Computational Methods in Solid State Theory

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1. Single particle methods

1.1 The tight binding method

There are two ways of dealing with the periodic arrays of atoms in crystals; in one picture which is suitable for simple metals and covalent semiconductors, Bloch electron wave functions are considered to be waves that are little affected by the positions of the atoms: this works whenever the crystal potential is a smooth function and the atomic positions are not critical for the understanding. A different picture, suitable for insulators, but also for covalent semiconductors, considers electrons to move through the crystal slowly (or not at all) and to therefore belong to an atom for some time before moving on. The electrons are "tightly bound" to the atom and only move on for energetic reasons.

We start to introduce this description¹ by writing the potential of the electrons $V(\vec{r})$ in a crystal as a sum of atomic potentials

$$\mathbf{V}(\vec{\mathbf{r}}) = \sum_{\vec{\mathbf{R}}} \mathbf{V}_{\text{atom}}(\vec{\mathbf{r}} - \vec{\mathbf{R}})$$
(1.1)

where the sum runs over the lattice vectors; first we treat the case of one atom per unit cell. This potential is periodic by construction because for a lattice vector \vec{R}_0

$$\mathbf{V}(\vec{\mathbf{r}}+\vec{\mathbf{R}}_{0}) = \sum_{\vec{\mathbf{R}}} \mathbf{V}_{\text{atom}}(\vec{\mathbf{r}}+\vec{\mathbf{R}}_{0}-\vec{\mathbf{R}}) \stackrel{\vec{\mathbf{R}}'=\vec{\mathbf{R}}-\vec{\mathbf{R}}_{0}}{=} \sum_{\vec{\mathbf{R}}'} \mathbf{V}_{\text{atom}}(\vec{\mathbf{r}}-\vec{\mathbf{R}}') = \mathbf{V}(\vec{\mathbf{r}}) \quad (1.2)$$

Setting $\frac{\hbar^2}{2m} = 1$, the crystal Hamiltonian is

$$\mathbf{H} = -\nabla^2 + \mathbf{V}(\vec{\mathbf{r}}) \,. \tag{1.3}$$

We now try to relate the electron wave function to the atomic orbitals satisfying

$$\mathbf{H}_{\mathrm{atom}} \boldsymbol{\Phi}_{\mathfrak{n}} \equiv \left(-\nabla^2 + \mathbf{V}_{\mathrm{atom}}(\vec{\mathbf{r}}) \right) \boldsymbol{\Phi}_{\mathfrak{n}} = \varepsilon_{\mathfrak{n}} \boldsymbol{\Phi}_{\mathfrak{n}} \,. \tag{1.4}$$

¹This closely follows a tight binding note by Warren Pickett.

With a simple linear combination $\Phi_n(\vec{r}) = \sum_{\vec{R}} \phi_n(\vec{r} - \vec{R})$ one has difficulties fulfilling the Bloch theorem but the *ansatz*

$$B_{n\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} \phi_n(\vec{r}-\vec{R})$$
(1.5)

fulfils the Bloch condition for the wave vector k:

$$\sqrt{N} B_{n\vec{k}}(\vec{r} + \vec{R}_0) = \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} \phi_n(\vec{r} + \vec{R}_0 - \vec{R})$$
$$\stackrel{\vec{R}' = \vec{R} - \vec{R}_0}{=} \sum_{\vec{R}'} e^{i\vec{k}\cdot(\vec{R}' + \vec{R}_0)} \phi_n(\vec{r} - \vec{R}') = e^{i\vec{k}\cdot\vec{R}_0} \sqrt{N} B_{n\vec{k}}(\vec{r})$$
(1.6)

Here, it is enough to consider \vec{k} vectors from the first Brillouin zone. The Bloch sum itself is not an eigenfunction for the crystal, but we can now try to expand the electron wave function in these Bloch sums:

$$\psi_{\vec{k}}(\vec{r}) = \sum_{n} b_{n}(\vec{k}) B_{n\vec{k}}(\vec{r}) . \qquad (1.7)$$

The functions $\psi_{\vec{k}}(\vec{r})$ should now solve the Schrödinger equation

$$\mathsf{H}\psi_{\vec{k}} = \varepsilon_{\vec{k}}\psi_{\vec{k}} \tag{1.8}$$

with the $\varepsilon_{\overrightarrow{k}}$ representing the energy bands of the crystal. In order to find the conditions for the solution, we now calculate matrix elements by multiplying from the left with Bloch sums $B^*_{\overrightarrow{mk}}$ and integrating over the crystal:

$$\sum_{n} H_{mn}(\vec{k}) b_{n}(\vec{k}) = \varepsilon_{\vec{k}} \sum_{n} S_{mn}(\vec{k}) b_{n}(\vec{k})$$
(1.9)

with

$$H_{mn}(\vec{k}) = \int d^3 r \, B^*_{m\vec{k}}(\vec{r}) H B_{n\vec{k}}(\vec{r})$$
$$S_{mn}(\vec{k}) = \int d^3 r \, B^*_{m\vec{k}}(\vec{r}) B_{n\vec{k}}(\vec{r}) \qquad (1.10)$$

which are called *Hamiltonian matrix* and *overlap matrix*. Written without indices the secular equation is

$$\left(\mathsf{H}(\vec{k}) - \varepsilon_{\vec{k}} S(\vec{k})\right) \mathsf{b}(\vec{k}) = 0 \tag{1.11}$$

Now we can work out what the matrixes are by substituting the Bloch sums:

$$H_{mn}(\vec{k}) = \frac{1}{N} \sum_{\vec{R}_1, \vec{R}_2} e^{i\vec{k}\cdot(\vec{R}_2 - \vec{R}_1)} \int d^3r \underbrace{\phi_m^*(\vec{r} - \vec{R}_1) H \phi_n(\vec{r} - \vec{R}_2)}_{H_{mn}(\vec{R}_2 - \vec{R}_1)}$$
(1.12)

The cell periodicity of the Hamiltonian means that we can change the summation to $\vec{R} = \vec{R}_2 - \vec{R}_1$ so that $\sum_{\vec{R}_1}$ just gives a factor N and we find

$$H_{mn}(\vec{k}) = \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} H_{mn}(\vec{R})$$
(1.13)

 $H_{mn}(\vec{k})$ and $H_{mn}(\vec{R})$ are lattice Fourier transforms of each other. Analogously one finds

$$S_{mn}(\vec{k}) = \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} S_{mn}(\vec{R})$$
(1.14)

The real space integral

$$H_{mn}(\vec{R}) = \int d^3 r \, \phi_m^*(\vec{r}) H \phi_n(\vec{r} - \vec{R})$$
(1.15)

indicates the amount of coupling between orbital ϕ_m at the origin and ϕ_n at the site \vec{R} ; it is the *hopping amplitude* of an electron in orbital ϕ_n at site \vec{R} to the orbital ϕ_m at the origin. The discussion can be limited to small $|\vec{R}|$ (few neighbours) as the integral will otherwise be negligible. The discussion for $S_{mn}(\vec{R})$, the overlap of $\phi_m(\vec{r})$ and $\phi_n(\vec{r}-\vec{R})$ runs very similarly.

Going beyond the elemental crystal, there can be various atoms at positions $\vec{\tau_i}$ (with respect to the origin \vec{R} of the cell); then the atomic basis orbitals are $\phi_m(\vec{r} - \vec{R} - \vec{\tau_i})$. The basis Bloch sums become

$$B_{mi\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k}\cdot(\vec{R}+\vec{\tau}_i)} \phi_n(\vec{r}-\vec{R}-\vec{\tau}_i)$$
(1.16)

We then get

$$\begin{split} H_{\text{mi},\text{nj}}(\vec{k}) &= \frac{1}{N} \sum_{\vec{k}_{1},\vec{k}_{2}} e^{i\vec{k}\cdot(\vec{R}_{2}+\vec{\tau}_{j}-\vec{R}_{1}-\vec{\tau}_{i})} \int d^{3}r \, \phi_{\text{m}}^{*}(\vec{r}-\vec{R}_{1}-\vec{\tau}_{i})) H \phi_{n}(\vec{r}-\vec{R}_{2}-\vec{\tau}_{j})) \\ &= \frac{1}{N} e^{-i\vec{k}\cdot\vec{\tau}_{i}} \sum_{\vec{k}_{1},\vec{k}_{2}} e^{i\vec{k}\cdot(\vec{R}_{2}-\vec{R}_{1})} H_{\text{mi},\text{nj}}(\vec{R}_{2}-\vec{R}_{1}+\vec{\tau}_{j}-\vec{\tau}_{i}) e^{i\vec{k}\cdot\vec{\tau}_{j}} \\ &= e^{-i\vec{k}\cdot\vec{\tau}_{i}} \left(\sum_{\vec{k}} H_{\text{mi},\text{nj}}(\vec{R}) e^{i\vec{k}\cdot\vec{R}} \right) e^{i\vec{k}\cdot\vec{\tau}_{j}} = e^{-i\vec{k}\cdot\vec{\tau}_{i}} H_{\text{mi},\text{nj}}(\vec{k}) e^{i\vec{k}\cdot\vec{\tau}_{j}} \end{split}$$

$$(1.17)$$

where the notation $H_{mi,nj}(\vec{R}) = H_{mi,nj}(\vec{R} + \vec{\tau}_j - \vec{\tau}_i)$ was used. This can be viewed as the matrix $H^0(\vec{k})$ transformed by the unitary transformation

$$U_{mi,nj}(\vec{k}) = e^{-i\vec{k}\cdot\vec{\tau}_{j}}\delta_{mn}\delta_{ij}$$
(1.18)

which obeys $U^+U = \mathbb{I} = U^{-1}U$. A unitary transformation of a Hermitian matrix does not affect its eigenvalues, it only transforms the eigenvectors. Thus, unless there is specific reason to include the phase factors in Eq. 1.17 (*i.e.* eigenvectors are needed for some further calculation like matrix elements, for example), they can be disregarded.

Now the terms entering the Hamiltonian can be determined. We start with the single site terms with $\vec{R} = 0$ when both orbitals are at the same site. We split the crystal Hamiltonian into the atomic Hamiltonian for the atom at the origin plus the potential for all the other atoms:

$$\begin{aligned} \mathsf{H} &= -\nabla^2 + \mathsf{V}_{\mathrm{atom}}(\vec{r}) + \sum_{\vec{k} \neq 0} \mathsf{V}_{\mathrm{atom}}(\vec{r} - \vec{R}) \\ &= -\nabla^2 + \mathsf{V}_{\mathrm{atom}}^{\mathrm{spherical}}(\vec{r}) + \mathsf{V}_{\mathrm{atom}}^{\mathrm{nonspherical}}(\vec{r}) + \sum_{\vec{k} \neq 0} \mathsf{V}_{\mathrm{atom}}(\vec{r} - \vec{R}) \\ &= \mathsf{H}_{\mathrm{atom}}^{\mathrm{spherical}}(\vec{r}) + \Delta \mathsf{V}(\vec{r}) \end{aligned}$$
(1.19)

The integral results primarily from the spherical atomic Hamiltonian, with orthogonal atomic orbitals

$$H_{mn}(0) = \int d^3 \mathbf{r} \, \phi_m^*(\vec{\mathbf{r}}) H_{atom}(\vec{\mathbf{r}}) \phi_n(\vec{\mathbf{r}}) = \varepsilon_n \delta_{mn} \tag{1.20}$$

which gives atomic eigenvalues ε_n .

The quantity $\Delta V(\vec{r})$ has the symmetry of the atom in the crystal which is not spherical but discrete (mirror planes, rotation or screw axes). This *crystal field*, *i.e.* the nonspherical potential due to the crystal, will split some eigenvalues that would be degenerate in a spherical potential. An example is the splitting in a cubic crystal field of the five **d** orbitals into the t_{2g} manifold (xy, yz, zx) and the e_g manifold ($x^2 - y^2, 3z^2 - 1$). This means that a transition metal ion in a cubic site has instead of a single onsite energy ε_d two energies $\varepsilon_{t_{2g}}$ and ε_{e_g} which can split further if the octahedral environment of the transition metal ion is distorted.

If we now consider the general integrals (1.15) they contain three center integrals $(\Phi_{\mathfrak{m}}(\vec{r}) \text{ is centered at } \vec{R} = 0, \ \Phi_{\mathfrak{n}}(\vec{r} - \vec{R}) \text{ is centered at } \vec{R} \text{ and } H$ involves potential contributions $V_{\text{atom}}(\vec{r}-R')$ centered at all R'). Following the important paper J. C. Slater, G. F. Koster, Phys. Rev. 94, 1498 (1954), the two center approximation is widely used. This means that the the multitude of integrals (1.15) is restricted to two center integrals denoted as $(ss\sigma), (sp\sigma), (pp\sigma), (pp\pi), (sd\sigma), (pd\sigma), (pd\pi), (dd\sigma), (dd\pi), (dd\delta)$ and so on. Arguments are i) three-center integrals are less important than two-center integrals in principle, and ii) the purpose of the tight binding method is often to represent the bandstructure of a material (calculated with more elaborate methods) with as few parameters as possible, and in the course of a fitting process some effect of the three-center integrals can be absorbed into the two-center parameters. Following this logic, the Hamiltonian matrix elements or hopping integrals are often called *tight* binding parameters (and denoted with the letter $t: t_{mn}(\overline{R}) \equiv H_{mn}(\overline{R})$). For the overlap matrix the usual notation is $s_{mn}(\vec{R}) \equiv S_{mn}(\vec{R})$ with $s_{mn}(0) =$ δ_{mn} expressing the orthonormality of the atomic orbitals.

Simple examples

We only consider the case of one s-like function on each atom; the tight binding matrix is then (1×1) and directly gives an expression for the energy bands $\varepsilon_{\vec{k}}$.

1D linear chain of atoms: The atom at the origin has two nearest neighbours at $\pm a$, and the hopping amplitude is t_1 . Eq. (1.13) yields

$$H_{ss}(k) = \varepsilon_s + t_1 \sum_{R} e^{ikR} = \varepsilon_s + t_1(e^{ika} + e^{-ika}) = \varepsilon_s + 2t_1 \cos(ka) \quad (1.21)$$

and the overlap is

$$S_{ss}(k) = 1 + s_1 \sum_{R} e^{ikR} = 1 + 2s_1 \cos(ka)$$
 (1.22)

Thus, the secular equation (1.11) is solved by

$$\varepsilon_{\mathbf{k}} = \frac{\varepsilon_{\mathbf{s}} + 2\mathbf{t}_1 \cos(\mathbf{k}\mathbf{a})}{1 + 2\mathbf{s}_1 \cos(\mathbf{k}\mathbf{a})} \tag{1.23}$$

Adding the effects of hopping to second neighbours at $\pm 2a$ with hopping amplitude t_2 involves doubled frequencies ($\cos(2ka)$):

$$\varepsilon_{\mathbf{k}} = \frac{\varepsilon_{\mathbf{s}} + 2\mathbf{t}_1 \cos(\mathbf{k}\mathbf{a}) + 2\mathbf{t}_2 \cos(2\mathbf{k}\mathbf{a})}{1 + 2\mathbf{s}_1 \cos(\mathbf{k}\mathbf{a}) + 2\mathbf{s}_2 \cos(2\mathbf{k}\mathbf{a})}$$
(1.24)

2D square lattice of atoms: The nearest neighbour sum runs over the sites $\vec{R} = (a, 0), (0, a), (-a, 0), (0, -a)$, and the lattice sum becomes

$$\sum_{\overrightarrow{R}} e^{i\overrightarrow{k}\cdot\overrightarrow{R}} = \sum_{p=\pm 1} e^{ik_xap} + \sum_{q=\pm 1} e^{ik_yaq} = 2\cos(k_xa) + 2\cos(k_ya) \quad (1.25)$$

leading to the dispersion relation (we neglect the overlap)

$$\varepsilon_{\vec{k}} = \varepsilon_{s} + 2t_{1}\cos(k_{x}a) + 2t_{1}\cos(k_{y}a)$$
(1.26)

To include second neighbours at points $\vec{R} = (a, a), (-a, a), (a, -a), (-a, -a)$ with amplitude t_2 , we use $e^{\nu+\omega} = e^{\nu}e^{\omega}$ and get

$$\varepsilon_{\mathbf{k}} = \varepsilon_{\mathbf{s}} + 2\mathbf{t}_1 \cos(\mathbf{k}_{\mathbf{x}} \mathbf{a}) + 2\mathbf{t}_1 \cos(\mathbf{k}_{\mathbf{y}} \mathbf{a}) + 4\mathbf{t}_2 \cos(\mathbf{k}_{\mathbf{x}} \mathbf{a}) \cos(\mathbf{k}_{\mathbf{y}} \mathbf{a}) \quad (1.27)$$

1.2 Integration over the Brillouin zone

Applications of electronic structure theory imply the calculation of many different \mathbf{k} space integrals over the Brillouin zone or its irreducible part.

$$I(\varepsilon) = \frac{1}{V_{G}} \sum_{n} \int_{\Omega_{BZ}} d\vec{k} f(\vec{k}) \Theta(\varepsilon - \varepsilon_{n,\vec{k}})$$
(1.28)

Typical examples are the total electron number $n(\varepsilon)$

$$n(\varepsilon) = \frac{1}{V_{\rm G}} \sum_{n} \int_{V_{\rm G}} d^3 k \,\Theta\left(\varepsilon - \varepsilon_n(\vec{k})\right) \tag{1.29}$$

and its energy derivative, the density of states $\rho(\varepsilon)$

$$\rho(\varepsilon) = \frac{1}{V_{\rm G}} \sum_{\rm n} \int_{V_{\rm G}} d^3 k \, \delta \left(\varepsilon - \varepsilon_{\rm n}(\vec{k}) \right) \tag{1.30}$$

where V_G is the volume of the primitive cell of the reciprocal lattice, and n is the band index.

One possibility of doing such integrals is by simply introducing a fine mesh in the reciprocal lattice and adding up the contributions from all \mathbf{k} points (histogram method). Due to the nature of the step and delta functions, the results for the two integrals given above are not going to be satisfactory with this most simple method. This method is illustrated in Fig. 1.1.



Figure 1.1: Example of simple Brillouin zone integration.

An alternative that is sometimes used is to do the summation (1.30) by approximating the delta function with a function that has a small finite width, for example a Gaussian:

$$\delta(\varepsilon) \approx g(\varepsilon) = \frac{2}{f} \sqrt{\frac{\ln 2}{\pi}} e^{-4\ln 2\frac{\varepsilon^2}{f^2}}$$
(1.31)

with full width at half maximum given by f.

Linear tetrahedron method

A far better method for Brillouin zone integration is the linear tetrahedron method. The idea is to do the integration by splitting the volume into tetrahedra, to evaluate the integrand at the corners of the tetrahedra and to use linear interpolation over the tetrahedra for the integration². An example of how the reciprocal space can be broken up into tetrahedra is given in Fig. 1.2. Each tetrahedron can then be split into two tetrahedra by introducing a new vertex in the middle of the longest edge of each tetrahedron.



Figure 1.2: Splitting of a cubic reciprocal space sector into six tetrahedra.

Derivation of the linear tetrahedron method

Let the irreducible Brillouin zone be split into n_{T_i} tetrahedra³. We can recast integral Eq. (1.28) as

$$\begin{split} I(\mathsf{E}_{\mathsf{F}}) &= \frac{1}{V_{\mathrm{BZ}}} \sum_{n} \int_{\Omega_{\mathrm{BZ}}} \mathrm{d}\vec{k} \; f(\vec{k}) \Theta(\mathsf{E}_{\mathsf{F}} - \varepsilon_{n,\vec{k}}) \\ &= \frac{1}{V_{\mathrm{BZ}}} \sum_{n} \sum_{i=1}^{n_{\mathrm{T}_{i}}} \int_{\mathrm{T}_{i}} \mathrm{d}\vec{k} \; f(\vec{k}) \Theta(\mathsf{E}_{\mathsf{F}} - \varepsilon_{n,\vec{k}}) \\ &= \sum_{i=1}^{n_{\mathrm{T}_{i}}} \frac{1}{V_{\mathrm{BZ}}} \sum_{n} \int_{\mathrm{T}_{i}} \mathrm{d}\vec{k} \; f(\vec{k}) \Theta(\mathsf{E}_{\mathsf{F}} - \varepsilon_{n,\vec{k}}) = \sum_{i=1}^{n_{\mathrm{T}_{i}}} I_{\mathrm{T}_{i}}, \end{split}$$

²O. Jepsen, O. K. Andersen, *The electronic structure of h.c.p. ytterbium*, Solid State Commun. **9**, 1763 (1971); P. E. Blöchl, O. Jepsen, O. K. Andersen, *Improved tetrahedron method for Brillouin-zone integrations*, Phys. Rev. B **49**, 16223 (1994); H. Eschrig, *Optimized LCAO Method and the Electronic Structure of Extended Systems*, Akademie-Verlag Berlin 1988.

³Thanks to Francesc Salvat-Pujol for the following derivation of the interpolation formulas.



Figure 1.3: Tetrahedron vertex labeling and definition of \vec{q}_1 , \vec{q}_2 , \vec{q}_3 .

where we have defined

$$I_{T_{i}} = \frac{1}{V_{BZ}} \sum_{n} \int_{T_{i}} d\vec{k} f(\vec{k}) \Theta(E_{F} - \epsilon_{n,\vec{k}})$$
(1.32)

as the integral over the *i*-th tetrahedron. We also take the upper limit of integration to be $\varepsilon = E_F$ but the method of course works for any BZ integral $I(\varepsilon)$. We shall now restrict ourselves to computing integrals of the form Eq. (1.32); the full integral will be a sum of such terms.

We proceed analogously to Chen ⁴, Reser⁵ and to Appendix A of Lehmann and Taut⁶ to derive expressions for the linear tetrahedron method. We assume that the integrand in the relevant part of the BZ has been tabulated on a tetrahedral mesh (a cubic mesh will do, since each cube can be decomposed into 6 tetrahedra). We shall now derive the integration formula for each tetrahedron.

Let us consider a tetrahedron with vertices \vec{k}_0 , \vec{k}_1 , \vec{k}_2 , \vec{k}_3 , see Fig. 1.3. We require that the tetrahedron-vertex labels are assigned such that

$$\mathsf{E}_0 \leqslant \mathsf{E}_1 \leqslant \mathsf{E}_2 \leqslant \mathsf{E}_3, \qquad \mathsf{E}_i = \mathsf{E}(\vec{\mathsf{k}}_i). \tag{1.33}$$

Without loss of generality we take \vec{k}_0 at the origin of reciprocal space. The first step consists in changing to a system of oblique coordinates where the integration volume is easier to deal with, *e. g.*, a cube as opposed to a

⁴A.-B. Chen, Simple Brillouin-zone scheme for the spectral properties of solids, Phys. Rev. B **16**, 3291 (1977).

