + i\eta\mathrm{sgn}\left(t\cos\left(\frac{\pi k}{N+1}\right)\right)}. \qquad (3.82)$$

Here we used Eqs. (3.69), (A.3.8) and (A.3.9). We continue by calculating $\Sigma(\omega)$ as $N \to \infty$. Then as before we may use the Dyson equation Eq. (2.40) to obtain the Green's function in molecule.

In the limit $N \to \infty$, Eq. (3.82) becomes

$$\begin{aligned}
\Sigma(\omega) &= t_{hyb}^2 \int_1^{\infty} \mathrm{d}k \, \frac{\frac{2}{N+1}\sin^2\left(\frac{\pi k}{N+1}\right)}{\omega - 2t\cos\left(\frac{\pi k}{N+1}\right) + i\eta\mathrm{sgn}\left(t\cos\left(\frac{\pi k}{N+1}\right)\right)}, \quad x = \frac{\pi k}{N+1} \\
&= t_{hyb}^2 \frac{2}{\pi} \int_0^{\pi} \mathrm{d}x \, \frac{\sin^2(x)}{\omega - 2t\cos(x) + i\eta\mathrm{sgn}(t\cos(x))} \\
&= t_{hyb}^2 \frac{2}{\pi} \left\{ \mathcal{P}\int_0^{\pi} \mathrm{d}x \, \frac{\sin^2(x)}{\omega - 2t\cos(x)} - i\int_0^{\pi} \mathrm{d}x \, \mathrm{sgn}(t\cos(x)) \frac{\eta\sin^2(x)}{(\omega - 2t\cos(x))^2 + \eta^2} \right\}, \qquad (3.83)
\end{aligned}$$

where $\mathcal{P}$ stands for the Cauchy principal value [2]. We thus obtain

$$\mathrm{Re}\Sigma(\omega) = t_{hyb}^2 \frac{2}{\pi} \mathcal{P} \int_0^{\pi} \mathrm{d}x \, \frac{\sin^2(x)}{\omega - 2t\cos(x)}, \qquad (3.84)$$

$$\mathrm{Im}\Sigma(\omega) = -t_{hyb}^2 \frac{2}{\pi} \int_0^{\pi} \mathrm{d}x \, \mathrm{sgn}(t\cos(x)) \frac{\eta\sin^2(x)}{(\omega - 2t\cos(x))^2 + \eta^2}. \qquad (3.85)$$

It is convenient to consider the retarded self-energy ($= \Sigma^R(\omega)$), since in the end we are interested in the spectral function and it can be calculated easily from retarded Green's function. The imaginary part of the retarded self-energy is calculated in Appendix A.7.1. The real part of the retarded self-energy is calculated from the imaginary part (A.7.2) by Kramer-Kronig relations in Appendix A.7.1. From (A.7.2), (A.7.9) and (A.7.10) we may deduce the form of $\Sigma^R(\omega)$. The retarded self-energy reads

$$\Sigma^R(\omega) = -\mathrm{sgn}(t)\frac{1}{2}\left(\frac{t_{hyb}}{t}\right)^2 \begin{cases} \omega + \sqrt{\omega^2 - 4t^2}, & \omega < -|2t| \\ \omega + i\mathrm{sgn}(t)\sqrt{4t^2 - \omega^2}, & \omega \in [2t, -2t] \\ \omega - \sqrt{\omega^2 - 4t^2}, & \omega > |2t|. \end{cases} \qquad (3.86)$$

We are now ready to deduce the form of the retarded Green's function in the molecule through the Dyson equation Eq. (A.6.5). The retarded Green's function becomes

$$
\begin{aligned}
G^R_{mol} &= ((G^R_{0,mol})^{-1} - \Sigma^R_{EM})^{-1} = \left(\begin{pmatrix} G^R_{0,mol,H} & 0 \\ 0 & G^R_{0,mol,L} \end{pmatrix}^{-1} - \Sigma^R \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \right)^{-1} \\
&= \begin{pmatrix} (G^R_{0,mol,H})^{-1} - \Sigma^R & -\Sigma^R \\ -\Sigma^R & (G^R_{0,mol,L})^{-1} - \Sigma^R \end{pmatrix}^{-1} \\
&= \frac{1}{\det(G^R_{mol})} \begin{pmatrix} (G^R_{0,mol,L})^{-1} - \Sigma^R & \Sigma^R \\ \Sigma^R & (G^R_{0,mol,H})^{-1} - \Sigma^R \end{pmatrix}.
\end{aligned}
\tag{3.87}
$$

As we have seen in chapter 2.4.2 the spectral function of the molecule can be deduced from the imaginary part of the retarded Green's function. We will now solve the imaginary part from (3.87).

We start by multiplying by the complex conjugate of the determinant to obtain a real denominator

$$
G^R_{mol} = \frac{1}{|\det(G^R_{mol})|^2} \begin{pmatrix} \det(G^R_{mol})^* \left[(G^R_{0,mol,L})^{-1} - \Sigma^R \right] & \det(G^R_{mol})^* \Sigma^R \\ \det(G^R_{mol})^* \Sigma^R & \det(G^R_{mol})^* \left[(G^R_{0,mol,H})^{-1} - \Sigma^R \right] \end{pmatrix}.
\tag{3.88}
$$

Now, for example, the HOMO component of the retarded self-energy reads

$$
\begin{aligned}
G^R_{mol,HH} &= \frac{1}{|\Lambda|^2} \Big[\mathrm{Re}\Lambda \left(\mathrm{Re}\Gamma_L - \mathrm{Re}\Sigma^R \right) + \mathrm{Im}\Lambda \left(\mathrm{Im}\Gamma_L - \mathrm{Im}\Sigma^R \right) \\
&- i\mathrm{Im}\Lambda \left(\mathrm{Re}\Gamma_L - \mathrm{Re}\Sigma^R \right) + i\mathrm{Re}\Lambda \left(\mathrm{Im}\Gamma_L - \mathrm{Im}\Sigma^R \right) \Big],
\end{aligned}
\tag{3.89}
$$

where we defined

$$
\begin{aligned}
\Gamma_{L/H} &= (G^R_{0,mol,L/H})^{-1} \\
\Lambda &= \det(G^R_{mol,L}).
\end{aligned}
\tag{3.90}
$$

We see that the imaginary component becomes

$$
\mathrm{Im}G^R_{mol,HH} = \frac{\mathrm{Re}\Lambda \left(\mathrm{Im}\Gamma_L - \mathrm{Im}\Sigma^R \right) - \mathrm{Im}\Lambda \left(\mathrm{Re}\Gamma_L - \mathrm{Re}\Sigma^R \right)}{|\Lambda|^2}.
\tag{3.91}
$$

It turns out that $\mathrm{Im}G^R_{mol,HH}$ divides into two pieces, one being a delta peak and the other the continuum, for details see A.7.2. We recall the relation between the imaginary part of the retarded self-energy and spectral function (2.60) to deduce from (A.7.22) that the spectral function at the HOMO/LUMO level becomes

$$
A_{HH/LL}(\omega) = \begin{cases} \frac{\left(\omega_{L/H} - \mathrm{Re}\Sigma^R\right)^2 + \left(\mathrm{Re}\Sigma^R\right)^2}{\sqrt{\omega_L^2 + \omega_H^2 + 4(\mathrm{Re}\Sigma^R)^2}} \frac{1}{\left| \frac{\mathrm{d}}{\mathrm{d}\omega} (\omega_H \omega_L - \mathrm{Re}\Sigma^R (\omega_L + \omega_H)) \right|_{\omega = a}} \delta(\omega - a), & \omega \notin [2t, -2t] \\ -\frac{1}{\pi} \frac{\mathrm{Im}\Sigma^R \omega_{L/H}^2}{(\omega_H \omega_L - \mathrm{Re}\Sigma^R(\omega_L + \omega_H))^2 + (\mathrm{Im}\Sigma^R)^2 (\omega_L + \omega_H)^2}, & \omega \in [2t, -2t], \end{cases}
\tag{3.92}
$$

where the LUMO component is calculated identically to the HOMO component.

3.3 Numerics

The quantities introduced in previous sections require some programming if one wants to plot the results. Moreover, as mentioned already, the real part of the self-energy in HFB Eq. (3.33) requires the use of Hilbert transform [14] since we were not able to find any analytical form for the imaginary part Eqs. (3.31) and (3.32).

After having the self-energy in HFB we may calculate the spectral function Eq. (3.36) and from it we can easily obtain, for example, the peak shift w.r.t. U_{ext} in Eqs. (3.51) and (3.52). Thus we may also deduce the approximate density at the terminal site of the chain. Moreover, the exact density can be obtained from Eq. (3.61). Here we again calculate the integral numerically exactly.

The results presented below have been obtained by the attached code "SigmaIntegral.f". After the data files are produced we use Gnuplot to plot the data. Also when calculating the peak shifts out of the spectral function Eq. (3.36) we fit a fourth-order polynomial to the data and take the derivative out of this polynomial to avoid numerical inaccuracies.

For the Fano model we have a separate code "FanoSpectral.f" which, as the name suggests, calculates the spectral function for the two-level Fano model Eq. (3.92).

Chapter 4

Results

In this chapter I will present the results obtained considering the models presented in Chapter 3. The main focus is given on the HOMO/LUMO level peak shifts w.r.t. U_{ext} and the connection of this shift to the image-charge at the terminal site of the chain. We start by introducing the self-energies and then go on to study the spectral functions for each system separately. In the end we will do some comparison about the peak behauviour and draw conclusions about the systems separately.

4.1 Interacting model

For the case of an interacting model we can calculate the self-energy in molecular orbitals from (3.31) and (3.32) numerically exactly. With the self energies obtained the rest of the properties are easy to deduce through Eqs. (3.35) and (3.36). We start by introducing the form of the self energies.

4.1.1 Self-energy

The two different approximations for the self-energy namely, the Hartree-Fock and HFB are presented in Eqs. (3.11), (3.31) and (3.32). The form of the Hartree-Fock self-energy is simply a constant as a function o ω. The part of self-energy coming from the bubble diagram (Σ^B) is shown in Fig. 4.1. The parameters are chosen as Eq. (3.49) suggests.

As indicated by Eqs. (3.31) and (3.32) the effect of U_{ext} to the second-order self-energy is just a multiplication. The curve remains unchanged; only the height changes w.r.t. U_{ext}. Hence we see that the larger U_{ext} the more important the second-order diagrams become.

4.1.2 Spectral functions

We now turn our attention to the peak shifts w.r.t. U_{ext}. The peak shifts are easy to deduce from the spectral function which can be read from Eq. (3.36).

A numerical solution is given for the case $\mathrm{Im}\Sigma_{HH} = \mathrm{Im}\Sigma^B_{HH} + \Sigma^{HF}_{HH} = 0$. Note that we are now dealing with the full self-energy, i.e., we also include the Hartree-Fock contribution. From Eq. (3.36) we see that to obtain a peak two conditions must be satisfied:

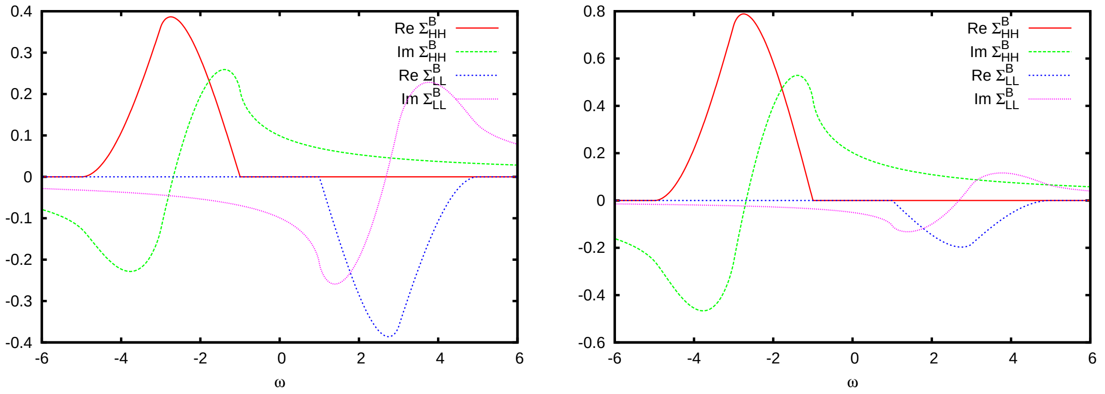


Figure 4.1: Left: The real and imaginary parts of the second-order self-energy contribution at HOMO and LUMO with $U_{ext} = 0.7$. Right: The real and imaginary parts of second order self-energy contribution at molecular orbitals. For HOMO $U_{ext} = 1$ and for LUMO $U_{ext} = 0.5$. The parameter values are $U_0 = U_{HL} = 1$, $\xi_H = -2$, $\xi_L = -1$ and $t = -1$.

1. $\text{Im}\Sigma_{ii}(\omega) = 0$,
2. $\omega - \xi_i + U_{ext} - \text{Re}\Sigma^{HF}_{ii}(\omega) = \text{Re}\Sigma^{B}_{ii}(\omega)$.

The numerical result is shown in Fig. 4.2.

