The DMFT object of the CP-PAW code

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Contents

Chapter 1

Purpose and theoretical background

The purpose of the DMFT object is to prepare an interface to the solver for a quantum impurity in the context of dynamical mean-field theory. The derivations follow closely the paper of Blöchl, Pruschke and Potthoff[1], in the following referred to **BPP**.

1.1 Grand potential and density-matrix functional as starting point

The **grand potential** has the form[1]

$$
\Omega_{\beta,\mu}^{KB}[\hat{h} + \hat{W}] = \min_{|\psi_n\rangle, f_n \in [0,1]} \operatorname*{stat}_{\Lambda} \Bigg\{ \sum_n f_n \langle \psi_n | \hat{h} | \psi_n \rangle + \tilde{F}_{\beta}^{\hat{W}} \Big[\sum_n |\psi_n\rangle f_n \langle \psi_n| \Big] - \mu \sum_n f_n
$$
$$
- \sum_{m,n} \Lambda_{m,n} \Big(\langle \psi_n | \psi_m \rangle - \delta_{m,n} \Big) \Bigg\} \tag{1.1}
$$

where the **density-matrix functional** $\tilde{F}_{\beta}^{\hat{W}}$ is expressed[1] by the **Luttinger-Ward functional** [2] $\Phi^{LW}[\boldsymbol{G}, \hat{W}]$ as

$$
\tilde{F}_{\beta}^{\hat{W}}[\boldsymbol{\rho}] = \frac{1}{\beta} \operatorname{Tr} \Big[\boldsymbol{\rho} \ln(\boldsymbol{\rho}) + (\mathbf{1} - \boldsymbol{\rho}) \ln(\mathbf{1} - \boldsymbol{\rho}) \Big]
$$
$$
+ \operatorname*{stat}_{\boldsymbol{h}'} \operatorname*{stat}_{\boldsymbol{G}, \boldsymbol{\Sigma}} \Bigg\{ \Phi_{\beta}^{LW}[\boldsymbol{G}, \hat{W}] - \frac{1}{\beta} \sum_{\nu} \operatorname{Tr} \Big\{ \ln \Big[\mathbf{1} - \big(i\hbar\omega_{\nu} + \mu \big) \mathbf{1} - \bar{\boldsymbol{h}} \big)^{-1} \big(\boldsymbol{h}' + \boldsymbol{\Sigma}(i\omega_{\nu}) - \bar{\boldsymbol{h}} \big) \Big]
$$
$$
+ (\boldsymbol{h}' + \boldsymbol{\Sigma}(i\omega_{\nu}) - \bar{\boldsymbol{h}}) \boldsymbol{G}(i\omega_{\nu}) - \Big[\boldsymbol{G}(i\omega_{\nu}) - \big(i\hbar\omega_{\nu} + \mu \big) \mathbf{1} - \bar{\boldsymbol{h}} \big)^{-1} \Big] \big(\boldsymbol{h}' - \bar{\boldsymbol{h}} \big) \Big\} \Bigg\} \tag{1.2}
$$

Here, $|\psi_n\rangle$ are one-particle wave functions. They play the role of **natural orbitals**, the eigenstates of the **one-particle density matrix** $\boldsymbol{\rho}$. f_n are the **occupations**, the eigenvalues of the one-particle density matrix. The orthonormality of the natural orbitals is enforced with the method of Lagrange multipliers. The Lagrange multipliers are Λ. The chemical potential is μ and $\beta = 1/(k_B T)$. The full Hamiltonian consists of a non-interacting part $\hat{h} = \frac{\hat{p}^2}{2m_0} + \hat{v}_{ext}$ and an electron-electron interaction $\hat{W}$.

With $\operatorname{stat}_x Y$, we denote the **stationary condition**, which requires that the partial derivative of Y with respect to the variable x vanishes. It explicitly does not require the stationary point to be an extremum.

$\boldsymbol{G}(i\omega)$ is the Green's function and $\boldsymbol{\Sigma}(i\omega_\nu)$ is the self energy. The Matsubara sum runs over the **Matsubara frequencies** (see appendix A on p. 38)

$$\omega_\nu = (2\nu - 1)\frac{\pi}{\hbar\beta} \qquad \text{for } \nu \in \mathbb{Z} \tag{1.3}$$

h' are the Lagrange multipliers for the **density-matrix constraint**.

$$\boldsymbol{\rho} = \frac{1}{\beta}\sum_\nu e^{i\beta\hbar\omega_\nu 0^+} \boldsymbol{G}(i\omega_\nu) \tag{1.4}$$

The Hamiltonian $\bar{\boldsymbol{h}}$ is a non-local Hamiltonian directly related to the one-particle density matrix via (see Eq. BPP24)

$$\bar{\boldsymbol{h}} = \mu\mathbf{1} + k_B T \ln\left[\frac{\mathbf{1} - \boldsymbol{\rho}}{\boldsymbol{\rho}}\right] \tag{1.5}$$

In practice, we perform calculations at fixed particle number. Therefore, we calculate the **Helmholtz potential** by adding the term with the particle number N to the grand potential.

$$\begin{aligned}
A_{\beta,N}[\hat{h} + \hat{W}] &= \underset{\mu}{\text{stat}}\left\{\Omega_{\beta,\mu} + \mu N\right\} \\
&= \underset{|\psi_n\rangle, f_n \in [0,1]}{\min} \underset{\mu,\Lambda}{\text{stat}}\left\{\sum_n f_n\langle\psi_n|\hat{h}|\psi_n\rangle + Q_\beta^{\hat{W}}\left[\sum_n |\psi_n\rangle f_n \langle\psi_n|\right]\right. \\
&\quad + \frac{1}{\beta}\sum_n\left[f_n\ln(f_n) + (1 - f_n)\ln(1 - f_n)\right] \\
&\quad \left. -\mu\left[\sum_n f_n - N\right] - \sum_{m,n}\Lambda_{m,n}\left(\langle\psi_n|\psi_m\rangle - \delta_{m,n}\right)\right\}
\end{aligned} \tag{1.6}$$

where $Q_\beta^{\hat{W}}$ is the density-matrix functional without the entropy contribution of a non-interacting electron gas with the same density matrix. The entropy contribution is taken care of with the **Mermin functional**[3] to describe DFT calculations with electrons at finite temperature.

$$\begin{aligned}
Q_\beta^{\hat{W}}[\boldsymbol{\rho}] &= \tilde{F}_\beta^{\hat{W}}[\boldsymbol{\rho}] - \frac{1}{\beta}\text{Tr}\left[\boldsymbol{\rho}\ln(\boldsymbol{\rho}) + (\mathbf{1} - \boldsymbol{\rho})\ln(\mathbf{1} - \boldsymbol{\rho})\right] \\
&= \underset{h'}{\text{stat}}\underset{\boldsymbol{G},\boldsymbol{\Sigma}}{\text{stat}}\left\{\Phi_\beta^{LW}[\boldsymbol{G},\hat{W}] - \frac{1}{\beta}\sum_\nu \text{Tr}\left\{\ln\left[\mathbf{1} - \left(i\hbar\omega_\nu + \mu\right)\mathbf{1} - \bar{\boldsymbol{h}}\right)^{-1}\left(h' + \boldsymbol{\Sigma}(i\omega_\nu) - \bar{\boldsymbol{h}}\right)\right]\right.\right. \\
&\quad \left.\left. + (h' + \boldsymbol{\Sigma}(i\omega_\nu) - \bar{\boldsymbol{h}})\boldsymbol{G}(i\omega_\nu) - \left[\boldsymbol{G}(i\omega_\nu) - \left(i\hbar\omega_\nu + \mu\right)\mathbf{1} - \bar{\boldsymbol{h}}\right)^{-1}\right]\left(h' - \bar{\boldsymbol{h}}\right)\right\}\right\}
\end{aligned} \tag{1.7}$$

1.2 Separate out static correlations: Towards DFT+

In appendix D it is shown that the correlation contribution $Q_\beta^{\hat{W}}$ can be divided into one part having a frequency-dependent **self energy** and several contributions having a frequency-independent self energy. When we talk about a self energy in the context of the density-matrix functional theory, we refer to the construction of the density matrix functional from an optimization of Green's functions.[1] The Luttinger-Ward functional with frequency-independent self energy can

be expressed by the density matrix alone, that is, the Green's function enters always in the form of the integral

$$\frac{1}{\beta}\sum_\nu \boldsymbol{G}(i\omega_\nu)e^{i\hbar\omega\beta0^+} \tag{1.8}$$

According to appendix D on p. 57, this notion allows us to split the interaction contribution $Q^{\hat{W}}$ into different parts as

$$Q^{\hat{W}}[\boldsymbol{\rho}] \approx Q^{DFT,\hat{W}}[\boldsymbol{\rho}] - Q^{DFT,\hat{W}_1}[\boldsymbol{\rho}] + Q^{HF,\hat{W}_1}[\boldsymbol{\rho}] - Q^{HF,\hat{W}_2}[\boldsymbol{\rho}] + Q^{\hat{W}_2}[\boldsymbol{\rho}] \tag{1.9}$$

of which only the last term has a frequency-dependent self energy.

In order to keep the computational effort at a reasonable level, we consider three different interactions, namely the full interaction $\hat{W}$, a simplified interaction $\hat{W}_1$ used for static correlations, and interaction $\hat{W}_2$, which is even further simplified, and which is used for dynamic correlations. The full interaction is treated on the most simple level of the description, namely DFT, while the most complex many-particle treatment is limited to the most approximate interaction, namely $\hat{W}_2$.

With a density-functional contribution $Q^{DFT,\hat{W}}[\hat{\rho}]$ acting as double-counting term and a screened Hartree-Fock contribution $Q^{HF,\hat{W}}[\hat{\rho}]$ described later, we obtain

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HELMHOLTZ POTENTIAL

$$
\begin{aligned}
A_{\beta,N}[\hat{h}+\hat{W}] = \min_{|\psi_n\rangle, f_n\in[0,1]} \operatorname*{stat}_{\mu,\Lambda} \Bigg\{ &\sum_n f_n \langle\psi_n| \frac{\hat{\vec{p}}^2}{2m_e} |\psi_n\rangle + \int d^3r\, n(\vec{r}) v_{ext}(\vec{r}') \\
&+ \frac{1}{2}\int d^3r \int d^3r' \frac{e^2 n(\vec{r})n(\vec{r}')}{4\pi\epsilon_0|\vec{r}-\vec{r}'|} + E_{xc}[n] + \frac{1}{\beta}\sum_n \Big[f_n\ln(f_n) + (1-f_n)\ln(1-f_n) \Big] \\
&+ \underbrace{Q^{HF,\hat{W}_1}_\beta[\boldsymbol{\rho}] - Q^{DFT,\hat{W}_1}_\beta[\boldsymbol{\rho},n]}_{\text{local hybrid functional}} \quad + \quad \underbrace{Q^{\hat{W}_2}_\beta[\boldsymbol{\rho}] - Q^{HF,\hat{W}_2}_\beta[\boldsymbol{\rho}]}_{Q^{dyn,\hat{W}_2}_\beta[\boldsymbol{\rho}]} \\
&- \mu\Big[\sum_n f_n - N\Big] - \sum_{m,n}\Lambda_{m,n}\Big(\langle\psi_n|\psi_m\rangle - \delta_{m,n}\Big) \Bigg\}
\end{aligned}
\tag{1.10}
$$

where

$$n(\vec{r},\sigma,\sigma') = \sum_n \langle\vec{r},\sigma|\psi_n\rangle f_n \langle\psi|\vec{r},\sigma'\rangle$$

$$n(\vec{r}) = \sum_\sigma n(\vec{r},\sigma,\sigma)$$

$$\rho_{a,b} = \sum_n \langle\pi_a|\psi_n\rangle f_n \langle\psi|\pi_b\rangle \tag{1.11}$$

We distinguish two different corrections:

1. a screened Hartree-Fock correction with an interaction $\hat{W}_1$.

The Hartree-Fock term $Q_\beta^{HF,\hat{W}}$ is equal to $Q_\beta^{\hat{W}}$ when only the first-order term of the Luttinger-Ward functional in the interaction is considered. It is obtained as (BPP-Eq.43)

$$Q_\beta^{HF,\hat{W}}[\rho] = \frac{1}{2} \sum_{a,b,c,d} U_{a,b,d,c} \left[\rho_{d,a}\rho_{c,b} - \rho_{c,a}\rho_{d,b} \right] \quad (1.12)$$

(See also appendix E on p.60.)

The first term, E_H, is the **Hartree energy** and the second term, E_X, is the **exchange energy**

$$E_H = \frac{1}{2} \sum_{a,b,c,d} U_{a,b,d,c}\rho_{d,a}\rho_{c,b}$$

$$E_X = -\frac{1}{2} \sum_{a,b,c,d} U_{a,b,d,c}\rho_{c,a}\rho_{d,b} \quad (1.13)$$

For the Hartree-Fock contribution we restrict the U-tensor to on-site contributions and certain bond-terms. In the spirit of the hybrid functionals or the GW method, we scale the U-tensor. The neglect of U-tensor elements that do not reside on an atom pair is motivated by the fact that screening becomes stronger with increasing distance. Part of this approximation is to neglect the interactions not captured by the local orbital basis. This term is evaluated in the `paw_lmto`-object.