⁵B. I. Reser, On the Brillouin Zone Integration, Phys. Stat. Sol. B **116**, 31 (1983)

⁶G. Lehmann, M. Taut, On the Numerical Calculation of the Density of States and Related Properties, Phys. Stat. Sol. B **54**, 469 (1972)

tetrahedron. We define the following vectors,

$$\vec{\mathbf{q}}_{1} = \vec{\mathbf{k}}_{1} - \vec{\mathbf{k}}_{0}$$

$$\vec{\mathbf{q}}_{2} = \vec{\mathbf{k}}_{2} - \vec{\mathbf{k}}_{1}$$

$$\vec{\mathbf{q}}_{3} = \vec{\mathbf{k}}_{3} - \vec{\mathbf{k}}_{2},$$
 (1.34)

represented in red in Fig. 1.3. Any point k in the volume delimited by the tetrahedron can be expressed as a linear combination of these vectors:

$$\vec{k} = k_x \vec{e}_x + k_y \vec{e}_y + k_z \vec{e}_z = \alpha \vec{q}_1 + \alpha \beta \vec{q}_2 + \alpha \beta \gamma \vec{q}_3, \qquad \alpha, \beta, \gamma \in [0, 1].$$
(1.35)

Indeed, for $\gamma = 0$, varying α and β from 0 to 1 we sweep the back side of the tetrahedron, $\vec{k}_0 \vec{k}_1 \vec{k}_2$. Varying γ from 0 to 1 we can move from the back side of the tetrahedron, $\vec{k}_0 \vec{k}_1 \vec{k}_2$, to the front side, $\vec{k}_0 \vec{k}_1 \vec{k}_3$. Note that α appears also in the second term, and $\alpha\beta$ appear in the third term, effectively limiting the integration volume to the tetrahedron. Thus, an integral over \vec{k} in the tetrahedron volume is trivially recast as an integral over a unit cube in the (α, β, γ) system of coordinates:

$$I_{T_{i}} = \frac{1}{V_{BZ}} \sum_{n} \int_{0}^{1} d\alpha \int_{0}^{1} d\beta \int_{0}^{1} d\gamma \ f(\alpha, \beta, \gamma) \Theta(E_{F} - \epsilon_{n, \vec{k}}) \left| \frac{d(k_{x}, k_{y}, k_{z})}{d(\alpha, \beta, \gamma)} \right|,$$
(1.36)

where the last term is the Jacobian of the coordinate transformation $(k_x, k_y, k_z) \rightarrow (\alpha, \beta, \gamma)$. To evaluate the Jacobian, we first express \vec{k} explicitly. From Eq. (1.35) we have:

$$\vec{k} = (\alpha q_{1x} + \alpha \beta q_{2x} + \alpha \beta \gamma q_{3x}) \vec{e}_{x} + (\alpha q_{1y} + \alpha \beta q_{2y} + \alpha \beta \gamma q_{3y}) \vec{e}_{y} + (\alpha q_{1z} + \alpha \beta q_{2z} + \alpha \beta \gamma q_{3z}) \vec{e}_{z}.$$
(1.37)

The Jacobian is

$$\left|\frac{\mathrm{d}(\mathbf{k}_{\mathrm{x}},\mathbf{k}_{\mathrm{y}},\mathbf{k}_{z})}{\mathrm{d}(\alpha,\beta,\gamma)}\right| = \left|\begin{array}{ccc} \frac{\partial \mathbf{k}_{\mathrm{x}}}{\partial \alpha} & \frac{\partial \mathbf{k}_{\mathrm{x}}}{\partial \beta} & \frac{\partial \mathbf{k}_{\mathrm{x}}}{\partial \gamma} \\ \frac{\partial \mathbf{k}_{\mathrm{y}}}{\partial \alpha} & \frac{\partial \mathbf{k}_{\mathrm{y}}}{\partial \beta} & \frac{\partial \mathbf{k}_{\mathrm{y}}}{\partial \gamma} \\ \frac{\partial \mathbf{k}_{z}}{\partial \alpha} & \frac{\partial \mathbf{k}_{z}}{\partial \beta} & \frac{\partial \mathbf{k}_{z}}{\partial \gamma} \end{array}\right|$$

$$= \begin{vmatrix} q_{1x} + \beta q_{2x} + \beta \gamma q_{3x} & \alpha q_{2x} + \alpha \gamma q_{3x} & \alpha \beta q_{3x} \\ q_{1y} + \beta q_{2y} + \beta \gamma q_{3y} & \alpha q_{2y} + \alpha \gamma q_{3y} & \alpha \beta q_{3y} \\ q_{1z} + \beta q_{2z} + \beta \gamma q_{3z} & \alpha q_{2z} + \alpha \gamma q_{3z} & \alpha \beta q_{3z} \end{vmatrix}$$
$$= \alpha \beta \begin{vmatrix} \alpha q_{1x} + \alpha \beta q_{2x} + \alpha \beta \gamma q_{3x} & q_{2x} + \gamma q_{3x} & q_{3x} \\ \alpha q_{1y} + \alpha \beta q_{2y} + \alpha \beta \gamma q_{3y} & q_{2y} + \gamma q_{3y} & q_{3y} \\ \alpha q_{1z} + \alpha \beta q_{2z} + \alpha \beta \gamma q_{3z} & q_{2z} + \gamma q_{3z} & q_{3z} \end{vmatrix}$$
$$= \alpha \beta \epsilon_{ijk} k_i (q_{2j} + \gamma q_{3j}) q_{3k}$$
$$= \alpha \beta \epsilon_{ijk} k_i q_{2j} q_{3k} + \alpha \beta \gamma \epsilon_{ijk} k_i q_{3j} q_{3k}$$
$$= \alpha \beta \epsilon_{ijk} (\alpha q_{1i} + \alpha \beta q_{2i} + \alpha \beta \gamma q_{3i}) q_{2j} q_{3k}$$
$$= \alpha^2 \beta \epsilon_{ijk} (q_{1i} q_{2j} q_{3k})$$
$$= \alpha^2 \beta \epsilon_{ijk} q_{1i} q_{2j} q_{3k}$$
$$= \alpha^2 \beta \delta q_{1} \cdot (\vec{q}_2 \times \vec{q}_3)$$
$$= 6\alpha^2 \beta V_{T}, \qquad (1.38)$$

where

$$\mathbf{V}_{\mathsf{T}} = \frac{1}{6}\vec{\mathbf{q}}_1 \cdot (\vec{\mathbf{q}}_2 \times \vec{\mathbf{q}}_3) = \frac{1}{6}\vec{\mathbf{k}}_1 \cdot (\vec{\mathbf{k}}_2 \times \vec{\mathbf{k}}_3)$$
(1.39)

is the volume of the tetrahedron. Thus,

$$I_{T_{i}} = \frac{6V_{T_{i}}}{V_{BZ}} \sum_{n} \int_{0}^{1} d\alpha \int_{0}^{1} d\beta \int_{0}^{1} d\gamma \ \alpha^{2} \beta f(\alpha, \beta, \gamma) \Theta(E_{F} - \epsilon_{n,\vec{k}}).$$
(1.40)

The next step consists in carrying out a three-dimensional interpolation of $f(\alpha, \beta, \gamma)$ in the volume of the tetrahedron, that is, in the unit cube of the (α, β, γ) coordinates. Even though we shall be only interested in linear interpolation, let us assume that the function values have been tabulated in a mesh of points $(\alpha_i, \beta_j, \gamma_m)$ in the tetrahedron:

$$\begin{aligned} \boldsymbol{\alpha} &= \boldsymbol{\alpha}_0, ..., \boldsymbol{\alpha}_{n_{\boldsymbol{\alpha}}} \\ \boldsymbol{\beta} &= \boldsymbol{\beta}_0, ..., \boldsymbol{\beta}_{n_{\boldsymbol{\beta}}} \\ \boldsymbol{\gamma} &= \boldsymbol{\gamma}_0, ..., \boldsymbol{\gamma}_{n_{\boldsymbol{\gamma}}}. \end{aligned}$$
(1.41)

This will allow us to write down general expressions, which we will then recast for the particular case of linear interpolation. A conversion between relevant values of (α, β, γ) and (k_x, k_y, k_z) is given below.

Let us consider first an interpolation along $\alpha,$ that is, for a fixed β and $\gamma.$ We then have

$$f(\alpha) = \sum_{j=0}^{n_{\alpha}} L_j(\alpha) f(\alpha_j), \qquad (1.42)$$

where $L_j(\alpha)$ are the Lagrange interpolation coefficients, given by ⁷

$$L_{j}(\alpha) = \prod_{0 \leq m \leq n_{\alpha}, m \neq j} \frac{\alpha - \alpha_{m}}{\alpha_{j} - \alpha_{m}}$$
(1.43)

In the three-dimensional case we have

$$f(\alpha, \beta, \gamma) = \sum_{i=0}^{n_{\alpha}} \sum_{j=0}^{n_{\beta}} \sum_{k=0}^{n_{\gamma}} L_i(\alpha) L_j(\beta) L_k(\gamma) f(\alpha_i, \beta_j, \gamma_k).$$
(1.44)

For a linear three-dimensional interpolation we have $n_{\alpha} = n_{\beta} = n_{\gamma} = 1$, so that the linear interpolation formula reads

$$f(\alpha, \beta, \gamma) = \sum_{i=0}^{1} \sum_{j=0}^{1} \sum_{k=0}^{1} L_i(\alpha) L_j(\beta) L_m(\gamma) f(\alpha_i, \beta_j, \gamma_k), \qquad (1.45)$$

where $\alpha_0 = \beta_0 = \gamma_0 = 0$ and $\alpha_1 = \beta_1 = \gamma_1 = 1$. The expressions of $L_i(\alpha)$, $L_j(\beta)$, and $L_k(\gamma)$ are

$$L_{0}(\alpha) = \frac{\alpha - \alpha_{1}}{\alpha_{0} - \alpha_{1}} = 1 - \alpha, \qquad L_{1}(\alpha) = \frac{\alpha - \alpha_{0}}{\alpha_{1} - \alpha_{0}} = \alpha,$$

$$L_{0}(\beta) = \frac{\beta - \beta_{1}}{\beta_{0} - \beta_{1}} = 1 - \beta, \qquad L_{1}(\beta) = \frac{\beta - \beta_{0}}{\beta_{1} - \beta_{0}} = \beta,$$

$$L_{0}(\gamma) = \frac{\gamma - \gamma_{1}}{\gamma_{0} - \gamma_{1}} = 1 - \gamma, \qquad L_{1}(\gamma) = \frac{\gamma - \gamma_{0}}{\gamma_{1} - \gamma_{0}} = \gamma, \qquad (1.46)$$

Table 1.1 summarizes the conversion of relevant values of (α, β, γ) to tetrahedron-vertex coordinates.

Case $E_F > E_3$

Let us first consider the case where the tetrahedron is completely contained within the Fermi surface, that is

$$\epsilon_{n,\vec{k}} < \mathsf{E}_{\mathsf{F}} \tag{1.47}$$

for all vertices of the tetrahedron, $\vec{k_i}$. Under these circumstances, the Heaviside step function in equation (1.40) is always unity, so the volume integral over the tetrahedron becomes

$$I_{T_{i}} = \frac{6V_{T}}{V_{BZ}} \int_{0}^{1} d\alpha \int_{0}^{1} d\beta \int_{0}^{1} d\gamma \ \alpha^{2} \beta f(\alpha, \beta, \gamma).$$
(1.48)

⁷A. Ralston and P. Rabinowitz, A First Course in Numerical Analysis, Dover 2001.

α	β	γ	\vec{k}	$E(\alpha, \beta, \gamma)$	$f(\alpha, \beta, \gamma)$
0	0	0	\vec{k}_0	E ₀	$f(\vec{k}_0)$
0	0	1	$ \vec{\mathbf{k}}_0 $	E_0	$f(\vec{k}_0)$
0	1	0	$ \vec{\mathbf{k}}_0 $	E_0	$f(\vec{k}_0)$
0	1	1	$ \vec{\mathbf{k}}_0 $	E ₀	$f(\vec{k}_0)$
1	0	0	$ \vec{\mathbf{k}}_1 $	E_1	$f(\vec{k}_1)$
1	0	1	$ \vec{\mathbf{k}}_1 $	E_1	$f(\vec{k}_1)$
1	1	0	$ \vec{\mathbf{k}}_2 $	E_2	$f(\vec{k}_2)$
1	1	1	$ \vec{k}_3 $	E_3	$f(\vec{k}_3)$

Table 1.1: Conversion between the (α, β, γ) system of coordinates and known points.

For the time being we suppose there is only one band, so we drop the sum over band indices n. We can then write the integral explicitly:

$$\begin{split} I_{T_{i}} &= \frac{6V_{T}}{V_{BZ}} \int_{0}^{1} d\alpha \ \alpha^{2} \int_{0}^{1} d\beta \ \beta \int_{0}^{1} d\gamma \ \sum_{i=0}^{1} \sum_{j=0}^{1} \sum_{m=0}^{1} L_{i}(\alpha) L_{j}(\beta) L_{m}(\gamma) f(\alpha_{i}, \beta_{j}, \gamma_{m}) \\ &= \frac{6V_{T}}{V_{BZ}} \sum_{i=0}^{1} \sum_{j=0}^{1} \sum_{m=0}^{1} f(\alpha_{i}, \beta_{j}, \gamma_{m}) \int_{0}^{1} d\alpha \ \alpha^{2} L_{i}(\alpha) \int_{0}^{1} d\beta \ \beta L_{j}(\beta) \int_{0}^{1} d\gamma \ L_{m}(\gamma) \\ &(1.49) \end{split}$$

Using the abbreviations

$$I_{\alpha_{i}} = \int_{0}^{1} \mathrm{d}\alpha \ \alpha^{2} L_{i}(\alpha), \qquad I_{\beta_{j}} = \int_{0}^{1} \mathrm{d}\beta \ \beta L_{j}(\beta), \qquad I_{\gamma_{m}} = \int_{0}^{1} \mathrm{d}\gamma \ L_{m}(\gamma)$$
(1.50)

we have

$$\begin{split} I_{T_{i}} &= \frac{6V_{T}}{V_{BZ}} \sum_{i=0}^{1} \sum_{j=0}^{1} \sum_{m=0}^{1} f(\alpha_{i}, \beta_{j}, \gamma_{m}) I_{\alpha_{i}}(\alpha) I_{\beta_{i}}(\beta) I_{\gamma_{i}}(\gamma) \\ &= \frac{6V_{T}}{V_{BZ}} \left[f(\alpha_{0}, \beta_{0}, \gamma_{0}) I_{\alpha_{0}} I_{\beta_{0}} I_{\gamma_{0}} + f(\alpha_{0}, \beta_{0}, \gamma_{1}) I_{\alpha_{0}} I_{\beta_{0}} I_{\gamma_{1}} + f(\alpha_{0}, \beta_{1}, \gamma_{0}) I_{\alpha_{0}} I_{\beta_{1}} I_{\gamma_{0}} + f(\alpha_{0}, \beta_{1}, \gamma_{1}) I_{\alpha_{0}} I_{\beta_{1}} I_{\gamma_{1}} + f(\alpha_{1}, \beta_{0}, \gamma_{0}) I_{\alpha_{1}} I_{\beta_{0}} I_{\gamma_{0}} + f(\alpha_{1}, \beta_{0}, \gamma_{1}) I_{\alpha_{1}} I_{\beta_{0}} I_{\gamma_{1}} + f(\alpha_{1}, \beta_{0}, \gamma_{0}) I_{\alpha_{1}} I_{\beta_{0}} I_{\gamma_{0}} + f(\alpha_{1}, \beta_{0}, \gamma_{1}) I_{\alpha_{1}} I_{\beta_{0}} I_{\gamma_{1}} + f(\alpha_{1}, \beta_{0}, \gamma_{0}) I_{\alpha_{1}} I_{\beta_{0}} I_{\gamma_{0}} + f(\alpha_{1}, \beta_{0}, \gamma_{1}) I_{\alpha_{1}} I_{\beta_{0}} I_{\gamma_{1}} + f(\alpha_{1}, \beta_{0}, \gamma_{0}) I_{\alpha_{1}} I_{\beta_{0}} I_{\gamma_{0}} + f(\alpha_{1}, \beta_{0}, \gamma_{1}) I_{\alpha_{1}} I_{\beta_{0}} I_{\gamma_{1}} + f(\alpha_{1}, \beta_{0}, \gamma_{0}) I_{\alpha_{1}} I_{\beta_{0}} I_{\gamma_{0}} + f(\alpha_{1}, \beta_{0}, \gamma_{1}) I_{\alpha_{1}} I_{\beta_{0}} I_{\gamma_{1}} + f(\alpha_{1}, \beta_{0}, \gamma_{0}) I_{\alpha_{1}} I_{\beta_{0}} I_{\gamma_{0}} + f(\alpha_{1}, \beta_{0}, \gamma_{1}) I_{\alpha_{1}} I_{\beta_{0}} I_{\gamma_{1}} + f(\alpha_{1}, \beta_{0}, \gamma_{0}) I_{\alpha_{1}} I_{\beta_{0}} I_{\gamma_{0}} + f(\alpha_{1}, \beta_{0}, \gamma_{1}) I_{\alpha_{1}} I_{\beta_{0}} I_{\gamma_{1}} + f(\alpha_{1}, \beta_{0}, \gamma_{0}) I_{\alpha_{1}} I_{\beta_{0}} I_{\gamma_{0}} + f(\alpha_{1}, \beta_{0}, \gamma_{1}) I_{\alpha_{1}} I_{\beta_{0}} I_{\gamma_{1}} + f(\alpha_{1}, \beta_{0}, \gamma_{0}) I_{\alpha_{1}} I_{\beta_{0}} I_{\gamma_{0}} + f(\alpha_{1}, \beta_{0}, \gamma_{1}) I_{\alpha_{1}} I_{\beta_{0}} I_{\gamma_{1}} + f(\alpha_{1}, \beta_{0}, \gamma_{0}) I_{\alpha_{1}} I_{\beta_{0}} I_{\gamma_{0}} + f(\alpha_{1}, \beta_{0}, \gamma_{1}) I_{\alpha_{1}} I_{\beta_{0}} I_{\gamma_{1}} + f(\alpha_{1}, \beta_{0}, \gamma_{1}) I_{\alpha_{1}} I_{\beta_{1}} + f(\alpha_{1}, \beta_{0}, \gamma_{1}) I_{\alpha_{1}} I_{\beta_{1}} + f(\alpha_{1}, \beta_{1}, \gamma_{1}) I_{\alpha_{1}} I_{\beta$$

$$f(\boldsymbol{\alpha}_{1},\boldsymbol{\beta}_{1},\boldsymbol{\gamma}_{0})I_{\boldsymbol{\alpha}_{1}}I_{\boldsymbol{\beta}_{1}}I_{\boldsymbol{\gamma}_{0}} + f(\boldsymbol{\alpha}_{1},\boldsymbol{\beta}_{1},\boldsymbol{\gamma}_{1})I_{\boldsymbol{\alpha}_{1}}I_{\boldsymbol{\beta}_{1}}I_{\boldsymbol{\gamma}_{1}}]$$
(1.51)

The integral values are

$$\begin{split} I_{\alpha_{0}} &= \int_{0}^{1} d\alpha \ \alpha^{2} L_{0}(\alpha) = \int_{0}^{1} d\alpha \ \alpha^{2}(1-\alpha) = \int_{0}^{1} d\alpha \ (\alpha^{2}-\alpha^{3}) = \left[\frac{\alpha^{3}}{3} - \frac{\alpha^{4}}{4}\right]_{0}^{1} = \frac{1}{3} - \frac{1}{4} = \frac{1}{12} \\ I_{\alpha_{1}} &= \int_{0}^{1} d\alpha \ \alpha^{2} L_{1}(\alpha) = \int_{0}^{1} d\alpha \ \alpha^{3} = \frac{1}{4} \\ I_{\beta_{0}} &= \int_{0}^{1} d\beta \ \beta L_{0}(\beta) = \int_{0}^{1} d\beta \ \beta(1-\beta) = \int_{0}^{1} d\beta \ (\beta-\beta^{2}) = \left[\frac{\beta^{2}}{2} - \frac{\beta^{3}}{3}\right]_{0}^{1} = \frac{1}{2} - \frac{1}{3} = \frac{1}{6} \\ I_{\beta_{1}} &= \int_{0}^{1} d\beta \ \beta L_{1}(\beta) = \int_{0}^{1} d\beta \ \beta^{2} = \frac{1}{3} \\ I_{\gamma_{0}} &= \int_{0}^{1} d\gamma \ L_{0}(\gamma) = \int_{0}^{1} d\gamma \ \beta(1-\gamma) = \left[\gamma - \frac{\gamma^{2}}{2}\right]_{0}^{1} = 1 - \frac{1}{2} = \frac{1}{2} \\ I_{\gamma_{1}} &= \int_{0}^{1} d\gamma \ L_{1}(\gamma) = \int_{0}^{1} d\gamma \ \gamma = \frac{1}{2}. \end{split}$$

$$(1.52)$$

Inserting these values in Eq. (1.51) we have

$$I_{T_{i}} = \frac{6V_{T}}{V_{BZ}} \left[f(\vec{k}_{0}) \frac{1}{12} \frac{1}{6} \frac{1}{2} + f(\vec{k}_{0}) \frac{1}{12} \frac{1}{6} \frac{1}{2} + f(\vec{k}_{0}) \frac{1}{12} \frac{1}{3} \frac{1}{2} + f(\vec{k}_{0}) \frac{1}{12} \frac{1}{3} \frac{1}{2} \right] + f(\vec{k}_{1}) \frac{1}{4} \frac{1}{6} \frac{1}{2} + f(\vec{k}_{1}) \frac{1}{4} \frac{1}{6} \frac{1}{2} + f(\vec{k}_{2}) \frac{1}{4} \frac{1}{3} \frac{1}{2} + f(\vec{k}_{3}) \frac{1}{4} \frac{1}{3} \frac{1}{2} \right] = \frac{6V_{T}}{V_{BZ}} \frac{1}{2} \left[\frac{f(\vec{k}_{0})}{12} \left(\frac{1}{6} + \frac{1}{6} + \frac{1}{3} + \frac{1}{3} \right) + \frac{f(\vec{k}_{1})}{12} + \frac{f(\vec{k}_{2})}{12} + \frac{f(\vec{k}_{3})}{12} \right] = \frac{V_{T}}{V_{BZ}} \frac{1}{4} \left[f(\vec{k}_{0}) + f(\vec{k}_{1}) + f(\vec{k}_{2}) + f(\vec{k}_{3}) \right].$$
(1.53)

Thus, if the volume of the tetrahedron is fully contained within the Fermi surface, the contribution of the tetrahedron volume to the total integral is an average of the vertex values, as it should be.

$\mathbf{Case} \ \mathsf{E}_0 < \mathsf{E}_{\mathsf{F}} \leqslant \mathsf{E}_1 \leqslant \mathsf{E}_2 \leqslant \mathsf{E}_3$

In this case the Fermi surface crosses the tetrahedron, with crossing points \vec{k}_{01} , \vec{k}_{02} , and \vec{k}_{03} along the $\vec{k}_0\vec{k}_1$, $\vec{k}_0\vec{k}_2$, and $\vec{k}_0\vec{k}_3$ axes, respectively, see Fig. 1.4.

The Fermi surface separates the tetrahedron into two regions:

• a smaller tetrahedron $k_0 k_{01} k_{02} k_{03}$ which is contained within the integration region (below the Fermi surface), and



• the rest of the tetrahedron, which lies above the Fermi surface and therefore does not contribute to the integral, due to the factor $\Theta(E_F - \epsilon_{n,\vec{k}})$.

Thus, we have to restrict our volume integral to the small tetrahedron determined by \vec{k}_0 , \vec{k}_{01} , \vec{k}_{02} , \vec{k}_{03} . The coordinates of the intersection points can be found in a straightforward way:

$$\vec{k}_{01} = \frac{E_{F} - E_{0}}{E_{1} - E_{0}} \vec{k}_{1} \equiv \Delta_{10} \vec{k}_{1}$$
$$\vec{k}_{02} = \frac{E_{F} - E_{0}}{E_{2} - E_{0}} \vec{k}_{2} \equiv \Delta_{20} \vec{k}_{2}$$
$$\vec{k}_{03} = \frac{E_{F} - E_{0}}{E_{3} - E_{0}} \vec{k}_{3} \equiv \Delta_{30} \vec{k}_{3},$$
(1.54)

where

$$\Delta_{ij} = \frac{\mathsf{E}_{\mathsf{F}} - \mathsf{E}_j}{\mathsf{E}_i - \mathsf{E}_j}.\tag{1.55}$$

The values of $f(\vec{k})$ at the intersection points read

$$\begin{aligned} f(\vec{k}_{01}) &= f(\vec{k}_0) + \Delta_{10}[f(\vec{k}_1) - f(\vec{k}_0)] \\ f(\vec{k}_{02}) &= f(\vec{k}_0) + \Delta_{20}[f(\vec{k}_2) - f(\vec{k}_0)] \\ f(\vec{k}_{03}) &= f(\vec{k}_0) + \Delta_{30}[f(\vec{k}_3) - f(\vec{k}_0)]. \end{aligned}$$
(1.56)

The volume of the small tetrahedron reads

$$\mathbf{V} = \frac{1}{6}\vec{k}_{01} \cdot (\vec{k}_{02} \times \vec{k}_{03}) = \frac{1}{6}\Delta_{10}\Delta_{20}\Delta_{30}\vec{k}_1 \cdot (\vec{k}_2 \times \vec{k}_3) = \Delta_{10}\Delta_{20}\Delta_{30}\mathbf{V}_{\mathrm{T}_{\mathrm{i}}}$$
(1.57)

Using Eq. (1.53) for the small tetrahedron contained within the Fermi surface, we have

$$\begin{split} \mathbf{I}_{\mathrm{T}_{i}} &= \frac{V_{\mathrm{T}_{i}}}{4V_{\mathrm{BZ}}} \Delta_{10} \Delta_{20} \Delta_{30} [f(\vec{k}_{0}) + f(\vec{k}_{01}) + f(\vec{k}_{02}) + f(\vec{k}_{03})] \\ &= \frac{V_{\mathrm{T}_{i}}}{4V_{\mathrm{BZ}}} \Delta_{10} \Delta_{20} \Delta_{30} [4f(\vec{k}_{0}) + \Delta_{10} [f(\vec{k}_{1}) - f(\vec{k}_{0})] \\ &+ \Delta_{20} [f(\vec{k}_{2}) - f(\vec{k}_{0})] + \Delta_{30} [f(\vec{k}_{3}) - f(\vec{k}_{0})] \} \end{split}$$

Thus, in the case $E_0 < E_F \leqslant E_1 \leqslant E_2 \leqslant E_3$ we have

$$I_{T_{i}} = \frac{V_{T_{i}}}{4V_{BZ}} \Delta_{10} \Delta_{20} \Delta_{30} [(4 - \Delta_{10} - \Delta_{20} - \Delta_{30})f(\vec{k}_{0}) + \Delta_{10}f(\vec{k}_{1}) + \Delta_{20}f(\vec{k}_{2}) + \Delta_{30}f(\vec{k}_{3})].$$
(1.58)

 $\mathbf{Case} \ \mathsf{E}_0 \leqslant \mathsf{E}_1 < \mathsf{E}_\mathsf{F} \leqslant \mathsf{E}_2 \leqslant \mathsf{E}_3$



This case is the most involved one as the integration volume needs to be split into tetrahedra (see Fig. 1.5).