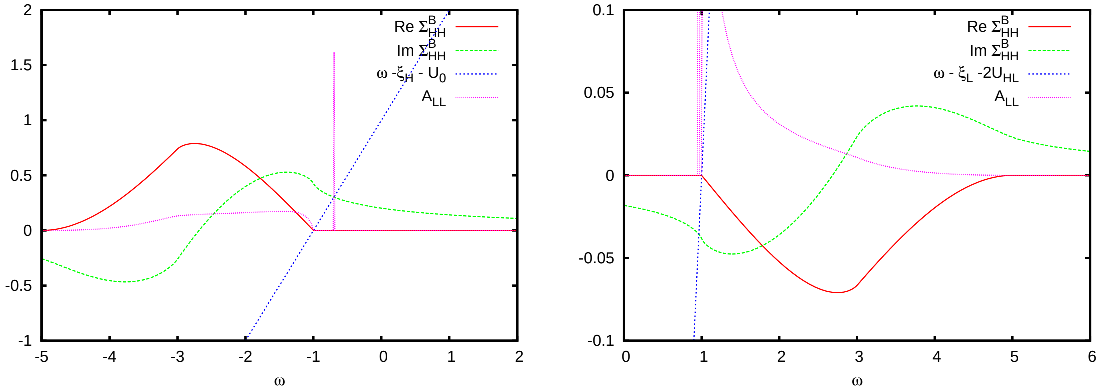


Figure 4.2: Left: Solution to determine the position of the split-off state peak for the HOMO level $U_{ext} = 1$. Right: Same as the previous but with $U_{ext} = 0.3$ and LUMO level. The corresponding spectral functions are also plotted. Note that the spectral function integrates to two. $U_0 = U_{HL} = 1$, $\xi_H = -2$, $\xi_L = -1$ and $t = -1$.

Now that we know how to deduce the peak shift it is convenient to see how the HOMO/LUMO level peaks shift w.r.t. U_{ext}. We also present the exact peaks shift which are calculated using the Hellman-Feynman theorem [Eq. (3.53)]. The peak shifts are presented in Fig. 4.3. One can actually see that with large U_{ext} the peaks would intersect. The method by which these plots are generated becomes clear as we introduce the way of deducing the density at the terminal site of the chain.

Image-charge

We may deduce the densities at the terminal site of the chain through Eqs. (3.51) and (3.52) and the exact density through Eq. (3.66). We plot first the spectral function at the terminal site for

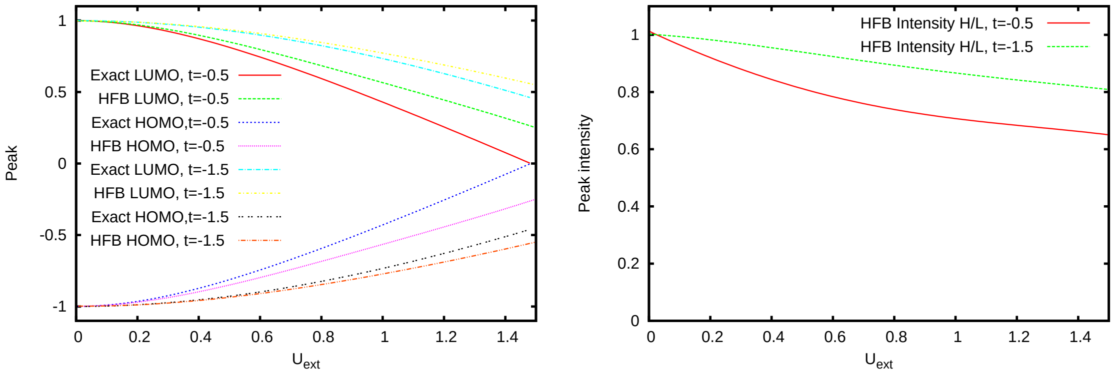


Figure 4.3: Left: The peak position in HFB and in the exact solution for HOMO and LUMO levels w.r.t. U_{ext}. Right: The peak intensity in HFB for HOMO and LUMO levels w.r.t. U_{ext}. Here $U_0 = U_{HL} = 1$, $\xi_H = -2$, $\xi_L = -1$ and $t = -1$.

one particle removed from the HOMO level. The exact spectral function are plotted in Fig. 4.4 and the corresponding density and the HOMO level peak shift are also presented.

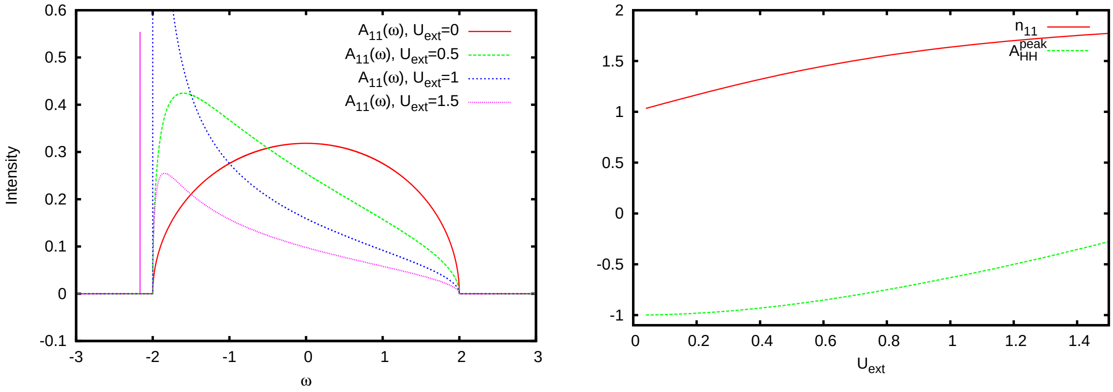


Figure 4.4: Left: Spectral function at the terminal site of the chain with different U_{ext}. Note the forming of peak when $|U_{ext}| > |t|$. Right: The corresponding exact density integrated out of the spectral functions and the HOMO peak shift calculated from density using Hellman-Feynman theorem. Here $t = -1, U_0 = U_{HL} = 1$, $\xi_H = -2$ and $\xi_L = -1$.

The peak positions at the level of Hartree-Fock are independent of U_{ext} thus at Hartree-Fock level we do not see any image-charge effect in the chain. However if we take our HFB approximation we may calculate the densities at the terminal site w.r.t. U_{ext} through Eq. (3.53). The densities with different values of t are plotted in Fig. 4.5. The exact densities are obtained through Eq. (3.66) as already introduced in Fig. (4.4).

We also plot the density for LUMO level w.r.t. $U_{ext}/|t|$. This shows the property already deduced in Eq. (3.66), i.e., the exact density at the terminal site is a function only of $U_{ext}/|t|$. Howeve,r in HFB the density is a function of U_{ext} and t separately. Thus we get a large deviation from the exact density depending on the values of U_{ext} and t, see Fig. 4.6.

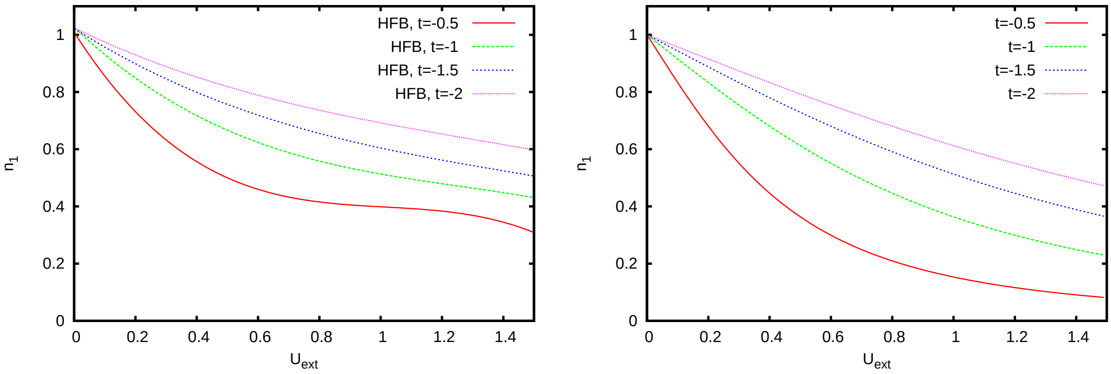


Figure 4.5: Left: Density at terminal site calculated at HFB for LUMO level with different hopping parameters t. Right: The exact densities at the terminal site for LUMO level with different hoppings t. Here $U_0 = U_{HL} = 1$, $\xi_H = -2$ and $\xi_L = -1$.

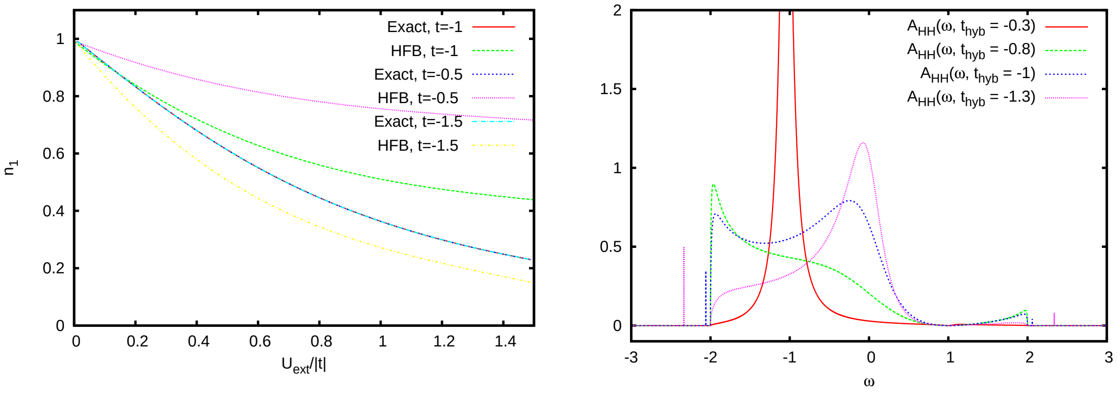


Figure 4.6: Left: Density at terminal site of the chain w.r.t U_{ext}/t in HFB and exact. Right: two-level Fano model Spectral function with different t_{hyb}, $\xi_H = \xi_L = -1, \quad t = -1$

4.2 Fano model

So far we have seen that one can deduce the image-charge at the terminal site through the spectral peak shifts in the interacting model. However, there are also other possibilities to obtain peaks in the spectral function. In Fig. 4.6 we plot also the spectral function (eq. 3.92) at the HOMO level for the two-level Fano model. Even though there are no interactions in the Fano model, and thus all image-charge effects are impossible, we see that with large t_{hyb} we obtain spectral peaks, which also seem to shift w.r.t. different parameters in the model. This is not too suprising since we have already seen the forming of a split-off state in the case of a one-level Fano model, i.e., at the terminal site of the chain, see Fig. 4.4.

4.3 Discussions

1. In our image-charge model we may a find correspondance between the density at the terminal site of the chain and the HOMO/LUMO level spectral peak shift. This correspondence can be used to deduce the exact peak shift from the exact density and the approximate density from approximate peak shifts. With these results we may compare our approximation with the exact results.
2. For the image-charge model we do not find any image-charge effect at the Hartree-Fock level.

This can be seen immediately from Eq. (3.16), which does not contain U_{ext} at all. The fact that the Hartree-Fock approximation is independent of U_{ext} is due to the nature of this approximation: in our calculation the Hartree diagram just probes the density at the terminal site of the chain; the density is naturally constant since we always plug the non-interacting Green's function into the diagrams. Since the density at the terminal site is constant and the Fock diagram only gives on-site corrections, and hence we do not see any U_{ext} dependence at the Hartree-Fock level.

However, for $U_{ext} = 0$ the Hartree-Fock approximation predicts the addition and removal energies for the molecule correctly. This is not too surprising due to the fact that the Hartree-Fock practically takes the Slater determinant and finds optimal orbitals to minimize the ground-state energy. However, in our case with $U_{ext} = 0$ the Hamiltonian is diagonal in the molecule, and hence the exact ground state in the molecule is just a Slater determinant. For a diagonal Hamiltonian the energy levels become just the spectral peaks, and hence the peak positions are predicted correctly by the Hartree-Fock method for $U_{ext} = 0$.

3. In the second order only the "bubble" diagram gives a non-zero contribution. This is a consequence of the structure of our Hamiltonian, which only permits the bubble and "ladder" diagrams to exist. Unlike in the Hartree-Fock case, we now obtain the density response at the terminal cite of the chain to the additional charge in the molecule.

   The fact that the terminal site of the chain now "sees" the additional charge can be understood by considering the "bubble" diagram. The particle-hole "bubble" can be shown to be the first-order approximation of the density response function [4]. In our approximation the additional particle/hole in the molecule interacts with the terminal site of the chain creating a particle-hole "bubble", i.e., a density change to the terminal site of the chain (=image-charge). After this density change the terminal site acts back to the molecule and hence the image-charge effect is, to some extent, encoded into our HFB approximation. It turns out that the value of the "bubble" diagram (at HOMO and LUMO levels) is proportional to $(U_{ext}/t)^2$.

   The self-energies calculated from the "bubble" diagram can be seen in Fig. 4.1. The U_{ext} dependence of the self-energy starts to play a role in the spectral functions as we see in Fig. 4.2. From the spectral function we deduce now the density at the terminal site, and hence we obtain U_{ext} dependence in the density at the HFB level, see Fig. 4.5.

4. From the spectral function at the HOMO/LUMO level, Fig. 4.2, we may notice the peak outside of the continuum. This split-off state forms below/above the energy band immediately as the two conditions given in chapter 4.1.2 are satisfied. The forming of a split-off state is due to the fact that the additional charge creates an effective potential to the terminal site of the chain. If this potential is large enough it can push one state out of the band. This state is then seen as a peak in the spectral function.

5. The densities at the terminal site of the chain are calculated from the spectral peak shifts w.r.t. U_{ext}, see Eqs. 3.52 and 3.51. One can observe that the formation of the bound state does not give any discontinuity into the density.

   An interesting property of the densities is the fact that the larger the hopping parameter the less the additional charge is able to polarize the terminal site. This may be seen as a consequence of the fact that the value of the density-response function is proportional to $1/t^2$, i.e., the smaller t the more the terminal site responds to additional charge in the molecule. Physically one can think the effect through the fact that for small t one has a narrow band and hence a large density of states which in turn implies large density response function [11].