2. a **DFT double counting term** $Q_\beta^{DFT,\hat{W}_1}$:

$$Q^{DFT,\hat{W}}[\hat{\rho}] = \underbrace{\frac{1}{2} \int d^3r \int d^3r' \frac{e^2 n(\vec{r})n(\vec{r}')}{4\pi\epsilon_0|\vec{r}-\vec{r}'|}}_{\frac{1}{2}\sum_{a,b,c,d}U_{a,b,d,c}\rho_{d,a}\rho_{c,b}} + \underbrace{E_{xc}[n] + T_s[n] - \text{Tr}[\frac{\hat{\vec{p}}^2}{2m_e}\hat{\rho}]}_{U_{xc}}, \quad (1.14)$$

where $n(r) = \langle \vec{r}|\hat{\rho}|\vec{r}\rangle$. U_{xc} is the interaction part at full interaction strength.

In practice the we use E_{xc} instead of U_{xc}

The term $Q_\beta^{DFT,\hat{W}_1}$ describes the DFT contribution when the interaction is limited to $\hat{W}_1$. The basic ideas behind the double-counting correction have been described in a previous paper[4].

Both, the Hartree-Fock term and the DFT double-counting term contain the same Hartree energy, which cancels exactly. Therefore the Hartree terms are not evaluated.

3. a **dynamic-correlation correction**

$$Q_\beta^{dyn,\hat{W}_2} \overset{\text{def}}{=} Q_\beta^{\hat{W}_2} - Q_\beta^{HF,\hat{W}_2} \quad (1.15)$$

contains an interaction term calculated on the highest level of theory such as a many-body calculation. The corresponding Hartree-Fock term is immediately substracted as double counting correction.

The dynamic-correlation correction uses an interaction $\hat{W}_2$. In the spirit of the local approximation, the interaction of this term is limited to on-site terms only. The evaluation of the dynamic correlations is the only contribution that requires expensive many-particle calculations.

This term is further elaborated in section 1.3

1.3   Dynamic-correlation correction

The dynamical term $Q^{\hat{W}}_{\text{dyn},\beta}$ is simply the difference of the complete term minus the Hartree-Fock contribution.

$$Q^{\hat{W}_2}_{dyn,\beta}[\boldsymbol{\rho}] = \tilde{F}^{\hat{W}_2}_\beta[\boldsymbol{\rho}] - \frac{1}{\beta}\text{Tr}\Big[\boldsymbol{\rho}\ln(\boldsymbol{\rho}) + (\mathbf{1} - \boldsymbol{\rho})\ln(\mathbf{1} - \boldsymbol{\rho})\Big] - \frac{1}{2}\sum_{a,b,c,d} U^{\hat{W}_2}_{a,b,d,c}\Big[\rho_{d,a}\rho_{c,b} - \rho_{c,a}\rho_{d,b}\Big]$$

$$= \underset{\boldsymbol{h}'_{dyn}}{\text{stat}}\ \underset{\boldsymbol{G},\boldsymbol{\Sigma}_{dyn}}{\text{stat}}\ \Big\{\Phi^{LW}_\beta[\boldsymbol{G},\hat{W}_2] - \Phi^{HF,LW}_\beta[\boldsymbol{G},\hat{W}_2]$$

$$-\frac{1}{\beta}\sum_\nu \text{Tr}\Big\{\ln\Big[\mathbf{1} - \big((i\hbar\omega_\nu + \mu)\mathbf{1} - \bar{\boldsymbol{h}}\big)^{-1}\big(\boldsymbol{h}'_{dyn} + \boldsymbol{\Sigma}_{dyn}(i\omega_\nu) - \bar{\boldsymbol{h}}\big)\Big]$$

$$+(\boldsymbol{h}'_{dyn} + \boldsymbol{\Sigma}_{dyn}(i\omega_\nu) - \bar{\boldsymbol{h}})\boldsymbol{G}(i\omega_\nu) - \Big[\boldsymbol{G}(i\omega_\nu) - \big(i\hbar\omega_\nu + \mu)\mathbf{1} - \bar{\boldsymbol{h}}\big)^{-1}\Big]\big(\boldsymbol{h}'_{dyn} - \bar{\boldsymbol{h}}\big)\Big\}\Big\}$$

$$\tag{1.16}$$

We introduce a new variable

$$\boldsymbol{\Gamma} \overset{\text{def}}{=} \bar{\boldsymbol{h}} - \boldsymbol{h}'_{dyn} \tag{1.17}$$

so that

DYNAMIC CORRELATION CORRECTION

$$Q^{\hat{W}_2}_{dyn,\beta}[\boldsymbol{\rho}] = \underset{\boldsymbol{\Gamma}}{\text{stat}}\ \underset{\boldsymbol{G},\boldsymbol{\Sigma}_{dyn}}{\text{stat}}\ \Big\{\Phi^{LW}_\beta[\boldsymbol{G},\hat{W}_2] - \Phi^{HF,LW}_\beta[\boldsymbol{G},\hat{W}_2]$$

$$-\frac{1}{\beta}\sum_\nu \text{Tr}\Big\{\ln\Big[\mathbf{1} - \big((i\hbar\omega_\nu + \mu)\mathbf{1} - \bar{\boldsymbol{h}}\big)^{-1}\big(\boldsymbol{\Sigma}_{dyn}(i\omega_\nu) - \boldsymbol{\Gamma}\big)\Big]$$

$$+(\boldsymbol{\Sigma}_{dyn}(i\omega_\nu) - \boldsymbol{\Gamma})\boldsymbol{G}(i\omega_\nu) + \Big[\boldsymbol{G}(i\omega_\nu) - \big(i\hbar\omega_\nu + \mu)\mathbf{1} - \bar{\boldsymbol{h}}\big)^{-1}\Big]\boldsymbol{\Gamma}\Big\}\Big\}$$

$$\tag{1.18}$$

If the Luttinger-Ward functional is expressed by Feynman diagrams, we can simply avoid the Hartree and the exchange term instead of subtracting the exchange contribution externally.

According to appendix D, the Hartree-Fock contribution can also be moved out of the variational part, where it can be calculated directly from the density matrix. In that case, however, the values of $\boldsymbol{h}'_{dyn}$ and $\boldsymbol{\Sigma}_{dyn}$ have different values than if they are kept inside the variational part. It is beneficial to keep it inside the variational principle, because the values of the self energy and the Lagrange multipliers will be smaller.

Derivative of the dynamical correlation

Let us form the derivative of $Q^{\hat{W}_2}_{\text{dyn},\beta}[\boldsymbol{\rho}]$ in all detail to avoid using inappropriate assumptions.

In order to simplify the discussion we introduce the non-interacting density matrix, which produces a given density matrix as

$$\bar{\boldsymbol{G}}(i\omega_\nu) = \left[(i\hbar\omega_\nu + \mu)\boldsymbol{1} - \bar{\boldsymbol{h}}\right]^{-1} \tag{1.19}$$

with $\bar{\boldsymbol{h}}$ defined in Eq. 1.5 as a functional of the density matrix.

During the derivation, we use the rule for derivatives of an inverse of a matrix[1] $d(\bar{\boldsymbol{G}}^{-1}) = +\bar{\boldsymbol{G}}\,d\bar{\boldsymbol{h}}\,\bar{\boldsymbol{G}}$.

We form the first variation with respect to the density matrix.

$$
\begin{aligned}
d\mathcal{Q}_\beta^{dyn,\hat{W}_2} = &-\frac{1}{\beta}\sum_\nu \text{Tr}\Bigg\{ \left(-\frac{\beta\delta\Phi_\beta^{LW}}{\delta\boldsymbol{G}(i\omega_\nu)} + \frac{\beta\delta\Phi_{\beta,HF}^{LW}}{\delta\boldsymbol{G}(i\omega_\nu)}\right)d\boldsymbol{G} \\
&+ \left[\boldsymbol{1} - \bar{\boldsymbol{G}}\left(\boldsymbol{\Sigma}_{dyn} - \boldsymbol{\Gamma}\right)\right]^{-1}\left(-d\bar{\boldsymbol{G}}(\boldsymbol{\Sigma}_{dyn} - \boldsymbol{\Gamma}) - \bar{\boldsymbol{G}}(d\boldsymbol{\Sigma}_{dyn} - d\boldsymbol{\Gamma})\right) \\
&+ (d\boldsymbol{\Sigma}_{dyn} - \underbrace{d\boldsymbol{\Gamma}}_{(A)})\boldsymbol{G} + (\boldsymbol{\Sigma}_{dyn} - \underbrace{\boldsymbol{\Gamma}}_{(B)})d\boldsymbol{G} + (\underbrace{d\boldsymbol{G}}_{(B)} - d\bar{\boldsymbol{G}})\boldsymbol{\Gamma} + (\underbrace{\boldsymbol{G}}_{(A)} - \bar{\boldsymbol{G}})d\boldsymbol{\Gamma}\Bigg\} \\
= &-\frac{1}{\beta}\sum_\nu \text{Tr}\Bigg\{ \left[\boldsymbol{\Sigma}_{dyn} - \frac{\beta\delta\Phi_\beta^{LW}}{\delta\boldsymbol{G}(i\omega_\nu)} + \frac{\beta\delta\Phi_{\beta,HF}^{LW}}{\delta\boldsymbol{G}(i\omega_\nu)}\right]d\boldsymbol{G} \\
&+ \left[-\left[\boldsymbol{1} - \bar{\boldsymbol{G}}\left(\boldsymbol{\Sigma}_{dyn} - \boldsymbol{\Gamma}\right)\right]^{-1}\bar{\boldsymbol{G}} + \boldsymbol{G}\right]d\boldsymbol{\Sigma}_{dyn} \\
&+ \left[\left[\boldsymbol{1} - \bar{\boldsymbol{G}}\left(\boldsymbol{\Sigma}_{dyn} - \boldsymbol{\Gamma}\right)\right]^{-1}\bar{\boldsymbol{G}} - \bar{\boldsymbol{G}}\right]d\boldsymbol{\Gamma} \\
&- \left[\bar{\boldsymbol{G}}(\boldsymbol{\Sigma}_{dyn} - \boldsymbol{\Gamma})\left[\boldsymbol{1} - \bar{\boldsymbol{G}}\left(\boldsymbol{\Sigma}_{dyn} - \boldsymbol{\Gamma}\right)\right]^{-1}\bar{\boldsymbol{G}}\right]d\bar{\boldsymbol{h}} \\
&- d\bar{\boldsymbol{G}}\boldsymbol{\Gamma}\Bigg\} \\
= &-\frac{1}{\beta}\sum_\nu \text{Tr}\Bigg\{ \left[\boldsymbol{\Sigma}_{dyn} - \frac{\beta\delta\Phi_\beta^{LW}}{\delta\boldsymbol{G}(i\omega_\nu)} + \frac{\beta\delta\Phi_{\beta,HF}^{LW}}{\delta\boldsymbol{G}(i\omega_\nu)}\right]d\boldsymbol{G} \\
&+ \left[\boldsymbol{G} - \left[\boldsymbol{1} - \bar{\boldsymbol{G}}\left(\boldsymbol{\Sigma}_{dyn} - \boldsymbol{\Gamma}\right)\right]^{-1}\bar{\boldsymbol{G}}\right]d\boldsymbol{\Sigma}_{dyn} \\
&+ \left[\left[\boldsymbol{1} - \bar{\boldsymbol{G}}\left(\boldsymbol{\Sigma}_{dyn} - \boldsymbol{\Gamma}\right)\right]^{-1}\bar{\boldsymbol{G}} - \bar{\boldsymbol{G}}\right]\left(d\boldsymbol{\Gamma} - d\bar{\boldsymbol{h}}\right) \\
&+ \underbrace{\left[\left[\boldsymbol{1} - \bar{\boldsymbol{G}}\left(\boldsymbol{\Sigma}_{dyn} - \boldsymbol{\Gamma}\right)\right]^{-1}\bar{\boldsymbol{G}} - \bar{\boldsymbol{G}} - \bar{\boldsymbol{G}}(\boldsymbol{\Sigma}_{dyn} - \boldsymbol{\Gamma})\left[\boldsymbol{1} - \bar{\boldsymbol{G}}\left(\boldsymbol{\Sigma}_{dyn} - \boldsymbol{\Gamma}\right)\right]^{-1}\bar{\boldsymbol{G}}\right]}_{=-\bar{\boldsymbol{G}}+[\boldsymbol{1}-\bar{\boldsymbol{G}}(\boldsymbol{\Sigma}_{dyn}-\boldsymbol{\Gamma})]\left[\boldsymbol{1}-\bar{\boldsymbol{G}}\left(\boldsymbol{\Sigma}_{dyn}-\boldsymbol{\Gamma}\right)\right]^{-1}=0}d\bar{\boldsymbol{h}} \\
&- d\bar{\boldsymbol{G}}\boldsymbol{\Gamma}\Bigg\} \tag{1.21}
\end{aligned}
$$