Final formulas of linear tetrahedron method

Note that here we label the tetrahedron vertices from 1 to 4 as in P. Blöchl *et al.*, Phys. Rev. B **49**, 16223 (1994). For the calculation of the electron

number and the density of states, the only information that is required is the volume V_T of the tetrahedra; for a tetrahedron given by the vectors \vec{k}_1 , \vec{k}_2 , \vec{k}_3 , \vec{k}_4 , this can be calculated by

$$\mathbf{V}_{\mathsf{T}} = \frac{1}{6} \left| \det(\vec{k}_2 - \vec{k}_1, \vec{k}_3 - \vec{k}_1, \vec{k}_4 - \vec{k}_1) \right|$$
(1.59)

Then we denote the energies of a given band by $\varepsilon(\vec{k}_i) \equiv \varepsilon_i$ and energy differences by $\varepsilon_{ij} = \varepsilon_i - \varepsilon_j$; we also sort the energies at the corners of the tetrahedron as

$$\varepsilon_1 < \varepsilon_2 < \varepsilon_3 < \varepsilon_4$$

Now the contribution of the tetrahedron to the number of states $n(\varepsilon)$ at a given energy ε is

$$n_{T}(\varepsilon) = \begin{cases} 0 & \text{for } \varepsilon < \varepsilon_{1} \\ \frac{V_{T}}{V_{G}} \frac{(\varepsilon - \varepsilon_{1})^{3}}{\varepsilon_{21}\varepsilon_{31}\varepsilon_{41}} & \text{for } \varepsilon_{1} < \varepsilon < \varepsilon_{2} \\ \frac{V_{T}}{V_{G}} \frac{1}{\varepsilon_{31}\varepsilon_{41}} \left[\varepsilon_{21}^{2} + 3\varepsilon_{21}(\varepsilon - \varepsilon_{2}) + 3(\varepsilon - \varepsilon_{2})^{2} - \frac{\varepsilon_{31} + \varepsilon_{42}}{\varepsilon_{32}\varepsilon_{42}}(\varepsilon - \varepsilon_{2})^{3} \right] & \text{for } \varepsilon_{2} < \varepsilon < \varepsilon_{3} \\ \frac{V_{T}}{V_{G}} \left(1 - \frac{(\varepsilon_{4} - \varepsilon)^{3}}{\varepsilon_{41}\varepsilon_{42}\varepsilon_{43}} \right) & \text{for } \varepsilon_{3} < \varepsilon < \varepsilon_{4} \\ \frac{V_{T}}{V_{G}} & \text{for } \varepsilon_{4} < \varepsilon \\ \frac{V_{T}}{V_{G}} & (1.60) \end{cases}$$

 V_G is the volume of the primitive cell of the reciprocal lattice. The contribution of the tetrahedron to the density of states $\rho(\epsilon)$ is simply the energy derivative of $n_T(\epsilon)$:

$$\rho_{\mathsf{T}}(\varepsilon) = \begin{cases}
0 & \text{for } \varepsilon < \varepsilon_{1} \\
\frac{V_{\mathsf{T}}}{V_{\mathsf{G}}} \frac{3(\varepsilon - \varepsilon_{1})^{2}}{\varepsilon_{21}\varepsilon_{31}\varepsilon_{41}} & \text{for } \varepsilon_{1} < \varepsilon < \varepsilon_{2} \\
\frac{V_{\mathsf{T}}}{V_{\mathsf{G}}} \frac{1}{\varepsilon_{31}\varepsilon_{41}} \left[3\varepsilon_{21} + 6(\varepsilon - \varepsilon_{2}) - 3\frac{(\varepsilon_{31} + \varepsilon_{42})(\varepsilon - \varepsilon_{2})^{2}}{\varepsilon_{32}\varepsilon_{42}} \right] & \text{for } \varepsilon_{2} < \varepsilon < \varepsilon_{3} \\
\frac{V_{\mathsf{T}}}{V_{\mathsf{G}}} \frac{3(\varepsilon_{4} - \varepsilon)^{2}}{\varepsilon_{41}\varepsilon_{42}\varepsilon_{43}} & \text{for } \varepsilon_{3} < \varepsilon < \varepsilon_{4} \\
0 & \text{for } \varepsilon_{4} < \varepsilon \end{cases}$$
(1.61)

1.3 Some results of crystal field theory

Crystal field theory ⁸ analyzes the splitting of one electron states, for example transition metal d states, in the electrical field caused by the surrounding ligands in the crystal, the so called ligand field. Ligand field theory is a more complicated approach that goes beyond crystal field theory and deduces the chemical bonding in transition metal complexes. We discuss the principal idea of crystal field theory for the example of a single d electron in an octahedral environment.



Figure 1.6: (Left) Octahedron of ligands (black spheres), inscribed into a cube. (Center) Tetrahedron of ligands. (Right) Square of ligands.

In the octahedral ligand field, the d orbitals split into two groups, based on stronger and less strong interaction with the ligands. As demonstrated in Fig. 1.7, d_{z^2} and $d_{x^2-y^2}$ have lobes pointing directly towards the ligands, leading to a strong interaction, because the highest densitiy overlaps with that of the ligand. The three orbitals d_{xy} , d_{xz} and d_{yz} all have exactly the same orientation towards the ligands, pointing along the angle bisectrix; they have the highest charge density between two metal-ligand bonds. This leads to the term scheme 1.8. The crystal field splitting energy Δ is traditionally written as $\Delta_0 = 10$ Dq where Dq is called ligand field splitting parameter. Perturbation theory yields

$$\mathsf{E}(\mathsf{t}_{2\mathsf{g}}) = \varepsilon_0 - 4\mathsf{D}\mathsf{q}, \qquad \mathsf{E}(\mathsf{e}_{\mathsf{g}}) = \varepsilon_0 + 6\mathsf{D}\mathsf{q}$$

where ε_0 is the shift due to the spherically symmetric part of the potential; is called barycenter.

⁸This chapter is based on A. R. West, *Grundlagen der Festkörperchemie*, Wiley-VCH (1992), und H. L. Schläfer, G. Gliemann, *Einführung in die Ligandenfeldtheorie*. Akademische Verlagsgesellschaft, Frankfurt (1967).



Figure 1.8: Splitting of energy levels in an octahedral ligand field.

The naming of t_{2g} and e_g is derived from the theory of molecular symmetry. Small t and e indicate one-electron states. The irreducible representations of the point group are labeled as follows:

- one dimensional representations are labeled with a and b; a when rotation around the principal axis is symmetrical, b when rotation around the principal axis is asymmetrical.
- e and t are doubly and triply degenerate representations respectively
- the subscript g (for german gerade) indicates no sign change with respect to inversion, and n indicates sign change.
- subscript numbers distinguish between the various one-, two-, threeand four dimensional representations; t_2 carries the index 2 to distinguish it from the triply degenerate p state which is named t_1 .

The crystal field stabilization energy arises from the fact that some **d** levels become more stable compared to a spherical field. In the same way, we can understand the splitting in the tetrahedral ligand field. Here, d_{z^2} and $d_{x^2-y^2}$ are always pointing along the angle bisectrix, putting the highest charge density between the bonds (see Fig. 1.9); these two states have lower energies and are labeled **e**. The orbitals d_{xy} , d_{xz} and d_{yz} each have higher density pointing towards ligands leading to larger interaction an thus higher energy; they are labeled t_2 . The term scheme for tetrahedral field is shown in Fig. 1.10.



Figure 1.10: Splitting of energy levels in a tetrahedral ligand field.

Another example is the square planar ligand field which leads to the term scheme shown in Fig. 1.11. It can be considered as the extreme limit of an octahedral environment elongated along z, with ligands above and below

the plane moved away from the center. A small distortion of this kind will be discussed below.



Figure 1.11: Splitting of energy levels in a square planar ligand field.

If we now consider more than one d electron in an octahedral field, we find a crystal field stabilization energy

$$CFSE = n_{t_{2g}}(-4D_{q}) + n_{eg}(+6D_{q}) = -0.4\Delta_0 n_{t_{2g}} + 0.6\Delta_0 n_{eg}$$

See Fig. 1.12 for examples. Between d^3 and d^7 , low spin or high spin configurations are possible depending on the crystal field splitting energy Δ_0 compared to the so called pairing energy P that consists in Coulomb repulsion U and loss of Hund's rule coupling energy J_H . There is a low spin energy gain Δ_0 for d^4 , d^7 and $2\Delta_0$ for d^5 , d^6 .



Figure 1.12: Spin configurations for transition metal ions in an octahedral field; in four cases, high and low spin configurations are possible.

Jahn Teller distortion

The Jahn Teller effect leads to a distortion of the ligand positions in case the resulting lifting of a degeneracy due to lowering of the symmetry leads to an energy gain. An important example is the Cu²⁺ ion which has a d^9 configuration. In octahedral symmetry, one of the two degenerate e_g orbitals (either d_{z^2} or $d_{x^2-y^2}$) holds one electron, the other two. Now the doubly occupied orbital leads to a stronger repulsion of the ligands than the simply occupied orbital; this would elongate the corresponding metalligand bonds, the four xy plane bonds in the case of doubly occupied $d_{x^2-y^2}$ or the two axial bonds in the case of doubly occupied d_{z^2} . This elongation leads to a lowering of the corresponding energy level.



Figure 1.13: Energy level diagram of a d ion with Jahn Teller distortion. The bonds along z are longer than the other four bonds. the energy gain is $1/2\delta_2$ compared to the undistorted octahedral ligand field.

2. Density functional theory

The widely used and extremely successful density functional theory is based on the exact theorem that the ground state energy is determined only by the density. In particular, the theorem guarantees that all ground state properties are unique functionals of the electron density and that the electron density can be obtained from a Schrödinger equation in an effective potential. Thus the interacting electron system is mapped onto a system of noninteracting electrons in an effective potential. This potential depends on the electron distribution and describes the interactions between the electrons in an effective way.

Density functional theory provides a total energy functional of the form

$$\mathsf{E}[\mathsf{n}(\vec{r})] = \underbrace{\sum_{n} \left\langle \phi_{n} \left| \frac{\hat{p}^{2}}{2m_{e}} \right| \phi_{n} \right\rangle}_{\mathsf{T}_{s}[\mathsf{n}(\vec{r})]} + \int d^{3}r \, \mathsf{n}(\vec{r}) v_{\mathrm{ext}}(\vec{r}) + \frac{1}{2} \int d^{3}r \int d^{3}r' \, \frac{\mathsf{n}(\vec{r})\mathsf{n}(\vec{r}')}{4\pi\epsilon_{0}|\vec{r} - \vec{r}'}$$

$$(2.1)$$

 T_s is the kinetic energy of the noninteracting reference system, not that of the many body system. It can be written as a functional of the density. $E_{xc}[n(\vec{r})]$ is the exchange and correlation functional which is not known and has to be approximated .

The minimum principle leads to the Kohn-Sham equations for the one particle orbitals

$$\left[\frac{\hat{\mathbf{p}}^2}{2\mathbf{m}_e} + \mathbf{v}_{\text{eff}}(\vec{\mathbf{r}}) - \varepsilon_{\mathbf{n}}\right] |\phi_{\mathbf{n}}\rangle = 0$$
(2.2)

with the effective potential

$$\nu_{\rm eff}(\vec{r}) = \nu_{\rm ext}(\vec{r}) + \frac{e^2}{4\pi\epsilon_0} \int d^3r' \frac{n(\vec{r})}{|\vec{r} - \vec{r}'|} + \frac{\partial E_{\rm xc}}{\partial n(\vec{r})}$$
(2.3)

and the density

$$\mathfrak{n}(\vec{r}) = \sum_{n=1}^{N} \phi_n^*(\vec{r}) \phi_n(\vec{r})$$
(2.4)

Thus, a conventional selfconsistency cycle to solve this system of equations looks like this:



2.1 Local spin density approximation

In order to describe magnetic systems (called open shell molecules by chemists), one uses the local spin density approximation where the spin dependent density $n(\vec{r}, \sigma)$ is used instead of the total density $n(\vec{r}) =$

 $\sum_{\sigma} \mathbf{n}(\mathbf{r}, \mathbf{\sigma})$. This leads to one-particle wave functions with spin up and spin down character and to two effective potentials, one for spin up electrons and one for spin down electrons. The difference between the effective potentials acts like a magnetic field even though its origin is purely electrostatic, *i.e.* exchange and correlation; it is called the **exchange interaction**.

2.2 Interpretation of Kohn-Sham energies

The Kohn-Sham eigenvalues, introduced as Lagrange multipliers, have no direct physical meaning, at least not that of the energies to add or substract electrons from the interacting manybody system (in analogy to Koopmas theorem for Hartree Fock). The exception is the highest eigenvalue in a finite system which is minus the ionization energy.

Nevertheless, the eigenvalues have a well defined meaning within the theory and can be used to construct physically meaningful quantities. For example, they can be used to develop perturbation expressions for excitation energies, either in the form of a functional or in the form of explicit manybody calculations that use the Kohn-Sham eigenfunctions and eigenvalues as an input.

Within the Kohn-Sham formalism, the meaning of the eigenvalues, known as Janak theorem, is that the eigenvalue is the derivative of the total energy with respect to the occupation of a state:

$$\varepsilon_{i} = \frac{dE_{\text{total}}}{dn_{i}} = \int d^{3}r \, \frac{dE_{\text{total}}}{dn(\vec{r})} \frac{dn(\vec{r})}{dn_{i}} \,.$$
(2.5)

2.3 Basis sets

Here we give a very brief overview over the different basis sets that are in use for the solution of the Kohn Sham equations.

1) Plane waves

Plane waves are conceptionally very simple but they are not well adapted to describe strongly varying potentials. Therefore, they are usually used in conjunction with pseudopotentials or their more recent generalization, projector augmented waves (PAW).

2) Augmented functions

Mixed basis sets that treat the region close to the atomic cores differently from the interstitial region are often computationally efficient as they lead to a small (or even minimal) basis. Examples are augmented plane wave (APW), muffin tin orbital (MTO) and the Korringa-Kohn-Rostoker (KKR) multiple scattering Green function method. Linear augmented function methods were invented to deal with the energy dependence of the basis functions.

3) Localized orbitals

Here, we give slightly more detail about methods using localized orbitals as we will use one of them in this course.

The following expansion theorem is important for the usefulness of analytical basis functions:

$$\chi_{\alpha}(\vec{r} - \vec{R}) = \sum_{\alpha'} B_{\alpha\alpha'}(\vec{R}, \vec{R}') \chi_{\alpha'}(\vec{r} - \vec{R}')$$
(2.6)

This is an expansion in terms of basis functions on neighbouring sites. Examples are: Gaussians times polynomials $r^{\beta}e^{-\alpha r^2}$, Slater type orbitals (STO) $r^{\beta}e^{-\alpha r}$, Bessel, Neumann and Hankel functions.

a) Gaussians

Gaussians have the nice property that the product of any two Guassians is a Gaussian:

$$\gamma = \alpha + \beta, \qquad \vec{\mathsf{R}}_{\mathrm{C}} = \frac{\alpha \mathsf{R}_{\mathrm{A}} + \beta \mathsf{R}_{\mathrm{B}}}{\alpha + \beta}, \qquad \mathsf{K}_{\mathrm{AB}} = \left[\frac{2\alpha\beta}{\pi(\alpha + \beta)}\right]^{3/4} e^{\frac{\alpha\beta}{\gamma} |\vec{\mathsf{R}}_{\mathrm{A}} - \vec{\mathsf{R}}_{\mathrm{B}}|^{2}}$$
(2.7)

Thus, all multicenter integrals can be done analytically. This is why most molecular calculations and quantum chemistry codes use Gaussians. They are also very suitable for Coulomb integrals which is important for Hartree Fock and hybrid functionals. Many commercial codes based on Gaussians exist.

b) Numerial atomic orbitals

These basis sets rely on the solution of the atomic Schrödinger equation with spherically symmetric potentials; confining potentials are used for compression (*i.e.* for limiting the range of the overlap of the basis functions). An example is the SIESTA code with has rather low precision due to its use of pseudopotentials.

The full potential local orbital (FPLO) minimum basis band structure code

uses the crystal potential decomposition

$$\nu(\vec{r}) = \sum_{\vec{R}+\vec{\tau},L} \nu_{\vec{\tau},L} (|\vec{r}-\vec{R}-\vec{\tau}|) Y_L(\vec{r}-\vec{R}-\vec{\tau})$$
(2.8)

where L=l,m and Y_L are spherical harmonics. Extended states are expanded in localized atomic basis orbitals

$$\langle \vec{\mathbf{r}} | \vec{\mathbf{R}} \vec{\tau} L \rangle = \phi_{\vec{\tau}}^{1} (| \vec{\mathbf{r}} - \vec{\mathbf{R}} - \vec{\tau} |) Y_{L} (\vec{\mathbf{r}} - \vec{\mathbf{R}} - \vec{\tau})$$
(2.9)

The basis orbitals solve the Schrödinger equation with spherical potential

$$\nu^{\text{atom}}(\mathbf{r}) = \frac{1}{4\pi} \int d\Omega \,\nu(\vec{\mathbf{r}} - \vec{\mathbf{R}} - \vec{\tau}) + \nu^{\text{confinement}}$$
(2.10)

FPLO uses a confinement potential growing as r^4 ,

$$v^{\text{confinement}} = \left(\frac{\mathbf{r}}{\mathbf{r}_0}\right)^4 \tag{2.11}$$

but there are several other choices in the literature.

3. Greens functions

3.1 Introduction

Greens functions appear naturally as response functions, *i.e.* as answers to the function how a quantum mechanical system responds to an external perturbation, like for example electrical or magnetic fields; the corresponding response functions would then describe the electrical conductivity or the magnetic susceptibility of a system. Here we will be concerned with small perturbations and thus only the linear response of the system. We describe the system by a Hamiltonian

$$\mathsf{H} = \mathsf{H}_0 + \mathsf{V}_\mathsf{t} \tag{3.1}$$

where V_t represents the interaction with an external field. H_0 describes the system with the external field switched off; due to interactions H_0 is not necessarily exactly solvable. The external field F_t couples to the observable \hat{B} of the system:

$$V_{t} = \hat{B}F_{t} \tag{3.2}$$

Here, \hat{B} is an operator and F_t is a complex number. We now consider an observable \hat{A} of the system that is not explicitly time dependent and ask how the dynamic expectation value $\langle \hat{A} \rangle$ reacts to the perturbation V_t . Without field we have

$$\langle \hat{A} \rangle_0 = \operatorname{Tr}(\rho_0 \hat{A})$$
 (3.3)

where ρ_0 is the density matrix of the system without external fields:

$$\rho_0 = \frac{e^{-\beta \mathcal{H}}}{\mathrm{Tr} e^{-\beta \mathcal{H}}} \tag{3.4}$$

in the grand canonical ensemble $\mathcal{H} = H - \mu \hat{N}$ (with chemical potential μ , particle number operator \hat{N}). The density matrix will change if we switch on the field:

$$\rho_0 \to \rho_t$$
(3.5)

This means for the expectation value of \hat{A}

$$\langle \hat{A} \rangle_{t} = \text{Tr}(\rho_{t} \hat{A})$$
 (3.6)

In the Schrödinger picture, the equation of motion of the density matrix (the statistical operator) is determined by the von Neumann equation

$$i\hbar \frac{\partial \rho_t}{\partial t} = \left[\mathcal{H} + V_t, \rho_t \right] \tag{3.7}$$

We consider a perturbation that is switched on at some time so that the boundary condition for our first order differential equation is an unperturbed system for $t \to -\infty$

$$\lim_{t \to -\infty} \rho_t = \rho_0 \,. \tag{3.8}$$

We now switch to the Dirac picture where we have

$$\rho_{t}^{D}(t) = e^{\frac{i}{\hbar}\mathcal{H}_{0}t}\rho_{t}e^{-\frac{i}{\hbar}\mathcal{H}_{0}t}$$
(3.9)

with the equation of motion

$$\rho_t^{\rm D}(t) = \frac{i}{\hbar} \left[\rho_t^{\rm D}, V_t^{\rm D} \right]_{-}(t) \,. \tag{3.10}$$

Integrating with the boundary condition

$$\lim_{t \to \infty} \rho_t^{\mathsf{D}}(t) = \rho_0 \tag{3.11}$$

leads to

$$\rho_{t}^{D}(t) = \rho_{0} - \frac{i}{\hbar} \int_{-\infty}^{t} dt' \left[V_{t'}^{D}(t'), \rho_{t'}^{D}(t') \right]_{-}$$
(3.12)

This equation can be solved by iteration (by substituting $\rho_t^D(t)$ repeatedly on the right hand side):

$$\begin{split} \rho_{t}^{D}(t) &= \rho_{0} + \sum_{n=1}^{\infty} \rho_{t}^{D(n)}(t) \quad \text{with} \\ \rho_{t}^{D(n)}(t) &= \left(-\frac{i}{\hbar}\right)^{n} \int_{-\infty}^{t} dt_{1} \int_{-\infty}^{t_{1}} dt_{2} \cdots \int_{-\infty}^{t_{n-1}} dt_{n} \\ &\times \left[V_{t_{1}}^{D}(t_{1}), \left[V_{t_{2}}^{D}(t_{2}), \left[\cdots \left[V_{t_{n}}^{D}(t_{n}), \rho_{0}\right] \cdots \right]_{-}\right]_{-}\right]_{-} \end{split}$$
(3.13)

While this formula is exact, it is not practical. For sufficiently small external perturbations, we can restrict to linear terms in the perturbation V_t which is called **linear response**:

$$\rho_{t} \approx \rho_{0} - \frac{i}{\hbar} \int_{-\infty}^{t} dt' \, e^{-\frac{i}{\hbar} \mathcal{H}_{0} t} \left[V_{t'}^{D}(t'), \rho_{0} \right]_{-} e^{\frac{i}{\hbar} \mathcal{H}_{0} t} \tag{3.14}$$

Here, we have returned to the Schrödinger representation for the density matrix. We can use this result to determine the perturbed expectation value of (3.6):

$$\begin{split} \langle \hat{A} \rangle_{t} &= \operatorname{Tr}(\rho_{t} \hat{A}) = \langle \hat{A} \rangle_{0} - \frac{i}{\hbar} \int_{-\infty}^{t} dt' \operatorname{Tr} \Big\{ e^{-\frac{i}{\hbar} \mathcal{H}_{0} t} \big[V_{t'}^{D}(t'), \rho_{0} \big]_{-} e^{\frac{i}{\hbar} \mathcal{H}_{0} t} \hat{A} \Big\} \\ &= \langle \hat{A} \rangle_{0} - \frac{i}{\hbar} \int_{-\infty}^{t} dt' F_{t'} \operatorname{Tr} \underbrace{\Big\{ \big[\hat{B}^{D}(t'), \rho_{0} \big]_{-} \hat{A}^{D}(t) \Big\}}_{=\hat{B} \rho_{0} \hat{A} - \rho_{0} \hat{B} \hat{A} = \rho_{0} \hat{A} \hat{B} - \rho_{0} \hat{B} \hat{A}} \\ &= \langle \hat{A} \rangle_{0} - \frac{i}{\hbar} \int_{-\infty}^{t} dt' F_{t'} \operatorname{Tr} \Big\{ \rho_{0} \big[\hat{A}^{D}(t), \hat{B}^{D}(t') \big]_{-} \Big\} \end{split}$$
(3.15)

Here, cyclic invariance of the trace was exploited. This shows how the system reacts to the external perturbation, as measured from the observable \hat{A} :

$$\Delta A_{t} = \langle \hat{A} \rangle_{t} - \langle \hat{A} \rangle_{0} = -\frac{i}{\hbar} \int_{-\infty}^{t} dt' F_{t'} \langle [\hat{A}^{D}(t), \hat{B}^{D}(t')]_{-} \rangle_{0} \qquad (3.16)$$

This response is determined by an expectation value of the unperturbed system. The Dirac representation of the operators $\hat{A}^{D}(t)$, $\hat{B}^{D}(t')$ corresponds to the Heisenberg representation when the field is switched off. Now we define the retarded two-time greens function

$$G_{AB}^{r}(t,t') = \langle\!\langle A(t); B(t') \rangle\!\rangle = -i\Theta(t,t') \big\langle \big[A(t), B(t')\big]_{-} \big\rangle_{0} \quad (3.17)$$

The operators are to be taken in Heisenberg representation of the field free system. The retarded Greens function describes the response of a system as manifested in observable \hat{A} when the perturbation couples to observable \hat{B} :

$$\Delta A_{t} = -\frac{1}{\hbar} \int_{-\infty}^{\infty} dt' F_{t'} G^{r}_{AB}(t,t') \qquad (3.18)$$

It is called retarded because due to the Heaviside function, only perturbations for $t < t^\prime$ contribute.

With the Fourier transform $F(\omega)$ of the perturbation

$$F_{t} = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega F(\omega) e^{-i(\omega+i\delta)t}$$
(3.19)

where $\delta > 0$ is infinitesimally small and using the later result that with a Hamiltonian that is not explicitly time dependent the Greens function depends only on time differences t - t', we can rewrite (3.18) in the form of the **Kubo formula**

$$\Delta A_{t} = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} d\omega F(\omega) G_{AB}^{r}(\omega + i\delta) e^{-i(\omega + i\delta)t}$$
(3.20)

The $\delta > 0$ in the exponent enforces the boundary condition (3.8). We will now look into two applications of response functions.

Magnetic Susceptibility

The perturbation is a spatially homogeneous magnetic field that oscillates in time:

$$B_{t} = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega B(\omega) e^{-i(\omega+i\delta)t}, \qquad (3.21)$$

which couples to the magnetic moment

$$\vec{m} = \sum_{i} m_{i} = \frac{g\mu_{B}}{\hbar} \sum_{i} \vec{S}_{i}. \qquad (3.22)$$

Thus, the perturbing potential term in the Hamiltonian becomes

$$V_{t} = -\vec{m} \cdot \vec{B}_{t} = -\frac{1}{2\pi} \sum_{\alpha} \int_{-\infty}^{\infty} d\omega \, m^{\alpha} B^{\alpha}(\omega) e^{-i(\omega+i\delta)t}$$
(3.23)

where $\alpha = x, y, z$ are Cartesian directions. An interesting quantity is now the magnetization in response to the applied field. As it is

$$\vec{\mathcal{M}} = \frac{1}{\mathbf{V}} \langle \vec{\mathfrak{m}} \rangle = \frac{g\mu_B}{\hbar \mathbf{V}} \sum_{i} \langle \vec{S}_i \rangle , \qquad (3.24)$$

we have to choose the magnetic momentum operator for both \hat{A} and \hat{B} operators in the Kubo formula:

$$\mathcal{M}_{t}^{\beta} - \mathcal{M}_{0}^{\beta} = -\frac{1}{V} \sum_{\alpha} \int_{-\infty}^{\infty} dt' \, \mathcal{B}_{t'}^{\alpha} \langle\!\langle \mathfrak{m}^{\beta}(t); \mathfrak{m}^{\alpha}(t') \rangle\!\rangle \,. \tag{3.25}$$

Only in a ferromagnet there is a finite magnetization \mathcal{M}_0^{β} without a field. Eq. (3.25) defines the **magnetic susceptibility tensor**

$$\chi_{ij}^{\beta\alpha}(\mathbf{t},\mathbf{t}') = -\frac{\mu_0}{V} \frac{g\mu_B^2}{\hbar^2} \left\langle\!\!\left\langle S_i^\beta(\mathbf{t}); S_j^\alpha(\mathbf{t}') \right\rangle\!\!\right\rangle$$
(3.26)

as a retarded Greens function. Thus

$$\Delta \mathcal{M}_{t}^{\beta} = \frac{1}{\mu_{0}} \sum_{ij} \int_{-\infty}^{\infty} dt' B_{t'}^{\alpha} \chi_{ij}^{\beta\alpha}(t,t')$$
(3.27)

or in terms of frequency

$$\Delta \mathcal{M}_{t}^{\beta} = \frac{1}{2\pi\mu_{0}} \sum_{ij} \sum_{\alpha} \int_{-\infty}^{\infty} d\omega \, e^{-i(\omega+i\delta)t} \chi_{ij}^{\beta\alpha}(\omega) \mathcal{B}^{\alpha}(\omega)$$
(3.28)

We have implicitly assumed that the system we consider has permanent localized moments.