6. There is value of $t \equiv t_e \approx 1.3$ for which the HFB approximation gives an almost exact density, see Fig. 4.6. The fact that there is some t_e for which the approximation works nicely for only one value of t can be viewed as a consequence of the fact that we have made only "single-shot" approximation instead of fully self-consistent series of iterations. If we did a self-consistent calculation we would definetly get less deviation in the results for the HFB approximation, Fig. 4.6, with different t. Doing the fully self-consistent scheme one would get the same results with all different approximations for initial Green's functions. This consideration shows that one must be really careful when doing single-shot approximations.

7. Even though there are no interactions and thus no ”external potential” at the terminal site of the chain in the two-level Fano model, we may see that for large hybridization also here we get split-off states outside the band, see Fig. 4.6.

Appendix A

A.1 Intermediate steps

A.1.1 Operation of the annihilation operator

We consider the operation of $\hat{\psi}(\mathbf{y})$ in the matrix element $\langle\Psi|\hat{\psi}(\mathbf{y})|\mathbf{x}_1\dots\mathbf{x}_n\rangle = \langle\mathbf{x}_1\dots\mathbf{x}_n|\hat{\psi}^\dagger(\mathbf{y})|\Psi\rangle^*$. Here $|\Psi\rangle$ is some general $n-1$ particle state and thus has expansion

$$\begin{aligned}
|\Psi\rangle &= \frac{1}{(n-1)!}\int d\mathbf{y}_2\dots d\mathbf{y}_n \; |\mathbf{y}_2\dots\mathbf{y}_n\rangle\,\langle\mathbf{y}_2\dots\mathbf{y}_n|\Psi\rangle \\
&= \frac{1}{(n-1)!}\int d\mathbf{y}_2\dots d\mathbf{y}_n \; \Psi(\mathbf{y}_2\dots\mathbf{y}_n)|\mathbf{y}_2\dots\mathbf{y}_n\rangle
\end{aligned} \tag{A.1.1}$$

Inserting this (A.1.1) into the matrix element we obtain

$$\begin{aligned}
&\langle\Psi|\hat{\psi}(\mathbf{y}_1)|\mathbf{x}_1\dots\mathbf{x}_n\rangle \\
=\;& \frac{1}{(n-1)!}\int d\mathbf{y}_2\dots d\mathbf{y}_n \; \Psi^*(\mathbf{y}_2\dots\mathbf{y}_n)\,\langle\mathbf{y}_1\mathbf{y}_2\dots\mathbf{y}_n|\mathbf{x}_1\dots\mathbf{x}_n\rangle \\
=\;& \frac{1}{(n-1)!}\int d\mathbf{y}_2\dots d\mathbf{y}_n \; \Psi^*(\mathbf{y}_2\dots\mathbf{y}_n)\sum_\sigma(-1)^\sigma\prod_{i=1}^{n}\delta(\mathbf{y}_i-\mathbf{x}_{\sigma(i)}) \\
=\;& \frac{1}{(n-1)!}\sum_\sigma(-1)^\sigma\delta(\mathbf{y}_1-\mathbf{x}_{\sigma(1)})\Psi^*(\mathbf{x}_{\sigma(2)}\dots\mathbf{x}_{\sigma(n)}) \\
=\;& \sum_{k=1}^{n}\delta(\mathbf{y}_1-\mathbf{x}_k)\frac{1}{(n-1)!}\sum_{\sigma,\sigma(1)=k}(-1)^\sigma\Psi^*(\mathbf{x}_{\sigma(2)}\dots\mathbf{x}_{\sigma(n)}),
\end{aligned} \tag{A.1.2}$$

where on the last line we just wrote the sum over all the permutations as a sum of n classes of $(n-1)!$ permutations that map 1 to k. The permutation of 1 to k gives rise to sign $(-1)^{k-1}$. Any permutation can be obtained by permuting the remaining $n-1$ indices. Now we consider the last term on the last line of (A.1.2)

$$\begin{aligned}
&\frac{1}{(n-1)!}\sum_{\sigma,\sigma(1)=k}(-1)^\sigma\Psi^*(\mathbf{x}_{\sigma(2)}\dots\mathbf{x}_{\sigma(n)}) \\
=\;& \frac{1}{(n-1)!}\sum_{\sigma'}(-1)^{k-1}(-1)^{\sigma'}\Psi^*(\mathbf{x}_{\sigma'(1)}\dots\mathbf{x}_{\sigma'(k-1)}\mathbf{x}_{\sigma'(k+1)}\dots\mathbf{x}_{\sigma'(n)}) \\
=\;& \frac{(-1)^{k-1}}{(n-1)!}\sum_{\sigma'}(-1)^{2\sigma'}\Psi^*(\mathbf{x}_1\dots\mathbf{x}_{k-1}\mathbf{x}_{k+1}\dots\mathbf{x}_n) \\
=\;& \frac{(-1)^{k-1}}{\cancel{(n-1)!}}\cancel{(n-1)!}\Psi^*(\mathbf{x}_1\dots\mathbf{x}_{k-1}\mathbf{x}_{k+1}\dots\mathbf{x}_n),
\end{aligned} \tag{A.1.3}$$

where we used the antisymmetry of the wave function. Now plugging (A.1.3) into (A.1.2) we may deduce

$$\langle\Psi|\hat{\psi}(\mathbf{y}_1)|\mathbf{x}_1\dots\mathbf{x}_n\rangle = \sum_{k=1}^{n}(-1)^{k-1}\delta(\mathbf{y}_1-\mathbf{x}_k)\,\langle\Psi|\mathbf{x}_1\dots\mathbf{x}_{k-1}\mathbf{x}_{k+1}\dots\mathbf{x}_n\rangle\,. \tag{A.1.4}$$

The relation (A.1.4) is valid for any state $n-1$ particle state $\langle\Psi|$ and thus

$$\hat{\psi}(\mathbf{y}_1)|\mathbf{x}_1\dots\mathbf{x}_n\rangle = \sum_{k=1}^{n}(-1)^{k-1}\delta(\mathbf{y}_1-\mathbf{x}_k)|\mathbf{x}_1\dots\mathbf{x}_{k-1}\mathbf{x}_{k+1}\dots\mathbf{x}_n\rangle + |\varphi\rangle, \tag{A.1.5}$$

where $|\Psi\rangle\langle\varphi| = 0$. Thus $|\varphi\rangle$ does not have any component in $n-1$ particle Hilbert space. Taking inner product of both sides (A.1.5) with $\langle\varphi|$ we may conclude

$$\langle\varphi|\varphi\rangle = \langle\varphi|\hat{\psi}(\mathbf{y}_1)|\mathbf{x}_1\dots\mathbf{x}_n\rangle = \langle\mathbf{x}_1\dots\mathbf{x}_n|\hat{\psi}^\dagger(\mathbf{y}_1)|\varphi\rangle^* = 0, \tag{A.1.6}$$

since $\hat{\psi}^\dagger(\mathbf{y}_1)|\varphi\rangle$ cannot have any component in the n particle Hilbert space. Thus $|\varphi\rangle = 0$ and we obtain

$$\hat{\psi}(\mathbf{y}_1)|\mathbf{x}_1\dots\mathbf{x}_n\rangle = \sum_{k=1}^{n}(-1)^{k-1}\delta(\mathbf{y}_1-\mathbf{x}_k)|\mathbf{x}_1\dots\mathbf{x}_{k-1}\mathbf{x}_{k+1}\dots\mathbf{x}_n\rangle. \tag{A.1.7}$$

We quickly check that (A.1.7) is consistent with our normalization of basis states. We may calculate

$$\begin{aligned}
&\langle\mathbf{y}_1\dots\mathbf{y}_n|\mathbf{x}_1\dots\mathbf{x}_n\rangle = \langle 0|\hat{\psi}(\mathbf{y}_n)\dots\hat{\psi}(\mathbf{y}_1)|\mathbf{x}_1\dots\mathbf{x}_n\rangle \\
=\ & \langle 0|\sum_{k_1=1}^{n}(-1)^{k_1-1}\delta(\mathbf{y}_1-\mathbf{x}_{k_1})\hat{\psi}(\mathbf{y}_1)\dots\hat{\psi}(\mathbf{y}_{n-1})|\mathbf{x}_1\dots\mathbf{x}_{k_1-1}\mathbf{x}_{k_1+1}\dots\mathbf{x}_n\rangle \\
=\ & \langle 0|\sum_{k_1=1}^{n}(-1)^{k_1-1}\delta(\mathbf{y}_1-\mathbf{x}_{k_1})\sum_{k_2}^{n-1}(-1)^{k_2-1}\delta(\mathbf{y}_2-\mathbf{x}_{k_2}) \\
\times\ & \hat{\psi}(\mathbf{y}_n)\dots\hat{\psi}(\mathbf{y}_3)|\mathbf{x}'_1\dots\mathbf{x}'_{k_2-1}\mathbf{x}'_{k_2+1}\dots\dots\mathbf{x}'_{n-1}\rangle,
\end{aligned} \tag{A.1.8}$$

where $\{\mathbf{x}'_1\dots\mathbf{x}'_{n-1}\}$ is now the group where $\mathbf{x}_{k_1}$ has been removed from $\{\mathbf{x}_1\dots\mathbf{x}_n\}$. By continuing in this manner we arrive at

$$\begin{aligned}
&\langle\mathbf{y}_1\dots\mathbf{y}_n|\mathbf{x}_1\dots\mathbf{x}_n\rangle \\
=\ & \langle 0|\sum_{k_1=1}^{n}(-1)^{k_1-1}\delta(\mathbf{y}_1-\mathbf{x}_{k_1})\sum_{k_2}^{n-1}(-1)^{k_2-1}\delta(\mathbf{y}_2-\mathbf{x}^{(2)}_{k_2})\dots \\
\times\ & \sum_{k_{n-1}=1}^{2}(-1)^{k_{n-1}-1}\delta(\mathbf{y}_{n-1}-\mathbf{x}^{(n-1)}_{k_{n-1}})\delta(\mathbf{y}_n-\mathbf{x}^{(n)}_{k_n})|0\rangle, \\
=\ & \sum_{k_1=1}^{n}\cdots\sum_{k_{n-1}=1}^{2}(-1)^{k_1+\dots+k_{n-1}-n+1}\prod_{i=1}^{n}\delta(\mathbf{y}_i-\mathbf{x}^{(i)}_{k_i}).
\end{aligned} \tag{A.1.9}$$

We see that every $\mathbf{x}_i$ appear in the product exactly once and the prefactor appears to be the sign of the permutation over $\mathbf{x}_i$'s. We thus conclude

$$\langle\mathbf{y}_1\dots\mathbf{y}_n|\mathbf{x}_1\dots\mathbf{x}_n\rangle = \sum_{\sigma}(-1)^{\sigma}\prod_{i=1}^{n}\delta(\mathbf{y}_i-\mathbf{x}_{\sigma(i)}). \tag{A.1.10}$$

A.1.2 Anti-commutator

To deduce the operation of $\left\{\hat{\psi}^\dagger(\mathbf{x}),\hat{\psi}(\mathbf{y})\right\}$ to arbitrary ket state $|x_1\dots x_n\rangle$ we use the operation of the annihilation operator to the general ket state (1.26). We write

$$\begin{aligned}
\left\{\hat{\psi}^\dagger(\mathbf{x}),\hat{\psi}(\mathbf{y})\right\}|\mathbf{x}_1\dots\mathbf{x}_n\rangle &= \left(\hat{\psi}^\dagger(\mathbf{x})\hat{\psi}(\mathbf{y})+\hat{\psi}(\mathbf{y})\hat{\psi}^\dagger(\mathbf{x})\right)|\mathbf{x}_1\dots\mathbf{x}_n\rangle \\
&= \hat{\psi}^\dagger(\mathbf{x})\sum_{k=1}^{n}(-1)^{k-1}\delta(\mathbf{y}-\mathbf{x}_k)|\mathbf{x}_1\dots\mathbf{x}_{k-1}\mathbf{x}_{k+1}\dots\mathbf{x}_n\rangle \\
&+ \sum_{k=1}^{n+1}(-1)^{k-1}\delta(\mathbf{x}-\mathbf{x}'_k)|\mathbf{x}'_1\dots\mathbf{x}'_{k-1}\mathbf{x}'_{k+1}\dots\mathbf{x}'_{n+1}\rangle,
\end{aligned} \tag{A.1.11}$$

where on the last line we redefined $\mathbf{x},\mathbf{x}_1,\dots,\mathbf{x}_n\to\mathbf{x}'_1,\dots,\mathbf{x}'_{n+1}$. We continue by considering the last line of (A.1.11)

$$\begin{aligned}
&\sum_{k=1}^{n+1}(-1)^{k-1}\delta(\mathbf{x}-\mathbf{x}'_k)|\mathbf{x}'_1\dots\mathbf{x}'_{k-1}\mathbf{x}'_{k+1}\dots\mathbf{x}'_{n+1}\rangle, \\
= \;& \delta(\mathbf{x}-\mathbf{x}'_k)|\mathbf{x}'_2\dots\mathbf{x}'_{n+1}\rangle+\sum_{k=2}^{n+1}(-1)^{k-1}\delta(\mathbf{x}-\mathbf{x}'_k)|\mathbf{x}'_1\dots\mathbf{x}'_{k-1}\mathbf{x}'_{k+1}\dots\mathbf{x}'_n\rangle, \\
= \;& \delta(\mathbf{x}-\mathbf{x}'_k)|\mathbf{x}'_2\dots\mathbf{x}'_{n+1}\rangle+\sum_{k'=1}^{n}(-1)^{k'}\delta(\mathbf{x}-\mathbf{x}'_{k'+1})|\mathbf{x}'_1\dots\mathbf{x}'_{k'}\mathbf{x}'_{k'+2}\dots\mathbf{x}'_n\rangle, \\
= \;& \delta(\mathbf{x}-\mathbf{x}'_k)|\mathbf{x}'_2\dots\mathbf{x}'_{n+1}\rangle-\sum_{k'=1}^{n}(-1)^{k'-1}\delta(\mathbf{x}-\mathbf{x}_{k'})|\mathbf{x}\mathbf{x}_1\dots\mathbf{x}_{k'-1}\mathbf{x}_{k'+1}\dots\mathbf{x}_n\rangle.
\end{aligned} \tag{A.1.12}$$