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[1]

$$\boldsymbol{A}\boldsymbol{A}^{-1} = \boldsymbol{1} \quad \Rightarrow \quad \left(d\boldsymbol{A}\right)\boldsymbol{A}^{-1} + \boldsymbol{A}\left(d\boldsymbol{A}^{-1}\right) = 0 \quad \Rightarrow \quad d\boldsymbol{A}^{-1}) = -\boldsymbol{A}^{-1}\left(d\boldsymbol{A}\right)\boldsymbol{A}^{-1} \tag{1.20}$$

Thus we obtain

$$
\begin{aligned}
d\mathcal{Q}_\beta^{dyn,\hat{W}_2} = & -\frac{1}{\beta}\sum_\nu \mathrm{Tr}\left\{ \left[\mathbf{\Sigma}_{dyn}(i\omega_\nu) - \frac{\beta\delta\Phi_\beta^{LW}}{\delta\mathbf{G}(i\omega_\nu)} + \frac{\beta\delta\Phi_{\beta,HF}^{LW}}{\delta\mathbf{G}(i\omega_\nu)} \right] d\mathbf{G}(i\omega_\nu) \right\} \\
& -\frac{1}{\beta}\sum_\nu \mathrm{Tr}\left\{ \left[\mathbf{G}(i\omega_\nu) - \left[\mathbf{1} - \bar{\mathbf{G}}(i\omega_\nu)\left(\mathbf{\Sigma}_{dyn}(i\omega_\nu) - \mathbf{\Gamma}\right) \right]^{-1} \bar{\mathbf{G}}(i\omega_\nu) \right] d\mathbf{\Sigma}_{dyn}(i\omega_\nu) \right\} \\
& -\frac{1}{\beta}\sum_\nu \mathrm{Tr}\left\{ \left[\mathbf{1} - \bar{\mathbf{G}}\left(\mathbf{\Sigma}_{dyn} - \mathbf{\Gamma}\right) \right]^{-1}\bar{\mathbf{G}} - \bar{\mathbf{G}} \right\}\left(d\mathbf{\Gamma} - d\bar{\mathbf{h}} \right) \\
& +\mathrm{Tr}\left[\mathbf{\Gamma}\, d\boldsymbol{\rho} \right]
\end{aligned}
\tag{1.22}
$$

Thus the stationary conditions are

- the definition of the dynamic self energy from $\partial\mathcal{Q}_\beta^{dyn,\hat{W}_2}/\partial\mathbf{G}$

$$
\mathbf{\Sigma}_{dyn}(i\omega_\nu) = \frac{\beta\delta\Phi_\beta^{LW}}{\delta\mathbf{G}(i\omega_\nu)} - \frac{\beta\delta\Phi_{\beta,HF}^{LW}}{\delta\mathbf{G}(i\omega_\nu)}
\tag{1.23}
$$

- Dyson's equation defining the Green's function from $\partial\mathcal{Q}_\beta^{dyn,\hat{W}_2}/\partial\mathbf{\Sigma}$

$$
\begin{aligned}
\mathbf{G}(i\omega_\nu) &= \left[\mathbf{1} - \bar{\mathbf{G}}(i\omega_\nu)\left(\mathbf{\Sigma}_{dyn}(i\omega_\nu) - \mathbf{\Gamma}\right) \right]^{-1}\bar{\mathbf{G}}(i\omega_\nu) \\
&= \left[(i\hbar\omega_\nu + \mu)\mathbf{1} - \left(\bar{\mathbf{h}} - \mathbf{\Gamma}\right) - \mathbf{\Sigma}_{dyn}(i\omega_\nu) \right]^{-1}\bar{\mathbf{G}}(i\omega_\nu)
\end{aligned}
\tag{1.24}
$$

- and the density-matrix constraint from $\partial\mathcal{Q}_\beta^{dyn,\hat{W}_2}/\partial\mathbf{\Gamma}$

$$
\frac{1}{\beta}\sum_\nu \mathrm{Tr}\left\{ \underbrace{\left[\mathbf{1} - \bar{\mathbf{G}}\left(\mathbf{\Sigma}_{dyn} - \mathbf{\Gamma}\right) \right]^{-1}\bar{\mathbf{G}}}_{\mathbf{G}} - \bar{\mathbf{G}} \right\} = 0
\tag{1.25}
$$

If the stationary conditions with respect to Green's function, self energy and $\mathbf{\Gamma}$ are obeyed, the derivative with respect to the density matrix is simply the matrix $\mathbf{\Gamma}$.

DENSITY-MATRIX DERIVATIVE OF THE DYNAMIC CORRELATION CORRECTION

$$
\frac{\delta\mathbf{Q}_\beta^{dyn,\hat{W}_2}[\boldsymbol{\rho}]}{\delta\boldsymbol{\rho}} = \mathbf{\Gamma}
\tag{1.26}
$$

The matrix $\mathbf{\Gamma}$ replaces $\mathbf{h}'$ as Lagrange parameter for the density matrix constraint. It vanishes in the Hartree-Fock approximation as seen from BPP-Eq.45-46[1]. Instead of the Hartree-Fock self energy $\mathbf{\Sigma}^{HF}$, we could have taken any other static self energy.

One may ask, where the self energy contribution from static correlations is, because both, $\mathbf{\Sigma}$ and $\mathbf{\Sigma}^{HF}$ mentioned here refer to the second interaction using $\hat{W}_2$. The Terms related to $\hat{W}_1$ are contained in the density matrix and $\bar{\mathbf{h}}$.

Stationary conditions for wave functions and occupations

Let us now explore the stationary conditions in Eq. 1.10: We use the representation of the wave functions $|\psi_n\rangle = \sum_a |\chi_a\rangle\langle\pi_a|\psi_n\rangle$ in terms of local orbitals $|\chi_a\rangle$.

$$\left[\frac{\hat{\bar{p}}^2}{2m_e} + v_{ext} + v_{Hartree} + v_{xc} + \sum_{a,b}|\pi_a\rangle\left(\frac{\delta Q_{HF,\beta}^{\hat{W}_1}}{\delta\rho_{a,b}} - \frac{\delta Q_{DFT,\beta}^{\hat{W}_1}}{\delta\rho_{a,b}} + \frac{\delta Q_{dyn,\beta}^{\hat{W}_2}}{\delta\rho_{a,b}}\right)\langle\pi_b|\right]|\psi_n\rangle$$
$$= \sum_m |\psi_m\rangle\Lambda_{m,n}\frac{1}{f_n} \tag{1.27}$$

$$\langle\psi_n|\left[\frac{\hat{\bar{p}}^2}{2m_e} + v_{ext} + v_{Hartree} + v_{xc} + \sum_{a,b}|\pi_a\rangle\left(\frac{\delta Q_{HF,\beta}^{\hat{W}_1}}{\delta\rho_{a,b}} - \frac{\delta Q_{DFT,\beta}^{\hat{W}_1}}{\delta\rho_{a,b}} + \frac{\delta Q_{dyn,\beta}^{\hat{W}_2}}{\delta\rho_{a,b}}\right)\langle\pi_b|\right]|\psi_n\rangle$$
$$- \mu + \frac{1}{\beta}\ln\left[\frac{f_n}{1-f_n}\right] = 0 \tag{1.28}$$

These equations specify the optimum density matrix as

EQUILIBRIUM DENSITY MATRIX

$$\hat{\rho} = \left[\hat{1} + e^{\beta(\hat{h}_{eff}-\mu)}\right]^{-1} \tag{1.29}$$

with the effective Hamiltonian

$$\hat{h}_{eff} = \frac{\hat{\bar{p}}^2}{2m_e} + v_{ext} + v_{Hartree} + v_{xc} + \sum_{a,b}|\pi_a\rangle\left(\underbrace{\frac{\delta Q_{HF,\beta}^{\hat{W}_1}}{\delta\rho_{a,b}} - \frac{\delta Q_{DFT,\beta}^{\hat{W}_1}}{\delta\rho_{a,b}}}_{\Delta\Sigma_{static}} + \underbrace{\frac{\delta Q_{dyn,\beta}^{\hat{W}_2}}{\delta\rho_{a,b}}}_{\Gamma_{b,a}}\right)\langle\pi_b|$$
$$\tag{1.30}$$

Note, that, in equilibrium, $\hat{h}_{eff} = \hat{\bar{h}}$. The latter defined in Eq. 1.5.

Eq. 1.29 can be veryfied from the stationary conditions by going into a basis of eigenstates of $\hat{h}_{eff}$.

The Hamiltonian $\hat{h}_{eff}$ has, like $\bar{h}$, no spectral information. It simply reflects the occupations. If an orbital obtains partial occupations due to quantum fluctuations[2], $\hat{h}_{eff}$ places this state near the Fermi level, where the Fermi distribution give it the desired occupation.

The spectral information is contained in the Hamiltonian

$$\hat{h}_{bare} = \frac{\hat{\bar{p}}^2}{2m_e} + v_{ext} + v_{Hartree} + v_{xc} \tag{1.31}$$

which reflects the Kohn-Sham energy levels. When the Green's function is calculated we will see that this Hamiltonian, respectively $\bar{\boldsymbol{h}} - \boldsymbol{\Gamma}$ acts as "non-interacting" Hamiltonian to which the self energy (including double counting) is added to give the quasi-particle spectrum.

---

[2]With quantum fluctuations we mean for example electron-hole pairs, which screen the bare interaction. Electron-hole pairs lead fractional occupations beyond the effect of thermal fluctuations.

1.4 Local orbitals

1.4.1 Projection onto local orbitals

In order to integrate DMFT into the DFT code, we define first a local basis set of orbitals $|\chi_a\rangle$. These orbitals are not orthogonal. The orbitals are spin orbitals, that is, each is a two-component wave function with a spin-up and a spin-down component. If the spin orbitals are eigenstates of $\hat{S}_z$, one or the other of the components vanishes.

The decomposition of the Kohn-Sham wave functions, which in the the context of rDMFT are the natural orbitals, is obtained via the projector functions $\langle\pi_a|$ as

$$|\psi_n\rangle = \sum_a |\chi_a\rangle\langle\pi_a|\psi_n\rangle + |\delta\psi_n\rangle \tag{1.32}$$

where the projector functions obey the bi-orthogonality condition

$$\langle\pi_a|\chi_b\rangle = \delta_{a,b} \ , \tag{1.33}$$

and where $|\delta\psi_n\rangle$ is a remainder which is left over if the local orbitals do not form a complete basis set. This remainder has the property

$$\langle\pi_a|\delta\psi_n\rangle = 0 \tag{1.34}$$

However, there is no orthogonality between the orbitals and the remainder, that is $\langle\chi_\alpha|\delta\phi_n\rangle \neq 0$.

In order to estimate the importance of the remainder, consider the following thought experiment: Perform a calculation with the self-consistent potential and introduce the constraints $\langle\pi_\alpha|\bar{\psi}_n\rangle = 0$ for all α. The constraints will push the wave functions up in energy. These wave functions serve as basis functions for the remainder $|\delta\psi_n\rangle = \sum_m |\bar{\psi}_m\rangle c_{m,n}$. If there are many constraints and there are no larger gaps between the atoms, the constrained wave functions $|\bar{\psi}_m\rangle$ will have high energies and therefore we can assume that they do not contribute much to the wave functions. As conclusion from our thought experiment comes the notion that we can assume the remainder to be unimportant, if there are many projectors and if they do not leave any large gaps in space.

1.4.2 Energy correction

Here we consider changes of the correlation corrections when we move from a Bra-Ket notation to a matrix notation.

$$Q_\beta^{\hat{W}}[\hat{\rho}] = Q_\beta^{\hat{W}}\left[\sum_n |\psi_n\rangle f_n \langle\psi_n|\right] = Q_\beta^{\hat{W}}\left[\sum_{a,b} |\chi_a\rangle \underbrace{\left(\sum_n \langle\pi_a|\psi_n\rangle f_n \langle\psi_n|\pi_b\rangle\right)}_{\rho_{a,b}} \langle\chi_b|\right] \tag{1.35}$$

Below we consider also the energy contribution as functional of the density matrix in matrix form

$$Q_\beta^{\hat{W}}[\boldsymbol{\rho}] \stackrel{\text{def}}{=} Q_\beta^{\hat{W}}\left[\sum_{a,b} |\chi_a\rangle \rho_{a,b} \langle\chi_b|\right] \tag{1.36}$$

The derivatives are

$$\frac{\delta Q_\beta^{\hat{W}}}{\delta \langle \psi_n |} \frac{1}{f_n} = \sum_{a,b} |\pi_b\rangle \langle \chi_b | \frac{\delta Q_\beta^{\hat{W}}}{\delta \hat{\rho}} | \chi_a \rangle \langle \pi_a | \psi_n \rangle$$

$$\frac{\delta Q_\beta^{\hat{W}}}{\delta f_n} = \sum_{a,b} \langle \psi_n | \pi_b \rangle \langle \chi_b | \frac{\delta Q_\beta^{\hat{W}}}{\delta \hat{\rho}} | \chi_a \rangle \langle \pi_a | \psi_n \rangle \tag{1.37}$$

In the following we introduce a new symbol, namely

$$\frac{\delta Q_\beta^{\hat{W}}}{\delta \rho_{b,a}} \overset{\text{def}}{=} \langle \chi_b | \frac{\delta Q_\beta^{\hat{W}}}{\delta \hat{\rho}} | \chi_a \rangle \tag{1.38}$$

1.4.3   Overlap matrix

The overlap matrix is

$$S_{a,b} = \langle \chi_a | \chi_b \rangle \tag{1.39}$$

.