Two types of susceptibilities are interesting: The **longitudinal susceptibility**

$$\chi_{ij}^{zz}(\omega) = \frac{\mu_0}{V} \frac{g\mu_B^2}{\hbar^2} \left\langle\!\!\left\langle \mathbf{S}_i^z; \mathbf{S}_j^z \right\rangle\!\!\right\rangle_{\omega} \tag{3.29}$$

where the index indicates the Fourier transform of the retarded Greens function. This can be used to obtain information about the stability of magnetic orderings. For the paramagnetic phase, one calculates the spatial Fourier transform

$$\chi_{\vec{q}}^{zz}(\omega) = \frac{1}{N} \sum_{ij} \chi_{ij}^{zz}(\omega) e^{i\vec{q}\cdot\left(\vec{R}_i - \vec{R}_j\right)}$$
(3.30)

At the singularities of this response function, an infinitesimally small field is sufficient to create a finite magnetization, *i.e.* a spontaneous ordering of the moments. For that purpose, the conditions under which

$$\left\{\lim_{(\vec{q},\omega)\to\infty}\chi_{\vec{q}}^{zz}(\omega)\right\}^{-1} = 0$$
(3.31)

are studied; they indicate the paramagnetic \leftrightarrow ferromagnetic transition. The other interesting case is the **transversal susceptibility**

$$\chi_{ij}^{+-}(\omega) = -\frac{\mu_0}{V} \frac{g\mu_B^2}{\hbar^2} \left\langle\!\!\left\langle S_i^+; S_j^- \right\rangle\!\!\right\rangle_{\omega} \quad \text{where} \quad S_i^{\pm} = S_i^{x} \pm i S_i^{y} \qquad (3.32)$$

Poles of this susceptibility correspond to spin wave (magnon) energies:

$$\left\{\chi_{\vec{q}}^{+-}(\omega)\right\}^{-1} = 0 \iff \omega = \omega(\vec{q}).$$
(3.33)

The examples show that linear response theory not only treats weak external perturbations but also yields information about the unperturbed system.

Electrical conductivity

Now we consider a spatially homogeneous electrical field that oscillates in time:

$$\vec{\mathsf{E}}_{\mathsf{t}} = \frac{1}{2\pi} \int_{-\infty}^{\infty} \mathrm{d}\omega \, \vec{\mathsf{E}}(\omega) e^{-\mathsf{i}(\omega+\mathsf{i}\delta)\mathsf{t}} \,. \tag{3.34}$$

The electrical field couples to the electrical dipole moment \vec{P}

$$\vec{\mathsf{P}} = \int d^3 r \, \vec{r} n(\vec{r}) \,. \tag{3.35}$$

We consider N point changes q_i at positions $\vec{r}_i(t)$; the charge density is

$$n(\vec{r}) = \sum_{i=1}^{N} q_i \delta(\vec{r} - \vec{r}_i). \qquad (3.36)$$

This gives a dipole moment operator

$$\vec{\mathsf{P}} = \sum_{i=1}^{\mathsf{N}} \mathsf{q}_i \vec{\mathsf{r}}_i \,. \tag{3.37}$$

The electrical field causes the additional external potential term in the Hamiltonian

$$V_{t} = -\vec{P} \cdot \vec{E}_{t} = -\frac{1}{2\pi} \sum_{\alpha} \int_{-\infty}^{\infty} d\omega P^{\alpha} E^{\alpha}(\omega) e^{-i(\omega+i\delta)t}.$$
(3.38)

An interesting quantity is the response of the current density to the external field:

$$\vec{j} = \frac{1}{V} \sum_{i=1}^{N} q_i \vec{r}_i = \frac{1}{V} \vec{P}$$
 (3.39)
Its expectation value without field disappears:

$$\langle \vec{\mathbf{j}} \rangle_0 = 0. \tag{3.40}$$

After switching the field on, we have

$$\langle \mathbf{j}^{\beta} \rangle_{\mathbf{t}} = -\frac{1}{\hbar} \sum_{\alpha} \int_{-\infty}^{\infty} d\mathbf{t}' \, \mathsf{E}^{\alpha}_{\mathbf{t}'} \big\langle \! \big\langle \mathbf{j}^{\beta}(\mathbf{t}); \mathsf{P}^{\alpha}(\mathbf{t}') \big\rangle \! \big\rangle \,. \tag{3.41}$$

In terms of the Fourier transforms this becomes

$$\langle \mathfrak{j}^{\beta} \rangle_{\mathfrak{t}} = \frac{1}{2\pi} \sum_{\alpha} \int_{-\infty}^{\infty} d\omega \, e^{-\mathfrak{i}(\omega + \mathfrak{i}\delta)\mathfrak{t}} \sigma^{\beta\alpha}(\omega) \mathsf{E}^{\alpha}(\omega) \tag{3.42}$$

This is Ohms law, defining the electrical conductivity tensor

$$\sigma^{\beta\alpha}(\omega) \equiv -\langle\!\langle j^{\beta}; \mathsf{P}^{\alpha} \rangle\!\rangle_{\omega} \tag{3.43}$$

that has retarded Greens functions as components. This can be rewritten as

$$\sigma^{\beta\alpha}(\omega) = i \frac{N}{V} \frac{q^2}{m(\omega + i\delta)} \delta_{\alpha\beta} + \frac{i}{\hbar} \frac{\langle\!\langle j^\beta; j^\alpha \rangle\!\rangle}{\omega + i\delta}$$
(3.44)

The first term represents the conductivity of a noninteracting electron system as given by classical Drude theory, and the second one involving a retarded current-current Greens function represents the interaction between the particles.

3.2 Matsubara method

In the solid state theory class, Greens functions were introduced as response functions; they can be used to determine the quasiparticle density of states. They also appear as correlation functions, and they give us access to excitation energies. But so far, everything was done at zero temperature. The ojective is now to extend the methods for T = 0 to finite temperatures.¹ As a reminder, the two-time Greens functions were defined as (with $\varepsilon = -1$ for fermionic operators, $\varepsilon = +1$ for bosonic operators)

retarded:	$G_{AB}^{r}(t,t') \equiv \langle\!\langle A(t); B(t') \rangle\!\rangle^{r} = -i\theta(t-t')\langle [A(t), B(t')]_{-\varepsilon} \rangle$
advanced:	$G^{\mathfrak{a}}_{AB}(t,t') \equiv \langle\!\langle A(t); B(t') angle\!\rangle^{\mathfrak{a}} = \mathfrak{i} \theta(t-t') \langle [A(t), B(t')]_{-\epsilon} angle$
causal:	$G^{c}_{AB}(t,t') \equiv \langle\!\langle A(t); B(t') \rangle\!\rangle^{c} = -i \langle T_{\epsilon}(A(t)B(t')) \rangle$

¹This chapter is based on K. Elk, W. Gasser, "Die Methode der Greenschen Funktionen in der Festkörperphysik", Akademie-Verlag Berlin 1979, and W. Nolting, "Grundkurs Theoretische Physik 7, Viel-Teilchen-Theorie", Springer 2009.

(3.45)

with the Wick time ordering operator $T_\epsilon :$

$$\mathsf{T}_{\varepsilon}(\mathsf{A}(\mathsf{t})\mathsf{B}(\mathsf{t}')) = \theta(\mathsf{t}-\mathsf{t}')\mathsf{A}(\mathsf{t})\mathsf{B}(\mathsf{t}') + \varepsilon\theta(\mathsf{t}'-\mathsf{t})\mathsf{B}(\mathsf{t}')\mathsf{A}(\mathsf{t})$$
(3.46)

 $\langle \dots \rangle$ indicates an average over the grand canonical ensemble

$$\langle X \rangle = \frac{\operatorname{Tr}(e^{-\beta \mathcal{H}}X)}{\operatorname{Tr}(e^{-\beta \mathcal{H}})} \quad \text{where } \beta = \frac{1}{k_{\mathrm{B}}T}, \quad \mathcal{H} = H - \mu N \quad (3.47)$$

If the Hamiltonian has no explicit time dependence, the Greens functions are homogeneous in time:

$$\frac{\partial \mathcal{H}}{\partial t} = 0 \Rightarrow G^{\alpha}_{AB}(t, t') = G^{\alpha}_{AB}(t - t'), \qquad \alpha = r, a, c \qquad (3.48)$$

This can be shown using the cyclic invariance of the trace. For the correlation functions that are needed for G^r and G^a , we have

$$\langle (\mathbf{A}(\mathbf{t})\mathbf{B}(\mathbf{t}')\rangle = \langle \mathbf{A}(\mathbf{t} - \mathbf{t}')\mathbf{B}(0)\rangle = \langle \mathbf{A}(0)\mathbf{B}(\mathbf{t}' - \mathbf{t})\rangle \langle (\mathbf{B}(\mathbf{t}')\mathbf{A}(\mathbf{t})\rangle = \langle \mathbf{B}(\mathbf{t}' - \mathbf{t})\mathbf{A}(0)\rangle = \langle \mathbf{B}(0)\mathbf{A}(\mathbf{t} - \mathbf{t}')\rangle$$
(3.49)

We now allow the time variables to formally take complex values:

$$Tre^{-\beta\mathcal{H}}\langle A(t-i\hbar\beta)B(t')\rangle = Tr\left\{e^{-\beta\mathcal{H}}e^{\frac{i}{\hbar}\mathcal{H}(t-i\hbar\beta)}A(0)e^{-\frac{i}{\hbar}\mathcal{H}(t-i\hbar\beta)}B(t')\right\}$$
$$= Tr\left\{B(t')e^{-\beta\mathcal{H}}e^{+\beta\mathcal{H}}e^{\frac{i}{\hbar}\mathcal{H}t}A(0)e^{-\frac{i}{\hbar}\mathcal{H}t}e^{-\beta\mathcal{H}}\right\}$$
$$= Tr\left\{e^{-\beta\mathcal{H}}B(t')A(t)\right\}$$
$$\Rightarrow \langle A(t-i\hbar\beta)B(t')\rangle = \langle B(t')A(t)\rangle$$
(3.50)

As two different correlation functions become related in this way, the extension of the Greens function to complex time seems to be advantageous. In particular, in perturbation theory in V where $\mathcal{H} = \mathcal{H}_0 + V$, V would, for finite temperatures, appear in two places, in the Heisenberg representation of time dependent operators $e^{\pm \frac{1}{\hbar}\mathcal{H}t}$ and in the density operator of the grand canonical averaging $e^{-\beta\mathcal{H}}$; two perturbation expansions would be necessary. Therefore, we join the exponential functions by introducing a complex time.

The Matsubara method introduces purely imaginary times so that the quantity $\tau = it$ is real. This leads to a modified Heisenberg representation of operators:

$$A(\tau) = e^{\frac{1}{\hbar}\mathcal{H}\tau} A(0) e^{-\frac{1}{\hbar}\mathcal{H}\tau}$$
(3.51)

Note that the operator $e^{\frac{i}{\hbar}\mathcal{H}\tau}$ creating imaginary time shifts is not unitary. The equation of motion (EOM) for an operator $A(\tau)$

$$-\hbar\frac{\partial}{\partial\tau}A(\tau) = -\hbar\frac{\partial}{\partial\tau}\left[e^{\frac{1}{\hbar}\mathcal{H}\tau}A(0)e^{-\frac{1}{\hbar}\mathcal{H}\tau}\right] = -\mathcal{H}A(\tau) + A(\tau)\mathcal{H} \quad (3.52)$$

thus becomes:

$$-\hbar \frac{\partial}{\partial \tau} A(\tau) = \left[A(\tau), \mathcal{H} \right]_{-}$$
(3.53)

Here, we use the (conventional) step function

$$\theta(\tau) = \begin{cases} 1 & \text{for } \tau > 0 \ (t = -\tau i \text{ negative imaginary}) \\ 0 & \text{for } \tau < 0 \ (t = |\tau| i \text{ positive imaginary}) \end{cases}$$
(3.54)

It can be used to introduce the time ordering operator.

$$T_{\tau} \{ A(\tau) B(\tau') \} = \theta(\tau - \tau') A(\tau) B(\tau') + \varepsilon^{p} \theta(\tau' - \tau) B(\tau') A(\tau) \quad (3.55)$$

where p is the number of permutations of creation operators. We assume pure Fermi/Bose operators so that p = 1.

The definition of the Matsubara function is:

$$G_{AB}^{M}(\tau,\tau') = \langle\!\langle A(\tau); B(\tau') \rangle\!\rangle^{M} = -\langle T_{\tau}(A(\tau)B(\tau')) \rangle$$
(3.56)

Using (3.53) and (3.55) we get the EOM

$$-\hbar \frac{\partial}{\partial \tau} G^{\mathsf{M}}_{\mathsf{A}\mathsf{B}}(\tau, \tau') = \hbar \delta(\tau - \tau') \langle [\mathsf{A}, \mathsf{B}]_{-\varepsilon} \rangle + \langle \!\langle [\mathsf{A}(\tau), \mathcal{H}]_{-}; \mathsf{B}(\tau') \rangle\!\rangle \quad (3.57)$$

Properties of the Matsubara Greens function introduced in this way are: 1) it depends only on time differences

$$G_{AB}^{M}(\tau,\tau') = G_{AB}^{M}(\tau-\tau',0) = G_{AB}^{M}(0,\tau'-\tau)$$
(3.58)

2) it is periodic in time: Take
$$\hbar\beta > \tau - \tau' + n\hbar\beta > 0, n \in \mathbb{Z}$$
; then

$$Tre^{-\beta\mathcal{H}}G_{AB}^{\mathcal{M}}(\underline{\tau-\tau'+n\hbar\beta}) = -Tr\{e^{-\beta\mathcal{H}}T_{\tau}(A(\tau-\tau'+n\hbar\beta)B(0))\} = -Tr\{e^{-\beta\mathcal{H}}A(\tau-\tau'+n\hbar\beta)B(0)\} = -Tr\{e^{-\beta\mathcal{H}}A(\tau-\tau'+n\hbar\beta)A(0)e^{-\frac{\mathcal{H}}{\hbar}(\tau-\tau'+n\hbar\beta)}B(0)\} = -Tr\{e^{-\beta\mathcal{H}}e^{\frac{\mathcal{H}}{\hbar}(\tau-\tau'+(n-1)\hbar\beta)}A(0)e^{-\frac{\mathcal{H}}{\hbar}(\tau-\tau'+(n-1)\hbar\beta)}e^{-\beta\mathcal{H}}B(0)\} = -Tr\{e^{-\beta\mathcal{H}}B(0)A(\underline{\tau-\tau'+(n-1)\hbar\beta})\} = -Tr\{e^{-\beta\mathcal{H}}T_{\tau}(B(0)A(\tau-\tau'+(n-1)\hbar\beta))\} = -\varepsilon Tr\{e^{-\beta\mathcal{H}}T_{\tau}(A(\tau-\tau'+(n-1)\hbar\beta)B(0))\}$$
(3.59)

This gives us the important result:

$$\hbar\beta > \tau - \tau' + n\hbar\beta > 0: \quad G^{M}_{AB}(\tau - \tau' + n\hbar\beta) = \varepsilon G^{M}_{AB}(\tau - \tau' + (n-1)\hbar\beta)$$
(3.60)

In particular, for n = 1:

$$G_{AB}^{M}(\tau - \tau' + \hbar\beta) = \varepsilon G_{AB}^{M}(\tau - \tau') \quad \text{for } -\hbar\beta < \tau - \tau' < 0 \quad (3.61)$$

Thus the Matsubara Greens function is periodic in an interval $2\hbar\beta$; it is enough to consider the time interval $-\hbar\beta < \tau - \tau' < 0$. This periodicity allows the Fourier expansion:

$$G^{M}(\tau) = \frac{1}{2}a_{0} + \sum_{n=1}^{\infty} \left[a_{n}\cos\frac{n\pi}{\hbar\beta}\tau + b_{n}\sin\frac{n\pi}{\hbar\beta}\tau \right]$$
$$a_{n} = \frac{1}{\hbar\beta} \int_{-\hbar\beta}^{\hbar\beta} d\tau G^{M}(\tau)\cos\left(\frac{n\pi}{\hbar\beta}\tau\right)$$
$$b_{n} = \frac{1}{\hbar\beta} \int_{-\hbar\beta}^{\hbar\beta} d\tau G^{M}(\tau)\sin\left(\frac{n\pi}{\hbar\beta}\tau\right)$$
(3.62)

Now we define discrete energies

$$\mathsf{E}_{\mathsf{n}} = \frac{\mathsf{n}\pi}{\beta} \tag{3.63}$$

and the Matsubara Greens function on the imaginary energy (frequency) axis

$$G(E_n) = \frac{1}{2}\hbar\beta(a_n + ib_n)$$
(3.64)

Then

$$G^{\mathcal{M}}(\tau) = \frac{1}{\hbar\beta} \sum_{n=-\infty}^{\infty} e^{-\frac{i}{\hbar}E_{n}\tau} G^{\mathcal{M}}(E_{n})$$

$$G^{\mathcal{M}}(E_{n}) = \frac{1}{2} \int_{-\hbar\beta}^{\hbar\beta} d\tau \, G^{\mathcal{M}}(\tau) e^{\frac{i}{\hbar}E_{n}\tau}$$
(3.65)

Still, we can simplify a bit more:

$$\begin{split} \mathsf{G}^{\mathsf{M}}(\mathsf{E}_{\mathsf{n}}) &= \frac{1}{2} \int_{0}^{\hbar\beta} d\tau \, \mathsf{G}^{\mathsf{M}}(\tau) e^{\frac{\mathrm{i}}{\hbar} \mathsf{E}_{\mathsf{n}} \tau} + \frac{1}{2} \int_{-\hbar\beta}^{0} d\tau \, \mathsf{G}^{\mathsf{M}}(\tau) e^{\frac{\mathrm{i}}{\hbar} \mathsf{E}_{\mathsf{n}} \tau} \\ &= \frac{1}{2} \int_{0}^{\hbar\beta} d\tau \, \mathsf{G}^{\mathsf{M}}(\tau) e^{\frac{\mathrm{i}}{\hbar} \mathsf{E}_{\mathsf{n}} \tau} + \frac{1}{2} \int_{0}^{\hbar\beta} d\tau \, \mathsf{G}^{\mathsf{M}}(\tau' - \hbar\beta) e^{\frac{\mathrm{i}}{\hbar} \mathsf{E}_{\mathsf{n}} \tau'} e^{-\mathrm{i}\mathsf{E}_{\mathsf{n}}\beta} \\ &= \left[1 + \varepsilon e^{-\mathrm{i}\mathsf{E}_{\mathsf{n}}\beta} \right] \frac{1}{2} \int_{0}^{\hbar\beta} d\tau \, \mathsf{G}^{\mathsf{M}}(\tau) e^{\frac{\mathrm{i}}{\hbar} \mathsf{E}_{\mathsf{n}} \tau} \end{split}$$
(3.66)

where $\tau' = \tau + \hbar\beta$ was introduced. The bracket [...] disappears for fermions ($\varepsilon = -1$) if n is even, for bosons ($\varepsilon = 1$) if n is odd. Thus

$$G^{\mathcal{M}}(\tau) = \frac{1}{\hbar\beta} \sum_{n=-\infty}^{\infty} e^{-\frac{i}{\hbar}E_{n}\tau} G^{\mathcal{M}}(E_{n})$$
$$G^{\mathcal{M}}(E_{n}) = \int_{0}^{\hbar\beta} d\tau G^{\mathcal{M}}(\tau) e^{\frac{i}{\hbar}E_{n}\tau}$$
(3.67)

with

$$\mathsf{E}_{\mathsf{n}} = \begin{cases} 2\mathsf{n}\frac{\pi}{\beta} & \text{for bosons} \\ (2\mathsf{n}+1)\frac{\pi}{\beta} & \text{for fermions} \end{cases}$$
(3.68)

Now we need to work out a spectral representation for the Matsubara Greens function in order to relate it to the retarded Greens function. We first consider the correlation function

$$\langle \mathsf{A}(\tau)\mathsf{B}(0)\rangle = \frac{1}{\mathrm{Tr}e^{-\beta\mathcal{H}}} \sum_{n} \langle \mathsf{E}_{n}|\mathsf{A}(\tau)\mathsf{B}(0)|\mathsf{E}_{n}\rangle e^{-\beta\mathsf{E}_{n}} = \frac{1}{\mathrm{Tr}e^{-\beta\mathcal{H}}} \sum_{n} \langle \mathsf{E}_{n}|\mathsf{A}|\mathsf{E}_{m}\rangle \langle \mathsf{E}_{m}|\mathsf{B}|\mathsf{E}_{n}\rangle e^{-\beta\mathsf{E}_{n}} e^{-\frac{1}{\hbar}(\mathsf{E}_{n}-\mathsf{E}_{m})\tau}$$
(3.69)

where we introduced the eigenstates of the Hamiltonian $|E_n\rangle$: $\mathcal{H}|E_n\rangle = E_n|E_n\rangle$. We recall the spectral density on the real energy axis:

$$S_{AB}(E) = \frac{\hbar}{\mathrm{Tr}e^{-\beta\mathcal{H}}} \sum_{n,m} \langle E_n | A | E_m \rangle \langle E_m | B | E_n \rangle e^{-\beta E_n} (1 - \varepsilon e^{-\beta E}) \delta \left(E - (E_m - E_n) \right)$$
$$\sim \langle A(\tau) B(0) \rangle = \frac{1}{\hbar} \int_{-\infty}^{\infty} dE \frac{S_{AB}(E)}{1 - \varepsilon e^{-\beta E}} e^{-\frac{1}{\hbar}E\tau}$$
(3.70)

In the integration interval in (3.67), τ is positive; we need to evaluate

$$G_{AB}^{M}(E_{n}) = -\int_{0}^{\hbar\beta} d\tau \, e^{\frac{i}{\hbar}E_{n}\tau} \langle A(\tau)B(0) \rangle \tag{3.71}$$

Now we use the integral

$$\int_{0}^{\hbar\beta} d\tau \, e^{\frac{1}{\hbar}(i\mathsf{E}_{n}-\mathsf{E})\tau} = \frac{\hbar}{i\mathsf{E}_{n}-\mathsf{E}} \big(e^{i\beta\mathsf{E}_{n}} e^{-\beta\mathsf{E}} - 1 \big) = \frac{\hbar}{i\mathsf{E}_{n}-\mathsf{E}} \big(\varepsilon e^{-\beta\mathsf{E}} - 1 \big)$$
(3.72)

and put Eq. (3.70) into Eq. (3.71) to obtain

$$G_{AB}^{M}(E_{n}) = \int_{-\infty}^{\infty} dE' \frac{S_{AB}(E')}{iE_{n} - E'}$$
(3.73)

If we compare this to the spectral representation of the retarded Greens function, we only need to replace $iE_n \rightarrow E + i0^+$; thus, the retarded Greens function can be obtained from the Matsubara Greens function by analytic continuation!

3.3 Some methods for Matsubara axis functions

- The Green's function on the Matsubara axis is fairly smooth and featureless so that the determination of the sums poses no problems. But there are two points to be considered:
- (1) Terms falling off as $1/(i\omega_n)$ will be badly represented by any number of frequency points; therefore, high frequency corrections are needed.
- (2) In order to obtain a spectral function, we need to analytically continue the Greens function to the real axis. This is done by the Padé method.

High frequency correction

The idea is to subtract the leading terms of the high frequency expansion and calculate them analytically, e.g.

$$F_{m}(i\omega_{n}) = \frac{1 - n_{f} + \frac{n_{f}}{N}}{i\omega_{n}} + O\left(\frac{1}{(i\omega_{n})^{2}}\right)$$
(3.74)
$$\sim n_{f} = T \sum_{i\omega_{n}'} \left(F_{m}(i\omega_{n}') - \frac{1 - n_{f} + \frac{n_{f}}{N}}{i\omega_{n}'}\right) e^{i\omega_{n}'0^{+}} + \frac{1 - n_{f} + \frac{n_{f}}{N}}{2}$$
(3.75)

The last term of Eq. (3.75) is obtained by explicit calculation of the sum:

$$T\sum_{n=-\infty}^{\infty} \frac{1}{i\omega_n} e^{i\omega_n \tau} = T\sum_{n=0}^{\infty} \frac{2i\sin(\omega_n \tau)}{i\omega_n}$$
$$= \frac{2}{\pi} \sum_{n=0}^{\infty} \frac{\sin[(2n+1)\pi T\tau]}{2n+1} = \frac{1}{2}$$
(3.76)

because $\tau = 0^+ \in \left]0; 1/T\right[$ and

$$\frac{4}{\pi} \sum_{n=0}^{\infty} \frac{\sin[(2n+1)x]}{2n+1} = \begin{cases} -1 & \text{for } -\pi < x < 0\\ 0 & \text{for } x = -\pi, 0, \pi\\ 1 & \text{for } 0 < x < \pi \end{cases}$$
(3.77)

In practice, the $1/(i\omega_n)^2$ is taken into account in the same way.

(2) Pade approximation

This method for analytic continuation can be used

- 1. when the function to be continued is not given analytically (in that case, use $i\omega_n \rightarrow \omega + i\delta$)
- 2. when the function is given without statistical errors (for Quantum Monte Carlo Green's functions, use Maximum Entropy Method)

One has to keep in mind one drawback of the Padé approximation: it is a polynomial representation that has limited precision for functions which are hard to approximate by a polynomial. It can show the wiggles that are typical for polynomial interpolations.

The algorithm for calculating the Padé approximant was written down nicely by Vidberg and Serene (H. J. Vidberg and J. W. Serene, Solving the Eliashberg Equations by Means of N-Point Padé Approximants, J. Low Temp. Phys. **29**, 179 (1977)).