Plugging this (A.1.12) into (A.1.11) we may deduce

$$\left\{\hat{\psi}^\dagger(\mathbf{x}),\hat{\psi}(\mathbf{y})\right\}=\delta(\mathbf{x}-\mathbf{y}). \tag{A.1.13}$$

A.1.3 Slater Determinant

We want to calculate the inner-product $\langle\mathbf{x}_1\dots\mathbf{x}_N\hat{n}_1\dots\hat{n}_N\rangle$. To get started use the definitions of operators $\hat{a}^\dagger_{n_i}$ (1.31)

$$\begin{aligned}
&\langle\mathbf{x}_1\dots\mathbf{x}_N|\hat{n}_1\dots\hat{n}_N\rangle=\langle\mathbf{x}_1\dots\mathbf{x}_N|\hat{a}^\dagger_{n_1}\dots\hat{a}^\dagger_{n_N}|0\rangle \\
= \;& \int d\mathbf{y}_1\dots d\mathbf{y}_N\,\overbrace{\langle\mathbf{x}_1\dots\mathbf{x}_N|\hat{\psi}^\dagger(\mathbf{y}_1)\dots\hat{\psi}^\dagger(\mathbf{y}_N)|0\rangle}^{\overset{(1.15)}{=}\sum_\sigma(-1)^\sigma\prod_{i=1}^n\delta(\mathbf{y}_i-\mathbf{x}_{\sigma(i)})}\varphi_{n_1}(\mathbf{y}_1)\dots\varphi_{n_N}(\mathbf{y}_N) \\
= \;& \int d\mathbf{y}_1\dots d\mathbf{y}_N\,\sum_\sigma(-1)^\sigma\prod_{i=1}^n\delta(\mathbf{y}_i-\mathbf{x}_{\sigma(i)})\varphi_{n_1}(\mathbf{y}_1)\dots\varphi_{n_N}(\mathbf{y}_N) \\
= \;& \sum_\sigma(-1)^\sigma\varphi_{n_1}(\mathbf{x}_{\sigma(1)})\dots\varphi_{n_N}(\mathbf{x}_{\sigma(N)}), \qquad \text{(A.1.14)}
\end{aligned} \tag{A.1.15}$$

but this last line is nothing but the definition of the determinant of a matrix of $\varphi_i(\mathbf{x}_j)$ and thus

$$\langle\mathbf{x}_1\dots\mathbf{x}_N|\hat{n}_1\dots\hat{n}_N\rangle=\begin{vmatrix}\varphi_{n_1}(\mathbf{x}_1) & \dots & \varphi_{n_1}(\mathbf{x}_N) \\ \vdots & & \vdots \\ \varphi_{n_N}(\mathbf{x}_1) & \dots & \varphi_{n_N}(\mathbf{x}_N)\end{vmatrix} \tag{A.1.16}$$

A.1.4 Operators in second quantization

In this part we will deduce the form of different operators in terms of $\hat{\psi}$ and $\hat{\psi}^\dagger$. We will prove a couple of relations and state the rest due to the fact that all the calculations are quite similar. Consider first

$$\begin{aligned}
\hat{\psi}^\dagger(\mathbf{x})\hat{\psi}(\mathbf{y})|\mathbf{x}_1\ldots\mathbf{x}_n\rangle &\overset{(1.26)}{=} \sum_i (-1)^{i-1}\hat{\psi}^\dagger(\mathbf{x})\delta(\mathbf{y}-\mathbf{x}_i)|\mathbf{x}_1\ldots\mathbf{x}_{i-1}\mathbf{x}_{i+1}\ldots\mathbf{x}_n\rangle \\
&\overset{(1.27)}{=} \sum_i (-1)^{i-1}(-1)^{i-1}\delta(\mathbf{y}-\mathbf{x}_i)|\mathbf{x}_1\ldots\mathbf{x}_{i-1}\mathbf{x}\mathbf{x}_{i+1}\ldots\mathbf{x}_n\rangle \\
&= \sum_i \delta(\mathbf{y}-\mathbf{x}_i)|\mathbf{x}_1\ldots\mathbf{x}_{i-1}\mathbf{x}\mathbf{x}_{i+1}\ldots\mathbf{x}_n\rangle, \qquad \text{(A.1.17)}
\end{aligned}$$

thus we find for $\mathbf{x}=\mathbf{y}$

$$\begin{aligned}
\hat{\psi}^\dagger(\mathbf{x})\hat{\psi}(\mathbf{x})|\mathbf{x}_1\ldots\mathbf{x}_n\rangle &= \sum_k \delta(\mathbf{x}_k-\mathbf{x})|\mathbf{x}_1\ldots\mathbf{x}_n\rangle \\
\Rightarrow \hat{\psi}^\dagger(\mathbf{x})\hat{\psi}(\mathbf{x}) &= \hat{n}(\mathbf{x}). \qquad \text{(A.1.18)}
\end{aligned}$$

Now for example the external potential $\hat{U}$ is easy to deduce. Define

$$\hat{U} = \int \mathrm{d}\mathbf{x}\; u(\mathbf{r})\hat{n}(\mathbf{x}), \tag{A.1.19}$$

then

$$\begin{aligned}
(\hat{U}\Psi)(\mathbf{x}_1,\ldots,\mathbf{x}_n) &= \langle\mathbf{x}_1\ldots\mathbf{x}_n|\hat{U}|\Psi\rangle \\
&= \int \mathrm{d}\mathbf{x}\; u(\mathbf{r})\langle\Psi|\hat{n}(\mathbf{x})|\mathbf{x}_1\ldots\mathbf{x}_n\rangle^* \\
&= \int \mathrm{d}\mathbf{x} \sum_k (\mathbf{x}_k-\mathbf{x})\; u(\mathbf{r})\Psi(\mathbf{x}_1,\ldots,\mathbf{x}_n) \\
&= u(\mathbf{r}_k)\Psi(\mathbf{x}_1,\ldots,\mathbf{x}_n), \qquad \text{(A.1.20)}
\end{aligned}$$

which is the definition of the external potential in coordinate representation. Let us then define the kinetic energy operator as

$$\hat{T} = -\frac{\hbar^2}{2m}\int \mathrm{d}\mathbf{x}\; \hat{\psi}^\dagger(\mathbf{x})\nabla^2\hat{\psi}(\mathbf{x}). \tag{A.1.21}$$

Then we may calculate

$$\begin{aligned}
(\hat{T}\Psi)(\mathbf{x}_1\ldots\mathbf{x}_n) &= -\frac{\hbar^2}{2m}\int \mathrm{d}\mathbf{x}\; \langle\Psi|\hat{\psi}^\dagger(\mathbf{x})\nabla^2\hat{\psi}(\mathbf{x})|\mathbf{x}_1\ldots\mathbf{x}_n\rangle^* \\
&= -\frac{\hbar^2}{2m}\int \mathrm{d}\mathbf{x}\; \nabla^2_{\mathbf{y}}\langle\Psi|\hat{\psi}^\dagger(\mathbf{x})\hat{\psi}(\mathbf{y})|\mathbf{x}_1\ldots\mathbf{x}_n\rangle^*_{|y=x} \\
&\overset{(A.1.17)}{=} -\frac{\hbar^2}{2m}\int \mathrm{d}\mathbf{x}\; \nabla^2_{\mathbf{y}}\sum_i \delta(\mathbf{y}-\mathbf{x}_i)_{|y=x}\Psi(\mathbf{x}_1\ldots\mathbf{x}_{i-1}\mathbf{x}\mathbf{x}_{i+1}\ldots\mathbf{x}_n) \\
&= -\frac{\hbar^2}{2m}\int \mathrm{d}\mathbf{x}\; \sum_i \Psi(\mathbf{x}_1\ldots\mathbf{x}_{i-1}\mathbf{x}\mathbf{x}_{i+1}\ldots\mathbf{x}_n)\nabla^2_{\mathbf{x}}\delta(\mathbf{x}-\mathbf{x}_i), \qquad \text{(A.1.22)}
\end{aligned}$$

partial integrate twice to obtain

$$\begin{aligned}
(\hat{T}\Psi)(\mathbf{x}_1\ldots\mathbf{x}_n) &= -\frac{\hbar^2}{2m}\int \mathrm{d}\mathbf{x}\; \sum_i \delta(\mathbf{x}-\mathbf{x}_i)\nabla^2_{\mathbf{x}}\Psi(\mathbf{x}_1\ldots\mathbf{x}_{i-1}\mathbf{x}\mathbf{x}_{i+1}\ldots\mathbf{x}_n) \\
&= -\frac{\hbar^2}{2m}\sum_i \nabla^2_{x_i}\Psi(\mathbf{x}_1\ldots\mathbf{x}_n), \qquad \text{(A.1.23)}
\end{aligned}$$

i.e., our definition (A.1.21) for the kinetic energy operator is correct. The two body interaction can be found from [10] and it reads

$$\hat{V} = \frac{1}{2}\int \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' V(\mathbf{r},\mathbf{r}')\hat{\psi}^{\dagger}(\mathbf{x})\hat{\psi}^{\dagger}(\mathbf{x}')\hat{\psi}(\mathbf{x}')\hat{\psi}(\mathbf{x}). \tag{A.1.24}$$

A.1.5 Commutation under time ordered product

For the time ordered product defined as

$$\mathcal{T}(\hat{O}(t_{\sigma(n)})\ldots\hat{O}(t_{\sigma(1)})) = \hat{O}(t_n)\ldots\hat{O}(t_1), \tag{A.1.25}$$

with $t_n > \cdots > t_1$ we clearly see that one can order the operators in any order desired, since after time ordering they will turn out to be in same proper order. Now consider exponentials

$$\begin{aligned} e^{\hat{A}(t_2)}e^{\hat{B}(t_1)} &= \sum_{n,m=0}^{\infty}\frac{1}{n!}\hat{A}(t_2)^n\frac{1}{m!}\hat{B}(t_1)^m \\ &= 1+\hat{A}(t_2)+\hat{B}(t_1)+\frac{1}{2}(\hat{A}^2(t_2)+\hat{B}^2(t_1)+2\hat{A}(t_2)\hat{B}(t_1))+\ldots \end{aligned} \tag{A.1.26}$$

$$\begin{aligned} e^{\hat{A}(t_2)+\hat{B}(t_1)} &= \sum_{n=0}^{\infty}\frac{1}{n!}(\hat{A}(t_2)+\hat{B}(t_1))^n \\ &= 1+\hat{A}(t_2)+\hat{B}(t_1)+\frac{1}{2}(\hat{A}^2(t_2)+\hat{B}^2(t_1)+\hat{A}(t_2)\hat{B}(t_1)+\hat{B}(t_1)\hat{A}(t_2))+\ldots \end{aligned} \tag{A.1.27}$$

Taking time ordered product of (A.1.26) and (A.1.27) we see that $\mathcal{T}(e^{\hat{A}(t_2)}e^{\hat{B}(t_1)}) = \mathcal{T}(e^{\hat{A}(t_2)+\hat{B}(t_1)})$.

A.2 Two coupled systems

If two systems are in equilibrium with total energy E and particle number N we need maximize entropy $S = S_1 + S_2$ with the constraints arising from the energy and particle number. Find the extremum of S

$$\begin{aligned} \frac{\partial S}{\partial E_1} &= \frac{\partial S_1}{\partial E_1}+\frac{\partial S_2}{\partial E_1} = \frac{\partial S_1}{\partial E_1}+\overbrace{\frac{\partial E_2}{\partial E_1}}^{\frac{\partial E-E_1}{\partial E_1}=-1}\frac{\partial S_2}{\partial E_2} = \frac{\partial S_1}{\partial E_1}-\frac{\partial S_2}{\partial E_2} = 0 \\ \frac{\partial S}{\partial N_1} &= \frac{\partial S_1}{\partial N_1}+\frac{\partial S_2}{\partial N_1} = \frac{\partial S_1}{\partial N_1}+\overbrace{\frac{\partial N_2}{\partial N_1}}^{\frac{\partial N-N_1}{\partial N_1}=-1}\frac{\partial S_2}{\partial N_2} = \frac{\partial S_1}{\partial N_1}-\frac{\partial S_2}{\partial N_2} = 0. \end{aligned}$$

We demand that for two systems in equilibrium the temperature and chemical potential are equal. Thus we define

$$\frac{1}{T_1} = \frac{\partial S_1}{\partial E_1} = \frac{\partial S_2}{\partial E_2} = \frac{1}{T_2} \tag{A.2.1}$$

$$-\frac{\mu_1}{T_1} = \frac{\partial S_1}{\partial N_1} = \frac{\partial S_2}{\partial N_2} = -\frac{\mu_2}{T_2} \tag{A.2.2}$$

A.3 tight-binding chain

The tight binding model is widely used in condensed matter physics and it forms the basis for many approximations of many-particle systems, for example the Hubbard model [8]. The one dimensional tight binding Hamiltonian can, in second quantization, be written as

$$\hat{H} = \sum_{i,j} t_{ij}\hat{a}_i^\dagger \hat{a}_j. \tag{A.3.1}$$

The tight binding approximation assumes that the electrons are non-interacting and that the matrix elements t_{ij} with $j \neq i \pm 1$ are zero and for the $t_{i,i\pm1} = t$. Schematically the model can be viewed as chain of sites which the electron can occupy and hop from a site to the one next to it.