1.4.4   U-tensor

The interaction $\hat{W}$

$$\hat{W} = \frac{1}{2} \sum_{a,b,c,d} U_{a,b,d,c} \hat{c}_a^\dagger \hat{c}_b^\dagger \hat{c}_c \hat{c}_d \tag{1.40}$$

is expressed by the **U-tensor**

$$U_{a,b,c,d} = \sum_{\sigma,\sigma'} \int d^3r \int d^3r \, \frac{e^2 \chi_a^*(\vec{r},\sigma) \chi_b^*(\vec{r'},\sigma') \chi_c(\vec{r},\sigma) \chi_d(\vec{r'},\sigma')}{4\pi\epsilon_0 |\vec{r} - \vec{r'}|} \tag{1.41}$$

.

The U-tensor can then be approximated to yield $\hat{W}_1$ and $\hat{W}_2$. Typically, these approximations amount to multiplying matrix elements with scale factors and to leaving certain elements out completely.

1.4.5   Non-orthonormal orbitals

The main difference[4] between orthonormal and non-orthonormal basisets is that the commutator relation

$$\left[\hat{c}_a^\dagger, \hat{c}_b \right]_+ = \langle \pi_b | \pi_a \rangle \tag{1.42}$$

Feynman diagrams

A Feynmandiagram in terms of orthonormal orbitals can be transformed easily into any other one-particle basis, by introducing a unit matrix in the form $\boldsymbol{AA}^{-1}$ in between every Green's function and every interaction.

Let the original basis be $\{|\psi_n\rangle\}$ and a new basis $\{|\chi_a\rangle\}$ so that

$$|\psi_n\rangle = \sum_a |\chi_a\rangle\langle\pi_a|\psi_n\rangle \tag{1.43}$$

Then the Green's function has the form

$$\hat{G} = \sum_{m,n} |\psi_m\rangle\langle\psi_m|\hat{G}|\psi_n\rangle\langle\psi_n| = \sum_{a,b} |\chi_a\rangle\underbrace{\langle\pi_a|\hat{G}|\pi_b\rangle}_{G_{a,b}}\langle\chi_b| \tag{1.44}$$

Thus if the U-tensor is evaluated using the orbitals $|\chi\rangle$, it can directly be used with the Green's function $\langle\pi_a|\hat{G}|\pi_b\rangle$. The final result will be invariant if all sums are traced out.

1.4.6   Calculate $\bar{h}$ from the density matrix

The density matrix constraint has the form

$$\sum_\nu e^{i\hbar\omega_\nu\beta 0^+} G_{a,b}(i\omega_\nu) = \rho_{a,b} \quad \left(= \sum_n \langle\pi_a|\psi_n\rangle f_n\langle\psi_n|\pi_b\rangle\right) \tag{1.45}$$

Thus we look for a hamiltonian $\bar{h}$ whose non-interacting Greens function satisfies the constraint

$$\boldsymbol{\rho} = \sum_\nu e^{i\hbar\omega_\nu\beta 0^+} \left[(i\hbar\omega_\nu + \mu)\boldsymbol{S} - \bar{\boldsymbol{h}}\right]^{-1} \tag{1.46}$$

$$\Rightarrow \quad \sqrt{\boldsymbol{S}}\boldsymbol{\rho}\sqrt{\boldsymbol{S}} = \sum_\nu e^{i\hbar\omega_\nu\beta 0^+} \left[(i\hbar\omega_\nu + \mu)\boldsymbol{1} - (\boldsymbol{S})^{-\frac{1}{2}}\bar{\boldsymbol{h}}(\boldsymbol{S})^{-\frac{1}{2}}\right]^{-1} \tag{1.47}$$

In the next step we diagonalize $\sqrt{\boldsymbol{S}}\boldsymbol{\rho}\sqrt{\boldsymbol{S}}$

$$\sqrt{\boldsymbol{S}}\boldsymbol{\rho}\sqrt{\boldsymbol{S}}\boldsymbol{U} = \boldsymbol{U}\bar{\boldsymbol{f}} \tag{1.48}$$

which yields effective occupations $\bar{f}$. The eigenvalue equation is equivalent with the generalized eigenvalue problem

$$\boldsymbol{\rho}\left(\sqrt{\boldsymbol{S}}\boldsymbol{U}\right) = \boldsymbol{S}^{-1}\left(\sqrt{\boldsymbol{S}}\boldsymbol{U}\right)\bar{\boldsymbol{f}} \tag{1.49}$$

Now we calculate $\bar{\boldsymbol{\epsilon}}$ so that

$$\bar{\boldsymbol{f}} = \left[1 + e^{\beta(\bar{\epsilon}-\mu\boldsymbol{1})}\right]^{-1} \quad \Leftrightarrow \quad \bar{\boldsymbol{\epsilon}} = \mu\boldsymbol{1} + \frac{1}{\beta}\ln\left(\frac{\boldsymbol{1}-\bar{\boldsymbol{f}}}{\bar{\boldsymbol{f}}}\right) \tag{1.50}$$

Then we can represent $\bar{f}$ by the Matsubara sum

$$\bar{f} = \sum_{\nu} e^{i\hbar\omega_\nu\beta 0^+} \left[(i\hbar\omega_\nu + \mu)\mathbf{1} - \bar{\boldsymbol{\epsilon}} \right]^{-1} \tag{1.51}$$

In practice we face here a severe **N-representability problem**, namely that the occupations $\bar{f}_a$ do not necessarily lie within zero and one. For values outside the interval $]0, 1[$ the logarithm can no more be evaluated.[3] Therefore, we select a minimum and a maximum energy relative to the Fermi level and force the energies into this interval. Details of the implemented mapping are described in section 1.8.7 on page 31. This mapping affects those states that lie far from the Fermi level and thus are weakly correlated. Therefore, I expect the resulting error to be small.

This is a well-defined mapping of the initial density matrix onto one that is strictly N-representable. Thus all derivatives with respect to the original density matrix can be evaluated.

Thus we obtain

$$\boldsymbol{\rho} = \boldsymbol{S}^{-\frac{1}{2}}\boldsymbol{U}\bar{f}\boldsymbol{U}^\dagger\boldsymbol{S}^{-\frac{1}{2}} = \sum_{\nu} e^{i\hbar\omega_\nu\beta 0^+} \boldsymbol{S}^{-\frac{1}{2}}\boldsymbol{U} \left[(i\hbar\omega_\nu + \mu)\mathbf{1} - \bar{\boldsymbol{\epsilon}} \right]^{-1} \boldsymbol{U}^\dagger\boldsymbol{S}^{-\frac{1}{2}} \tag{1.52}$$

This yields

$$\begin{aligned}
\bar{\boldsymbol{G}} &= \boldsymbol{S}^{-\frac{1}{2}}\boldsymbol{U} \left[(i\hbar\omega_\nu + \mu)\mathbf{1} - \bar{\boldsymbol{\epsilon}} \right]^{-1} \boldsymbol{U}^\dagger\boldsymbol{S}^{-\frac{1}{2}} \\
&= \left[(i\hbar\omega_\nu + \mu)\boldsymbol{S} - \underbrace{\sqrt{\boldsymbol{S}}\boldsymbol{U}}_{\boldsymbol{V}}\bar{\boldsymbol{\epsilon}}\boldsymbol{U}^\dagger\sqrt{\boldsymbol{S}} \right]^{-1} = \left[(i\hbar\omega_\nu + \mu)\boldsymbol{S} - \underbrace{\boldsymbol{V}\bar{\boldsymbol{\epsilon}}\boldsymbol{V}^\dagger}_{\bar{h}} \right]^{-1}
\end{aligned} \tag{1.53}$$

Comparison yields

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HAMILTONIAN FOR DENSITY MATRIX CONSTRAINT

$$\bar{h} = \boldsymbol{V} \left[\mu\mathbf{1} + \frac{1}{\beta}\ln\left(\frac{\mathbf{1} - \bar{f}}{\bar{f}}\right) \right] \boldsymbol{V}^\dagger \tag{1.54}$$

where

$$\boldsymbol{\rho}\boldsymbol{V} = \boldsymbol{S}^{-1}\boldsymbol{V}\bar{f} \qquad \text{with} \qquad \boldsymbol{V}^\dagger\boldsymbol{S}^{-1}\boldsymbol{V} = \mathbf{1} \tag{1.55}$$

</div>

Derivatives

If the incompleteness is taken into account in the way suggested above, the density matrix functional not only depends on the density matrix, but also on the inverse overlap matrix.

$$F[\boldsymbol{\rho}, \boldsymbol{S}^{-1}] \tag{1.56}$$

---

[3]More accurately, the mapping $f \to \bar{\boldsymbol{\epsilon}}$ is no more unique.

The derivatives with respect to the natural orbitals and the occupations are

$$
\begin{aligned}
dF &= \frac{\partial F}{\partial \boldsymbol{\rho}} d\boldsymbol{\rho} + \frac{\partial F}{\partial \boldsymbol{S}^{-1}} d\boldsymbol{S}^{-1} \\
&= \sum_{\alpha,\beta} \frac{\partial F}{\partial \boldsymbol{\rho}_{\beta,\alpha}} \left(\sum_n \langle \pi_\beta | \delta\psi_n \rangle f_n \langle \psi_n | \pi_\alpha \rangle + \sum_n \langle \pi_\beta | \psi_n \rangle df_n \langle \psi_n | \pi_\alpha \rangle + \sum_n \langle \pi_\beta | \psi_n \rangle f_n \langle \delta\psi_n | \pi_\alpha \rangle \right) \\
&\quad + \frac{\partial F}{\partial \boldsymbol{S}^{-1}_{\beta,\alpha}} \left(\sum_n \langle \pi_\beta | \delta\psi_n \rangle \langle \psi_n | \pi_\alpha \rangle + \sum_n \langle \pi_\beta | \psi_n \rangle \langle \delta\psi_n | \pi_\alpha \rangle \right) \\
&= \sum_n df_n \left(\sum_{\alpha,\beta} \langle \psi_n | \pi_\alpha \rangle \frac{\partial F}{\partial \boldsymbol{\rho}_{\beta,\alpha}} \langle \pi_\beta | \psi_n \rangle \right) \\
&\quad + \sum_n f_n \sum_{\alpha,\beta} \langle \delta\psi_n | \pi_\alpha \rangle \left[\frac{\partial F}{\partial \boldsymbol{\rho}_{\beta,\alpha}} \langle \pi_\beta | \psi_n \rangle + \frac{\partial F}{\partial \boldsymbol{S}^{-1}_{\beta,\alpha}} \langle \pi_\beta | \psi_n \rangle \frac{1}{f_n} \right] + c.c.
\end{aligned}
\tag{1.57}
$$

Problematic is the term $\frac{1}{f_n}$, which diverges for empty states.

For fully occupied states the two terms, those containing the derivative with respect to the density matrix and those with respect to the inverse overlap, act simultaneously. I believe that the two terms together suppress changes in the total energy that are due that the natural orbitals overlap better with the correlated orbitals.

Let us single out the term that acts on empty or partially occupied states.

$$
\begin{aligned}
dF &= \sum_n df_n \sum_{\alpha,\beta} \left[\langle \psi_n | \pi_\alpha \rangle \left(\frac{\partial F}{\partial \boldsymbol{\rho}_{\beta,\alpha}} + \frac{\partial F}{\partial \boldsymbol{S}^{-1}_{\beta,\alpha}} \right) \langle \pi_\beta | \psi_n \rangle + \langle \psi_n | \pi_\alpha \rangle \frac{\partial F}{\partial \boldsymbol{S}^{-1}_{\beta,\alpha}} \langle \pi_\beta | \psi_n \rangle \frac{1-f_n}{f_n} \right] \\
&\quad + \sum_n df_n \underbrace{\sum_{\alpha,\beta} \left[-\langle \psi_n | \pi_\alpha \rangle \frac{\partial F}{\partial \boldsymbol{S}^{-1}_{\beta,\alpha}} \langle \pi_\beta | \psi_n \rangle - \langle \psi_n | \pi_\alpha \rangle \frac{\partial F}{\partial \boldsymbol{S}^{-1}_{\beta,\alpha}} \langle \pi_\beta | \psi_n \rangle \frac{1-f_n}{f_n} \right]}_{\text{correction}} \\
&\quad + \sum_n f_n \sum_{\alpha,\beta} \langle \delta\psi_n | \pi_\alpha \rangle \left[\left(\frac{\partial F}{\partial \boldsymbol{\rho}_{\beta,\alpha}} + \frac{\partial F}{\partial \boldsymbol{S}^{-1}_{\beta,\alpha}} \right) \langle \pi_\beta | \psi_n \rangle + \frac{\partial F}{\partial \boldsymbol{S}^{-1}_{\beta,\alpha}} \langle \pi_\beta | \psi_n \rangle \frac{1-f_n}{f_n} \right] + c.c.
\end{aligned}
\tag{1.58}
$$

The term in the last line is a contribution to the force acting on the wave functions. The kohn-sham energies ϵ_n are usually determined from this force acting on the wave functions. In the present case, however, we need to add the term marked "correction" in the second line to the Kohn-Sham energies.