Given the values u_i of a function at N complex points $z_i (i=1,\ldots,N),$ we define the continued fraction

$$C_{N}(z) = \frac{a_{1}}{1 + \frac{a_{2}(z - z_{1})}{1 + \dots a_{N}(z - z_{N-1})}}$$
(3.78)

Here, the coefficients a_i are to be determined so that

$$C_{N}(z_{i}) = u_{i}, \quad i = 1, \dots, N$$

$$(3.79)$$

The coefficients are then given by the recursion

$$a_{i} = g_{i}(z_{i}), \quad g_{1}(z_{i}) = u_{i}, \quad i = 1, ..., N$$

$$g_{p}(z) = \frac{g_{p-1}(z_{p-1}) - g_{p-1}(z)}{(z - z_{p-1})g_{p-1}(z)}, \quad p \ge 2$$
(3.80)

This requires the following calculation:

$$g_{1}(z_{1}) = a_{1} = u_{1} \quad g_{1}(z_{2}) = u_{2} \quad g_{1}(z_{3}) = u_{3} \quad g_{1}(z_{4}) = u_{4} \dots$$

$$g_{2}(z) = \frac{g_{1}(z_{1}) - g_{1}(z)}{(z - z_{1})g_{1}(z)} \quad g_{2}(z_{2}) = a_{2} = \frac{a_{1} - g_{1}(z_{2})}{(z_{2} - z_{1})g_{1}(z_{2})} = \frac{a_{1} - u_{2}}{(z_{2} - z_{1})u_{2}}$$

$$g_{2}(z_{3}) = \frac{a_{1} - g_{1}(z_{3})}{(z_{3} - z_{1})g_{1}(z_{3})} = \frac{a_{1} - u_{3}}{(z_{3} - z_{1})u_{3}} \quad g_{2}(z_{4}) = \frac{a_{1} - u_{4}}{(z_{4} - z_{1})u_{4}} \dots$$

$$g_{3}(z) = \frac{g_{2}(z_{2}) - g_{2}(z)}{(z - z_{2})g_{2}(z)} \quad g_{3}(z_{3}) = a_{3} = \frac{a_{2} - g_{2}(z_{3})}{(z_{3} - z_{2})g_{2}(z_{3})}$$

$$g_{3}(z_{4}) = \frac{a_{2} - g_{2}(z_{4})}{(z_{4} - z_{2})g_{2}(z_{4})} \dots$$

$$g_{4}(z) = \frac{g_{3}(z_{3}) - g_{3}(z)}{(z - z_{3})g_{3}(z)} \quad g_{4}(z_{4}) = a_{4} = \frac{a_{3} - g_{3}(z_{4})}{(z_{4} - z_{3})g_{3}(z_{4})} \dots$$
(3.81)

Thus, the following triangular matrix $p_{i,\,j}$ has to be calculated:

$$j = 1$$
 $j = 2$ $j = 3$ $j = 4$...
 $i = 1$ $a_1 = u_1$ u_2 u_3 u_4 ...
 $i = 2$ a_2 $g_2(z_3)$ $g_2(z_4)$...
 $i = 3$ a_3 $g_3(z_4)$...
...

This can be done as follows:

$$p_{1,j} = u_j, \quad j = 1, \dots, N$$

$$p_{i,j} = \frac{p_{i-1,i-1} - p_{i-1,j}}{(z_j - z_{i-1})p_{i-1,j}}, \quad j = 2, \dots, N \text{ and } i = 2, \dots, j$$
(3.82)

The diagonal of this matrix then contains the coefficients a_i which are needed for the recursion formula for $C_N(z)$:

$$C_{N}(z) = \frac{A_{N}(z)}{B_{N}(z)}$$
with $A_{n+1}(z) = A_{n}(z) + (z - z_{n}) a_{n+1}A_{n-1}(z)$
 $B_{n+1}(z) = B_{n}(z) + (z - z_{n}) a_{n+1}B_{n-1}(z)$
and $A_{0} = 0$, $A_{1} = a_{1}$, $B_{0} = B_{1} = 1$
(3.83)

An important fact to keep in mind: the bigger you chose N, *i.e.* the more coefficients a_i you calculate, the bigger the numbers $A_N(z)$ and $B_N(z)$ are going to be for a given z. N = 128 will already lead to values of order 10^{115} .

Comparing functions on real and imaginary axes

For a first check if an analytic continuation makes sense, there are exact relations at zero frequency.

If a complex function is given around z = 0 as

$$f(z) = \alpha + \beta z + \gamma z^2 + \dots$$
(3.84)

with complex coefficients $\alpha = \alpha' + i\alpha''$ etc., we can write it in terms of imaginary frequencies $i\omega_n$ as

$$f(i\omega_{n}) = \alpha' + i\alpha'' - \beta''\omega_{n} + i\beta'\omega_{n} - \gamma'\omega_{n}^{2} - i\gamma''\omega_{n}^{2} + \dots \quad (3.85)$$

or of real frequencies as

$$f(\omega) = \alpha' + i\alpha'' + \beta'\omega + i\beta''\omega + \gamma'\omega^2 + i\gamma''\omega^2 + \dots$$
(3.86)

and thus by comparing coefficients we find for the function value at zero

$$f(\mathbf{i}\omega_n)|_{\omega_n=0} = f(\omega)|_{\omega=0}$$
(3.87)

For the derivatives of f we find

$$\frac{\mathrm{d}}{\mathrm{d}\omega_{\mathrm{n}}}\operatorname{Re} f(\mathrm{i}\omega_{\mathrm{n}})\Big|_{\omega_{\mathrm{n}}=0} = -\frac{\mathrm{d}}{\mathrm{d}\omega}\operatorname{Im} f(\omega)\Big|_{\omega=0}$$
(3.88)

$$\frac{\mathrm{d}}{\mathrm{d}\omega_{n}}\operatorname{Im} f(\mathfrak{i}\omega_{n})\Big|_{\omega_{n}=0} = \frac{\mathrm{d}}{\mathrm{d}\omega}\operatorname{Re} f(\omega)\Big|_{\omega=0}$$
(3.89)

$$\frac{\mathrm{d}^2}{\mathrm{d}\omega_n^2} \operatorname{Re} f(\mathfrak{i}\omega_n) \Big|_{\omega_n = 0} = -\frac{\mathrm{d}^2}{\mathrm{d}\omega^2} \operatorname{Im} f(\omega) \Big|_{\omega = 0}$$
(3.90)

$$\frac{d^2}{d\omega_n^2} \operatorname{Im} f(i\omega_n) \Big|_{\omega_n = 0} = -\frac{d^2}{d\omega^2} \operatorname{Re} f(\omega) \Big|_{\omega = 0}$$
(3.91)

Kramers Kronig relations

If the function we try to calculate is analytic in the upper complex plane as well as in the lower complex plane (this is the case for all response functions of physical systems) it must obey the Kramers-Kronig relation

$$g'(\mathbf{y}) = -P \int_{-\infty}^{\infty} \frac{\mathrm{d}x}{\pi} \frac{g''(\mathbf{x})}{\mathbf{y} - \mathbf{x}}$$
(3.92)

where the notation g(z) = g'(z) + ig''(z) is used. x, y are used for real, z and u for complex variables. This is the real-axis analog of the more general Cauchy integral formula

$$g(z) = \frac{1}{2\pi i} \oint du \frac{g(u)}{u - z}$$
(3.93)

which says that a holomorphic function defined on a disk is completely determined by its values on the boundary of the disk. Response functions are not analytic on the real axis, but otherwise we can deform the contour arbitrarily on the complex plane.

If g(z) falls off in infinity, we can write

$$g(z) = \int_{-\infty}^{\infty} \frac{\mathrm{d}x}{2\pi \mathrm{i}} \frac{[g(x+\mathrm{i}\delta) - g(x-\mathrm{i}\delta)]}{x-z}$$
(3.94)

which yields

$$g(z) = -\int_{-\infty}^{\infty} \frac{\mathrm{d}x}{\pi} \frac{g''(x)}{z - x}$$
(3.95)

The real part of this equation is equal to Eq. (3.92).

The practical calculation of a Kramers Kronig transformation is straightforward but requires the subtraction of the divergent part. It will usually be implemented on a mesh from a to b large enough so that g''(a) and g''(b) are negligibly small. Then

$$g'(y) = \int_{a}^{b} \frac{dx}{\pi} \frac{g''(x) - g''(y)}{x - y} + \frac{g''(y)}{\pi} \operatorname{Re} \left[\log(b - y) - \log(a - y) \right]$$

(3.96)

$$= \int_{a}^{b} \frac{dx}{\pi} \frac{g''(x) - g''(y)}{x - y} + \frac{g''(y)}{\pi} \log\left(\frac{b - y}{y - a}\right)$$
(3.97)

Now the integrand is smooth everywhere. At x = y it should be estimated using the derivative dg''(y)/dy.

Kramers Kronig relations can become very useful if real or imaginary part of a Greens function are easier than the full function. Typically, the imaginary part falls off abruptly at the band edges and is exactly zero beyond. Then the imaginary part is perfectly suited for calculation on a mesh, but the corresponding real part only falls off as $1/\omega$.

4. Exact diagonalization

4.1 Hamiltonian operators for strongly correlated electron systems

4.1.1 The Hubbard model

The **Hubbard model** represents interacting electrons in narrow bands. It was originally proposed to study metal-insulator transitions and ferromagnetism of itinerant electrons in narrow bands but it has also acquired importance in the study of high temperature superconductors. Assuming localized orbitals and a strong screening of the Coulomb interaction, only the local density-density repulsion is included. The model is defined by

$$H = -t \sum_{\substack{\langle i,j \rangle, \sigma \\ H_0}} a_{i\sigma}^{\dagger} a_{j\sigma} + \underbrace{U \sum_{i} n_{i\downarrow} n_{i\uparrow}}_{H_1} - \mu \hat{N}$$

$$(4.1)$$

where $\mathbf{a}_{i\sigma}^{\dagger}(\mathbf{a}_{i\sigma})$ create (annihilate) fermions of spin $\sigma = \downarrow, \uparrow$ in a Wannier orbital centered at site \mathbf{i} . $\mathbf{n}_{i\sigma} = \mathbf{a}_{i\sigma}^{\dagger}\mathbf{a}_{i\sigma}$ represents the occupation number operator. The electrons move in tight binding bands, with a transfer integral \mathbf{t} between nearest neighbor sites, as indicated by $< \mathbf{i}, \mathbf{j} >$. The Coulomb interaction strength is \mathbf{U} . The chemical potential $\boldsymbol{\mu}$ couples to the particle number operator $\hat{\mathbf{N}} = \sum_{i} (\mathbf{n}_{i\downarrow} + \mathbf{n}_{i\uparrow})$.

4.1.2 The t-J model

The t-J model consists of a constrained hopping term for the charge degrees of freedom, allowing no double occupancies. It can be derived as strong U limit of the Hubbard model. In the restricted space the eliminated double occupancies result in an effective spin-spin interaction:

$$\mathbf{H} = \mathbf{t} \sum_{\langle \mathbf{i}, \mathbf{j} \rangle, \sigma} (1 - \mathbf{n}_{\mathbf{i}-\sigma}) \mathbf{a}_{\mathbf{i}\sigma}^{\dagger} \mathbf{a}_{\mathbf{j}\sigma} (1 - \mathbf{n}_{\mathbf{j}-\sigma}) + \mathbf{J} \sum_{\langle \mathbf{i}, \mathbf{j} \rangle} \left(\mathbf{S}_{\mathbf{i}} \mathbf{S}_{\mathbf{j}} - \frac{\mathbf{n}_{\mathbf{i}} \mathbf{n}_{\mathbf{j}}}{4} \right)$$
(4.2)

The projection operators $(1 - n_{i-\sigma})$ in the kinetic term ensure that no site is occupied by more than two electrons. The spin operators at site i

are $\mathbf{S}_{i} = \sum_{\sigma\sigma'} \mathbf{a}_{i\sigma}^{\dagger} \boldsymbol{\sigma}_{\sigma\sigma'} \mathbf{a}_{i\sigma'}^{\dagger}$ with Pauli matrices $\boldsymbol{\sigma}_{\sigma\sigma'}$. S_{i} describes magnetic moments with S = 1/2 for occupied sites and S = 0 for empty sites. The t-J model can be viewed as a generic model for the interplay of spin and charge degrees of freedom.

4.1.3 The Heisenberg model

While the Hubbard type models treat itinerant electrons, the **Heisenberg Hamiltonian** describes the situation that the charge degrees of freedom are bound to the atomic positions and only the spin degrees of freedom remain active. This fundamental model in the theory of magnetism of local magnetic moments is defined by

$$H = \sum_{ij} J_{ij}^{z} S_{i}^{z} S_{j}^{z} + J_{ij}^{\perp} (S_{i}^{x} S_{j}^{x} + S_{i}^{y} S_{j}^{y}) + B \sum_{i} S_{i}^{z}$$
(4.3)

where S_i^{α} , $\alpha = x, y, z$ is the α component of the spin operator and J stands for the exchange integrals. The last term describes the coupling to an external magnetic field B in z direction. Special cases are the isotropic Heisenberg model $J^z = J^{\perp}$, the Ising model $J^{\perp} = 0$ and the XY model $J^z = 0$. The spin operators obey

$$[S_{i}^{\alpha}, S_{j}^{\beta}] = i\delta_{ij}\epsilon_{\alpha\beta\gamma}S_{i}^{\gamma}$$

$$(4.4)$$

For numerical purposes it is convenient to use ladder operators

$$\mathbf{S}_{\mathbf{i}}^{\pm} = \mathbf{S}_{\mathbf{i}}^{\mathbf{x}} \pm \mathbf{i} \, \mathbf{S}_{\mathbf{i}}^{\mathbf{y}} \tag{4.5}$$

so that the operators $S^{\boldsymbol{x}}$ and $S^{\boldsymbol{y}}$ can be written as

$$S_{i}^{x} = \frac{1}{2}(S_{i}^{+} + S_{i}^{-}) \qquad S_{i}^{y} = \frac{1}{2i}(S_{i}^{+} - S_{i}^{-})$$
 (4.6)

Replacing $S^{\boldsymbol{x}}$ and $S^{\boldsymbol{y}}$ in the Hamiltonian leads to

$$H = \sum_{i \neq j} \left(J_{ij}^{z} S_{i}^{z} S_{j}^{z} + \frac{1}{2} (S_{i}^{+} S_{j}^{-} + S_{i}^{-} S_{j}^{+}) \right) + B \sum_{i} S_{i}^{z}$$
(4.7)

4.2 Principle of the exact diagonalization method

To see why we have to employ special methods to make the diagonalization of Hamilton matrices possible, we have to consider the dimension of the Hamilton matrix produced by a given lattice and model.

If we study the Heisenberg Hamiltonian on a lattice of N sites, we have two possible states for each site: Spin up and spin down. Thus the lattice has 2^{N} states, and this is the dimension of the Hamilton matrix. Similarly we find for the t-J model 3^{N} states and for the Hubbard model 4^{N} states. This exponential growth of the matrix with lattice size makes even small lattices of typically 10 sites difficult to handle with standard diagonalization techniques.

In order to make the matrix size for a given lattice size accessible to the available computing power, it is important to exploit the **model symmetries**.

Many models, including those given above, show conservation of total spin number, total spin in the z direction and total charge, *i.e.*

$$\left[\mathsf{H}, \mathbf{S}^{2}\right] = \left[\mathsf{H}, \mathsf{S}^{z}\right] = \left[\mathsf{H}, \hat{\mathsf{N}}\right] = 0 \tag{4.8}$$

where \boldsymbol{H} is the model Hamiltonian and

$$\mathbf{S} = \sum_{i} \mathbf{S}_{i} \qquad \hat{\mathbf{N}} = \sum_{i} n_{i} \tag{4.9}$$

In addition, these operators also commute with each other

$$\left[\mathbf{S}^{2}, \mathbf{S}^{z}\right] = \left[\mathbf{S}^{z}, \hat{\mathbf{N}}\right] = \left[\hat{\mathbf{N}}, \mathbf{S}^{2}\right] = 0 \tag{4.10}$$

so that the eigenvalues of H, S^2 , S^z and \hat{N} are simultaneous good quantum numbers which we can denote by E, S(S + 1), S^z and N.

In order to build the Hamilton matrix, we have to choose a basis set that is easily generated, allows fast computation of matrix elements, is economical with memory and allows us to access states quickly. We also have to find a numerical representation of the basis set.

For representing spin-1/2 systems, we can use integers $n_i = (\sigma_i + 1)/2 \in \{0, 1\}$. If we identify the sequence of n_i values with the bit pattern of the integer $I = \sum_{l=1}^{N} n_l 2^{l-1}$, the basis state $|\psi\rangle = |-1, +1, -1, +1\rangle$ is represented by $n = \{0101\}$ and mapped onto I = 5. This representation saves memory and speeds up some numerical operations.

As $S^z = \sum_{i=1}^{N} S_i^z$ commutes with the Hamiltonian, the Hamilton matrix is block diagonal in the sectors with fixed S^z values, *i.e.* fixed numbers N^{σ} of σ spins.

For a given S^z sector, the number of ones in the bit pattern is fixed which reduces the number of basis states to

$$\mathbf{L} = \begin{pmatrix} \mathbf{N} \\ \mathbf{N}^{\uparrow} \end{pmatrix} \tag{4.11}$$

where N is the number of lattice sites and

$$\mathbf{S}^{\mathbf{z}} = \frac{1}{2} \left(2\mathbf{N}^{\uparrow} - \mathbf{N} \right) \tag{4.12}$$

For example, if the number of sites is N = 16 there are $2^{16} = 65536$ possible basis states in total, but only $\binom{16}{8} = 12870$ for $S^z = 0$, *i.e.* $N^{\uparrow} = N^{\downarrow} = 8$. In principle, translation and rotation could be exploited to reduce the number of basis states even further.

Now we are ready to list all permissible configurations. Not every integer is included since the number of ones and zeros in the bit pattern is fixed. We generate the basis states in such a way that the corresponding integer values are in increasing order. The basis states and their integer representations are therefore

$$\begin{split} |\phi_{1}\rangle &= \{ \overbrace{0,0,\ldots,0,0}^{N}, \overbrace{1,1,1,\ldots,1}^{N^{\uparrow}} \}; \quad I_{1} = 2^{N^{\uparrow}} - 1 \\ |\phi_{2}\rangle &= \{0,0,\ldots,0,1,0,1,1,\ldots,1\}; \quad I_{2} = 2^{N^{\uparrow}+1} - 1 - 2^{N^{\uparrow}-1} \\ |\phi_{3}\rangle &= \{0,0,\ldots,0,1,1,0,1,\ldots,1\}; \quad I_{3} = 2^{N^{\uparrow}+1} - 1 - 2^{N^{\uparrow}-2} \\ \vdots & \vdots \\ |\phi_{L}\rangle &= \{\underbrace{1,1,\ldots,1,1}_{N^{\uparrow}}, \underbrace{0,0,0,\ldots,0}_{N-N^{\uparrow}} \}; \quad I_{L} = 2^{N} - 2^{N-N^{\uparrow}} \end{split}$$
(4.13)

Consider a four site cluster with $S^z = 0$ as an example:

number 1 2 3 4 56 1010 bit 0011 0101 0100 1001 11003 5 6 12integer 9 10

As the basis states are ordered, their spin representations can be found rapidly by bisection search.

Representation of **electronic systems**: The basis for Hubbard, Anderson or t-J Hamiltonians can be conveniently constructed in real space. Restricting the discussion to a single orbital per lattice site, the state vector can be writen as

$$|\psi\rangle = \prod_{i=1}^{N^{\uparrow}} a_{\Gamma_{i}^{\uparrow}}^{\dagger} \prod_{j=1}^{N^{\downarrow}} a_{\Gamma_{j}^{\downarrow}}^{\dagger} |0\rangle$$
(4.14)

where $|0\rangle$ denotes the vacuum state and Γ_i^{\uparrow} is the lattice site of the *i*-th spin up electron and Γ_j^{\downarrow} is the lattice site of the *j*-th spin down electron. For example

$$|\psi\rangle = \begin{vmatrix} 1 & 2 & 3 & 4 \\ \uparrow & \sqcup & \downarrow & \uparrow \downarrow \end{vmatrix}$$

$$(4.15)$$

is represented by $\Gamma^{\uparrow} = \{1, 4\}$ and $\Gamma^{\downarrow} = \{3, 4\}$

Another way of representing this basis is by

$$|\psi\rangle = \prod_{i=1}^{N} \left(a_{i\uparrow}^{\dagger}\right)^{n_{i}^{\dagger}} \prod_{j=1}^{N} \left(a_{j\downarrow}^{\dagger}\right)^{n_{j}^{\downarrow}} |0\rangle$$
(4.16)

where $\mathbf{n}_{i}^{\uparrow}, \mathbf{n}_{j}^{\downarrow} \in \{0, 1\}$ indicate whether or not site i is occupied by a spin up or spin down electron. The state Eq. (4.15) is represented by $\mathbf{n}^{\uparrow} = \{1, 0, 0, 1\}$ and $\mathbf{n}^{\downarrow} = \{0, 0, 1, 1\}$.

Yet another way to encode the same basis is

$$|\psi\rangle = \prod_{i=1}^{N} O_{i}|0\rangle \quad O_{i} \in \{\hat{1}, a_{i\uparrow}^{\dagger}, a_{i\downarrow}^{\dagger}, a_{i\uparrow}^{\dagger}a_{i\downarrow}^{\dagger}\}$$
(4.17)

where the operator O_i creates either an empty site, a site occupied by an up or down electron, or a doubly occupied site.

The number of basis states is 4^{N} . In the case of the t-J model, doubly occupied site are forbidden and therefore the number of basis states reduces to 3^{N} .

Since the electronic spin is conserved, N^{\uparrow} and N^{\downarrow} are good quantum numbers. For spin σ there are

$$\mathcal{L}^{\sigma} = \begin{pmatrix} \mathsf{N} \\ \mathsf{N}^{\sigma} \end{pmatrix} \tag{4.18}$$

basis states. The total number of basis states in the sector of fixed N^σ values N^\uparrow, N^\downarrow is therefore

$$\mathbf{L} = \mathbf{L}^{\uparrow} \mathbf{L}^{\downarrow} = \binom{\mathbf{N}}{\mathbf{N}^{\uparrow}} \binom{\mathbf{N}}{\mathbf{N}^{\downarrow}}$$
(4.19)

For example, N = 16 and $N^{\uparrow} = N^{\downarrow} = 8$. The number of basis states is then $4^{16} = 4\,294\,967\,296$, while $\binom{16}{8}\binom{16}{8} = 165\,636\,900$.

In the t-J model there the additional constraint of no double occupancy reduces the number of basis states to (below half-filling)

$$\mathbf{L} = \frac{\mathbf{N}!}{\mathbf{N}^{\downarrow}! \, \mathbf{N}^{\uparrow}! \, \mathbf{N}^{\mathbf{h}}!} \tag{4.20}$$

where $N^{h} = N - N^{\downarrow} - N^{\uparrow}$ is the number of empty sites (holes). In the previous example, the number of states would only be L = 12870.

As before, it is recommended to use a memory saving representation, and for that Eq. (4.16) is well suited because the two spin species are separately treated and we can interpret the sequence of values of \mathbf{n}_i^{σ} as a bit pattern. Then in the example above $\mathbf{n}^{\uparrow} = \{1, 0, 0, 1\}$ corresponds to the integer $\mathbf{I}^{\uparrow} = 9$, $\mathbf{n}^{\downarrow} = \{0, 0, 1, 1\}$ corresponds to $\mathbf{I}^{\downarrow} = 3$. Each basis state is therefore represented as a pair of integers $(\mathbf{I}^{\uparrow}, \mathbf{I}^{\downarrow})$.

The generation of basis states is now similar to that of spin-1/2 systems. The only difference is that we have to generate two integers for the two spin species.

4.2.1 Computation of the Hamilton matrix

Now we have to calculate the matrix elements

$$\mathbf{h}_{\mathbf{v}'\mathbf{v}} = \left\langle \Phi_{\mathbf{v}'} | \mathbf{H} | \Phi_{\mathbf{v}} \right\rangle \tag{4.21}$$

of the Hamiltonian H in suitable basis states $|\Phi_{\nu}\rangle$. For this purpose we split the Hamiltonian into individual contributions $H^{(1)}$

$$\mathsf{H} = \sum_{\mathfrak{l}} \mathsf{H}^{(\mathfrak{l})} \tag{4.22}$$

such that the application of one term $H^{(1)}$ to a basis state $|\Phi_{\nu}\rangle$ yields again a basis state or the null vector:

$$\mathsf{H}^{(l)}|\Phi_{\mathbf{v}}\rangle = \mathsf{h}^{(l)}_{\mathbf{v}'\mathbf{v}}|\Phi_{\mathbf{v}'}\rangle \tag{4.23}$$

The full matrix element $\langle \Phi_{\nu'} | H | \Phi_{\nu} \rangle$ is obtained by summing up all contributions $h_{\nu'\nu}^{(l)}$. If there is only one term $H^{(l)}$ in the Hamiltonian that mediates between the two basis states $|\Phi_{\nu}\rangle$ and $|\Phi_{\nu'}\rangle$ then $h_{\nu'\nu} = h_{\nu'\nu}^{(l)}$.