As the electrons do not interact they see each other only through the Pauli exclusion principle, which states that two fermions with all same quantum numbers can not occupy the same site. For tight binding Hamiltonian this leads to the fact that there cannot be more than two electrons at one site and these two must have opposite spins.

There are many ways to diagonalize the above Hamiltonian. We will go it through in detail since I have been using these eigenenergies and states a lot. We start by writing the Eq. (A.3.1) in the form

$$\hat{H} = \sum_{i,j} t_{ij}\hat{a}_i^\dagger \hat{a}_j = \sum_{i,j} \langle i|\hat{h}|j\rangle \hat{a}_i^\dagger \hat{a}_j, \tag{A.3.2}$$

where $\hat{h} = t\sum_{i=1}^{N-1} |i+1\rangle\langle i| + |i\rangle\langle i+1|$, where N is the number of sites. Let the eigenstate of $\hat{h}$ be $|\phi_k\rangle$ with eigenvalue ϵ_k. Since the states $|i\rangle$ form complete set we can expand the eigenstate $|\phi_k\rangle$ with these basis states yielding $|\phi_k\rangle = \sum_i c_i^k|i\rangle$. Now we use the Schrödinger equation to obtain

$$\begin{aligned}
\epsilon_k|\phi_k\rangle &= \epsilon_k\sum_i c_i^k|i\rangle = \hat{h}\sum_i c_i^k|i\rangle \\
&= t\sum_{j=1}^{N-1}\sum_{i=1}^{N} |j+1\rangle\langle j|c_i^k|i\rangle + |j\rangle\langle j+1|c_i^k|i\rangle \\
&= t\sum_{j=1}^{N-1} c_j^k|j+1\rangle + t\sum_{j=1}^{N-1} c_{j+1}^k|j\rangle \\
&= t\sum_{j=2}^{N} c_{j-1}^k|j\rangle + t\sum_{j=1}^{N-1} c_{j+1}^k|j\rangle \\
&= t\left[c_{N-1}^k|N\rangle + c_2^k|1\rangle + \sum_{i=2}^{N-1}(c_{i-1} + c_{i+1}^k)|i\rangle\right].
\end{aligned} \tag{A.3.3}$$

Now comparing the first and the last lines of (A.3.3) one can deduce properties of the factors c_i^k. The relations read

$$\begin{aligned}
\epsilon_k c_j^k &= t(c_{j+1} + c_{j-1}) \quad \forall\ j \in \{2,\dots,N-1\} \\
\epsilon_k c_1^k &= t c_2^k \\
\epsilon_k c_N^k &= t c_{N-1}^k.
\end{aligned} \tag{A.3.4}$$

Next we make ansatz: let the factors be of the form $c_j^k = \alpha_k \sin(\beta_k j)$. Now the first condition of (A.3.4) gives

$$\begin{aligned}
\epsilon_k\alpha_k\sin(\beta_k j) &= t[\alpha_k\sin(\beta_k(j+1)) + \alpha_k\sin(\beta_k(j-1))] \\
&= t\alpha_k[\sin(\beta_k(j+1)) + \sin(\beta_k(j-1))] \\
&= \frac{t\alpha_k}{2}[\mathrm{e}^{\beta_k(j+1)} - \mathrm{e}^{-\beta_k(j+1)} + \mathrm{e}^{\beta_k(j-1)} - \mathrm{e}^{-\beta_k(j-1)}] \\
&= \frac{t\alpha_k}{2}\left(\mathrm{e}^{\beta_k} + \mathrm{e}^{-\beta_k}\right)\left(\mathrm{e}^{\beta_k j} - \mathrm{e}^{-\beta_k j}\right) \\
&= 2t\alpha_k\sin(\beta_k j)\cos(\beta_k) \\
\Rightarrow \epsilon_k &= 2t\cos(\beta_k j).
\end{aligned} \tag{A.3.5}$$

Next we use the third equality of (A.3.4) and the result obtained above (A.3.5) to find

$$\begin{aligned}
\epsilon_k \sin(\beta_k N) &= t\sin(\beta_k(N-1)) \\
2t\cos(\beta_k)\sin(\beta_k N) &= t\sin(\beta_k(N-1)) \\
t[\sin(\beta_k(N+1)) + \cancel{\sin(\beta_k(N-1))}] &= \cancel{t\sin(\beta_k(N-1))} \\
\Rightarrow \sin(\beta_k(N+1)) &= 0 \\
\Rightarrow \beta_k = \frac{k\pi}{N+1} & \quad \forall \quad k \in \{1,\dots,N\}. \qquad \text{(A.3.6)}
\end{aligned}$$

Here from the second to the third line we used a result that can be read from the intermediate steps of Eq. (A.3.5). The last task to do is to determine the coefficients α_k. This is done by requiring that the eigenstates are normalized to unity, i.e., $\sum_{j=1}^{N} |c_j^k|^2 = 1$. In the limit $N \to \infty$ we may show

$$\begin{aligned}
1 &= \sum_{j=1}^{N} |c_j^k|^2 \xrightarrow{N\to\infty} \int_1^N \mathrm{d}j \ \alpha_k^2 \sin^2(\frac{\pi k}{N+1} j), \quad \text{let } \pi k j/(N+1) = x \\
&= \int_0^{\pi k} \mathrm{d}x \ \frac{N+1}{\pi k} \alpha_k^2 \sin^2(x) = \alpha_k^2 \frac{N+1}{\cancel{\pi k}} \frac{\cancel{\pi k}}{2} \\
\Rightarrow \quad & \alpha_k = \sqrt{\frac{2}{N+1}} \qquad \text{(A.3.7)}
\end{aligned}$$

where we chose the plus sign for the factor α_k. Note also that the factor is independent of the index k. We are now ready to present the eigenenergies and -states of the one dimensional tight binding Hamiltonian system

$$\epsilon_k = 2t\cos\left(\frac{k\pi}{N+1}\right) \qquad \text{(A.3.8)}$$

$$c_i^k = \sqrt{\frac{2}{N+1}} \sin\left(\frac{k\pi}{N+1} i\right), \quad \forall \ k, i \in \{1,\dots,N\}. \qquad \text{(A.3.9)}$$

Now the TB Hamiltonian can be expressed as

$$\begin{aligned}
\hat{H}_{\mathrm{TB}} &= \sum_k \epsilon_k \hat{c}_k^\dagger \hat{c}_k, \qquad \text{where} && \text{(A.3.10)} \\
\hat{c}_k^\dagger &= \sum_i c_i^k \hat{a}_i^\dagger && \text{(A.3.11)} \\
\hat{c}_k &= \sum_i c_k^{i*} \hat{a}_i. && \text{(A.3.12)}
\end{aligned}$$

A.4 Green's function in different exactly solvable systems

A.4.1 Non-interacting Green's function

In zero temperature the Green's function becomes (2.44)

$$G_0(xt, x't') = -i\langle \Psi_0 | \mathcal{T}(\hat{\psi}_H(x,t)\hat{\psi}_H^\dagger(x',t')) | \Psi_0 \rangle, \qquad \text{(A.4.1)}$$

where $\mathcal{T}(A(t)B(t')) = \theta(t-t')A(t)B(t') - \theta(t'-t)B(t')A(t)$, i.e., $\mathcal{T}$ is the time-ordering operator ordering last time to left. As usual $x = (r, \sigma)$ is the space-spin coordinate. Operators $\hat{\psi}_H(x,t)$ and

$\hat{\psi}^\dagger_H(x',t')$ can be expanded with the energy eigenstates[1]

$$\begin{aligned} \hat{\psi}_H(x,t) &= \sum_k \phi_k(r)\hat{a}_{k,H}(t) \\ \hat{\psi}^\dagger_H(x',t') &= \sum_k \phi^*_k(r')\hat{a}^\dagger_{k,H}(t'), \qquad k=(k,\sigma) \end{aligned} \tag{A.4.2}$$

Now plug these (A.4.2) into (A.4.1). With time ordering written open this yields

$$\begin{aligned} G_0(xt,x't') &= -i\sum_{k,k'}\theta(t-t')\phi_k(r)\phi^*_{k'}(r')\langle\Psi_0|\hat{a}_{k,H}(t)\hat{a}^\dagger_{k',H}(t')|\Psi_0\rangle \\ &+ \theta(t'-t)\phi_k(r)\phi^*_{k'}(r')\langle\Psi_0|\hat{a}^\dagger_{k',H}(t')\hat{a}_{k,H}(t)|\Psi_0\rangle. \end{aligned} \tag{A.4.3}$$

Next we transform the operators $\hat{a}^\dagger_{k',H}(t')$ and $\hat{a}_{k,H}(t)$ from the Heisenberg to the Schrödinger picture. Since our Hamiltonian is constant in time the transformation is just

$$\hat{O}_H(t) = e^{i\hat{H}t}\hat{O}_S e^{-i\hat{H}t}. \tag{A.4.4}$$

Inserting the identity $\sum_n |\Psi^{N\pm1}_n\rangle\langle\Psi^{N\pm1}_n|$, where $\langle\Psi^{N\pm1}_i|$ are energy eigenstates with one particle added/removed in comparison to ground state, between the creation and annihilation operators, transforming to the Schrödinger picture and operating with the exponentials one obtains

$$\begin{aligned} G_0(xt,x't') &= -i\sum_{k,k',n}\theta(t-t')\phi_k(r)\phi^*_{k'}(r')e^{i(E_0-E^{N+1}_n)(t-t')} \\ &\times \langle\Psi_0|\hat{a}_k|\Psi^{N+1}_n\rangle\langle\Psi^{N+1}_n|\hat{a}^\dagger_{k'}|\Psi_0\rangle \\ &+ \theta(t'-t)\phi_k(r)\phi^*_{k'}(r')e^{i(E_0-E^{N-1}_n)(t'-t)} \\ &\times \langle\Psi_0|\hat{a}^\dagger_{k'}|\Psi^{N-1}_n\rangle\langle\Psi^{N-1}_n|\hat{a}_k|\Psi_0\rangle. \end{aligned} \tag{A.4.5}$$

To proceed we make the observation that the ground state $|\Psi_0\rangle$ is the Fermi sphere and thus to obtain a non-zero overlap with the states where one electron has been added/removed we must have $|\Psi^{N+1}_k\rangle = \hat{a}^\dagger_k|\Psi_0\rangle$ where k such that it is out of the Fermi sphere. Now $\hat{H}|\Psi^{N+1}_k\rangle = \hat{H}\hat{a}^\dagger_k|\Psi_0\rangle = (\epsilon_k + E_0)|\Psi^{N+1}_k\rangle$, moreover, $\hat{H}|\Psi^{N-1}_p\rangle = \hat{H}\hat{a}_p|\Psi_0\rangle = (\epsilon_p + E_0)|\Psi^{N-1}_p\rangle$ where $k \notin \{FS\}$ and $p \in \{FS\}$. With the requirement of non-vanishing overlaps we may restrict the summation indices to be outside/inside of the Fermi sphere. moreover, both of the matrix elements must be non-zero which leads to $k = k'$. Furthermore we define $\tau = t - t'$, now Eq. (A.4.5) may be written

$$\begin{aligned} G_0(xt,x't') &= -i\sum_{k>N/2}\theta(\tau)\phi_k(r)\phi^*_{k'}(r')e^{-i\epsilon_k\tau} \\ &+ \sum_{k\le N/2}\theta(-\tau)\phi_k(r)\phi^*_{k'}(r')e^{-i\epsilon_k\tau}. \end{aligned} \tag{A.4.6}$$

The fact that $k \gtrless N/2$ is not a problem since as we remember k is a space-spin index and thus the half integer numbers correspond to different spin orientations.

In this particular thesis we work most of the time in frequency space. We may obtain the Green's function in frequency space by a Fourier transform [2]. We have to use the known identity [2]

$$\theta(\tau) = \lim_{\eta\to0^+} -\frac{1}{2\pi i}\int \mathrm{d}\omega\frac{e^{-i\omega\tau}}{w+i\eta}. \tag{A.4.7}$$

---

[1] Note that since our Hamiltonian is of the form $\hat{H} = \sum_i \epsilon_i\hat{a}^\dagger_i\hat{a}_i$, where $\hat{a}^\dagger$ and $\hat{a}$ are operators in site basis, the Hamiltonian has common energy and site eigenstates.