One potential remedy of the singularity for empty states is to replace $\frac{1-f}{f}$ by $1-f$. For states that are strongly occupied, that is for $f \to 1$ the two functions are similar. For weakly occupied states, that is for $f \to 0$ the term is there, but not divergent.

1.5   Variational parameters for the Green's function

Representation of the Green's function

The Green's function is expressed in a Bloch representation.

$$
\boldsymbol{G}_{\vec{t},\vec{t}'}(i\omega_\nu) = \frac{1}{N_k} \sum_{\vec{k}} \boldsymbol{G}_{\vec{k}}(i\omega_\nu) e^{i\vec{k}(\vec{t}-\vec{t}')}
\tag{1.59}
$$

where N_k is the number of $\vec{k}$ points on the chosen numerical grid in the first unit cell. $\boldsymbol{G}_{\vec{t},\vec{t}'}$ is a matrix with dimension equal to the number of local orbitals in a given unit cell, and it connects these orbitals in two unit cells specified by the translation vectors $\vec{t}$ and $\vec{t}$. Check the sign in the exponential!

The Green's function can be expressed by the values at the positive Matsubara frequencies up to a maximum value ω_x and the first three Laurent expansion terms.

$$\boldsymbol{G}_{\vec{k}}(i\omega_\nu) = \begin{cases} \boldsymbol{G}_{\vec{k}}(i\omega_\nu) & \text{for } 0 < \omega_\nu \leq \omega_x \\ \boldsymbol{G}_{\vec{k}}^\dagger(-i\omega_\nu) & \text{for } -\omega_x \leq \omega_\nu < 0 \\ \sum_{j=1,2} \frac{1}{(i\hbar\omega_\nu)^j} \mathcal{G}_{\vec{k}}^{(j)} & \text{for } |\omega_\nu| > \omega_x \end{cases} \tag{1.60}$$

where $\mathcal{G}_{\vec{k}}^{(0)} = \boldsymbol{S}_{\vec{k}}^{-1}$.

Variational parameters

However, we treat this representation as the derived form. By employing the stationary condition for the self energy, we obtain Dyson's equation, which expresses the Green's function by the self energy. Using the same stationary condition with respect to the Laurent expansion terms of the self energy, one obtaines a consisent definition for the Laurent expansion terms of the Green's function.

The parameters entering in the representation Eq. 1.60 of the Greens function given above are obtained from the fundamental variables as.

$$\boldsymbol{G}_{\vec{k}}(i\omega_\nu) = \left[(i\hbar\omega_\nu + \mu)\boldsymbol{S}_{\vec{k}} - \bar{\boldsymbol{h}}_{\vec{k}} - \left[\boldsymbol{\Sigma}_{dyn}(i\omega_\nu) - \boldsymbol{\Gamma}_k\right]\right]^{-1} \quad \text{for } 0 < \omega_\nu \leq \omega_x$$

$$\mathcal{G}_{\vec{k}}^{(1)} \overset{\text{Eq. } B.38}{=} \boldsymbol{S}_{\vec{k}}^{-1}$$

$$\mathcal{G}_{\vec{k}}^{(2)} \overset{\text{Eq. } B.38}{=} -\boldsymbol{S}_{\vec{k}}^{-1}\left[\mu\boldsymbol{S}_{\vec{k}} - \bar{\boldsymbol{h}}_{\vec{k}} + \boldsymbol{\Gamma}_{\vec{k}} - \mathcal{S}_{dyn}^{(0)}\right]\boldsymbol{S}_{\vec{k}}^{-1} \tag{1.61}$$

The leading order in the Laurent expansion of the Green's function is not a dynamical variable, because it does not depend on any of the variational parameters in the definition of the dynamical correlation.

Thus the self energy is treated as variable that is iteratively optimized. This optimization is guided by the derivative with respect to the Green's function.

$$\boldsymbol{\Sigma}_{dyn}(+) = \boldsymbol{\Sigma}_{dyn}(0) + \alpha\left[\left.\frac{\beta\delta\Phi^{LW,dyn}}{\delta\boldsymbol{G}}\right|_{\boldsymbol{G}[\boldsymbol{\Sigma}(0)]} - \boldsymbol{\Sigma}_{dyn}(0)\right] \tag{1.62}$$

The fundamental variables are

- the site-diagonal and therefore k-independent dynamic self energy $\boldsymbol{\Sigma}_{dyn,R}(i\omega_\nu) = \boldsymbol{\Sigma}_R(i\omega_\nu) - \boldsymbol{\Sigma}_{HF,R}(i\omega_\nu)$. The self energy for positive and negative Matsubara frequencies are related by a hermitean conjugation $\boldsymbol{\Sigma}_{dyn,R}(-i\omega_\nu) = \boldsymbol{\Sigma}_{dyn,R}^\dagger(i\omega_\nu)$

- the Hamiltonian $\bar{\boldsymbol{h}}_{\vec{k}}$, which produces the one-particle reduced density matrix as $\boldsymbol{\rho}_{\vec{k}} = \left[\boldsymbol{1} + e^{\beta(\bar{\boldsymbol{h}}_{\vec{k}} - \mu\boldsymbol{1})}\right]^{-1}$.

- the static correction $\boldsymbol{\Gamma}_{\vec{k}}$, that ensures that the original density matrix is obtained from the Green's function, if the dynamic self energy is taken into account.

From the site-diagonal self energies $\boldsymbol{\Sigma}_{dyn,R}$, we obtain the global self energy $\boldsymbol{\Sigma}_{dyn}$ as direct sum. The global self energy is formally a matrix that connects each orbital in a unit cell with each other one.

$$\boldsymbol{\Sigma}_{dyn}(i\omega_\nu) = \bigoplus_{R \in \text{unit cell}} \boldsymbol{\Sigma}_{dyn,R}(i\omega_\nu) \tag{1.63}$$

This self energy is independent of $\vec{k}$.

Local Green's function

Then local Green's function is obtained as Brillouin-zone integral

$$\boldsymbol{G}_R(i\omega_\nu) = \frac{1}{N_k} \sum_{\vec{k}} \boldsymbol{P}_R \boldsymbol{G}_{\vec{k}}(i\omega_\nu) \boldsymbol{P}_R^\dagger \tag{1.64}$$

where $\boldsymbol{P}_R$ is a non-square diagonal matrix, which projects the matrix onto the subspace of orbitals on a given site.

1.5.1 High-Freqency expansion of Matsubara sum

A consistent choice for the Laurent expansion for the Green's function and self energy has turned out to be non-trivial. The most consistent approach appears to write down an approximate form for the high-frequency tail of the Matsubara sum in the dynamic correlation correction, and to extract the Laurent expansion coefficients from the stationary conditions.

With the high-frequency tail, we obtain

$$\ln\left[\mathbf{1} - \bar{\boldsymbol{G}}\left(\boldsymbol{\Sigma} - \boldsymbol{\Gamma}\right)\right] + \left(\boldsymbol{\Sigma} - \boldsymbol{\Gamma}\right)\boldsymbol{G} + \left(\boldsymbol{G} - \bar{\boldsymbol{G}}\right)\boldsymbol{\Gamma}$$

$$= -\bar{\boldsymbol{G}}\left(\boldsymbol{\Sigma} - \boldsymbol{\Gamma}\right) - \sum_{n=2}^{\infty} \frac{1}{n}\left[\bar{\boldsymbol{G}}\left(\boldsymbol{\Sigma} - \boldsymbol{\Gamma}\right)\right]^n + \left(\boldsymbol{\Sigma} - \boldsymbol{\Gamma}\right)\boldsymbol{G} + \left(\boldsymbol{G} - \bar{\boldsymbol{G}}\right)\boldsymbol{\Gamma}$$

$$= \left(\boldsymbol{G} - \bar{\boldsymbol{G}}\right)\left(\boldsymbol{\Sigma} - \boldsymbol{\Gamma}\right) - \sum_{n=2}^{\infty} \frac{1}{n}\left[\bar{\boldsymbol{G}}\left(\boldsymbol{\Sigma} - \boldsymbol{\Gamma}\right)\right]^n + \underbrace{\left(\boldsymbol{G} - \bar{\boldsymbol{G}}\right)\boldsymbol{\Gamma}}_{\rightarrow\text{number constraint}}$$

$$= \left(\boldsymbol{G} - \bar{\boldsymbol{G}}\right)\boldsymbol{\Sigma} - \sum_{n=2}^{\infty} \frac{1}{n}\left[\bar{\boldsymbol{G}}\left(\boldsymbol{\Sigma} - \boldsymbol{\Gamma}\right)\right]^n \tag{1.65}$$

Side Remark:[4]

---

[4]In order to rationalize the form of the Kadanoff-Baym functional, we look for a functional X , that provides Dyson's equation as functional derivative of the self energy. We do not make any reference regarding the representation of the Green's function. We only require $d\text{Tr}[A^n] = nA^{n-1}dA$ and $\ln[1-A] = -\sum_{n=1}^{\infty} \frac{1}{n}A^n$.

We start with Dyson's equation

$$G = G_0 + G_0\Sigma G = G_0 + \sum_{n=1} G_0\left(\Sigma G_0\right)^n = \sum_{n=0} G_0\left(\Sigma G_0\right)^n \tag{1.66}$$

Now we insert the Laurent expansions into Eq. 1.65

$$\left(\boldsymbol{G} - \bar{\boldsymbol{G}}\right)\boldsymbol{\Sigma} - \sum_{n=2}^{\infty} \frac{1}{n}\left[\bar{\boldsymbol{G}}\left(\boldsymbol{\Sigma} - \boldsymbol{\Gamma}\right)\right]^n$$

$$= \left[\sum_{j=2}^{\infty} \frac{1}{(i\hbar\omega_\nu)^j}\left(\mathcal{G}^{(j)} - \bar{\mathcal{G}}^{(j)}\right)\right]\left[\sum_{j'=0}^{\infty} \frac{1}{(i\hbar\omega_\nu)^{j'}}\mathcal{S}^{(j')}\right]$$

$$- \sum_{n=2}^{\infty} \frac{1}{n}\left[\left(\sum_{j=1}^{\infty} \frac{1}{(i\hbar\omega_\nu)^j}\bar{\mathcal{G}}^{(j)}\right)\left(\mathcal{S}^{(0)} - \boldsymbol{\Gamma} + \sum_{j'=1}^{\infty} \frac{1}{(i\hbar\omega_\nu)^{j'}}\mathcal{S}^{(j')}\right)\right]^n \qquad (1.72)$$

So-far, no approximations have been made: Now we introduce an approximation by truncating the Laurent expansions.

- We choose to include terms in the Matsubara sum up to the second order of the inverse Matsubara frequency.

- we include only the leading order of the Laurent expansion, namely $\mathcal{G}^{(2)}$ and $\mathcal{S}^{(0)}$ for the self energy.

Alternatively one could include terms in the Matsubara sum up to fourth order in the inverse temperature and to include the also $\mathcal{G}^{(3)}$ and $\mathcal{S}^{(1)}$. Note that the third order term in inverse temperature of the Matsubara sum does not contribute. However we will postpone this for the time being.

Another alternative would be to truncate the power-series expansion of the logarithm beyond a certain value and to include all Laurent expansion terms of the Matsubara sum which are produced by the Green's-function and self-energy expansion up to a certain order.

We define a functional $X[G, \Sigma]$ so that

$$\left.\frac{\delta X[G, \Sigma]}{\delta \Sigma}\right|_{G_0} = G - \sum_{n=0} G_0\left(\Sigma G_0\right)^n \qquad (1.67)$$

The functional has the form

$$X[G, \Sigma] \quad = \quad \mathrm{Tr}\left[G\Sigma - \sum_{n=0} \frac{1}{n+1}\left(\Sigma G_0\right)^{n+1}\right] = \mathrm{Tr}\left[G\Sigma - \sum_{n=1} \frac{1}{n}\left(\Sigma G_0\right)^n\right]$$

$$\overset{\text{Eq. } B.28}{=} \mathrm{Tr}\left[G\Sigma + \ln\left(1 - \Sigma G_0\right)\right] \qquad (1.68)$$

The functional derivative of X with respect to the Green's function is the self energy

$$\left.\frac{\delta X[G, \Sigma]}{\delta G}\right|_{G_0} = \Sigma \qquad (1.69)$$

Thus, if one finds a functional $\Phi[G]$ of the Green's function alone, which produces the self energy as derivative,

$$\frac{\delta\Phi[G]}{\delta G} = \Sigma \qquad (1.70)$$

we can produce a functional

$$\Phi[G] - X[G, \Sigma] \qquad (1.71)$$

which produces Dyson's equation as stationary condition with respect to Green's function and self energy. The connection to the total energy is, however, no clear from this argument.