Let's consider building the Hubbard Hamilton matrix in the real space basis of Eq. (4.16) characterized by the set of occupation numbers $|\Phi_{\nu}\rangle = |\{n_{i\sigma}^{\nu}\}\rangle$ for all lattice sites *i* and the two spin directions, with $n_{i\sigma}^{\nu} \in \{0, 1\}$. The Hubbard interaction H_1 of Eq. (4.1) is diagonal in this basis, so we have

$$h_{\nu\nu} = U \sum_{i} n_{i\uparrow}^{\nu} n_{i\downarrow}^{\nu}$$
(4.24)

There are no other contributions to the diagonal elements. Each summand in the kinetic energy of Eq. (4.1) represents an individual contribution to Eq.(4.22). But it is better to combine the back-and-forth hopping processes for a particular nearest-neighbour pair (i_0, j_0)

$$\mathsf{H}_{0}^{(\mathfrak{l})} = -\mathsf{t} \left(\mathfrak{a}_{\mathfrak{i}_{0}\sigma_{0}}^{\dagger} \mathfrak{a}_{\mathfrak{j}_{0}\sigma_{0}} + \mathfrak{a}_{\mathfrak{j}_{0}\sigma_{0}}^{\dagger} \mathfrak{a}_{\mathfrak{i}_{0}\sigma_{0}} \right)$$
(4.25)

Application of this term $H_0^{(l)}$ to a basis state $|\Phi_{\nu}\rangle = |\{n_{i\sigma}^{\nu}\}\rangle$ results either in the null vector if $n_{i_0\sigma_0}^{\nu}$ and $n_{j_0\sigma_0}^{\nu}$ are both occupied or empty

$$|\mathsf{H}_{0}^{(1)}|\{\mathsf{n}_{i\sigma}^{\gamma}\}\rangle = 0 \quad \text{if } \mathsf{n}_{i_{0}\sigma_{0}}^{\gamma} = \mathsf{n}_{j_{0}\sigma_{0}}^{\gamma}$$

$$(4.26)$$

Otherwise the hopping process is possible and results in another basis state $|\Phi_{\nu'}\rangle = |\{n_{i\sigma}^{\nu'}\}\rangle$ which differs from $|\Phi_{\nu}\rangle$ only in the exchange of the occupation number $n_{i_0\sigma_0}^{\nu}$ and $n_{j_0\sigma_0}^{\nu}$, *i.e.*

$$\begin{aligned}
\mathbf{n}_{i-\sigma_{0}}^{\mathbf{v}'} &= \mathbf{n}_{i-\sigma_{0}}^{\mathbf{v}} \quad \forall \mathbf{i} \\
\mathbf{n}_{i\sigma_{0}}^{\mathbf{v}'} &= \mathbf{n}_{i\sigma_{0}}^{\mathbf{v}} \quad \forall \mathbf{i} \neq \mathbf{i}_{0}, \mathbf{j}_{0} \\
\mathbf{n}_{i_{0}\sigma_{0}}^{\mathbf{v}'} &= \mathbf{n}_{j_{0}\sigma_{0}}^{\mathbf{v}} \quad \mathbf{n}_{j_{0}\sigma_{0}}^{\mathbf{v}'} &= \mathbf{n}_{i_{0}\sigma_{0}}^{\mathbf{v}}
\end{aligned} \tag{4.27}$$

There is only one hopping process $\mathsf{H}^{(l)}$ mediating between the two basis states under consideration.

The respective matrix element is therefore

$$\mathbf{h}_{\mathbf{v}'\mathbf{v}} = \begin{cases} -\mathbf{t} \, \mathbf{S} & \text{if } \mathbf{n}_{\mathbf{i}_0\sigma_0}^{\mathbf{v}} \neq \mathbf{n}_{\mathbf{j}_0\sigma_0}^{\mathbf{v}} \text{ for one set } (\mathbf{i}_0\sigma_0, \mathbf{j}_0\sigma_0) \\ 0 & \text{otherwise} \end{cases}$$
(4.28)

The hopping process can result in a sign S due to the Fermi statistics of the electrons. Consider for example a two-dimensional (4x4) lattice with sites enumerated as

1	2	3	4
5	6	$\overline{7}$	8
9	10	11	12
13	14	15	16

(The numbering of sites is arbitrary but must be kept fixed.)

Now we consider hopping between sites 2 and 6 of one spin species The state $|\Phi_{\nu}\rangle$ be given by $\{n_{i\sigma}\} = \{0, 0, 1, 1, 1, 1, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0\}$ (we suppress the spin indices from now on). The state reads according to Eq. (4.16)

$$|\Phi_{\nu}\rangle = a_3^{\dagger} a_4^{\dagger} a_5^{\dagger} a_6^{\dagger} |0\rangle \tag{4.29}$$

Application of the hopping operator

$$\mathsf{H}_{0}^{(1)} = -\mathsf{t}\left(\mathfrak{a}_{2}^{\dagger}\mathfrak{a}_{6} + \mathfrak{a}_{6}^{\dagger}\mathfrak{a}_{2}\right) \tag{4.30}$$

results in the state

$$|\Phi_{\nu'}\rangle = a_3^{\dagger} a_4^{\dagger} a_5^{\dagger} a_2^{\dagger} |0\rangle = -a_2^{\dagger} a_3^{\dagger} a_4^{\dagger} a_5^{\dagger} |0\rangle$$

$$(4.31)$$

Thus, the new state is given by

$$|\Phi_{\mathbf{v}'}\rangle = -\{0, 1, 1, 1, 1, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0\}$$
(4.32)

The hopping operator has shifted a bit and created a fermionic phase factor. For periodic boundary conditions, care must be taken of possible minus signs whenever an electron is wrapped around the boundary and the number of electrons it commutes through is odd. The sign is given by

$$\mathbf{S} = (-1)^{\Delta \mathbf{n}} \tag{4.33}$$

where $\Delta \mathbf{n}$ is the number of electrons at the lattice sites between the site \mathbf{i}_0 and \mathbf{j}_0 , in the example $\Delta \mathbf{n} = 3$.

Now we know how the individual terms of the Hamiltonian $H^{(l)}$ couple a basis state $\{n_{i\sigma}^{\gamma}\}$ represented by a bit pattern to another basis state $\{n_{i\sigma}^{\gamma'}\}$ or to its integer representation $(I_{\uparrow}^{\gamma'}I_{\downarrow}^{\gamma'})$.

It is still necessary to find the index ν' of the basis state. As they have been generated in increasing order of their integer representation, we can apply a bisection search to find the index. This is important if we compare the computational cost O(L) steps of a brute force search to $O(\log_2 L)$ operations of the bisection search. For example, for $L = 10^8$ there is a factor of 10^6 between the two methods.

4.3 The Lanczos method

In the previous section, exact diagonalization was introduced as a method to solve manybody Hamiltonians by calculating the Hamiltonian matrix in a basis and diagonalizing it. But the corresponding matrices are of the order $(10^8 \times 10^8)$ or larger and cannot be treated by Householder tridiag-onalization.

The Lanczos method avoids the problem of calculating and saving huge matrices in the computer memory by constructing a basis that directly leads to a tridiagonal matrix. It is an example of a family of projection techniques known as Krylov subspace methods.

The procedure is as follows. Consider an arbitrary normalized wave function $|\Phi_1\rangle$ which we assume not to be an eigenvector of the Hamiltonian \hat{H} . Then application of \hat{H} on this wave function produces a function $|\mathbf{U}_1\rangle$ that is different from $|\Phi_1\rangle$:

$$\hat{\mathsf{H}}|\Phi_1\rangle = |\mathbf{U}_1\rangle \tag{4.34}$$

In general, $|\mathbf{U}_1\rangle$ will not be normalized, and we can determine the normalization constant N_1 from

$$\langle \mathbf{U}_1 | \mathbf{U}_1 \rangle = \mathbf{N}_1^2 \tag{4.35}$$

A normalized vector $|\Psi_1\rangle$ is obtained by

$$|\Psi_1\rangle = \mathsf{N}_1^{-1}|\mathbf{U}_1\rangle \tag{4.36}$$

As $|\Phi_1\rangle$ is not an eigenvector of \hat{H} , $|\Psi_1\rangle$ and $|\Phi_1\rangle$ are different, and we can write $|\Psi_1\rangle$ as a linear combination of $|\Phi_1\rangle$ and another function $|\Phi_2\rangle$ which we conveniently chose to be normalized and orthogonal to $|\Phi_1\rangle$:

$$\langle \Phi_2 | \Phi_2 \rangle = 1 \qquad \langle \Phi_2 | \Phi_1 \rangle = 0$$

$$(4.37)$$

Now we can write $|\Psi_1\rangle$ as

$$|\Psi_1\rangle = \alpha_1 |\Phi_1\rangle + \beta_1 |\Phi_2\rangle \quad \text{with } \alpha_1^2 + \beta_1^2 = 1$$

$$(4.38)$$

If we multiply both sides of Eq. (4.34) by $\langle \Phi_1 |$ and integrate over all independent variables, we find

$$\langle \Phi_1 | \hat{\mathsf{H}} | \Phi_1 \rangle = \mathsf{N}_1 \langle \Phi_1 | \Psi_1 \rangle = \alpha_1 \mathsf{N}_1 \tag{4.39}$$

As N₁ is known from Eq. (4.35), we find α_1 by calculating the diagonal matrix element of \hat{H} with $|\Phi_1\rangle$. With Eq. (4.38) we find

$$|\Phi_2\rangle = \frac{1}{\beta_1} (|\Psi_1\rangle - \alpha_1 |\Phi_1\rangle) \tag{4.40}$$

The value of β_1 can be found from Eq. (4.38) or from the normalization requirement of $|\Phi_2\rangle$. This is very similar to the Gram-Schmidt orthogonalization method of constructing a set of orthonormal vectors from an arbitrary set. Now we can define two more quantities:

$$\mathbf{d}_1 \equiv \langle \Phi_1 | \hat{\mathbf{H}} | \Phi_1 \rangle = \alpha_1 \mathbf{N}_1 \tag{4.41}$$

$$\mathbf{f}_2 \equiv \langle \Phi_2 | \hat{\mathbf{H}} | \Phi_1 \rangle = \mathbf{N}_1 \langle \Phi_2 | \Psi_1 \rangle = \beta_1 \mathbf{N}_1 \tag{4.42}$$

These will turn out to be the first diagonal and superdiagonal elements we are looking for. Now we apply \hat{H} on $|\Phi_2\rangle$ which in general also will not be an eigenvector:

$$\hat{\mathsf{H}}|\Phi_2\rangle = \mathsf{N}_2|\Psi_2\rangle \tag{4.43}$$

where again $|\Psi_2\rangle$ is a normalized state, N₂ is a constant. $|\Psi_2\rangle$ cannot be a linear combination of $|\Phi_1\rangle$ and $|\Phi_2\rangle$ alone (the reason is given later), and we express it as a linear combination with yet another function $|\Phi_3\rangle$ thrown in:

$$|\Psi_2\rangle = \alpha_2 |\Phi_1\rangle + \beta_2 |\Phi_2\rangle + \gamma_2 |\Phi_3\rangle \tag{4.44}$$

Choosing $|\Phi_3\rangle$ normalized and orthogonal to $|\Phi_1\rangle$ and $|\Phi_2\rangle$ gives us the condition (obtained by squaring Eq. (4.44) and integrating over all independent variables).

$$\alpha_2^2 + \beta_2^2 + \gamma_2^2 = 1 \tag{4.45}$$

From the fact that the Hamiltonian is Hermitian, we find that

$$\langle \Phi_2 | \hat{\mathsf{H}} | \Phi_1 \rangle = \langle \Phi_1 | \hat{\mathsf{H}} | \Phi_2 \rangle = \mathsf{f}_2 \tag{4.46}$$

On the other hand, from Eqs. (4.43) and (4.44) we find

$$\langle \Phi_1 | \hat{\mathsf{H}} | \Phi_2 \rangle = \mathsf{N}_2 \langle \Phi_1 | \Psi_2 \rangle = \mathsf{N}_2 \alpha_2 \tag{4.47}$$

which gives us the value of $\alpha_2 = f_2/N_2$. With $|\Phi_2\rangle$ we obtain

$$\mathbf{d}_2 \equiv \langle \Phi_2 | \hat{\mathbf{H}} | \Phi_2 \rangle = \mathbf{N}_2 \langle \Phi_2 | \Psi_2 \rangle = \mathbf{N}_2 \boldsymbol{\beta}_2 \tag{4.48}$$

and thus $\beta_2 = d_2/N_2$. We can write

$$|\Phi_3\rangle = \frac{1}{\gamma_2} (|\Psi_2\rangle - \alpha_2 |\Phi_1\rangle - \beta_2 |\Phi_2\rangle)$$
(4.49)

and we define again

$$\mathbf{f}_3 \equiv \langle \Phi_3 | \hat{\mathbf{H}} | \Phi_2 \rangle \tag{4.50}$$

Note that the matrix element

$$\langle \Phi_3 | \hat{\mathsf{H}} | \Phi_1 \rangle = 0 \tag{4.51}$$

because the state produced by the action of H on $|\Phi_1\rangle$ is only a linear combination of $|\Phi_1\rangle$ and $|\Phi_2\rangle$, both orthogonal to $|\Phi_3\rangle$. Another application of the Hamiltonian gives the next step in this argument:

$$\hat{\mathsf{H}}|\Phi_3\rangle = \mathsf{N}_3|\Psi_3\rangle \tag{4.52}$$

Eq. (4.51) and the Hermitian Hamiltonian yield

$$\left\langle \Phi_1 | \hat{\mathsf{H}} | \Phi_3 \right\rangle = 0 \tag{4.53}$$

This is because by construction the only offdiagonal matrix element of H acting on $|\Phi_1\rangle$ is $\langle \Phi_2 | \hat{H} | \Phi_1 \rangle$. It also implies that $|\Psi_3\rangle$ is orthogonal to $|\Phi_1\rangle$. Thus, $|\Psi_3\rangle$ can only be a linear combination of $|\Phi_2\rangle$, $|\Phi_3\rangle$ and a new function $|\Phi_4\rangle$:

$$|\Psi_3\rangle = \alpha_3 |\Phi_2\rangle + \beta_3 |\Phi_3\rangle + \gamma_3 |\Phi_4\rangle \tag{4.54}$$

As before, $|\Phi_4\rangle$ is chosen normalized and orthogonal to $|\Phi_2\rangle$ and $|\Phi_3\rangle$. As $|\Psi_3\rangle$ is orthogonal to $|\Phi_1\rangle$, $|\Phi_4\rangle$ must also be orthogonal to $|\Phi_1\rangle$. Eq. (4.54) already provides the general relation. If we continue to construct basis vectors $|\Phi_1\rangle$, $|\Phi_2\rangle$,... until we get to $|\Phi_k\rangle$, we have the relation

$$\hat{\mathsf{H}}|\Phi_k\rangle = \mathsf{N}_k|\Psi_k\rangle$$
(4.55)

in analogy to Eq. (4.43).

It is always possible to express the new state $|\Psi_k\rangle$ as a linear combination of three components

$$|\Psi_{k}\rangle = \alpha_{k}|\Phi_{k-1}\rangle + \beta_{k}|\Phi_{k}\rangle + \gamma_{k}|\Phi_{k+1}\rangle$$
(4.56)

as demonstrated for $|\Psi_3\rangle$ in Eq. (4.54). The new vector $|\Phi_{k+1}\rangle$ can be made orthogonal to all the previous basis vectors $|\Phi_1\rangle, |\Phi_2\rangle, \ldots, |\Phi_k\rangle$. Furthermore, we see that the Hamiltonian matrix is tridiagonal in the basis formed by $|\Phi_1\rangle, |\Phi_2\rangle, \ldots$. An exception to Eq. (4.56) occurs when the dimension n of the Hilbert space is finite; in this case, the maximum number of linearly independent basis states that can be constructed is n.

When we reach k = n, all required states have been found and no new ones can be generated. Thus

$$|\Phi_{\mathfrak{n}+1}\rangle = 0 \tag{4.57}$$

What if $\gamma_k = 0$ at some stage for k < n of the basis state construction? This implies that the action of \hat{H} on $|\Phi_k\rangle$ does not contain any component that is not already in the basis states already found. Numerical inaccuracy aside this can only happen if the Hilbert space for the problem consists of two or more independent subspaces. This is closely related to the case when for a tridiagonalized matrix a superdiagonal element $f_k = 0$. This also explains why $|\Psi_2\rangle$ in Eq. (4.44) was written as a linear combination of three mutually orthogonal functions.

In practice, for large n values of γ_k that are close to zero can actually occur due to truncation errors, but the strength of the Lanczos method is that often it may be sufficient for a physical problem to generate only a small fraction of the total number of tridiagonal basis states.

For the general recursion, we label the tridiagonal matrix elements as

$$\mathbf{d}_{k} = \langle \Phi_{k} | \hat{\mathbf{H}} | \Phi_{k} \rangle \qquad \mathbf{f}_{k} = \langle \Phi_{k-1} | \hat{\mathbf{H}} | \Phi_{k} \rangle \tag{4.58}$$

and find that in general

$$\hat{\mathsf{H}}|\Phi_{k}\rangle = \mathsf{f}_{k}|\Phi_{k-1}\rangle + \mathsf{d}_{k}|\Phi_{k}\rangle + \mathsf{f}_{k+1}|\Phi_{k+1}\rangle \tag{4.59}$$

As an illustration to the working of the Lanczos method, consider finding the ground state energy of a system. From physical intuition we can often guess a starting state $|\Phi_1\rangle$ that is not too far away from the ground state. But as $|\Phi_1\rangle$ is not going to be an eigenfunction, the matrix element $\mathbf{d}_1 = \langle \Phi_1 | \hat{\mathbf{H}} | \Phi_1 \rangle$ is not the ground state energy. In fact, if the true ground state energy is denoted by \mathcal{E}_1 , we expect $\mathbf{d}_1 \ge \mathcal{E}_1$. Constructing a second basis state $|\Phi_2\rangle$, we can find \mathbf{d}_2 and \mathbf{f}_2 . In this enlarged active space of two tridiagonal basis states, we expect to produce an eigenvector that is a better approximation of the ground state. Let λ_1 be the lower of the eigenvalues formed by the (2×2) matrix formed from \mathbf{d}_1 , \mathbf{d}_2 and \mathbf{f}_2 . Being a better approximation, we expect λ_1 to be lower in value that \mathbf{d}_1 but still higher than \mathcal{E}_1 . If we proceed to add more tridiagonal basis states to the calculation, we will see the lowest eigenvalue of the growing matrix converge to the ground state. As in many physical problems this convergence is fast, an active space that is only a small fraction of the complete Hilbert space is sufficient to obtain the ground state energy.

Summary of the Lanczos method

- 1) Arbitrary normalized $|\Phi_1\rangle$ as starting point.
- 2) $|\Phi_2\rangle = \frac{1}{f_2} (H|\Phi_1\rangle d_1|\Phi_1\rangle)$
- 3) Iteration

$$|\Phi_{k+1}\rangle = \frac{1}{\mathsf{f}_{k+1}} \big(\mathsf{H}|\Phi_k\rangle - \mathsf{d}_k |\Phi_k\rangle - \mathsf{f}_k |\Phi_{k-1}\rangle \big) = \frac{|\gamma_k\rangle}{\mathsf{f}_{k+1}} \tag{4.60}$$

with

$$\mathbf{d}_{\mathbf{k}} = \langle \Phi_{\mathbf{k}} | \mathbf{H} | \Phi_{\mathbf{k}} \rangle, \qquad \mathbf{f}_{\mathbf{k}} = \langle \gamma_{\mathbf{k}} | \gamma_{\mathbf{k}} \rangle^{-1}$$

First $|\gamma_k\rangle$ is generated, then normalized to obtain f_{k+1} .

4) The Hamiltonian matrix is

$$\begin{split} \langle \Phi_{k-1} | \mathbf{H} | \Phi_k \rangle &= \mathbf{f}_k \\ \langle \Phi_k | \mathbf{H} | \Phi_k \rangle &= \mathbf{d}_k \\ \langle \Phi_{k+1} | \mathbf{H} | \Phi_k \rangle &= \mathbf{f}_{k+1} \end{split}$$
 (4.61)

4.3.1 Lanczos for the anharmonic oscillator

After the abstract discussion of the tridiagonal basis states $|\Phi_i\rangle$ we will now discuss the Lanczos method in terms of some known functions. Let us consider a complete set of orthonormal functions $|\phi_j\rangle$ for j = 1, 2, ..., nand express each tridiagonal state in terms of a linear combination

$$|\Phi_{i}\rangle = \sum_{j=1}^{n} c_{ij} |\phi_{j}\rangle$$
(4.62)

For a given set of $|\phi_j\rangle$ the function $|\Phi_i\rangle$ is completely specified by the coefficients c_{ij} . The $|\phi_j\rangle$ should be chosen both on physical grounds and for mathematical convenience. For example, as in the mentioned example of the anharmonic oscillator $\hat{H} = \mathcal{H}_0 + \mathcal{H}'$, the eigenfunctions of the harmonic oscillator \mathcal{H}_0 are a good choice.

Once we also chose a starting tridiagonal basis state $|\Phi_1\rangle$ we have

$$|\Phi_1\rangle = \sum_{j=1}^{n} c_{1j} |\phi_j\rangle \tag{4.63}$$

and proceed as in the abstract example starting with Eq. (4.34):

$$|\mathbf{U}_{1}\rangle = \hat{\mathbf{H}}|\Phi_{1}\rangle = \sum_{j=1}^{n} c_{1j}\hat{\mathbf{H}}|\phi_{j}\rangle$$
$$= \sum_{j=1}^{n} c_{1j}\sum_{k=1}^{n} |\phi_{k}\rangle\langle\phi_{k}|\hat{\mathbf{H}}|\phi_{j}\rangle = \sum_{k=1}^{n} g_{1k}|\phi_{k}\rangle \qquad (4.64)$$

where we used the closure property of the set of states and

$$g_{1k} = \sum_{j=1}^{n} c_{1j} \langle \phi_k | \hat{H} | \phi_j \rangle = \sum_{j=1}^{n} c_{1j} H_{kj}$$
(4.65)

The Hamiltonian matrix elements are abbreviated by $H_{kj} = \langle \varphi_k | \hat{H} | \varphi_j \rangle$. Thus we find for the first matrix element

$$\mathbf{d}_1 = \langle \Phi_1 | \hat{\mathbf{H}} | \Phi_1 \rangle = \sum_{\mathbf{i}, \mathbf{j}} \mathbf{c}_{1\mathbf{i}} \mathbf{c}_{1\mathbf{j}} \mathbf{H}_{\mathbf{i}\mathbf{j}}$$
(4.66)

This can be evaluated by calculating H_{ij} and from the known $c_{1i}.$ Next we determine

$$|\Phi_2\rangle = \sum_{j=1}^{n} c_{2j} \hat{H} |\phi_j\rangle \tag{4.67}$$

with the help of Eq. (4.59) and Eq. (4.64):

$$\hat{\mathsf{H}}|\Phi_1\rangle = \mathsf{d}_1|\Phi_1\rangle + \mathsf{f}_2|\Phi_2\rangle = \sum_{j=1}^n \mathfrak{g}_{1j}|\phi_j\rangle \tag{4.68}$$

Since the basis states are linearly independent, we obtain the relation for the c_{2i} by comparing coefficients:

$$f_2 c_{2j} = g_{1j} - d_1 c_{1j} \tag{4.69}$$

Using the normalization of $|\Phi_2\rangle$ we have $\sum_j c_{2j}^2 = 1$ and thus

$$f_2^2 = \sum_{j=1}^n (g_{1j} - d_1 c_{1j})^2$$
(4.70)

With f_2 we obtain the values of the coefficients

$$\mathbf{c}_{2j} = \frac{\mathbf{g}_{1j} - \mathbf{d}_1 \mathbf{c}_{1j}}{|\mathbf{f}_2|}$$
 for $j = 1, 2, \dots, n.$ (4.71)

There is an overall abiguity of the sign in all coefficients \boldsymbol{c}_{2j} which also affects \boldsymbol{f}_2

$$f_2 = \langle \Phi_1 | \hat{H} | \Phi_2 \rangle = \sum_{ij} c_{1i} c_{2j} H_{ij}$$
(4.72)

but not d_2

$$\mathbf{d}_2 = \langle \Phi_2 | \hat{\mathbf{H}} | \Phi_2 \rangle = \sum_{ij} \mathbf{c}_{2i} \mathbf{c}_{2j} \mathbf{H}_{ij} \tag{4.73}$$

and has no physical consequence.