Perform the Fourier transform as

$$\begin{aligned}
G_0(x,x',\omega) &= -i\sum_{k>N/2}\phi_k(r)\phi_k^*(r')\lim_{\eta\to0^+}\left(-\frac{1}{2\pi i}\right)\int \mathrm{d}\omega'\mathrm{d}\tau\frac{e^{-i\omega'\tau}}{\omega'+i\eta}e^{i\omega\tau}e^{-i\epsilon_k\tau}\\
&\quad +i\sum_{k\le N/2}\phi_k(r)\phi_k^*(r')\lim_{\eta\to0^+}\left(-\frac{1}{2\pi i}\right)\int \mathrm{d}\omega'\mathrm{d}\tau\frac{e^{i\omega'\tau}}{\omega'+i\eta}e^{i\omega\tau}e^{-i\epsilon_k\tau}\\
&= \sum_{k>N/2}\phi_k(r)\phi_k^*(r')\lim_{\eta\to0^+}\int \mathrm{d}\omega'\frac{\delta(\omega-\omega'-\epsilon_k)}{\omega'+i\eta}\\
&\quad -\sum_{k\le N/2}\phi_k(r)\phi_k^*(r')\lim_{\eta\to0^+}\int \mathrm{d}\omega'\frac{\delta(\omega+\omega'-\epsilon_k)}{\omega'+i\eta}\\
&= +\sum_{k>N/2}\phi_k(r)\phi_k^*(r')\lim_{\eta\to0^+}\frac{1}{\omega-\epsilon_k+i\eta}\\
&\quad -\sum_{k\le N/2}\phi_k(r)\phi_k^*(r')\lim_{\eta\to0^+}\frac{-1}{\omega-\epsilon_k-i\eta}\\
&= \sum_k\phi_k(r)\phi_k^*(r')\frac{1}{\omega-\epsilon_k+i\eta^+\mathrm{sgn}(\epsilon_k)}\\
&= \sum_{k,k'}\phi_k(r)\phi_{k'}^*(r')G^0_{kk'}(\omega), \qquad (A.4.8)
\end{aligned}$$

where we introduce $\mathrm{sgn}(\epsilon_k)=+1$ (-1) for k out (in) of the Fermi sphere and η^+ has the obvious meaning as $\lim_{\eta\to0^+}$. One may now finally write the components of the Green's function matrix for free electrons

$$G^0_{kk'}(\omega)=\frac{\delta_{kk'}}{\omega-\epsilon_k+i\eta^+\mathrm{sgn}(\epsilon_k)}. \qquad (A.4.9)$$

A.4.2 Green's function in a tight-binding chain

As above in A.4.1 we start with the definition of the Green's function at zero temperature

$$G_0(xt,x't')=-i\langle\Psi_0|\mathcal{T}(\hat\psi_H(x,t)\hat\psi_H^\dagger(x',t'))|\Psi_0\rangle. \qquad (A.4.10)$$

The operator $\mathcal{T}$ has the same meaning as in chapter A.4.1. Now we would again like to expand $\hat\psi_H(x,t)$ and $\hat\psi_H^\dagger(x',t')$ in energy eigenstates. This is a bit more tricky since the Hamiltonian for the tight binding model does not have common energy and occupation eigenstates. In order to proceed we need the relation between the operators in site basis and the operators in energy basis. For this Hamiltonian, these can be collected from A.3 by remembering that the transformation matrix c_i^k must be unitary and inverting Eqs. (A.3.11) and (A.3.12). The expansion becomes

$$\begin{aligned}
\hat\psi_H(x,t) &= \sum_k\phi_k(r)\hat a_{k,H}(t)=\sum_{k,j}\phi_k(r)c_j^k\hat c_{j,H}(t) \qquad (A.4.11)\\
\hat\psi_H^\dagger(x',t') &= \sum_k\phi_k^*(r')\hat a_{k,H}^\dagger(t')=\sum_{k,j}\phi_k(r')c_j^k\hat c_{j,H}^\dagger(t'), \qquad (A.4.12)
\end{aligned}$$

where in the former we used $c_k^{i*}=c_i^k$. Now these (A.4.11) and (A.4.12) can be plugged into (A.4.10). After writing the time ordering open and transforming from the Heisenberg to the Schrödinger picture the equation for the Green's function reads

$$\begin{aligned}
G_0^{\mathrm{TB}}\,(xt,x't') &= -i\sum_{k,k',j,j'}\theta(t-t')c_j^kc_{j'}^{k'}\phi_k(r)\phi_{k'}^*(r')\langle\Psi_0|\hat c_{j,H}(t)\hat c_{j',H}^\dagger(t')|\Psi_0\rangle\\
&\quad +\ \theta(t'-t)c_{j'}^{k'}c_j^k\phi_k(r)\phi_{k'}^*(r')\langle\Psi_0|\hat c_{j',H}^\dagger(t')\hat c_{j,H}(t)|\Psi_0\rangle. \qquad (A.4.13)
\end{aligned}$$

Transforming to the Schrödinger picture and inserting unit operators equivalently as in (A.4.4) and (A.4.5) we obtain

$$
\begin{aligned}
G_0^{\mathrm{TB}}\,(xt,x't') &= -i \sum_{k,k',j,j',n} \theta(t-t') c_j^k c_{j'}^{k'} \phi_k(r)\phi_{k'}^*(r') e^{i(E_0-E_n^{N+1})(t-t')} \\
&\times \langle \Psi_0|\hat{c}_j|\Psi_n^{N+1}\rangle\langle\Psi_n^{N+1}|\hat{c}_{j'}^\dagger|\Psi_0\rangle \\
&+ \theta(t'-t) c_{j'}^{k'} c_j^k \phi_k(r)\phi_{k'}^*(r') e^{i(E_0-E_n^{N-1})(t'-t)} \\
&\times \langle \Psi_0|\hat{c}_{j'}^\dagger|\Psi_n^{N-1}\rangle\langle\Psi_n^{N-1}|\hat{c}_j|\Psi_0\rangle. \qquad \text{(A.4.14)}
\end{aligned}
$$

Now we use similar arguing as in A.4.1 to show that one must have $j = j' = n$ and that the sums must run outside (inside) of the Fermi sphere for $\langle\Psi_0|\hat{c}_j|\Psi_n^{N+1}\rangle$ ($\langle\Psi_0|\hat{c}_{j'}^\dagger|\Psi_n^{N-1}\rangle$). After these considerations one has

$$
\begin{aligned}
G_0^{\mathrm{TB}}\,(xt,x't') &= -i \sum_{k,k',n>N/2} \theta(t-t') c_n^k c_n^{k'} \phi_k(r)\phi_{k'}^*(r') e^{i(E_0-E_n^{N+1})(t-t')} \\
&+ i \sum_{k,k',n\leq N/2} \theta(t'-t) c_n^{k'} c_n^k \phi_k(r)\phi_{k'}^*(r') e^{i(E_0-E_n^{N-1})(t'-t)}.
\end{aligned}
\qquad \text{(A.4.15)}
$$

We perform the Fourier transform completely analogously to Eq. (A.4.8) to yield

$$
\begin{aligned}
G_0^{\mathrm{TB}}\,(\omega,x,x') &= \sum_{k,k'} \phi_k(r)\phi_{k'}^*(r') \sum_{n=1}^{N} \frac{c_n^k c_n^{k'}}{\omega-\epsilon_n+i\eta^+\mathrm{sgn}(\epsilon_n)}, \\
&= \sum_{k,k'} \phi_k(r)\phi_{k'}^*(r') G_{0,kk'}^{\mathrm{TB}}(\omega) \qquad \text{(A.4.16)}
\end{aligned}
$$

where ϵ_n is the energy of a single-particle at level n and factors c_n^k and $c_n^{k'}$ come from (A.3.9). Thus the Green's function matrix for the TB chain becomes

$$
G_{0,kk'}^{\mathrm{TB}}(\omega) = \frac{2}{N+1} \sum_{n=1}^{N} \frac{\sin\left(\frac{k\pi}{N+1}n\right)\sin\left(\frac{k'\pi}{N+1}n\right)}{\omega - 2t\cos\left(\frac{n\pi}{N+1}\right) + i\eta^+\mathrm{sgn}\left(2t\cos\left(\frac{n\pi}{N+1}\right)\right)}. \qquad \text{(A.4.17)}
$$

A.5 Equations of motion in general bases

As it is in most cases useful to work in general bases we will derive the equations of motion for the single-particle Green's function in general bases here. We start by expanding the single-particle Green's function (2.7) in terms of general bases through (1.33) and (1.34). We obtain

$$
\begin{aligned}
G(\mathbf{x}z,\mathbf{x}'z') &= -i\left\langle \mathcal{T}_\gamma\left(\hat{\psi}_H(\mathbf{x}z)\hat{\psi}_H^\dagger(\mathbf{x}'z')\right)\right\rangle \\
&= -i\sum_{k,k'} \phi_k(\mathbf{r})\phi_{k'}^*(\mathbf{r}') \left\langle \mathcal{T}_\gamma\left(\hat{a}_{k,H}(z)\hat{a}_{k',H}^\dagger(z')\right)\right\rangle \\
&= \sum_{k,k'} \phi_k(\mathbf{r})\phi_{k'}^*(\mathbf{r}') G_{kk'}(z,z'), \qquad \text{(A.5.1)} \\
G(\mathbf{x}_1z_1,\mathbf{x}_2z_2;\mathbf{x}_1'z_1',\mathbf{x}_2'z_2') &= \sum_{\substack{k,k'\\ l,l'}} \phi_k(\mathbf{r}_1)\phi_l(\mathbf{r}_2)\phi_{k'}^*(\mathbf{r}_1')\phi_{l'}^*(\mathbf{r}_2') G_{kl,k'l'}(z_1z_2;z_1'z_2'), \qquad \text{(A.5.2)}
\end{aligned}
$$

for single and two-particle Green's functions respectively, where we defined the Green's function matrices as

$$
\begin{aligned}
G_{kk'}(z,z') &= -i\left\langle \mathcal{T}_\gamma\left(\hat{a}_{k,H}(z)\hat{a}_{k',H}^\dagger(z')\right)\right\rangle \qquad \text{(A.5.3)} \\
G_{kl,k'l'}(z_1z_2;z_1'z_2') &= -i\left\langle \mathcal{T}_\gamma\left(\hat{a}_{k,H}(z_1)\hat{a}_{l,H}(z_2)\hat{a}_{k',H}^\dagger(z_1')\hat{a}_{l',H}^\dagger(z_2')\right)\right\rangle. \qquad \text{(A.5.4)}
\end{aligned}
$$

Now we may plug these (A.5.1) and (A.5.2) into the equations of motion for the Green's function Eqs. (2.15) and (2.16) and solve the equation of motion for the single-particle Green's function matrix. For (2.15) we have

$$\begin{aligned} &\left[i\hbar\partial_z - \hat{h}(\mathbf{r}z)\right] \sum_{k,k'} \phi_k(\mathbf{r})\phi^*_{k'}(\mathbf{r}')G_{kk'}(z,z') \\ = \quad & \hbar\delta(z-z')\delta(\mathbf{x}-\mathbf{x}') - i\int \mathrm{d}\mathbf{x}''\mathrm{d}\mathbf{z}''\ v(\mathbf{r}^+,\mathbf{r}'')\sum_{\substack{k,k'\\ l,l'}} \phi_k(\mathbf{r})\phi_l(\mathbf{r}'')\phi^*_{k'}(\mathbf{r}')\phi^*_{l'}(\mathbf{r}'')G_{kl,k'l'}(zz'';z'z''^+). \end{aligned} \tag{A.5.5}$$

Integrating both sides with $\int \mathrm{d}\mathbf{r}\ \phi^*_j(\mathbf{r})$ and using (1.30) we may write

$$\begin{aligned} & i\hbar\partial_z \sum_{k'} \phi^*_{k'}(\mathbf{r}')G_{jk'}(z,z') - \sum_{k,k'} \phi^*_{k'}(\mathbf{r}')h_{jk}(z)G_{kk'}(z,z') \\ = \quad & \hbar\delta(z-z')\phi^*_j(\mathbf{r}')\delta_{\sigma_j\sigma_{\mathbf{x}'}} - i\sum_{\substack{k'\\ l,l'}} v_{ll'}\phi^*_{k'}(\mathbf{r}')G_{jl,k'l'}(zz'';z'z''^+), \end{aligned} \tag{A.5.6}$$

where

$$h_{jk}(z) = \int \mathrm{d}\mathbf{r}\ \phi^*_j(\mathbf{r})\hat{h}(\mathbf{r}z)\phi_k(\mathbf{r}) \tag{A.5.7}$$

$$v_{ll'} = \int \mathrm{d}\mathbf{x}''\mathrm{d}\mathbf{z}''\ \phi_l(\mathbf{r}'')v(\mathbf{r}^+,\mathbf{r}'')\phi^*_{l'}(\mathbf{r}''). \tag{A.5.8}$$

Integrating again but now with $\int \mathrm{d}\mathbf{r}'\ \phi_i(\mathbf{r}')$ we get from (A.5.6) to

$$i\hbar\partial_z G_{ji}(z,z') - \sum_k h_{jk}(z)G_{ki}(z,z') = \hbar\delta(z-z')\delta_{ij} - i\sum_{l,l'} v_{ll'}G_{jl,il'}(zz'';z'z''^+). \tag{A.5.9}$$

For non-interacting systems (A.5.9) can be written as a matrix equation

$$\left[i\hbar\partial_z - h(z)\right]G(z,z') = \hbar\delta(z-z'). \tag{A.5.10}$$

Similarly one can derive

$$G(z,z')\left[h(z) - i\hbar\overleftarrow{\partial}_z\right] = \hbar\delta(z-z'), \tag{A.5.11}$$

where $\overleftarrow{\partial}_z$ means that the derivative operates to left. Eqs. (A.5.10) and (A.5.11) must be solved with the boundary conditions

$$G(t_0,z') = -G(t_0-i\beta,z') \tag{A.5.12}$$

$$G(z,t_0) = -G(z,t_0-i\beta), \tag{A.5.13}$$

which follow directly from the fermionic time ordering in definition of the Green's function.