Then, the functional X

$$
\begin{aligned}
X \quad = \quad & -\frac{1}{\beta} \sum_{\nu, |\omega_\nu| > \omega_x} \mathrm{Tr}\left\{ \frac{1}{(i\hbar\omega_\nu)^2} \left\{ \left(\mathcal{G}^{(2)} - \bar{\mathcal{G}}^{(2)} \right) \mathcal{S}^{(0)} - \frac{1}{2} \left[\bar{\mathcal{G}}^{(1)} \left(\mathcal{S}^{(0)} - \mathbf{\Gamma} \right) \right]^2 \right\} \right\} \\
\overset{\text{Eq. } B.28}{=} \quad & -\frac{1}{\beta} \sum_{\nu, |\omega_\nu| > \omega_x} \mathrm{Tr}\left\{ \frac{1}{(i\hbar\omega_\nu)^2} \left\{ \left(\mathcal{G}^{(2)} - \bar{\mathcal{G}}^{(2)} \right) \mathcal{S}^{(0)} - \frac{1}{2} \left[\mathbf{S}^{-1} \left(\mathcal{S}^{(0)} - \mathbf{\Gamma} \right) \right]^2 \right\} \right\}
\end{aligned}
\tag{1.73}
$$

The functional derivatives of Eq. 1.73 with respect to the self energy is

$$
\frac{dX}{d\mathcal{S}^{(0)}} = \left\{ -\frac{1}{\beta} \sum_{\nu, |\omega_\nu| > \omega_x} \frac{1}{(i\hbar\omega_\nu)^2} \right\} \left[\mathcal{G}^{(2)} - \bar{\mathcal{G}}^{(2)} - \mathbf{S}^{-1} \left(\mathcal{S}^{(0)} - \mathbf{\Gamma} \right) \mathbf{S}^{-1} \right]
\tag{1.74}
$$

With the Laurent expansion of the non-interacting Green's function, Eq. B.28, we obtain

$$
\mathcal{G}^{(2)} = \mathbf{S}^{-1} \left(\bar{\mathbf{h}} - \mu\mathbf{S} - \left(\mathcal{S}^{(0)} - \mathbf{\Gamma} \right) \right) \mathbf{S}^{-1}
\tag{1.75}
$$

The derivative of Eq. 1.73 with respect to the Green's function yields

$$
\frac{dX}{d\mathcal{G}^{(2)}} = \left\{ -\frac{1}{\beta} \sum_{\nu, |\omega_\nu| > \omega_x} \frac{1}{(i\hbar\omega_\nu)^2} \right\} \mathcal{S}^{(0)}
\tag{1.76}
$$

The stationary condition with respect to the Laurent term of the Green's function yields

$$
\frac{1}{\beta} \sum_{\nu; |\omega_\nu| > \omega_x} \left[\frac{\beta \delta \Phi^{LW}}{\delta \mathbf{G}(i\omega_\nu)} - \frac{\beta \delta \Phi^{LW,HF}}{\delta \mathbf{G}(i\omega_\nu)} \right] \underbrace{\frac{\delta \mathbf{G}(i\omega_\nu)}{\delta \mathcal{G}^{(2)}}}_{\frac{1}{(i\hbar\omega_\nu)^2}} + \left\{ -\frac{1}{\beta} \sum_{\nu, |\omega_\nu| > \omega_x} \frac{1}{(i\hbar\omega_\nu)^2} \right\} \mathcal{S}^{(0)} = 0
$$

$$
\mathcal{S}^{(0)} = \left\{ +\frac{1}{\beta} \sum_{\nu, |\omega_\nu| > \omega_x} \frac{1}{(i\hbar\omega_\nu)^2} \right\}^{-1} \left\{ \frac{1}{\beta} \sum_{\nu; |\omega_\nu| > \omega_x} \frac{1}{(i\hbar\omega_\nu)^2} \left[\frac{\beta \delta \Phi^{LW}}{\delta \mathbf{G}(i\omega_\nu)} - \frac{\beta \delta \Phi^{LW,HF}}{\delta \mathbf{G}(i\omega_\nu)} \right] \right\}
\tag{1.77}
$$

1.6   Dynamic-correlation correction in non-orthonormal basis and in Bloch representation

<div style="border:1px solid">

DYNAMIC CORRELATION CORRECTION

$$Q_{dyn,\beta}^{\hat{W}_2}[\boldsymbol{\rho}] \overset{\text{Eq. }1.18}{=} \underset{\boldsymbol{\Gamma}_{\vec{k}}}{\text{stat}}\ \underset{\boldsymbol{G}_{\vec{k}},\boldsymbol{\Sigma}_{dyn,R}}{\text{stat}} \left\{ \sum_R \left(\Phi_\beta^{LW}[\boldsymbol{G}_R, \hat{W}_{2,R}] - \Phi_\beta^{HF,LW}[\boldsymbol{G}_R, \hat{W}_{2,R}] \right) \right.$$

$$-\frac{1}{N_k}\sum_k \frac{1}{\beta}\sum_{\nu,|\omega_\nu|<\omega_x} \text{Tr}\left\{ \ln\left[\mathbf{1} - \left((i\hbar\omega_\nu + \mu)\boldsymbol{S}_{\vec{k}} - \bar{\boldsymbol{h}}_{\vec{k}} \right)^{-1} \left(\boldsymbol{\Sigma}_{dyn}(i\omega_\nu) - \boldsymbol{\Gamma}_{\vec{k}} \right) \right] \right.$$

$$+ \left(\boldsymbol{\Sigma}_{dyn}(i\omega_\nu) - \boldsymbol{\Gamma}_{\vec{k}} \right)\boldsymbol{G}_{\vec{k}}(i\omega_\nu)$$

$$\left. + \left[\boldsymbol{G}_{\vec{k}}(i\omega_\nu) - \left((i\hbar\omega_\nu + \mu)\boldsymbol{S}_{\vec{k}} - \bar{\boldsymbol{h}}_{\vec{k}} \right)^{-1} \right]\boldsymbol{\Gamma}_{\vec{k}} \right\}$$

$$- \left[\frac{1}{\beta}\sum_{\nu,|\omega_\nu|>\omega_x}\frac{1}{(i\hbar\omega_\nu)^2} \right]\frac{1}{N_k}\sum_k \text{Tr}\left\{ \left[\mathcal{G}_{\vec{k}}^{(2)} - \boldsymbol{S}_{\vec{k}}^{-1}\left(\bar{\boldsymbol{h}}_{\vec{k}} - \mu\boldsymbol{S}_{\vec{k}} \right)\boldsymbol{S}_{\vec{k}}^{-1} \right]\mathcal{S}_{\vec{k}}^{(0)} \right.$$

$$\left.\left. -\frac{1}{2}\left[\boldsymbol{S}_{\vec{k}}^{-1}\left(\mathcal{S}_{\vec{k}}^{(0)} - \boldsymbol{\Gamma}_{\vec{k}} \right) \right]^2 \right\} \right\} \tag{1.78}$$

$\boldsymbol{G}_R$ is obtained from $\boldsymbol{G}_{\vec{k}}$ via Eq. 1.64 and $\boldsymbol{\Sigma}_{dyn}$ is obtained from the local contributions $\boldsymbol{\Sigma}_{dyn,R}$ via Eq. 1.63. If the initial density matrix is not N-representable, a transformation will turn it into a strictly N-respresentable form. This mapping will be considered consistently when evaluating the derivatives.

N_k is the number of k-points on the grid for the Brillouin-zone integration.

$$\bar{\boldsymbol{h}}_{a,b,\vec{k}} = \mu\boldsymbol{S}_{a,b,\vec{k}} + \sum_n \langle\chi_a|\psi_n'\rangle\frac{1}{\beta}\ln\left[\frac{1-f_n'}{f_n'}\right]\langle\psi_n'|\chi_b\rangle \tag{1.79}$$

where

$$\left(\sum_{a,b}|\chi_a\rangle\rho_{\vec{k},a,b}\langle\chi_b| \right)\left(\sum_c |\chi_c\rangle\langle\pi_c|\psi_{\vec{k},n}'\rangle \right) = \left(\sum_a |\chi_a\rangle\langle\pi_a|\psi_{\vec{k},n}'\rangle \right)f_{\vec{k},n}'$$

$$\Rightarrow \qquad \boldsymbol{S}_{\vec{k}}\boldsymbol{\rho}_{\vec{k}}\boldsymbol{S}_{\vec{k}}\vec{\psi}'_{\vec{k},n} = \boldsymbol{S}_{\vec{k}}\vec{\psi}'_{\vec{k},n}f_n' \tag{1.80}$$

and $\langle\chi_a|\chi_b\rangle = \boldsymbol{S}_k$.

In the high-frequency part, i.e. for $|\omega_\nu| > \omega_x$, the Green's function and the self energy are given by

$$\boldsymbol{G}_{\vec{k}}(i\omega_\nu) = \frac{1}{i\hbar\omega}\boldsymbol{S}_{\vec{k}}^{-1} + \frac{1}{(i\hbar\omega)^2}\mathcal{G}^{(2)}$$

$$\boldsymbol{\Sigma}_{dyn,R}(i\omega_\nu) = \mathcal{S}_{dyn,R}^{(0)} \tag{1.81}$$

The result is correct for $N_k \to \infty$ and for $\omega_x \to \infty$.

</div>

1.7   Spectral information

The Greens function and the self-energy produces only information that is relevant for the total energy. Energy levels that lie sufficiently far from the Fermi level that they are either completely filled or completely empty, do not contribute to correlations, because quantum fluctuations would make their occupations fractional. (compare CAS-SCF)

This implies that the spectral information obtained from the the Luttinger Ward functional is only valid in a limited energy region. Spectral information from the "inactive" region is ill-determined. There are many spectra, that would result in the same total energy. This implies that we may choose any set of energy levels for the inactive region and that one possible choice is to simply use the Kohn-Sham spectra.

The expression Eq. 1.30 makes an even stronger connection that the "inactive" region should be represented by the Kohn-Sham spectrum. This is however partly misleading, because the derivatives of the density matrix functional are not relevant for integer occupations. Lagrange multipliers which lower the energies of fully occupied states and those that rise the energy for empty states are equally tolerable.

A potential conclusion seems to be that the true spectrum may be wider spread out than the Kohn-Sham spectrum, which seems to be in line with the observations from the Band gap problem.

In order to obtain the final Green's function, we need to diagonalize the Koh-Sham Hamiltonian

$$
G(i\omega_\nu) = \left[(i\hbar\omega_\nu + \mu)S - S\langle\pi|\psi_m\rangle\langle\psi_m|\hat{h}|\psi_n\rangle\langle\psi_n|\pi\rangle S - \Sigma(i\omega_\nu) \right]^{-1} \tag{1.82}
$$

where

$$
\hat{h} = \frac{\hat{\vec{p}}^2}{2m_e} + \hat{v}_{ext} + \hat{v}_H + \hat{v}_{xc} - \sum_{a,b} |\pi_a\rangle\Gamma_{a,b}\langle\pi_b| \tag{1.83}
$$

Γ is nort included properly!

1.8   Description of Subroutines

Data structures

$\langle\pi_\alpha|\psi_{n,\vec{k}}\rangle$	`KSET(IKPT)%PIPSI(:NDIM,:NCHI,:NB,NSPIN)`
$\rho_{\vec{k}}$	`KSET(IKPT)%RHO(:NCHI,:NCHI,:NDIMD)`
$S_{\vec{k}}$	`KSET(IKPT)%SMAT(:NCHI,:NCHI,:NDIMD)`
$S_{\vec{k}}^{-1}$	`KSET(IKPT)%SINV(:NCHI,:NCHI,:NDIMD)`
$\Sigma_{dyn,R}(i\omega_\nu)$	`ATOMSET(IAT)%SLOC(:NLOC,:NLOC,:NDIMD,:NOMEGA)`
$\mathcal{S}_{dyn,R}^{(0)}$	`ATOMSET(IAT)%SLOClaur(:NLOC,:NLOC,:NDIMD,1)`
$\mathcal{S}_{dyn,R}^{(1)}$	`ATOMSET(IAT)%SLOClaur(:NLOC,:NLOC,:NDIMD,2)`
$\bar{h}_{\vec{k}}$	`KSET(IKPT)%HRHO(:NCHI,:NCHI,:NDIMD)`
$\Gamma_{\vec{k}}$	`KSET(IKPT)%GAMMA(:NCHI,:NCHI,:NDIMD)`

1.8.1   Data exchange of the Object wit the outer world

1.8.2   Flowchart
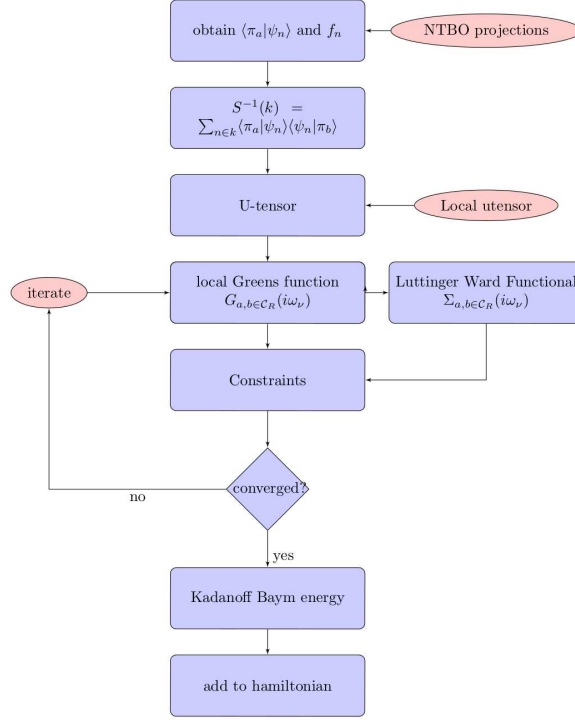
1.8.3   DMFT$GREEN

DMFT$GREEN is the main subroutine of the DMFT object. It is called from the LMTO object, which also provides the projections onto the tight-binding orbitals.