To derive the general equations, let us assume that we have already proceeded until $|\Phi_k\rangle$ with all coefficients $c_{1j}, c_{2j}, \ldots, c_{kj}$ known. The input quantities needed to calculate the state

$$|\Phi_{k+1}\rangle = \sum_{j=1}^{n} c_{k+1j} |\phi_j\rangle$$
(4.74)

are diagonal and superdiagonal elements d_k and f_k and coefficients $c_{k-1\,j}$ and $c_{kj}.$ Let

$$|\mathbf{U}_{k}\rangle = \hat{\mathbf{H}}|\Phi_{k}\rangle = \sum_{j=1}^{n} g_{kj}|\phi_{j}\rangle \quad \text{with } g_{kj} = \sum_{l=1}^{n} c_{kl}\mathbf{H}_{jl}$$
(4.75)

On the other hand, we have Eq. (4.59)

$$\hat{\mathsf{H}}|\Phi_{k}\rangle = \mathsf{f}_{k}|\Phi_{k-1}\rangle + \mathsf{d}_{k}|\Phi_{k}\rangle + \mathsf{f}_{k+1}|\Phi_{k+1}\rangle$$
(4.76)

At this point, f_{k+1} and the c_{k+1j} are still unknown. Using Eqs. (4.76) and (4.75), we find for the coefficients

$$f_{k+1}c_{k+1j} = g_{kj} - f_k c_{k-1j} - d_k c_{kj}$$
(4.77)

and with the normalization of $|\Phi_k\rangle$ giving $\sum_j c_{k+1j}^2 = 1$ we have

$$f_{k+1}^{2} = \sum_{j=1}^{n} \left(g_{kj} - f_{k} c_{k-1j} - d_{k} c_{kj} \right)^{2}$$
(4.78)

This yields the value of f_{k+1} up to a sign. Using this, we get the coefficients of $|\Phi_k\rangle$:

$$c_{k+1j} = \frac{g_{kj} - f_k c_{k-1j} - d_k c_{kj}}{|f_{k+1}|}$$
(4.79)

This also allows us to calculate

$$\mathbf{d}_{k+1} = \sum_{ij} c_{k+1\,i} c_{k+1\,j} \mathbf{H}_{ij} \tag{4.80}$$

This completes the calculations that are necessary for a new tridiagonal basis state. We can now proceed until we have a reasonable number of diagonal and superdiagonal elements and then diagonalize by bisection or QL decomposition. By comparing results for different matrix sizes we can decide whether we have enough tridiagonal basis states in the active space. Let us apply the Lanczos method to the anharmonic oscillator with the Hamiltonian

$$\hat{\mathsf{H}} = \mathcal{H}_0 + \mathcal{H}' = -\frac{\hbar}{2\mu} \frac{\mathrm{d}^2}{\mathrm{d}x^2} + \frac{1}{2}\mu\omega^2 x^2 + \epsilon\hbar\omega \left(\frac{\mu\omega}{\hbar}\right)^2 x^4 \tag{4.81}$$

With the dimensionless quantity $\rho = x \sqrt{\mu \omega / \hbar}$ the anharmonic term becomes

$$\mathcal{H}' = \epsilon \hbar \omega \rho^4 \tag{4.82}$$

Now we choose the harmonic oscillater wave function as basis states (with the notation $|\phi_i\rangle = |\psi_{i-1}(\rho)\rangle$):

$$\psi_{\mathfrak{m}}(\rho) = \frac{1}{\sqrt{2^{\mathfrak{m}}\mathfrak{m}!}\sqrt{\pi}} e^{-\rho^2/2} \,\mathcal{H}_{\mathfrak{m}}(\rho) \tag{4.83}$$

They are eigenfunctions of \mathcal{H}_0 :

$$\mathcal{H}_0 \psi_{\mathfrak{m}} = \left(\mathfrak{m} + \frac{1}{2}\right) \hbar \omega \psi_{\mathfrak{m}} \tag{4.84}$$

We now have to determine the matrix elements

$$\mathbf{H}_{ij} \equiv \langle \mathbf{\Phi}_{i} | \hat{\mathbf{H}} | \mathbf{\Phi}_{j} \rangle = \langle \mathbf{\psi}_{i-1} | \mathcal{H}_{0} + \epsilon \hbar \omega \rho^{4} | \mathbf{\psi}_{i-1} \rangle \tag{4.85}$$

With Eq. (4.84) we have

$$\langle \psi_{i-1} | \mathcal{H}_0 + \epsilon \hbar \omega \rho^4 | \psi_{i-1} \rangle = \left(i - \frac{1}{2} \right) \hbar \omega \delta_{ij} + \epsilon \hbar \omega \langle \psi_{i-1} | \rho^4 | \psi_{i-1} \rangle$$
(4.86)

For $\mathfrak{m} = \min(\mathfrak{i}, \mathfrak{j}) - 1$ the matrix elements of ρ^4 are

$$\begin{cases} \frac{3}{2} \left(\mathfrak{m}^2 + \mathfrak{m} + \frac{1}{2} \right) & \text{for } \mathfrak{i} = \mathfrak{j} \\ (\mathfrak{m}^2 + \mathfrak{m} + \frac{1}{2}) & \text{for } \mathfrak{i} = \mathfrak{j} \end{cases}$$

$$\langle \psi_{i-1} | \rho^4 | \psi_{i-1} \rangle = \begin{cases} \left(m + \frac{3}{2} \right) \sqrt{(m+1)(m+2)} & \text{for } i = j \pm 2 \\ \frac{1}{4} \sqrt{(m+1)(m+2)(m+3)(m+4)} & \text{for } i = j \pm 4 \\ 0 & \text{otherwise} \end{cases}$$

$$(4.87)$$

A reasonable starting point for constructing the tridiagonal basis states is the ground state of the harmonic oscillator:

$$|\Phi_1\rangle = |\phi_1\rangle \equiv |\psi_0(\rho)\rangle \tag{4.88}$$

This corresponds to the coefficients

$$\mathbf{c}_{1j} = \begin{cases} 1 & \text{for } \mathbf{j} = 1 \\ 0 & \text{otherwise} \end{cases}$$
(4.89)

The first diagonal matrix element in the tridiagonal basis is then

$$\mathbf{d}_1 = \langle \Phi_1 | \hat{\mathbf{H}} | \Phi_1 \rangle = \langle \psi_0 | \mathcal{H}_0 + \epsilon \hbar \omega \rho^4 | \psi_0 \rangle = \left(\frac{1}{2} + \frac{3\epsilon}{4}\right) \hbar \omega \qquad (4.90)$$

To obtain $|\Phi_2\rangle$ we use Eq. (4.64) to obtain

$$g_{1k} = \sum_{j=1}^{n} c_{1j} H_{kj} = H_{k1} = \begin{cases} d_1 & \text{for } k = 1 \\ \frac{3}{\sqrt{2}} \hbar \omega \epsilon & \text{for } k = 3 \\ \sqrt{\frac{3}{2}} \hbar \omega \epsilon & \text{for } k = 5 \\ 0 & \text{otherwise} \end{cases}$$
(4.91)

From these we get

$$f_2^2 = \hbar^2 \omega^2 \varepsilon^2 \left(\frac{9}{2} + \frac{3}{2}\right) = 6\hbar^2 \omega^2 \varepsilon^2$$
(4.92)

and the values of the coefficients c_{2j}

$$\mathbf{c}_{2j} = \left\{ 0, 0, \frac{\sqrt{3}}{2}, 0, \frac{1}{2}, 0, 0, \dots, 0 \right\}$$
(4.93)

The rest of the calculations can be carried out iteratively. For $k \geqslant 2$ we can calculate d_k from

$$\mathbf{d}_{\mathbf{k}} = \sum_{\mathbf{i}\mathbf{j}} = \mathbf{c}_{\mathbf{k}\mathbf{i}}\mathbf{c}_{\mathbf{k}\mathbf{j}}\mathbf{H}_{\mathbf{i}\mathbf{j}} \tag{4.94}$$

and the f_k can be obtained from Eq. (4.78). For each $k \ge 2$ the calculations proceeds in the order f_k , c_{kj} , d_k , g_{kj} .

If we repeatedly diagonalize the tridiagonal matrix for each k = 2, 3, ..., we obtain the following sequence of ground state energies \mathcal{E}_0 for $\boldsymbol{\epsilon} = 0.1$.



It is clear that with k = 10 steps we already have converged the ground state energy up to an error smaller than $10^{-3}\hbar\omega$.

4.4 Calculation of the Greens function

For an operator \hat{O} the retarded Green's function is defined by

$$\langle\!\langle \hat{O}(t); \hat{O}^{\dagger} \rangle\!\rangle \stackrel{\text{def}}{=} -i\Theta(t) \big(\langle \hat{O}(t)\hat{O}^{\dagger} \rangle - \varepsilon \langle \hat{O}^{\dagger}\hat{O}(t) \rangle \big)$$
(4.95)

where in the second line the symbol $\langle \rangle$ denotes the thermodynamic average. Commutator ($\varepsilon = +1$) and anticommutator ($\varepsilon = -1$) Green's functions can be chosen. At zero temperature, the average corresponds to the expectation value of the operators in the ground state $|\psi_0\rangle$ of the many-particle system. Here we focus on T = 0.

We proceed by inserting the Heisenberg time evolution of the operator O

$$\hat{O}(t) = e^{i\hat{H}t}\hat{O}(t)e^{-i\hat{H}t} \quad \text{with } \hat{O} = \hat{O}(t=0)$$
(4.96)

into Eq. (4.95).

Since $|\psi_0\rangle$ is the exact ground-state with energy E_0 we have

$$e^{-i\hat{H}t}|\psi_0\rangle = e^{-iE_0t}|\psi_0\rangle \qquad e^{i\hat{H}t}|\psi_0\rangle = e^{iE_0t}|\psi_0\rangle \tag{4.97}$$

and with $\omega^+=\omega+i\delta,$ where δ is an infinitesimal positive quantity, we obtain

$$\begin{split} \langle\!\langle \hat{O}; \hat{O}^{\dagger} \rangle\!\rangle_{\omega} &\stackrel{\text{def}}{=} \int_{-\infty}^{\infty} dt \, e^{i\omega^{+}t} \langle\!\langle \hat{O}(t); \hat{O}^{\dagger} \rangle\!\rangle \\ &= -i \int_{0}^{\infty} dt \, e^{i\omega^{+}t} \big(\langle e^{i\hat{H}t} \hat{O} e^{-i\hat{H}t} \hat{O}^{\dagger} \rangle - \varepsilon \langle \hat{O}^{\dagger} e^{i\hat{H}t} \hat{O} e^{-i\hat{H}t} \rangle \big) \\ &= -i \int_{0}^{\infty} dt \, e^{i\omega^{+}t} \big(\langle \hat{O} e^{-i(\hat{H}-E_{0})t} \hat{O}^{\dagger} \rangle - \varepsilon \langle \hat{O}^{\dagger} e^{i(\hat{H}-E_{0})t} \hat{O} \rangle \big) \\ &= -i \Big(\langle \hat{O} \int_{0}^{\infty} dt \, e^{i(\omega^{+}-\hat{H}+E_{0})t} \hat{O}^{\dagger} \rangle - \varepsilon \langle \hat{O}^{\dagger} \int_{0}^{\infty} dt \, e^{i(\omega^{+}+\hat{H}-E_{0})t} \hat{O} \rangle \big) \\ &= -i \Big(\langle \hat{O} \int_{0}^{\infty} dt \, e^{i(\omega^{+}-\hat{H}+E_{0})t} \hat{O}^{\dagger} \rangle - \varepsilon \langle \hat{O}^{\dagger} \int_{0}^{\infty} dt \, e^{i(\omega^{+}+\hat{H}-E_{0})t} \hat{O} \rangle \big) \\ &\qquad (4.98) \end{split}$$

With the aid of the spectral theorem the integral can be evaluated. We use relations like

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{i(\omega - \tilde{\omega})t} = \delta(\omega - \tilde{\omega})$$
(4.99)

Now, taking into account that we perform the average in the ground state $|\psi_0\rangle$, we obtain

$$\langle\!\langle \hat{O}; \hat{O}^{\dagger} \rangle\!\rangle_{\omega} = \left\langle \hat{O} \frac{1}{\omega^{+} - (\hat{H} - E_{0})} \hat{O}^{\dagger} \right\rangle - \varepsilon \left\langle \hat{O}^{\dagger} \frac{1}{\omega^{+} + (\hat{H} - E_{0})} \hat{O} \right\rangle$$

$$= \left\langle \psi_{0} \right| \hat{O} \hat{O}^{\dagger} |\psi_{0}\rangle \left\langle \phi_{0} \right| \frac{1}{\omega^{+} - (\hat{H} - E_{0})} \left| \phi_{0} \right\rangle$$

$$- \varepsilon \left\langle \psi_{0} \right| \hat{O}^{\dagger} \hat{O} |\psi_{0}\rangle \left\langle \tilde{\phi}_{0} \right| \frac{1}{\omega^{+} + (\hat{H} - E_{0})} \left| \tilde{\phi}_{0} \right\rangle$$

$$(4.100)$$

The normalized state vectors ϕ_0 and $\tilde{\phi}_0$, defined by

$$|\phi_{0}\rangle = \frac{\hat{O}^{\dagger}|\psi_{0}\rangle}{\sqrt{\langle\psi_{0}|\hat{O}\hat{O}^{\dagger}|\psi_{0}\rangle}} \qquad |\tilde{\phi}_{0}\rangle = \frac{\hat{O}|\psi_{0}\rangle}{\sqrt{\langle\psi_{0}|\hat{O}^{\dagger}\hat{O}|\psi_{0}\rangle}} \tag{4.101}$$

are used as initial vectors for two independent Lanczos sequences.

The tridiagonal form of \hat{H} , and likewise of the energy denominators $\tilde{H} = \omega \pm (H - E_0)$ in the Lanczos basis can be exploited to determine the expectation value of the inverse of $\tilde{H} = \omega \pm (H - E_0)$ in Eq. (4.100). As for the ground state we calculate the matrix elements for the Lanczos

vectors

$$\begin{aligned} \langle \phi_{i} | \hat{H} - E_{0} | \phi_{i} \rangle &= \Delta \varepsilon_{i} \\ \langle \phi_{i} | \hat{H} - E_{0} | \phi_{i+1} \rangle &= k_{i} \\ \langle \phi_{i} | \hat{H} - E_{0} | \phi_{j} \rangle &= 0 \quad \forall |i - j| > 1 \end{aligned}$$

$$(4.102)$$

Together with the orthonormality

$$\langle \phi_{i} | \phi_{j} \rangle = \delta_{ij} \tag{4.103}$$

we obtain the tridiagonal form

$$\begin{pmatrix} \omega^{+} \pm (\hat{H} - E_{0}) \end{pmatrix} \\ = \begin{pmatrix} \omega^{+} \pm \Delta \varepsilon_{0} & k_{1} & & \\ k_{1} & \omega^{+} \pm \Delta \varepsilon_{1} & k_{2} & & \\ & k_{2} & \omega^{+} \pm \Delta \varepsilon_{2} & k_{3} & \\ & & k_{3} & \omega^{+} \pm \Delta \varepsilon_{3} & k_{4} \\ & & & k_{4} & \ddots \end{pmatrix}$$
(4.104)

We need the (0,0) element of the inverse.

The (i, j) element of an inverse matrix can be expressed by

$$(A^{-1})_{ij} = (-1)^{i+j} \frac{\det \Delta_{ij}}{\det A}$$
 (4.105)

where Δ_{ij} denotes the submatrix of A obtained by eliminating from A the ith row and the jth column. Especially for the desired (0, 0) element of the inverse we have

$$(A^{-1})_{00} = \frac{\det \Delta_{00}}{\det A}$$
(4.106)

Because of the tridiagonal structure of the above matrix, the formula simplifies as follows. Consider the matrix

$$A = \begin{pmatrix} A_{00} & A_{01} & & \\ A_{10} & A_{11} & A_{12} & & \\ & A_{21} & A_{22} & A_{23} & \\ & & A_{32} & A_{33} & A_{34} \\ & & & A_{43} & A_{44} \end{pmatrix}$$
(4.107)

The determinant can be expanded along the first row and column:

$$\det A = A_{00} \det \begin{pmatrix} A_{11} & A_{12} & & \\ A_{21} & A_{22} & A_{23} & \\ & A_{32} & A_{33} & A_{34} \\ & & A_{43} & A_{44} \end{pmatrix} \\ - A_{01}A_{10} \det \begin{pmatrix} A_{22} & A_{23} & & \\ A_{32} & A_{33} & A_{34} \\ & & A_{43} & A_{44} \end{pmatrix}$$
(4.108)

We define the determinant of the submatrix of ${\sf A}$ beginning with the $i{\sf th}$ column and row, i.e.

$$D_{i} \stackrel{\text{def}}{=} \det \begin{pmatrix} A_{ii} & A_{ii+1} & & \\ A_{i+1i} & A_{i+1i+1} & A_{i+1i+2} & \\ & A_{i+2i+1} & A_{i+2i+2} & A_{i+2i+3} \\ & & & A_{i+3i+2} & A_{i+3i+3} \end{pmatrix}$$
(4.109)

Then, we can write the desired element of the inverse matrix (4.106) as

$$(\mathbf{A}^{-1})_{00} = \frac{1}{\frac{\mathbf{D}_0}{\mathbf{D}_1}} \tag{4.110}$$

We can now use Eq. (4.108) to express D_0/D_1 by D_1/D_2 :

$$\frac{\mathsf{D}_0}{\mathsf{D}_1} = \frac{\mathsf{A}_{00}\mathsf{D}_1 - |\mathsf{A}_{01}|^2\mathsf{D}_2}{\mathsf{D}_1} = \mathsf{A}_{00} - \frac{|\mathsf{A}_{01}|^2}{\frac{\mathsf{D}_1}{\mathsf{D}_2}} \tag{4.111}$$

Iterating the above reasoning yields

$$\frac{D_{l}}{D_{l+1}} = A_{ll} - \frac{|A_{ll+1}|^2}{\frac{D_{l+1}}{D_{l+2}}}$$
(4.112)

This leads to a continued fraction for the desired quantity

$$(A^{-1})_{00} = \frac{1}{\frac{D_0}{D_1}} = \frac{1}{A_{00} - \frac{|A_{01}|^2}{A_{11} - \frac{|A_{12}|^2}{A_{22} - \frac{|A_{23}|^2}{A_{33} - \ddots}}}$$
(4.113)

For the original problem $\big((\omega^+\pm(\hat{H}-E_0))^{-1}\big)_{00}$ the continued fraction reads

$$\left((\omega^{+} \pm (\hat{H} - E_{0}))^{-1} \right)_{00}$$

$$= \frac{1}{\omega^{+} \pm \Delta \varepsilon_{0} - \frac{|k_{1}|^{2}}{\omega^{+} \pm \Delta \varepsilon_{1} - \frac{|k_{2}|^{2}}{\omega^{+} \pm \Delta \varepsilon_{2} - \frac{|k_{3}|^{2}}{\omega^{+} \pm \Delta \varepsilon_{3} - \ddots}}$$

$$(4.114)$$

This expression is well suited for numerical treatment and can be iterated for arbitrary $\boldsymbol{\omega}$. To this end, we introduce the abbreviations

$$\begin{aligned} \mathbf{d}_{\mathbf{i}} &= \boldsymbol{\omega}^{+} \pm \Delta \boldsymbol{\varepsilon}_{\mathbf{i}} & \text{ for } \mathbf{i} = 0, 1, \dots \\ \mathbf{e}_{\mathbf{i}} &= |\mathbf{k}_{\mathbf{i}}|^{2} & \text{ for } \mathbf{i} = 1, 2, \dots \end{aligned}$$
(4.115)

Beginning with the upper left (2×2) submatrix of A the continued fraction has the form

$$\frac{1}{d_0 - \frac{e_1}{d_1 - R_1}} = \frac{d_1 - R_1}{d_0 d_1 - d_1 - d_0 R_1} \equiv \frac{a_1 + a_0 R_1}{b_1 + b_0 R_1}$$
(4.116)

In this equation we anticipated the general form. The remainder R_1 has again the form of a continued fraction. In general the remainder reads

$$R_{i} = \frac{e_{i+1}}{d_{i+1} - R_{i+1}}$$
(4.117)

By substituting this for i = 1 into Eq. (4.116) we obtain

$$\frac{a_1 + a_0 R_1}{b_1 + b_0 R_1} = \underbrace{\frac{a_1 d_1 + a_0 e_2}{b_1 d_2 + b_0 e_2} + \underbrace{(-a_1) R_2}_{b_0}}_{b_1 b_0}$$
(4.118)

which is again of the form

$$\frac{\mathbf{a}_1 + \mathbf{a}_0 \mathbf{R}}{\mathbf{b}_1 + \mathbf{b}_0 \mathbf{R}} \tag{4.119}$$

Thus the iteration formula for i = 1, 2, ... deduced from the considerations above is given by

$$\begin{array}{l} a_{1} \longrightarrow a_{1}d_{i+1} + a_{0}e_{i+1} \\ a_{0} \longrightarrow -a_{1} \\ b_{1} \longrightarrow b_{1}d_{i+1} + b_{0}e_{i+1} \\ b_{0} \longrightarrow -b_{1} \end{array}$$

$$(4.120)$$

with the initial values $a_1 = d_1$, $a_0 = -1$, $b_1 = d_0 d_1 - e_1$, $b_0 = -d_0$. The sequence is iterated for each ω individually and ends if the Krylov space is exhausted or if a desired convergence of

$$g(\omega) = \frac{a_1}{b_1} \tag{4.121}$$

is achieved. In order to avoid numerical instabilities, it is recommended to rescale all quantities $a_0, a_1, b_0, b_1 e.g.$ by b_1 after each iteration.

In some cases it may happen that the Green's function of interest is not diagonal in the operators, e.g.

$$g_{AB} = \left\langle \hat{A}^{\dagger} \frac{1}{\omega^{+} - (\hat{H} - E_{0})} \hat{B} \right\rangle$$
(4.122)

In this case we define two operators $\hat{O}_\alpha=\hat{A}+\alpha\hat{B}$ and determine the diagonal Green's functions

$$g_{\alpha} = \left\langle \hat{O}_{\alpha}^{\dagger} \frac{1}{\omega^{+} - (\hat{H} - E_{0})} \hat{O}_{\alpha} \right\rangle$$
(4.123)

It is easily possible to separate g_{AB} by linearly combining the four Green's functions for $\alpha = \{\pm 1, \pm i\}$.

Lehmann Representation

There is an alternative way of calculating Green's functions, the so-called Lehmann representation. Again we consider the matrix elements of the form

$$\left\langle \psi_{0} \middle| \hat{O}^{\dagger} \frac{1}{\omega^{+} \pm (\hat{H} - \mathsf{E}_{0})} \hat{O} \middle| \psi_{0} \right\rangle$$
(4.124)

where $|\psi_0\rangle$ represents the ground state. Like before we define $|\phi_0\rangle$ as the normalized vector $\hat{O}|\psi_0\rangle$, which serves as initial vector of a Lanczos sequence. We insert a complete orthonormal set of eigenvectors of \hat{H} given

by

$$\mathbb{I} = \sum_{\gamma} |\psi_{\gamma}\rangle \langle \psi_{\gamma}| \tag{4.125}$$

Then Eq. (4.124) can be cast into the form

$$\left\langle \psi_{0} \middle| \hat{O}^{\dagger} \frac{1}{\omega^{+} \pm (\hat{H} - \mathsf{E}_{0})} \hat{O} \middle| \psi_{0} \right\rangle = \sum_{\nu} \frac{\left\langle \psi_{0} \middle| \hat{O}^{\dagger} \middle| \psi_{\nu} \right\rangle \left\langle \psi_{\nu} \middle| \hat{O} \middle| \psi_{0} \right\rangle}{\omega^{+} \pm (\hat{H} - \mathsf{E}_{0})} \quad (4.126)$$

Next we expand the eigenvectors $|\psi_{\nu}\rangle$ in the Lanczos basis $\{|\phi_i\rangle\}$

$$|\psi_{\nu}\rangle = \sum_{i} c_{i}^{(\nu)} |\phi_{i}\rangle \quad \text{with } c_{i}^{(\nu)} = \langle \phi_{i} |\psi_{\nu}\rangle \tag{4.127}$$

to obtain

$$\begin{split} \langle \psi_{\nu} | \hat{O} | \psi_{0} \rangle &= \sum_{i} c_{i}^{(\nu)*} \langle \phi_{i} | \hat{O} | \psi_{0} \rangle = \sqrt{\langle \psi_{0} | \hat{O}^{\dagger} \hat{O} | \psi_{0} \rangle} \sum_{i} c_{i}^{(\nu)*} \langle \phi_{i} | \phi_{0} \rangle \\ &= \sqrt{\langle \psi_{0} | \hat{O}^{\dagger} \hat{O} | \psi_{0} \rangle} c_{i}^{(\nu)*} \end{split}$$

$$(4.128)$$

because $\langle \varphi_i | \varphi_0 \rangle = \delta_{i0}$. This means that except of the first terms all addends vanish.

Thus Eq. (4.124) can be approximated by

$$\left\langle \psi_{0} \middle| \hat{O}^{\dagger} \frac{1}{\omega^{+} \pm (\hat{H} - \mathsf{E}_{0})} \hat{O} \middle| \psi_{0} \right\rangle = \left\langle \psi_{0} \middle| \hat{O}^{\dagger} \hat{O} \middle| \psi_{0} \right\rangle \sum_{\nu=1}^{\mathsf{N}_{\mathsf{L}}} \frac{|\mathbf{c}_{0}^{(\nu)}|^{2}}{\omega^{+} \pm (\tilde{\mathsf{E}} - \tilde{\mathsf{E}}_{0})}$$

$$(4.129)$$

where only the first components $c_0^{(\nu)}$ of the expansion of the eigenvector $|\psi_{\nu}\rangle$ in the Lanczos basis are required. In general, the eigenstates $|\psi_{\nu}\rangle(\nu = 1, \ldots, N_L)$, computed by the Lanczos procedure, do not form a complete set of basis vectors, nor are the respective energies \tilde{E}_{ν} exact eigenvalues of \hat{H} . However, with increasing number of iterations, the Lanczos procedure converges towards the exact Green's function and the convergence can be monitored and stopped as soon as the desired accuracy is reached. The approximate Lehmann representation (4.129) is an explicit sum of simple poles. The same is true for the continued fraction.
5. Mean field approximation

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5.1 Hubbard model

The Hubbard model (5.1) is one of the simplest many particle models. However, its ground state is known to be complex. In general, exact solutions are unavailable. The exception are one dimensional systems where there are many possible methods; to cite only some of them: Bethe ansatz, bosonization, Luttinger and Tomonaga method. But these methods can't be used for two or three dimensional systems, and (approximate) numerical methods have to be employed to solve the Hubbard model.

The one band Hubbard model can be written as follows:

$$H = \sum_{\langle i,j \rangle,\sigma} t_{ij} c^{\dagger}_{i\sigma} c_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow} , \qquad (5.1)$$

where t_{ij} is the hopping amplitude, $\langle i, j \rangle$ indicates summation over the nearest neighbors. U is the value of the on-site Coulomb repulsion. $c_{i\sigma}^{\dagger}$, $c_{i\sigma}$ are the creation and annihilation operators, and $n_{i\sigma} = c_{i\sigma}^{\dagger}c_{i\sigma}$ is the local density of electrons for spin σ . In this case, the Coulomb interaction doesn't act between electrons of the same spin as the Pauli exclusion principle doesn't allow two electrons two be in identical states, so we can't consider the possibility of two electrons of the same spin on the same site of the lattice.

5.1.1 Simplest mean field approximation

After a direct Hartree-Fock decoupling of the four-operator terms, the mean field Hamiltonian (5.2) can be written as the sum of a Hamiltonian for spin

up, a Hamiltonian for spin down and a constant:

$$\begin{aligned} \mathsf{H}^{\mathsf{MF}} &= \mathsf{H}_{\uparrow} + \mathsf{H}_{\downarrow} + \mathsf{C}. \end{aligned} (5.2) \\ \mathsf{H}_{\uparrow} &= -\mathsf{t} \sum_{\langle i,j \rangle} c^{\dagger}_{i\uparrow} c_{j\uparrow} + \mathsf{U} \sum_{i} \mathsf{n}_{i\uparrow} \langle \mathsf{n}_{i\downarrow} \rangle, \end{aligned}$$

$$\begin{split} H_{\downarrow} &= -t \sum_{\langle i,j \rangle}^{\langle i,j \rangle} c^{\dagger}_{i\downarrow} c_{j\downarrow} + U \sum_{i}^{\iota} \langle n_{i\uparrow} \rangle n_{i\downarrow}, \\ C &= -U \sum_{i} \langle n_{i\uparrow} \rangle \langle n_{i\downarrow} \rangle. \end{split}$$

Now the Hamiltonian is reduced to two matrices of size $N\times N$ (where N is the system size), and we have 2N mean field parameters (N local densities $\langle n_{i\uparrow}\rangle$ and N local densities $\langle n_{i\downarrow}\rangle$) to determine the ground state.