A.6 Dyson equation in general bases

To express the Dyson equation Eq. (2.40) in terms of general operators $\hat{a}$ and $\hat{a}^\dagger$ we only need to expand the Green's function in terms of these operators and use the orthonormality of the basis functions. Use the expansion (A.5.1) for the single-particle Green's function to write (2.40) as

$$\begin{aligned}
&\sum_{k,k'} \phi_k(\mathbf{r})\phi^*_{k'}(\mathbf{r}')G_{kk'}(z,z') \\
=\;& \sum_{k,k'} \phi_k(\mathbf{r})\phi^*_{k'}(\mathbf{r}')G_{0,kk'}(z,z') \\
+\;& \int_\gamma \mathrm{d}1\mathrm{d}1' \sum_{\substack{k,k'\\p,p'}} \phi_k(\mathbf{r})\phi^*_{k'}(\mathbf{r}_1)G_{0,kk'}(z,z_1)\ \Sigma(1,1')\phi_p(\mathbf{r}_{1'})\phi^*_{p'}(\mathbf{r}')G_{pp'}(z_{1'},z') \\
=\;& \sum_{k,k'} \phi_k(\mathbf{r})\phi^*_{k'}(\mathbf{r}')G_{0,kk'}(z,z') + \sum_{\substack{k,k'\\p,p'}} \phi_k(\mathbf{r})\phi^*_{p'}(\mathbf{r}')G_{0,kk'}(z,z_1)\ \Sigma_{k'p}G_{pp'}(z_{1'},z'), \qquad \text{(A.6.1)}
\end{aligned}$$

where we defined the self-energy matrix as

$$\Sigma_{k'p} = \int_\gamma \mathrm{d}1\mathrm{d}1'\ \phi^*_{k'}(\mathbf{r}_1)\ \Sigma(1,1')\phi_p(\mathbf{r}_{1'}). \tag{A.6.2}$$

Integrating over $\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\ \phi^*_j(\mathbf{r})\phi_i(\mathbf{r}')$ and using (1.30) we obtain

$$\begin{aligned}
G_{ji}(z,z') &= G_{0,ji}(z,z') + \sum_{k'p} G_{0,jk'}(z,z_1)\ \Sigma_{k'p}G_{pi}(z_{1'},z') && \text{(A.6.3)}\\
G &= G_0 + G_0\Sigma G. && \text{(A.6.4)}
\end{aligned}$$

From (A.6.4) we may solve for G

$$\begin{aligned}
G &= G_0 + G_0\Sigma G \qquad |G_0^{-1} \\
G_0^{-1}G &= 1 + \Sigma G \\
(G_0^{-1} - \Sigma)G &= 1 + \\
\Rightarrow G &= (G_0^{-1} - \Sigma)^{-1}. && \text{(A.6.5)}
\end{aligned}$$

A.7 Fano model intermediate steps

A.7.1 Embedding self-energy integrals

Imaginary part

For the retarded self-energy equation Eq. (3.82) turns into

$$\Sigma^R(\omega) = t^2_{hyb} \sum_{k=1}^{N} \frac{\frac{2}{N+1}\sin^2\left(\frac{\pi k}{N+1}\right)}{\omega - 2t\cos\left(\frac{\pi k}{N+1}\right) + i\eta}. \tag{A.7.1}$$

Taking the limit $N \to \infty$ we obtain for the imaginary part

$$\begin{aligned} \mathrm{Im}\Sigma^R(\omega) &= -t_{hyb}^2\frac{2}{\pi}\int_0^\pi \mathrm{d}x\ \sin^2(x)\frac{\eta}{(\omega-2t\cos(x))^2+\eta^2}\\ &= -2t_{hyb}^2\int_0^\pi \mathrm{d}x\ \sin^2(x)\delta(\omega-2t\cos(x))\\ &= -2t_{hyb}^2\int_0^\pi \mathrm{d}x\ \frac{\sin^2(x)}{|2t\sin(x)|}\delta(x-a)\\ &\overset{(A.7.3)}{=} -\frac{t_{hyb}^2}{|t|}\int_0^\pi \mathrm{d}x\ \sin(x)\delta(x-a)\\ &= -\frac{t_{hyb}^2}{|t|}\int_0^\pi \mathrm{d}x\ \sqrt{1-\cos^2(x)}\delta(x-a), \qquad \text{where } a=\arccos\left(\frac{\omega}{2t}\right)\\ &= -\frac{t_{hyb}^2}{|t|}\begin{cases}\sqrt{1-\left(\frac{\omega}{2t}\right)^2}=\frac{1}{2|t|}\sqrt{4t^2-\omega}, & \omega\in[2t,-2t]\\ 0, & \omega\notin[2t,-2t].\end{cases} \end{aligned} \tag{A.7.2}$$

Through this imaginary part we may obtain the real part of retarded self-energy through Kramer-Kronig relations, see Appendix A.9.

In the derivation we used $\frac{1}{\pi}\lim_{\eta\to 0^+}\frac{\eta}{f(x)^2+\eta^2} = \delta(f(x))$. In addition we derived

$$\begin{aligned} \int \mathrm{d}x\ \delta(f(x))g(x) &= \int \mathrm{d}x\frac{1}{\pi}\lim_{\eta\to 0^+}\frac{\eta}{f(x)^2+\eta^2}g(x)\\ &= \frac{1}{f'(x_0)^2}\int \mathrm{d}x\frac{1}{\pi}\lim_{\eta\to 0^+}\frac{\eta}{(x-x_0)^2-\left(\frac{\eta}{f'(x_0)}\right)^2}g(x)\\ &\overset{\frac{\eta}{|f'(x_0)|}\equiv\epsilon}{=} \frac{1}{f'(x_0)^2}\int \mathrm{d}x\frac{1}{\pi}\lim_{|f'(x_0)|\epsilon\to 0^+}\frac{|f'(x_0)|\epsilon}{(x-x_0)^2-\epsilon^2}g(x)\\ &= \frac{1}{f'(x_0)^2}\int \mathrm{d}x\frac{1}{\pi}\lim_{\epsilon\to 0^+}\frac{|f'(x_0)|\epsilon}{(x-x_0)^2+\epsilon^2}g(x)\\ &= \frac{1}{|f'(x_0)|}\int \mathrm{d}x\delta(x-x_0)g(x), \end{aligned}$$

from which we deduce

$$\delta(f(x)) = \frac{\delta(x-x_0)}{|f'(x_0)|}, \qquad \text{where } f(x_0)=0. \tag{A.7.3}$$

Real part

Using (A.9.1) we may deduce the form of the real part of the retarded self-energy

$$\mathrm{Re}\Sigma^R(\omega) = \frac{t_{hyb}^2}{\pi|t|}\mathcal{P}\int_{2t}^{-2t}\mathrm{d}z'\ \frac{\sqrt{1-\left(\frac{z'}{2t}\right)^2}}{\omega-z'}. \tag{A.7.4}$$

Changing variable $\frac{z'}{2t} = \cos(x)$ we obtain

$$\mathrm{Re}\Sigma^R(\omega) = -\mathrm{sgn}(t)t_{hyb}^2\frac{2}{\pi}\mathcal{P}\int_0^\pi \mathrm{d}x\ \frac{\sin^2(x)}{\omega-2t\cos(x)} \tag{A.7.5}$$

As one can notice from (A.7.5) we must calculate an integral of the form

$$\mathcal{P}\int_0^\pi \mathrm{d}x\ \frac{\sin^2(x)}{\omega-2t\cos(x)} \tag{A.7.6}$$

However this turns out to be quite tricky especially when the pole occurs inside the integration limits. We use the definition of the principal value integral to write (A.7.6) for $\omega \in [2t, -2t]$ as

$$\mathcal{P}\int_0^{\pi} \mathrm{d}x\; \frac{\sin^2(x)}{\omega - 2t\cos(x)} = \lim_{\eta\to 0}\left[\int_0^{p-\eta} \mathrm{d}x\; \frac{\sin^2(x)}{\omega - 2t\cos(x)} + \int_{p+\eta}^{\pi} \mathrm{d}x\; \frac{\sin^2(x)}{\omega - 2t\cos(x)}\right], \tag{A.7.7}$$

where $p = \arccos(\frac{\omega}{2t})$. Now Eq. (A.7.7) may be plugged into mathematica and after taking the limit $\eta \to 0$ we obtain

$$\mathcal{P}\int_0^{\pi} \mathrm{d}x\; \frac{\sin^2(x)}{\omega - 2t\cos(x)} = \frac{\pi\omega}{4t^2}, \tag{A.7.8}$$

and hence

$$\mathrm{Re}\Sigma^R(\omega) = -\mathrm{sgn}(t)\frac{\omega}{2}\left(\frac{t_{hyb}}{t}\right)^2 \tag{A.7.9}$$

For $\omega \notin [2t, -2t]$ we obtain, again by mathematica,

$$\Sigma^R(\omega) = -\mathrm{sgn}(t)\frac{1}{2}\left(\frac{t_{hyb}}{t}\right)^2 \begin{cases} \omega - \sqrt{\omega^2 - 4t^2}, & \omega > |2t| \\ \omega + \sqrt{\omega^2 - 4t^2}, & \omega < -|2t|. \end{cases} \tag{A.7.10}$$

A.7.2 Retarded Green's function considerations

Let us calculate a more explicit formula for (3.91).

$$\mathrm{Im}G^R_{mol,HH} = \frac{\mathrm{Re}\Lambda\left(\mathrm{Im}\Gamma_L - \mathrm{Im}\Sigma^R\right) - \mathrm{Im}\Lambda\left(\mathrm{Re}\Gamma_L - \mathrm{Re}\Sigma^R\right)}{|\Lambda|^2} \tag{A.7.11}$$

Use the definitions given in (3.90) to obtain for the denominator

$$\begin{aligned} |\Lambda|^2 &= \left|(\Gamma_H - \Sigma^R)(\Gamma_L - \Sigma^R) - \left(\Sigma^R\right)^2\right|^2 = \left|\Gamma_H\Gamma_L - \Sigma^R(\Gamma_L + \Gamma_H)\right|^2 \\ &= \Big|\mathrm{Re}\Gamma_H\mathrm{Re}\Gamma_L - \mathrm{Im}\Gamma_H\mathrm{Im}\Gamma_L - \mathrm{Re}\Sigma^R(\mathrm{Re}\Gamma_L + \mathrm{Re}\Gamma_H) + \mathrm{Im}\Sigma^R(\mathrm{Im}\Gamma_L + \mathrm{Im}\Gamma_H) \\ &+ i\left(\mathrm{Im}G_H\mathrm{Re}\Gamma_L + \mathrm{Im}G_L\mathrm{Re}\Gamma_H - \mathrm{Re}\Sigma^R(\mathrm{Im}\Gamma_L + \mathrm{Im}\Gamma_H) - \mathrm{Im}\Sigma^R(\mathrm{Re}\Gamma_L + \mathrm{Re}\Gamma_H)\right)\Big|^2. \end{aligned} \tag{A.7.12}$$

Now one may use

$$(G^R_{0,mol,L/H})^{-1} = \Gamma_{L/H} = \omega - \xi_{L/H} + i\eta \equiv \omega_{L/H} + i\eta \tag{A.7.13}$$

in (A.7.12) to obtain

$$\begin{aligned} |\Lambda|^2 &= \left|\omega_H\omega_L - \eta^2 - \mathrm{Re}\Sigma^R(\omega_L + \omega_H) + 2\eta\mathrm{Im}\Sigma^R + i\left[\eta\left(\omega_L + \omega_H - 2\mathrm{Re}\Sigma^R\right) - \mathrm{Im}\Sigma^R(\omega_L + \omega_H)\right]\right|^2 \\ &= \left(\omega_H\omega_L - \eta^2 - \mathrm{Re}\Sigma^R(\omega_L + \omega_H) + 2\eta\mathrm{Im}\Sigma^R\right)^2 + \left(\eta\left(\omega_L + \omega_H - 2\mathrm{Re}\Sigma^R\right) - \mathrm{Im}\Sigma^R(\omega_L + \omega_H)\right)^2 \\ &= \left(\omega_H\omega_L - \eta^2 - \mathrm{Re}\Sigma^R(\omega_L + \omega_H)\right)^2 + 4\eta\mathrm{Im}\Sigma^R\left(\omega_H\omega_L - \eta^2 - \mathrm{Re}\Sigma^R(\omega_L + \omega_H)\right) + 4\eta^2\mathrm{Im}\Sigma^R \\ &+ \eta^2\left(\omega_L + \omega_H - 2\mathrm{Re}\Sigma^R\right)^2 - 2\eta\left(\omega_L + \omega_H - 2\mathrm{Re}\Sigma^R\right)\mathrm{Im}\Sigma^R(\omega_L + \omega_H) + \left(\mathrm{Im}\Sigma^R\right)^2(\omega_L + \omega_H)^2 \end{aligned} \tag{A.7.14}$$

Next consider two separate cases

1. $\omega \notin [2t, -2t] \Rightarrow \mathrm{Im}\Sigma^R = 0$
2. $\omega \in [2t, -2t] \Rightarrow \mathrm{Im}\Sigma^R \neq 0$

Consider first case 1. In denominator we may not put $\eta \to 0$ since the denominator has poles in the interval under consideration. The denominator becomes

$$\begin{aligned}
|\Lambda|^2 &= \left(\omega_H\omega_L - \mathrm{Re}\Sigma^R(\omega_L+\omega_H)\right)^2 - 2\eta^2\left(\omega_H\omega_L - \mathrm{Re}\Sigma^R(\omega_L+\omega_H)\right) + \eta^2\left(\omega_L+\omega_H-2\mathrm{Re}\Sigma^R\right)^2 \\
&= \left(\omega_H\omega_L - \mathrm{Re}\Sigma^R(\omega_L+\omega_H)\right)^2 + \eta^2\left(\omega_L^2+\omega_H^2+4\left(\mathrm{Re}\Sigma^R\right)^2\right), \quad \omega \notin [2t,-2t]\,. \qquad \text{(A.7.15)}
\end{aligned}$$

Consider then case 2. Here we can safely put $\eta \to 0$ immediately and obtain

$$|\Lambda|^2 = \left(\omega_H\omega_L - \mathrm{Re}\Sigma^R(\omega_L+\omega_H)\right)^2 + \left(\mathrm{Im}\Sigma^R\right)^2(\omega_L+\omega_H)^2, \quad \omega \in [2t,-2t] \qquad \text{(A.7.16)}$$

We are left to consider the numerator of (A.7.11). We first deduce for the denominator from (A.7.12) with the aid of definition (A.7.13) that the real and imaginary parts become, respectively

$$\begin{aligned}
\mathrm{Re}\Lambda &= \omega_H\omega_L - \eta^2 - \mathrm{Re}\Sigma^R(\omega_L+\omega_H) + 2\eta\mathrm{Im}\Sigma^R \\
\mathrm{Im}\Lambda &= \eta\left(\omega_L+\omega_H-2\mathrm{Re}\Sigma^R\right) - \mathrm{Im}\Sigma^R(\omega_L+\omega_H).
\end{aligned}$$