We evaluate the functional $Q^{\hat{W}_2}_{dyn,\beta}[\boldsymbol{\rho}]$ following the recipy provided in section III of the BPP paper[1].

```
call dmft_ini()
call dmft_collectnatorb()
call dmft_rhoofk()
call dmft_utensor()
call dmft_natorb()
call dmft_hrho()
call dmft_constraints()
do iter=1,3
  call dmft_gloc()
  call dmft_solver(etot)
  call dmft_constraints()
enddo ! end of loop over iterations to enforce constraint
call dmft_rholocal()
call dmft_staticsolver(svar)
etot=etot+svar
```

```
call dmft_detot(svar)
etot=etot+svar
call energylist$set('dmft interface',etot)
call energylist$add('local correlation',etot)
call energylist$add('total energy',etot)
call dmft_addtohpsi()
```

1. `DMFT_COLLECTNATORB`: The orbital coefficients $\langle \pi_a | \psi_n \rangle$ have been calculated by the LMTO object and they are kept in the module of `paw_waves`. The orbital coefficients are placed into as `kset(ik)%pipsi(ndim,nchi,nb,nspin)`. Also the occupations are kept as `kset(ik)%f(nb,nspin)` (without spin degeneracy, i.e. $f_n \in [0, 1]$). The k-point weights are kept as `kset(ik)%wkpt`. Again the spin degeneracy has been removed. However special k-points have half the weight as general k-points. This should be checked explicitely!

2. `DMFT_rhoofk`: calculate the k-dependent density matrix, the inverse overlap matrix and the overlap matrix itself.

$$\rho_{a,b}(\vec{k}) = \sum_n \langle \pi_a | \psi_n(\vec{k}) \rangle f_n(\vec{k}) \langle \psi_n(\vec{k}) | \pi_b \rangle \tag{1.84}$$

$$\mathbf{S}_{a,b}^{-1}(\vec{k}) = \sum_n \langle \pi_a | \psi_n(\vec{k}) \rangle \langle \psi_n(\vec{k}) | \pi_b \rangle \tag{1.85}$$

$$\mathbf{S} = \left(\mathbf{S}^{-1} \right)^{-1} \tag{1.86}$$

The k-dependent density matrix is kept as `kset(ik)%rho(nchi,nchi,ndimd)`. The inverse overlap matrix is kept as `kset(ik)%sinv(nchi,nchi,ndimd)` and the overlap matrix is kept as `kset(ik)%smat(nchi,nchi,ndimd)`.

3. `DMFT_UTENSOR`: (see also section 1.8.5) The local U-tensor is collected from the onsite elements `POTPAR(ISP)%TAILED%U` calculated in the `paw_LMTO` object. It is directly converted from the "tailed representation" into the basis of local orbitals.

$$U_{a,b,c,d} = \alpha \int d^4x \int d^4x' \frac{e^2 \chi_a^*(\vec{x}) \chi_b^*(\vec{x'}) \chi_c(\vec{x}) \chi_d(\vec{x'})}{4\pi\epsilon_0 |\vec{r} - \vec{r'}|} \tag{1.87}$$

Only the U-tensor for equal spin-electrons is stored. α is a scale factor that mimics the screening of the U-tensor. It is called `LHFWEIGHT`.

The scaled U-tensor is kept as `ATOMSET(iat)%U`

4. `DMFT_HRHO`: (see also section 1.8.7 on p. 31.) Calculate the non-interacting Hamiltonian $\bar{h}_{\vec{k}}$ that produces the specified (k-dependent) density matrix.

$$\bar{h}_{\vec{k},a,b} = \mu S_{\vec{k},a,b} + \sum_n \langle \chi_a | \psi'_{\vec{k},n} \rangle \frac{1}{\beta} \ln \left[\frac{1 - f'_{\vec{k},n}}{f'_{\vec{k},n}} \right] \langle \psi'_{\vec{k},n} | \chi_b \rangle \tag{1.88}$$

$\bar{h}_{\vec{k}}$ is kept as `KSET(IKPT)%HRHO`.

5. `DMFT_NATORB`: (see also section 1.8.6) Despite the name we do no more use local natural orbitals. This is described in section 1.8.6. A this point we have three different settings for the routine `DMFT_NATORB`: "NATORB", "QUAMBO" and "ORTHO". QUAMBO stands for "quasi atomic molecular orbitals"[5], while it may or may not be related to it.

Construct the eigenstates $|\phi_j\rangle$ of the single-site matrix $\boldsymbol{A}$

$$\hat{A}_R|\phi_{R,i}\rangle = |\phi_{R,i}\rangle a_{R,i} \tag{1.89}$$

These states will be called local natural orbitals (This will be changed.).

The orbital coefficients $\langle\pi_a|\phi_{R,j}\rangle$ of the local orthonormal orbitals are calculated as [5]

$$\sum_b \langle\pi_a|\hat{\rho}_R|\pi_b\rangle y_{b,j} = \sum_b S_{R,a,b}^{-1} y_{b,j} f_{R,j}' \qquad \text{with } \vec{y}_i^\dagger \boldsymbol{S}_R^{-1} \vec{y}_j = \delta_{i,j} \tag{1.94}$$

$$\langle\pi_a|\phi_{R,j}\rangle = \sum_b S_{R,a,b}^{-1} y_{b,j} \tag{1.95}$$

The local density matrix $\boldsymbol{\rho}_R$ and the local inverse overlap matrix $\boldsymbol{S}_R^{-1}$ are obtained as Brillouin zone intergral projected onto the lcoal site

$$\boldsymbol{\rho}_R = \boldsymbol{P}_R\left[\sum_{\vec{k}} w_{\vec{k}}\boldsymbol{\rho}(\vec{k})\right]\boldsymbol{P}_R$$

$$\boldsymbol{S}_R^{-1} = \boldsymbol{P}_R\left[\sum_{\vec{k}} w_{\vec{k}}\boldsymbol{S}^{-1}(\vec{k})\right]\boldsymbol{P}_R \tag{1.96}$$

The transformation matrices are stored in the fully non-collinear data model in `atomset%natorb%piphi` and the vectors $\vec{y}_j$ are stored as `atomset%natorb%chiphi`.

The vector y is used for the transformation to the local natural orbitals in the solver interface. Check if this is correct. should it be the vector x?

---

[5] The spirit follows from the construction of local natural orbitals along the following lines

$$\underbrace{\sum_{a,b}|\chi_a\rangle\langle\pi_a|\hat{A}_R|\pi_b\rangle\langle\chi_b|}_{\hat{\rho}_R}\underbrace{\sum_c|\chi_c\rangle x_{c,j}}_{|\phi_{R,j}\rangle} = \underbrace{\sum_a|\chi_a\rangle x_{a,j}}_{|\phi_{R,j}\rangle} f_{R,j}'$$

$$\sum_{b,c}\langle\pi_a|\hat{\rho}_R|\pi_b\rangle\langle\chi_b|\chi_c\rangle x_{c,j} = x_{a,j} f_{R,j}' \tag{1.90}$$

Now, introduce $y_{a,j} = \sum_b\langle\chi_a|\chi_b\rangle x_{b,j}$

$$\sum_b\langle\pi_a|\hat{\rho}_R|\pi_b\rangle y_{b,j} = \sum_b S_{a,b}^{-1} y_{b,j} f_{R,j}' \tag{1.91}$$

which is a generalized eigenvalue problem for the vectors $\vec{y}_j$, which are converted into orbital coefficients by multiplication with $\boldsymbol{S}^{-1}$.

$$|\phi_{R,j}\rangle = \sum_{a,b}|\chi_a\rangle S_{a,b}^{-1} y_{b,j} \tag{1.92}$$

The local natural orbitals are orthonormal in the sense

$$\langle\phi_{R,i}|\phi_{R,j}\rangle = \sum_{a,b,c,d} y_{a,i}^* S_{a,c}^{-1}\underbrace{\langle\chi_c|\chi_d\rangle}_{(\boldsymbol{S}^{-1})^{-1}} S_{d,b}^{-1} y_{b,j} = \sum_{a,b} y_{a,i}^* S_{a,b}^{-1} y_{b,j} = \delta_{i,j} \tag{1.93}$$

6. `DMFT_GLOC`: The local Green's function is obtained as Brillouin zone integral over the k-dependent greens function after projecting onto the correlated orbitals on the specified site.

$$\boldsymbol{G}_R(i\omega_\nu) = \sum_{\vec{k}} w_{\vec{k}} \left[(i\omega_\nu + \mu)\boldsymbol{S}_{\vec{k}} - \bar{\boldsymbol{h}}_{\vec{k}} + \boldsymbol{\Gamma}_{\vec{k}} - \boldsymbol{\Sigma}_{dyn}^{\hat{W}_2}(i\omega_\nu) \right]_R^{-1} \tag{1.97}$$

The Laurent expansion is obtained as

$$\mathcal{G}_R^{(1)}(i\omega_\nu) = \sum_{\vec{k}} w_{\vec{k}} \boldsymbol{S}_{\vec{k}}^{-1}$$
$$\mathcal{G}_R^{(2)}(i\omega_\nu) = \sum_{\vec{k}} w_{\vec{k}} \boldsymbol{S}_{\vec{k}}^{-1} \left(\bar{\boldsymbol{h}} - \mu\boldsymbol{S}_{\vec{k}} + \boldsymbol{\Gamma}_{\vec{k}} - \mathcal{S}_{dyn}^{(0)} \right) \boldsymbol{S}_{\vec{k}}^{-1} \tag{1.98}$$

The result and its Laurent expansion terms are stored in `atomset%gloc` and `atomset%gloclaur`.

7. `DMFT_SOLVER`: Calculates the dynamic contribution $\Phi_\beta^{LW,\hat{W}_2} - \Phi_\beta^{HF,\hat{W}_2}$ to the Luttinger-Ward functional and the corresponding contribution $\boldsymbol{\Sigma}_{dyn}^{\hat{W}_2}$ to the self energy for the specified Green's function.

   (a) In a first loop over atoms the atoms are individually adressed and the routine `dmft_dynamicsolver` is called.

   (b) Inside `dmft_dynamicsolver` the U-tensor and the Green's function are converted into local natural orbitals and in a up-down spinor representation with all up-spin components first and the down-spin components second.

   (c) then the actual interface routine `DMFT_SOLVERIO` is called, which returns the value of the dynamic contribution to the Luttinger-Ward functional (HF subtracted), the coresponding contribution to the self energy and the derivative of the U-tensor.

$$\Phi_{dyn}^{LW}[\boldsymbol{G}(i\omega_\nu), \hat{W}_2] = \Phi^{LW}[\boldsymbol{G}(i\omega_\nu), \hat{W}_2] - \frac{1}{2} \sum_{a,b,c,d} U_{a,b,d,c}^{\hat{W}_2} \left(\rho_{d,a}\rho_{c,b} - \rho_{c,a}\rho_{d,b} \right)$$

$$\Sigma_{dyn,a,b}^{\hat{W}_2}(i\omega_\nu) = \frac{\beta \partial \Phi^{LW}}{\partial G_{b,a}(i\omega_\nu)} - \sum_{c,d} \left(U_{a,c,b,d}^{\hat{W}_2} - U_{a,c,d,b}^{\hat{W}_2} \right) \rho_{d,c}$$

$$\mathcal{S}_{dyn,a,b}^{(0)} = \frac{1}{\beta} \sum_{|\nu|>\nu_x} \frac{1}{(i\hbar\omega_\nu)^2} \left[\frac{\beta \partial \Phi^{LW}}{\partial G_{b,a}(i\omega_\nu)} - \sum_{c,d} \left(U_{a,c,b,d}^{\hat{W}_2} - U_{a,c,d,b}^{\hat{W}_2} \right) \rho_{d,c} \right]$$

$$\frac{\delta\Phi_\beta^{dyn,LW}}{\delta U_{a,b,c,d}} = \frac{\delta\Phi_\beta^{LW}}{\delta U_{a,b,d,c}} - \frac{1}{2} \left(\rho_{d,a}\rho_{c,b} - \rho_{c,a}\rho_{d,b} \right) \tag{1.99}$$

`pay attention to the reversed order of the indices c, d!`

$\frac{\delta\Phi_\beta^{dyn,LW}}{\delta U_{a,b,c,d}}$ is the difference of the two-particle density for the interacting and the non-interacting electron gas at the same density matrix. In contrast to the corresponding term in the density functional theory, this term does not contain a kinetic energy contribution as does $n(\vec{r}) \int_0^1 d\lambda\, h_\lambda(\vec{r}, \vec{r}')$, but rather $n(\vec{r}) \left[h_1(\vec{r}, \vec{r}') - h_0(\vec{r}, \vec{r}') \right]$

   (d) After `DMFT_SOLVERIO` is finished, the self energy and the derivative with respect to the U-tensor are transformed back.