This approximation allows us to reduce the problem to a one particle problem. There are a number of advantages:

- the study of big system sizes is possible (the size of the Hilbert space is reduced to the size of the system; the Hamiltonian corresponds just to an $N \times N$ matrix);
- the computation can be done in real space;
- there are no restrictions on the shape of the system (open boundary conditions, defects, any type of geometry and lattices); we can even do simulations based on specific experimental systems;
- the model is flexible (it is easy to add some tight-binding or interaction terms to the model, or to study a deformation of the lattice).

But all of this has a high price:

- The SU(2) symmetry is broken.
- Important effects of the electron interaction are not taken into account: only long range order can be considered, and the stability of magnetic order is overestimated.

In general, the mean field approximation is closer to an exact solution of the model at weak U. At larger U, in the best case the mean field approximation can give the qualitative behavior.

5.1.2 Self-consistent solution

An iterative solution of the mean field Hamiltonian (5.2) involves the following steps:

- The initial condition is applied: the mean field parameters are initialized by a local density of electrons of spin σ .
- The following steps are repeated until convergence:
 - Diagonalization of the Hamiltonians for spin up and down:
 - \Rightarrow This yields the one particle energy spectrum $\varepsilon_{\alpha,\sigma}$.
 - \Rightarrow Now the eigenstate can be constructed:

$$\begin{split} |\mathsf{GS}\rangle &= \prod_{\alpha=1}^{\mathsf{N}_{\uparrow}} d_{\alpha\uparrow}^{\dagger} \prod_{\beta=1}^{\mathsf{N}_{\downarrow}} d_{\beta\downarrow}^{\dagger} |0\rangle \,, \quad d_{\alpha,\sigma} = \sum_{i} Q_{\alpha i,\sigma}^{\dagger} c_{i\sigma} . \\ \mathsf{H}^{\mathsf{MF}} &= \sum_{\sigma} \sum_{\alpha} \varepsilon_{\alpha,\sigma} d_{\alpha,\sigma}^{\dagger} d_{\alpha,\sigma} + C \end{split}$$

 New mean field parameters are computed using the new eigenstate:

$$\langle \mathfrak{n}_{\mathfrak{i}\sigma}
angle = \sum_{lpha=1}^{N_{\sigma}} Q^{\dagger}_{lpha\mathfrak{i},\sigma} Q_{\mathfrak{i}lpha,\sigma}$$

Convergence means $\langle n_{i\sigma} \rangle_I = \langle n_{i\sigma} \rangle_{I-1}$, where I corresponds to the number of the iteration.

5.1.3 Frustrated systems

What is frustration?

If we consider the Hubbard model, the on-site Coulomb interaction leads at large U to antiferromagnetic order (for $U\to\infty$, the Hubbard model corresponds to a Heisenberg model with an antiferromagnetic coupling J corresponding to the hopping bond, $J=4t^2/u$). Frustration means that a system is not able to find any magnetic order which satisfies all the couplings of the model.

As illustrated in Figure 5.1, there are at least two types of frustration, geometrical frustration and frustration due to competing interactions.

The classical solution: commensurate spiral order



Figure 5.1: Types of frustration: Geometrical frustration (left), and competition between couplings (right).

The classical solution to this problem with periodic boundary conditions (PBC) is a commensurate spiral order (see Figure 5.2).



Figure 5.2: Spin spiral that is commensurate with the size of the system due to the periodic boundary condition (PBC).

A spiral order is a magnetic order where the difference of orientation between all first neighbor spins corresponds to a uniform angle θ_a (with athe direction considered). For a system with periodic boundary conditions this angle is not completely free; there is only a finite number of values determined by the system size:

$$\theta_a = \gamma \frac{2\pi}{L_a}$$
 with system size L_a in a direction and γ an integer.

For example, in a ring of six sites, θ can only take the values $\pi/3$, $2\pi/3$, and π .

Mean field approximation for a spiral state

The Hartree-Fock decoupling of the Hubbard model used in the previous section is not unique. The one chosen previously allows only magnetic order of Ising type (ferromagnetic or antiferromagnetic order). For frustrated systems, we want to have at least the possibility to study spiral states. To achieve this, we should choose a mean field approximation including the x and y components of the spin:

$$\begin{split} \mathsf{H}^{\mathsf{MF2}} &= -t \sum_{\langle i,j \rangle,\sigma} c^{\dagger}_{i\sigma} c_{j\sigma} + U \sum_{i} \left[\langle n_{i\downarrow} \rangle n_{i\uparrow} + \langle n_{i\uparrow} \rangle n_{i\downarrow} - \langle n_{i\uparrow} \rangle \langle n_{i\downarrow} \rangle \right] \\ &- U \sum_{i} \left[\langle S^{+}_{i} \rangle c^{\dagger}_{i\downarrow} c_{i\uparrow} + \langle S^{-}_{i} \rangle c^{\dagger}_{i\uparrow} c_{i\downarrow} - \langle S^{+}_{i} \rangle \langle S^{-}_{i} \rangle \right] \\ &= C^{\dagger} \left(\begin{array}{c} \mathsf{H}^{\uparrow\uparrow} & \mathsf{H}^{\uparrow\downarrow} \\ \mathsf{H}^{\downarrow\uparrow} & \mathsf{H}^{\downarrow\downarrow} \end{array} \right)_{2N \times 2N} \mathsf{C} + \mathrm{constant}, \end{split}$$
(5.3)

with:

$$\begin{split} S_i^- &= c_{i\downarrow}^{\dagger} c_{i\uparrow} \\ S_i^+ &= c_{i\uparrow}^{\dagger} c_{i\downarrow} \\ C^{\dagger} &= \left(c_{1\uparrow}^{\dagger}, ..., c_{N\uparrow}^{\dagger}, c_{1\downarrow}^{\dagger}, ..., c_{N\downarrow}^{\dagger}\right) \\ H_{ij}^{\uparrow\uparrow} &= \left(U\langle n_{i\downarrow}\rangle - \mu\right) \delta_{ij} + T_{ij} \\ H_{ij}^{\uparrow\downarrow} &= -U\langle S_i^-\rangle \delta_{ij} \\ H_{ij}^{\downarrow\uparrow} &= -U\langle S_i^+\rangle \delta_{ij} \\ H_{ij}^{\downarrow\downarrow} &= \left(U\langle n_{i\uparrow}\rangle - \mu\right) \delta_{ij} + T_{ij} \\ constant &= U\sum_i \left[\langle S_i^+\rangle \langle S_i^-\rangle - \langle n_{i\uparrow}\rangle \langle n_{i\downarrow}\rangle\right] \end{split}$$

We have now a Hamiltonian of size $2N \times 2N$ and 4N mean field parameters to compute (N values for the local operators $\langle S_i^+ \rangle$, $\langle S_i^- \rangle$, $\langle n_{i\uparrow} \rangle$ and $\langle n_{i\downarrow} \rangle$). But we can easily reduce the number of parameters by assuming that the spins are coplanar. We can choose the spin to lie in the xy plane or in the xz (yz) plane:

• To have the spin in the xy plane we should enforce:

$$\langle \mathbf{n}_{i\uparrow} \rangle = \langle \mathbf{n}_{i\downarrow} \rangle \Leftrightarrow \langle \mathbf{S}_i^z \rangle = \langle \mathbf{n}_{i\uparrow} \rangle - \langle \mathbf{n}_{i\downarrow} \rangle = 0.$$

• And to have them in the xz plane we should enforce:

$$\langle \mathbf{S}_{i}^{+} \rangle = \langle \mathbf{S}_{i}^{-} \rangle = \langle \mathbf{S}_{i}^{\mathbf{x}} \rangle \Leftrightarrow \langle \mathbf{S}_{i}^{\mathbf{y}} \rangle = \frac{\mathbf{i}}{2} (\langle \mathbf{S}_{i}^{+} \rangle - \langle \mathbf{S}_{i}^{-} \rangle) = 0.$$

Computation of the mean field parameters

From the diagonalization of $\mathsf{H}^{\mathsf{MF2}},$ we obtain:

- the one particle spectrum for spin up and down $\varepsilon_{\alpha},$
- and the ground state:

$$\begin{split} |\mathsf{GS}\rangle &= \Pi_{\alpha} d_{\alpha}^{\dagger} |0\rangle \qquad (5.4) \\ \mathrm{with} \ d_{\alpha} &= \sum_{i} Q_{\alpha i}^{\dagger} c_{i}, \ \mathrm{and} \ \mathsf{H}^{\mathsf{MF2}} = \sum_{\alpha} \varepsilon_{\alpha} d_{\alpha}^{\dagger} d_{\alpha} + \mathrm{Constant} \end{split}$$

And we can compute from the eigenstates the different mean field parameters:

$$\begin{array}{lll} \langle \mathbf{n}_{i\uparrow} \rangle &=& \displaystyle\sum_{\alpha \leqslant N_e} \mathbf{Q}_{\alpha i}^{\dagger} \mathbf{Q}_{i\alpha} \\ \langle \mathbf{n}_{i\downarrow} \rangle &=& \displaystyle\sum_{\alpha \leqslant N_e} \mathbf{Q}_{\alpha i+N}^{\dagger} \mathbf{Q}_{i+N\alpha} \\ \langle \mathbf{S}_i^+ \rangle &=& \displaystyle\sum_{\alpha \leqslant N_e} \mathbf{Q}_{\alpha i}^{\dagger} \mathbf{Q}_{i+N\alpha} \\ \langle \mathbf{S}_i^- \rangle &=& \displaystyle\sum_{\alpha \leqslant N_e} \mathbf{Q}_{\alpha i+N}^{\dagger} \mathbf{Q}_{i\alpha} \end{array}$$

Be careful: the indices now don't correspond anymore to the lattice indices, but to the ones you choose in C^{\dagger} , so here the formulas correspond to $C^{\dagger} = (c_{1\uparrow}^{\dagger}, ..., c_{N\uparrow}^{\dagger}, c_{1\downarrow}^{\dagger}, ..., c_{N\downarrow}^{\dagger}).$

5.1.4 Some methods to solve convergence issues

Self-consistent solution and ground state

One important point is to notice the difference between a self-consistent solution and the ground state. The ground state will be the the self-consistent solution of lowest total energy. To be sure that your solution is the ground state and not an exited state, repeat the whole procedure several times (varying the initial conditions) and take the solution of lowest energy. In most cases you will mostly converge to the ground state. But in the case of frustrated systems, the first exited states are really close in energy to the ground state, which can therefore be difficult to find.

Choice of the initial condition

Here you have several possibilities:

- Random initial condition: choose random numbers for your mean field parameter. This is probably the best method, but the convergence process can be really slow and difficult.
- Paramagnetic state: $\langle n_{i\sigma} \rangle = N_{\sigma}/N$. This state is a special one but in combination with the annealing method for the first iterations, it will give you a more or less "physical" random initial condition.
- Special initial conditions: choose a specific state (for example the classical antiferromagnetic order). This type of choice is dangerous as it will reduce the number of self-consistent solutions which would be reachable. In the case of frustrated systems, it can be a good way to investigate the whole set of possible spiral states by searching the self-consistent solutions corresponding to each classical spiral (reachable for the system size) as initial condition. Be careful: you are probably reducing your solution to the spiral state only and potentially missing the true ground state.

Annealing

In some cases the symmetry of the system makes the convergence difficult. A good solution in this case is to add a small temperature to the first iteration. In this case, the computation of your mean field parameter is a bit modified and takes the following shape:

$$\langle n_{i\sigma} \rangle = \sum_{\alpha \in \Omega} Q^{\dagger}_{\alpha i,\sigma} Q_{i\alpha,\sigma} \, , \label{eq:niss}$$

where Ω is a set of N_{σ} one-particle states chosen with a probability : $n(\epsilon_{\alpha,\sigma}) = 1/(1 + e^{\beta(\epsilon_{\alpha,\sigma} - \epsilon_F)})$ with Fermi energy ϵ_F . In this method you have several possibilities:

- A fixed temperature during a fixed number of iterations (for example 10 iterations at $\beta = t$),
- or you can smoothly reduce the value of β , until you reach zero temperature corresponding to your regular iterations.

Damping

A usual problem of convergence is the oscillation between two states:

$$\langle n_{i\sigma} \rangle_{I} \rightarrow \langle n_{i\sigma} \rangle_{I+1} \text{ and } \langle n_{i\sigma} \rangle_{I+1} \rightarrow \langle n_{i\sigma} \rangle_{I}.$$

So in this case a simple solution is to introduce a form of damping by averaging the results of an iteration with a previous one.

- the simplest possibility is : $\langle n_{i\sigma} \rangle_I = 0.5 \langle n_{i\sigma} \rangle_I + 0.5 \langle n_{i\sigma} \rangle_{I-1}$. But this is in general not sufficient to solve your problem.
- a better solution is to introduce a variable weight: $\langle n_{i\sigma} \rangle_I = P_I \langle n_{i\sigma} \rangle_I + (1 P_I) \langle n_{i\sigma} \rangle_{I-1}$ where P_I evolves with the number of iteration I.
- And you can imagine more complicated possibilities; any linear combination of previous solutions could work.

Be careful: The weight assigned to your new mean field parameters should not be lower that your criterion of convergence ($P_I > \delta$ if δ is the demanded precision).

Reduction of the number of parameters

Normally you have a number of mean field parameter proportional to the size of your system. You can reduce this number to the number of sublattices of your system (for example two sublattices for the square lattice with periodic boundary condition). To achieve this goal it is enough to enforce that $\langle n_{i\sigma} \rangle = n_X$ for all i which belong to the X sublattice. In practice, n_X corresponds to the average on your new $\langle n_{i\sigma} \rangle$ which belongs to the X sublattice:

$$n_X = \frac{1}{N_X} \sum_{i \in X} \langle n_{i\sigma} \rangle \ {\rm where} \ N_X \ {\rm is \ the \ number \ of \ sites \ in \ sublattice \ } X \, .$$

Be careful: If you didn't choose the appropriate sublattices, you will miss the ground state.

5.1.5 Limits of the mean field approximation

The mean field approximation of the Hubbard model is a powerful method to study large system sizes, compute real space quantities and consider systems with sophisticated geometry. It will give really good results in the case of weak interaction. Now you should keep in mind, that this method allows only long range order and overestimates magnetic order. So if you don't see something it doesn't mean it doesn't exist. In particular exotic phases like a spin liquid, for example, is not accessible by this approximation. 5.2 Details of the computation of $\langle n_{i\sigma} \rangle$.

$$d_{\alpha,\sigma} = \sum_{i} Q^{\dagger}_{\alpha i,\sigma} c_{i\sigma} \quad {\rm and} \quad d^{\dagger}_{\alpha,\sigma} = \sum_{i} Q_{i\alpha,\sigma} c^{\dagger}_{i\sigma}$$

$$|\mathrm{GS}
angle = \prod_{lpha=1}^{\mathsf{N}_{\uparrow}} \mathrm{d}_{lpha\uparrow}^{\dagger} \prod_{eta=1}^{\mathsf{N}_{\downarrow}} \mathrm{d}_{eta\downarrow}^{\dagger} |0
angle$$

$$\langle \mathbf{n}_{i\sigma} \rangle = \langle \mathbf{GS} | \mathbf{n}_{i,\sigma} | \mathbf{GS} \rangle = \langle 0 | \prod_{\beta'=1}^{\mathsf{N}_{\downarrow}} \mathbf{d}_{\beta'\downarrow} \prod_{\alpha'=1}^{\mathsf{N}_{\uparrow}} \mathbf{d}_{\alpha'\uparrow} \mathbf{c}_{i,\sigma}^{\dagger} \mathbf{c}_{i,\sigma} \prod_{\alpha=1}^{\mathsf{N}_{\uparrow}} \mathbf{d}_{\alpha\uparrow}^{\dagger} \prod_{\beta=1}^{\mathsf{N}_{\downarrow}} \mathbf{d}_{\beta\downarrow}^{\dagger} | 0 \rangle 5.5 \rangle$$

We will consider here only the special case $\sigma =\uparrow$ but the case $\sigma =\downarrow$ is strictly similar.

 $c_{i\uparrow}$ is operator annihilation of electron of spin up and so follow the following rules of commutation: $\{c_{i,\sigma},c_{j,\sigma'}^{\dagger}\}=\delta_{\sigma,\sigma'}\delta_{i,j}.$ And we can as well derive the relation of commutation between the operator c and d:

$$\begin{aligned} c_{i\uparrow}d^{\dagger}_{\alpha,\downarrow} &= c_{i\uparrow}\sum_{j}Q_{j\alpha,\downarrow}c^{\dagger}_{j\downarrow} = \sum_{j}Q_{j\alpha,\downarrow}c_{i\uparrow}c^{\dagger}_{j\downarrow} \\ &= \sum_{j}Q_{j\alpha,\downarrow}(-c^{\dagger}_{j\downarrow}c_{i\uparrow}) = -d^{\dagger}_{\alpha,\downarrow}c_{i\uparrow} \end{aligned}$$

$$c_{i\uparrow} \prod_{\beta=1}^{N_{\downarrow}} d^{\dagger}_{\alpha,\downarrow} = (-1)^{N_{\downarrow}} \prod_{\beta=1}^{N_{\downarrow}} d^{\dagger}_{\alpha,\downarrow} c_{i\uparrow}$$
(5.6)

$$\begin{split} c_{i\uparrow}d^{\dagger}_{\alpha,\uparrow} &= \sum_{j} Q_{j\alpha,\uparrow}c^{\dagger}_{j\uparrow} = \sum_{j} Q_{j\alpha,\uparrow}c_{i,\uparrow}c^{\dagger}_{j\uparrow} \\ &= \sum_{j} Q_{j\alpha,\uparrow}(\delta_{ij} - c^{\dagger}_{j\uparrow}c_{i,\uparrow}) = Q_{i\alpha,\uparrow} - d^{\dagger}_{\alpha,\uparrow}c_{i,\uparrow} \end{split}$$

$$\begin{split} c_{i,\uparrow} \prod_{\alpha=1}^{N_{\uparrow}} d_{\alpha,\uparrow}^{\dagger} &= (Q_{i1,\uparrow} - d_{1,\uparrow}^{\dagger} c_{i,\uparrow}) \prod_{\alpha=2}^{N_{\uparrow}} d_{\alpha,\uparrow}^{\dagger} \\ &= Q_{i1,\uparrow} \prod_{\alpha=2}^{\Lambda} d_{\alpha,\uparrow}^{\dagger} - d_{1,\uparrow}^{\dagger} c_{i,\uparrow} \prod_{\alpha=2}^{N_{\uparrow}} d_{\alpha,\uparrow}^{\dagger} \\ &= Q_{i1,\uparrow} \prod_{\alpha=2}^{\Lambda} d_{\alpha,\uparrow}^{\dagger} - d_{1,\uparrow}^{\dagger} (Q_{i2,\uparrow} - d_{2,\uparrow}^{\dagger} c_{i,\uparrow}) \prod_{\alpha=3}^{N_{\uparrow}} d_{\alpha,\uparrow}^{\dagger} \\ &= Q_{i1,\uparrow} \prod_{\alpha=2}^{\Lambda} d_{\alpha,\uparrow}^{\dagger} - Q_{i2,\uparrow} \prod_{\alpha\neq2}^{\Lambda} d_{\alpha,\uparrow}^{\dagger} + d_{1,\uparrow}^{\dagger} d_{2,\uparrow}^{\dagger} c_{i,\uparrow} \prod_{\alpha=3}^{N_{\uparrow}} d_{\alpha,\uparrow}^{\dagger} \\ &= \dots \\ &= \sum_{\beta}^{N_{\uparrow}} (-1)^{\beta+1} Q_{i\beta,\uparrow} \prod_{\alpha\neq\beta}^{N_{\uparrow}} d_{\alpha,\uparrow}^{\dagger} + (-1)^{N_{\uparrow}} \prod_{\alpha=1}^{\Lambda} d_{\alpha,\uparrow}^{\dagger} c_{i,\uparrow} (5.7) \end{split}$$

Using (5.6) and (5.7) and $c_{i,\sigma}|0\rangle = 0$ we obtain:

$$\begin{split} \mathbf{c}_{\mathbf{i},\uparrow} |GS\rangle &= \mathbf{c}_{\mathbf{i},\uparrow} \prod_{\alpha=1}^{N_{\uparrow}} \mathbf{d}_{\alpha\uparrow}^{\dagger} \prod_{\gamma=1}^{N_{\downarrow}} \mathbf{d}_{\gamma\downarrow}^{\dagger} |0\rangle \\ &= \left(\sum_{\beta}^{N_{\uparrow}} (-1)^{\beta+1} \mathbf{Q}_{\mathbf{i}\beta,\uparrow} \prod_{\alpha\neq\beta}^{N_{\uparrow}} \mathbf{d}_{\alpha,\uparrow}^{\dagger} + (-1)^{N_{\uparrow}} \prod_{\alpha=1}^{N_{\uparrow}} \mathbf{d}_{\alpha,\uparrow}^{\dagger} \mathbf{c}_{\mathbf{i},\uparrow} \right) \prod_{\gamma=1}^{N_{\downarrow}} \mathbf{d}_{\gamma\downarrow}^{\dagger} |0\rangle \\ &= \sum_{\beta}^{N_{\uparrow}} (-1)^{\beta+1} \mathbf{Q}_{\mathbf{i}\beta,\uparrow} \prod_{\alpha\neq\beta}^{N_{\uparrow}} \mathbf{d}_{\alpha,\uparrow}^{\dagger} \prod_{\gamma=1}^{N_{\downarrow}} \mathbf{d}_{\gamma\downarrow}^{\dagger} |0\rangle + \\ &+ (-1)^{N_{\uparrow}} (-1)^{N_{\downarrow}} \prod_{\alpha=1}^{N_{\uparrow}} \mathbf{d}_{\alpha,\uparrow}^{\dagger} \prod_{\gamma=1}^{N_{\downarrow}} \mathbf{d}_{\gamma\downarrow}^{\dagger} \mathbf{c}_{\mathbf{i},\uparrow} |0\rangle \\ &= \sum_{\beta}^{N_{\uparrow}} (-1)^{\beta+1} \mathbf{Q}_{\mathbf{i}\beta,\uparrow} \prod_{\alpha\neq\beta}^{N_{\uparrow}} \mathbf{d}_{\alpha,\uparrow}^{\dagger} \prod_{\gamma=1}^{N_{\downarrow}} \mathbf{d}_{\gamma\downarrow}^{\dagger} |0\rangle \end{split}$$

Using this equation and its Hermitian conjugate we can at last compute

 $\langle n_{i,\sigma}\rangle :$

$$\begin{split} \langle n_{i\uparrow} \rangle &= \langle GS | n_{i,\sigma} | GS \rangle = \langle 0 | \prod_{\gamma'=1}^{N_{\downarrow}} d_{\gamma'\downarrow} \prod_{\alpha'=1}^{N_{\uparrow}} d_{\alpha'\uparrow} c_{i,\sigma}^{\dagger} c_{i,\sigma} \prod_{\alpha=1}^{N_{\uparrow}} d_{\alpha\uparrow}^{\dagger} \prod_{\gamma=1}^{N_{\downarrow}} d_{\gamma\downarrow}^{\dagger} | 0 \rangle \\ &= \langle 0 | \prod_{\gamma'=1}^{N_{\downarrow}} d_{\gamma'\downarrow} \bigg(\sum_{\beta'}^{N_{\uparrow}} (-1)^{\beta'+1} Q_{\beta'i,\uparrow}^{\dagger} \prod_{\alpha\neq\beta'}^{N_{\uparrow}} d_{\alpha',\uparrow} \bigg) \times \\ &\times \bigg(\sum_{\beta}^{N_{\uparrow}} (-1)^{\beta+1} Q_{i\beta,\uparrow} \prod_{\alpha\neq\beta}^{N_{\uparrow}} d_{\alpha,\uparrow}^{\dagger} \bigg) \prod_{\gamma=1}^{N_{\downarrow}} d_{\gamma\downarrow}^{\dagger} | 0 \rangle \\ &= \sum_{\beta'}^{N_{\uparrow}} \sum_{\beta}^{N_{\uparrow}} (-1)^{\beta+1+\beta'+1} Q_{\beta'i,\uparrow}^{\dagger} Q_{i\beta,\uparrow} \langle 0 | \prod_{\gamma'=1}^{N_{\downarrow}} d_{\gamma'\downarrow} \prod_{\alpha\neq\beta'}^{N_{\uparrow}} d_{\alpha',\uparrow} \prod_{\alpha\neq\beta}^{N_{\uparrow}} d_{\alpha,\uparrow}^{\dagger} \prod_{\gamma=1}^{N_{\downarrow}} d_{\gamma\downarrow}^{\dagger} | 0 \rangle \end{split}$$

The eigenvector are orthogonal and normalized so:

$$\langle 0|\prod_{\gamma'=1}^{\mathsf{N}_{\downarrow}} \mathbf{d}_{\gamma'\downarrow} \prod_{\alpha \neq \beta'}^{\mathsf{N}_{\uparrow}} \mathbf{d}_{\alpha',\uparrow} \prod_{\alpha \neq \beta}^{\mathsf{N}_{\uparrow}} \mathbf{d}_{\alpha,\uparrow}^{\dagger} \prod_{\gamma=1}^{\mathsf{N}_{\downarrow}} \mathbf{d}_{\gamma\downarrow}^{\dagger} |0\rangle = \delta_{\beta\beta'}$$

And at the end:

$$\langle \mathbf{n}_{i\uparrow} \rangle = \sum_{\beta'} \sum_{\beta} (-1)^{\beta+1+\beta'+1} Q^{\dagger}_{\beta'i,\uparrow} Q_{i\beta,\uparrow} \delta_{\beta\beta'}$$

$$= \sum_{\alpha=1}^{N_{\uparrow}} Q_{i\alpha,\uparrow} Q^{\dagger}_{\alpha i,\uparrow}$$

$$(5.8)$$