Now it is again convenient to study both cases separately. We start with case 1. For the numerator we obtain

$$\begin{aligned}
&\mathrm{Re}\Lambda\left(\mathrm{Im}\Gamma_L - \mathrm{Im}\Sigma^R\right) - \mathrm{Im}\Lambda\left(\mathrm{Re}\Gamma_L - \mathrm{Re}\Sigma^R\right) \\
=\;& \eta\left[\omega_H\omega_L - \eta^2 - \mathrm{Re}\Sigma^R(\omega_L+\omega_H) - \left(\omega_L+\omega_H-2\mathrm{Re}\Sigma^R\right)\left(\omega_L - \mathrm{Re}\Sigma^R\right)\right] \\
=\;& \eta\left[\omega_H\omega_L - \eta^2 - \mathrm{Re}\Sigma^R(\omega_L+\omega_H) + \mathrm{Re}\Sigma^R(\omega_L+\omega_H) - \omega_L^2 - \omega_L\omega_H + 2\mathrm{Re}\Sigma^R\left(\omega_L - \mathrm{Re}\Sigma^R\right)\right] \\
=\;& \eta\left[-\omega_L^2 + 2\mathrm{Re}\Sigma^R\omega_L - 2\left(\mathrm{Re}\Sigma^R\right)^2\right] \\
=\;& -\eta\left[\left(\omega_L - \mathrm{Re}\Sigma^R\right)^2 + \left(\mathrm{Re}\Sigma^R\right)^2\right], \qquad \omega \notin [2t,-2t]\,. \qquad \text{(A.7.17)}
\end{aligned}$$

again we used (A.7.13). For case 2 we may put $\eta \to 0$ in the beginning because there are no poles in the denominator, we obtain for numerator similarly as in (A.7.17)

$$\begin{aligned}
&\mathrm{Re}\Lambda\left(\mathrm{Im}\Gamma_L - \mathrm{Im}\Sigma^R\right) - \mathrm{Im}\Lambda\left(\mathrm{Re}\Gamma_L - \mathrm{Re}\Sigma^R\right) \\
=\;& -\mathrm{Im}\Sigma^R\left(\omega_H\omega_L - \mathrm{Re}\Sigma^R(\omega_L+\omega_H)\right) + \mathrm{Im}\Sigma^R(\omega_L+\omega_H)\left(\omega_L - \mathrm{Re}\Sigma^R\right) \\
=\;& \mathrm{Im}\Sigma^R\left[-\omega_H\omega_L + \mathrm{Re}\Sigma^R(\omega_L+\omega_H) + (\omega_L+\omega_H)\left(\omega_L - \mathrm{Re}\Sigma^R\right)\right] \\
=\;& \mathrm{Im}\Sigma^R\omega_L^2, \qquad \omega \in [2t,-2t]\,. \qquad \text{(A.7.18)}
\end{aligned}$$

As we look the form of $\mathrm{Im}G^R_{mol,HH}(\omega)$ with $\omega \notin [2t,-2t]$

$$\mathrm{Im}G^R_{mol,HH}(\omega) = -\frac{\eta\left[\left(\omega_L - \mathrm{Re}\Sigma^R\right)^2 + \left(\mathrm{Re}\Sigma^R\right)^2\right]}{\left(\omega_H\omega_L - \mathrm{Re}\Sigma^R(\omega_L+\omega_H)\right)^2 + \eta^2\left(\omega_L^2+\omega_H^2+4\left(\mathrm{Re}\Sigma^R\right)^2\right)}, \qquad \omega \notin [2t,-2t] \qquad \text{(A.7.19)}$$

we may define $\epsilon = \eta\sqrt{\omega_L^2+\omega_H^2+4\left(\mathrm{Re}\Sigma^R\right)^2}$. This can be done since $\omega_L^2+\omega_H^2+4\left(\mathrm{Re}\Sigma^R\right)^2 \neq 0, \quad \forall\omega \notin [2t,-2t]$. With our new definition one can write (A.7.19) as

$$\begin{aligned}
\mathrm{Im}G^R_{mol,HH}(\omega) &= -\frac{\left(\omega_L - \mathrm{Re}\Sigma^R\right)^2 + \left(\mathrm{Re}\Sigma^R\right)^2}{\sqrt{\omega_L^2+\omega_H^2+4\left(\mathrm{Re}\Sigma^R\right)^2}}\overbrace{\frac{\epsilon}{\left(\omega_H\omega_L - \mathrm{Re}\Sigma^R(\omega_L+\omega_H)\right)^2+\epsilon^2}}^{=\pi\delta(\omega_H\omega_L - \mathrm{Re}\Sigma^R(\omega_L+\omega_H))} \\
&= -\pi\frac{\left(\omega_L - \mathrm{Re}\Sigma^R\right)^2 + \left(\mathrm{Re}\Sigma^R\right)^2}{\sqrt{\omega_L^2+\omega_H^2+4\left(\mathrm{Re}\Sigma^R\right)^2}}\delta(\omega_H\omega_L - \mathrm{Re}\Sigma^R(\omega_L+\omega_H)) \\
&\overset{(A.7.3)}{=} -\pi\frac{\left(\omega_L - \mathrm{Re}\Sigma^R\right)^2 + \left(\mathrm{Re}\Sigma^R\right)^2}{\sqrt{\omega_L^2+\omega_H^2+4\left(\mathrm{Re}\Sigma^R\right)^2}}\frac{1}{\left|\frac{\mathrm{d}}{\mathrm{d}\omega}\left(\omega_H\omega_L - \mathrm{Re}\Sigma^R(\omega_L+\omega_H)\right)\right|_{\omega=a}}\delta(\omega-a),
\end{aligned}$$

$$\text{(A.7.20)}$$

where $\omega \notin [2t, -2t]$. moreover, a is defined by

$$\left[\omega_H \omega_L - \mathrm{Re}\Sigma^R(\omega_L + \omega_H)\right]_{\omega=a} = 0. \tag{A.7.21}$$

We may now write (A.7.11) in the two cases separately as

$$\mathrm{Im}G^R_{mol,HH}(\omega) = \begin{cases} -\pi \frac{\left(\omega_L - \mathrm{Re}\Sigma^R\right)^2 + \left(\mathrm{Re}\Sigma^R\right)^2}{\sqrt{\omega_L^2 + \omega_H^2 + 4(\mathrm{Re}\Sigma^R)^2}} \frac{1}{\left|\frac{\mathrm{d}}{\mathrm{d}\omega}(\omega_H\omega_L - \mathrm{Re}\Sigma^R(\omega_L+\omega_H))\right|_{\omega=a}} \delta(\omega - a), & \omega \notin [2t, -2t]\,, \\ \frac{\mathrm{Im}\Sigma^R \omega_L^2}{(\omega_H\omega_L - \mathrm{Re}\Sigma^R(\omega_L+\omega_H))^2 + (\mathrm{Im}\Sigma^R)^2(\omega_L+\omega_H)^2}, & \omega \in [2t, -2t]\,. \end{cases} \tag{A.7.22}$$

A.8 Calculus of Residues

For example the perturbative expansion for the self-energy contains lot of integrals of the form

$$\int_{-\infty}^{\infty} \mathrm{d}\nu \frac{1}{\nu - a}, \quad \text{or} \quad \int_{-\infty}^{\infty} \mathrm{d}\nu \frac{1}{\nu - a} \frac{1}{\nu - b}, \tag{A.8.1}$$

where a, b are real and $\nu = \nu \pm i\eta$. The way to deal with integrals of the form (A.8.1) is Cauchy's residue theorem [2]

$$\oint_{\mathcal{C}} f(z)\mathrm{d}z = 2\pi i \sum_k \mathrm{Res}_{z=z_k} f(z), \tag{A.8.2}$$

where for a simple pole the residue is

$$\mathrm{Res}_{z=z_k} f(z) = \lim_{z \to z_k} \left[(z - z_k) f(z)\right] \tag{A.8.3}$$

Here $f(z)$ must be analytic everywhere in a simply connected region $\mathcal{R}$ except for isolated singularities z_k. $\mathcal{C}$ is a piecewise smooth simple contour inside $\mathcal{R}$, confining z_k:s and oriented counterclockwise.

Now we may calculate the integrals in (A.8.1) through (A.8.2) by transforming them into complex contour integrals in the complex plane through

$$\oint f(z)\mathrm{d}z = \int_{-\infty}^{\infty} f(z)\mathrm{d}z + \int_{\mathcal{C}_{\mathcal{R}}} f(z)\mathrm{d}z. \tag{A.8.4}$$

Now the first of the integrals is just an improper integral on real axis, i.e., just an integral of the form in (A.8.1). The latter integral is the semicircle in the UHP connecting the $+\infty$ to $-\infty$. Now we may show that the latter term vanishes provided that $f(z) \to 0$ faster that $1/|z|$ as $|z| \to \infty$.

$$\begin{aligned} \int_{\mathcal{C}_{\mathcal{R}}} f(z)\mathrm{d}z &\overset{z=\rho e^{i\theta}}{=} \lim_{\rho\to\infty} \int_0^{\pi} f(\rho e^{i\theta}) i\rho e^{i\theta} \mathrm{d}\theta \\ &= \lim_{\rho\to\infty} \int_0^{\pi} \frac{e^{i\theta}}{\rho^{s-1}} \mathrm{d}\theta \to 0, \quad s > 1. \end{aligned} \tag{A.8.5}$$

Now from (A.8.5), (A.8.4) and (A.8.2) we may deduce for the integrals of the form (A.8.1) that the integral becomes

$$\int_{-\infty}^{\infty} f(\nu)\mathrm{d}\nu = 2\pi i \sum_k \mathrm{Res}_{z=z_k} f(z). \tag{A.8.6}$$

Note that this result holds for poles in the UHP. One may go through similar steps also for a pole in the LHP to obtain

$$\int_{-\infty}^{\infty} f(\nu)\mathrm{d}\nu = -2\pi i \sum_k \mathrm{Res}_{z=z_k} f(z). \tag{A.8.7}$$

The minus sign is due to the fact that in residue theorem we always go counter clockwise along the curve and thus the real axis is integrated from ∞ to $-\infty$ giving rise to the extra minus.

We may immediately deduce some properties of the integrals (A.8.1). For $f(\nu)$ with two simple poles we may argue that to obtain a non-zero contribution the poles must not be in same plane. Formally

$$\begin{aligned} &\int \frac{\mathrm{d}\nu}{2\pi}\ \frac{1}{\nu - a \pm i\eta}\frac{1}{\nu - b \pm i\eta} = i\sum_j \mathrm{Res}_{\nu=\nu_j} f(\nu) \\ =\ & i\left(\mp\frac{1}{b-a} \mp \frac{1}{a-b}\right) = i\left(\mp\frac{1}{b-a} \pm \frac{1}{b-a}\right) = 0, \end{aligned} \tag{A.8.8}$$

whereas for different signs

$$\begin{aligned} &\int \frac{\mathrm{d}\nu}{2\pi}\ \frac{1}{\nu - a \pm i\eta}\frac{1}{\nu - b \mp i\eta} = i\sum_j \mathrm{Res}_{\nu=\nu_j} f(\nu) \\ =\ & i\left(\pm\frac{1}{b-a\pm 2i\eta}\right) = \pm\frac{i}{b-a}, \end{aligned} \tag{A.8.9}$$

where a and b are both real.

A.9 The Kramer-Kronig relation

There exists a theorem relating the real and imaginary parts of any analyti function which vanishes faster than $1/|z|$ as $|z| \to \infty$ in the UHP of the complex variable z. The relation is called the Kramer-Kronig relation and it reads for $X(z) = \mathrm{Re}X(z) + i\mathrm{Im}X(z)$

$$\mathrm{Re}X(a) = \frac{1}{\pi}\mathcal{P}\int \mathrm{d}z'\frac{\mathrm{Im}X(z')}{a-z'} \tag{A.9.1}$$

$$\mathrm{Im}X(a) = -\frac{1}{\pi}\mathcal{P}\int \mathrm{d}z'\frac{\mathrm{Re}X(z')}{a-z'}. \tag{A.9.2}$$

The proof takes advantage of Cauchy's residue theorem A.8. For $X(z)$ the assumptions stated above hold. Now in the UHP the function $X(z)/(z-a)$ is also analytic and since there are now poles in the UHP we may write the contour integral.

$$\begin{aligned} 0 &= \oint \frac{X(z)}{z-a}\mathrm{d}z \overset{a\to a+i\eta}{=} P\int \frac{X(z)}{z-a}\mathrm{d}z + i\int \frac{\eta X(z)}{(z-a)^2+\eta^2}\mathrm{d}z \\ &= P\int \frac{X(z)}{z-a}\mathrm{d}z + i\pi X(a), \qquad \delta(x) = \frac{1}{\pi}\lim_{\eta\to 0}\frac{\eta}{x^2+\eta^2} \end{aligned} \tag{A.9.3}$$

from which one may deduce (A.9.1) and (A.9.2). At the first equal sign we used (A.8.5) to get rid of the semicircle parts. Note that the integration limits run from $-\infty$ to ∞.

Similar calculations can be carried out for a pole on the LHP, i.e., $a \to a - i\eta$. The relations are

$$\mathrm{Re}X(a) = -\frac{1}{\pi}\mathcal{P}\int \mathrm{d}z'\frac{\mathrm{Im}X(z')}{a-z'} \tag{A.9.4}$$

$$\mathrm{Im}X(a) = +\frac{1}{\pi}\mathcal{P}\int \mathrm{d}z'\frac{\mathrm{Re}X(z')}{a-z'}. \tag{A.9.5}$$

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