The external solver may make additional approximations to the U-tensor or to the Kadanoff-Baym functional. However, these approximations must be consistent across the dynamical-correlation correction.

8. `DMFT_MIX` mixes the self energy: The self energy cannot simply be inserted into the Green's function for the next iteration, because the changes for small Matsubara frequencies would be too violent. Therefore, it needs some preconditioning.

   The underlying ideas related to the mixing are described in appendix F on p. 62.

$$\Sigma_{a,b}^{dyn}(i\omega_\nu) \leftarrow \Sigma_{a,b}^{dyn}(i\omega_\nu) + \frac{1}{C}\left(\frac{C}{M} + (\hbar\omega)^2\right)\left(\Sigma_{a,b}^{dyn}(i\omega_\nu) - \frac{\beta\delta\Phi_{dyn}^{LW}}{\partial G_{b,a}(i\omega_\nu)}\right)$$

$$\mathcal{S}_{dyn,a,b}^{(0)} \leftarrow \mathcal{S}_{dyn,a,b}^{(0)} + \frac{(\hbar\omega_x)^2}{C}\left(\mathcal{S}_{dyn,a,b}^{(0)} - \frac{\delta\Phi_{dyn}^{LW}}{\delta\mathcal{G}_{b,a}^{(2)}}\right) \tag{1.100}$$

   It seems that the sign for the mixing is incorrect!! I am changing it in the code to see what happens. $\mathbf{\Sigma}^{dyn}$ is the self energy that has been accumulated, and that is zero in the first iteration. $\frac{\beta\delta\Phi_{dyn}^{LW}}{\partial G_{b,a}(i\omega_\nu)}$ is the dynamic self-energy contribution produced by the solver. Note that this self energy does not contain the Hartree-Fock term. C and M are two mixing parameters, that control the behavior at small (M) and large (C) Matsubara frequencies.

9. `DMFT_CONSTRAINTS` enforced the density matrix constraint: The new Green's function $\mathbf{G}^{new}$ has the form

$$\mathbf{G}^{new}(i\omega_\nu) = \left[(i\hbar\omega_\nu + \mu)\mathbf{1} - \bar{\mathbf{h}} + \mathbf{\Gamma} - \mathbf{\Sigma}^{dyn}(i\omega_\nu)\right]^{-1} \tag{1.101}$$

   where the Lagrange multiplier $\mathbf{\Gamma}$ needs to be adjusted until the density matrix constraint

$$\boldsymbol{\rho} = \frac{1}{\beta}\sum_\nu e^{i\beta\hbar\omega_\nu 0^+}\mathbf{G}^{new}(i\omega_\nu) \tag{1.102}$$

   is fulfilled.

   For this purpose, we linearize the constraint equation in the Lagrange multiplier

$$\boldsymbol{\rho} = \frac{1}{\beta}\sum_\nu e^{i\beta\hbar\omega_\nu 0^+}\left[\mathbf{G}^{new}(i\omega_\nu) - \mathbf{G}^{new}(i\omega_\nu)\delta\mathbf{\Gamma}\mathbf{G}^{new}(i\omega_\nu)\right]$$

$$0 = \left[\frac{1}{\beta}\sum_\nu e^{i\beta\hbar\omega_\nu 0^+}G_{a,b}^{new}(i\omega_\nu)\right] - \rho_{a,b} - \sum_{c,d}\left[\frac{1}{\beta}\sum_\nu G_{a,c}^{new}(i\omega_\nu)G_{d,b}^{new}(i\omega_\nu)\right]\delta\Gamma_{c,d}$$

$$\delta\Gamma_{c,d} = \underbrace{\left[\frac{1}{\beta}\sum_\nu G_{a,c}^{new}(i\omega_\nu)G_{d,b}^{new}(i\omega_\nu)\right]^{-1}_{cd,ab}}_{\rightsquigarrow\ \alpha\delta_{c,a}\delta_{d,b}}\left(\underbrace{\left[\frac{1}{\beta}\sum_\nu e^{i\beta\hbar\omega_\nu 0^+}G_{a,b}^{new}(i\omega_\nu)\right] - \rho_{a,b}}_{\rho_{a,b}^{new}}\right) \tag{1.103}$$

   In this equation we can use the model Green's function to avoid the calculation and inversion of $\mathbf{G}^{new}\otimes\mathbf{G}^{new}$

   Note, that $\mathbf{\Gamma}$ is, like $\mathbf{h}'$, a non-local Hamiltonian, that in principle connects arbitrary local orbitals with each other. In a Bloch representation, $\mathbf{\Gamma}$ is a k-dependent matrix, which connects all local orbitals in the unit cell with each other.

Thus, we iterate the coupled equations

$$\boldsymbol{G}^{new}(i\omega_\nu) = \left[(i\hbar\omega_\nu + \mu)\boldsymbol{1} - \bar{\boldsymbol{h}} + \boldsymbol{\Gamma} - \boldsymbol{\Sigma}^{dyn}(i\omega_\nu) \right]^{-1}$$

$$\delta\boldsymbol{\rho} = \frac{1}{\beta} \sum_\nu e^{i\beta\hbar\omega_\nu 0^+} \boldsymbol{G}^{new}(i\omega_\nu) - \boldsymbol{\rho}$$

$$\boldsymbol{\Gamma} = \boldsymbol{\Gamma} + \alpha\delta\boldsymbol{\rho} \tag{1.104}$$

until $\delta\rho$ vanishes.

In practice we do not use α, but precondition with a Green's function with zero one-particle level. see section 1.8.8.

With the correct Lagrange multiplier, the new Green's function is obtained.

10. `DMFT_RHOLOCAL`: For the Hartree-Fock and DFT double-counting terms, we need the local density matrix, which is calculatecd directly form the k-dependent density matrix als Brillouin zone sum.

11. `DMFT_STATICSOLVER`: Calculates the static contribution to the correlation energy, i.e. the screened Hartree-Fock term and the DFT double counting correction and its derivatives. These terms do not affect the density matrix constraint.

    This term must be removed if the corresponding terms are treated in the PAW_LMTO object. The double counting for the correlation must however still be included.

    For the double counting in the HF approximation, only the exchange part is removed, while, here, also the correlation contribution should be taken out, because the correlation is explicitly added.

    The Hartree-Fock contribution is added directly to the double counting term. Thus the self energy `atomset%sigma` is only the dynamical contribution.

12. `DMFT_DETOT`: Adds the non-local contribution to the total energy

$$-\frac{1}{\beta} \sum_\nu \text{Tr}\left\{ \ln\left[\boldsymbol{1} - \left((i\hbar\omega_\nu + \mu)\boldsymbol{1} - \bar{\boldsymbol{h}} \right)^{-1} \left(\boldsymbol{\Sigma}^{\hat{W}_2}_{dyn}(i\omega_\nu) - \boldsymbol{\Gamma} \right) \right] \right.$$

$$\left. + \left(\boldsymbol{\Sigma}^{\hat{W}_2}_{dyn}(i\omega_\nu) - \boldsymbol{\Gamma} \right) \boldsymbol{G}(i\omega_\nu) + \left[\boldsymbol{G}(i\omega_\nu) - \left((i\hbar\omega_\nu + \mu)\boldsymbol{1} - \bar{\boldsymbol{h}} \right)^{-1} \left[\boldsymbol{\Gamma} \right] \right\} \tag{1.105}$$

In order to evaluate the logarithm, I diagonalize the non-hermitean matrix in the argument, and sum the absolute values of the eigenvalues. The complex logarithm is $\ln[z] = \ln(|z|) + iArg(z)$. The imaginary part cancels out with the negative Matsubara frequencies.

In a previous version I used the Dahlen trick, which is probably not quite correct. See appendix 1.8.10 on p. 36

13. `DMFT_ADDTOHPSI`: Adds the energy derivative to `this%htbc` of the `waves_module`. There are two contributions, a k-dependent term which is restricted to the correlated orbitals and an site-dependent term that acts on all local orbitals.

    - The site-specific term contains the double counting term for the DFT functional and the Hartree-Fock contribution to the self energy.

1.8.4   DMFT_INI

Hardwired data

- NOMEGA (N_ω)

Inherited data

- NDIM from `waves_module`

- NSPIN from `waves_module`

- NKPTL from `waves_module`

- NAT from `ATOMLIST` Object

- isp(IAT)

- WKPT and (NKPT,KMAP) from `DYNOCC` Object

- KBT from `dynocc$getr8a('temp')` from `paw_occupations.f90`

- `atomset(iat)%lhfweight` from `lmto_module`

Derived data

- NDIMD (=1 for NDIM=1,NSPIN=1; =2 for NDIM=1,NSPIN=2; =4 for NDIM=2,NSPIN=1)

- List of positive Matsubara frequencies

$$\omega_\nu = (2\nu - 1)\pi k_B T \qquad \text{for } \nu = 1, \ldots, N_\omega \tag{1.106}$$

- Atomset structure

`atomset\%nloc`	number of correlated orbits on this atom
`atomset\%ICHI1`	first value of ICHI index for this atom
`atomset\%ICHI2`	last value of ICHI index for this atom

- KSET structure

`KSET\%WKPT`	geometric k-point weight

1.8.5   DMFT_UTENSOR

Obtain the on-site U-tensor for all local orbitals from subroutine `dmft_ulocal` reduces it to the entries for the correlated orbitals.

In `DMFT_ULOCAL` it obtains the local U-tensor from the `POTPAR%TAILED%U` and `SBAR` of the LMTO Object. This object contains the extended ϕ and $\dot{\phi}$ functions

$$|\chi_a\rangle = |\phi_a\rangle - \sum_{b; R_b = R_a} |\dot{\bar{\phi}}_b\rangle \bar{S}_{a,b} \tag{1.107}$$

The U-tensor is constructed in `LMTO_MAKETAILEDPARTIALWAVES`. `LMTO_ULITTLE` constructs

$$u_{\ell,a,b,c,d} = \frac{2\ell+1}{4\pi} \int dr \, r^2 R_c(r) R_d(r) \left[\int d^3r' \, V_\ell(r,r') R_a(r') R_b(r') \right] \qquad (1.108)$$

where the kernel $V_\ell(r,r')$ is the one used by `RADIAL$POISSON`. **There is a input parameter that determines which ℓ values are considered.**

In `LMTO_UTENSOR` the U-tensor elements are composed according to

$$U_{a,b,c,d} = \sum_{ell} \frac{4\pi}{2\ell+1} \sum_{m=-\ell}^{\ell} u_{\ell,b,d,c,a} C_{L,L_b,L_d} C_{L,L_c,L_a} \qquad (1.109)$$

The U-tensor is screened by a factor `LHFWEIGHT`. It is obtained from the `lmto_module` either as the global value `HFWEIGHT` or the individual value from hybridsetting. This very same factor is used for the double counting term.

Thus the U-tensor is defined as[6] in Eq. 1.87, i.e. as

$$U_{a,b,c,d} = \int d^4x \int d^4x' \, \frac{e^2 \chi_a^*(\vec{x}) \chi_b^*(\vec{x'}) \chi_c(\vec{x}) \chi_d(\vec{x'})}{4\pi\epsilon_0 |\vec{r}-\vec{r'}|} \qquad (1.110)$$

The U-tensor contributes only if $\sigma_a = \sigma_c$ and if $\sigma_b = \sigma_d$. With this definition the Hartree and exchange energy have the form

$$E_H = \frac{1}{2} \sum_{a,b,c,d} U_{a,b,c,d} \, \rho_{c,a}\rho_{d,b}$$

$$E_X = \frac{1}{2} \sum_{a,b,c,d} U_{a,b,c,d} \, \rho_{c,b}\rho_{d,a} \qquad (1.111)$$

1.8.6 DMFT_NATORB

Construct a set of orthonormal states for the single-site problem. This section describes first the mapping to local natural orbitals. Later we will propose a different basisset, which avoids some of the problems.

For this purpose, I redefine the unity operator for the sub Hilbert space of correlated orbitals.

$$\hat{1}_{\mathcal{C}_R} = \sum_{\alpha,\beta} \sum_n |\chi_\alpha\rangle\langle\pi_\alpha|\psi_n\rangle\langle\psi_n|\pi_\beta\rangle\langle\chi_\beta| \qquad (1.112)$$

which allows one to identify the inverse overlap matrix in this sub-Hilbert space.

$$S_{\alpha,\beta}^{-1} = \sum_{\alpha,\beta} \sum_n \langle\pi_\alpha|\psi_n\rangle\langle\psi_n|\pi_\beta\rangle \qquad (1.113)$$

Note,however, that this matrix lives only on a single site! We can obtain it from the k-dependent S^{-1} by summing over k-points and cutting out the corresponding submatrix. However, it is not allowed to do the same thing for the overlap matrix itself!

---

[6]$\vec{x} = (\vec{r}, \sigma)$

We approach the problem by a formulation of natural orbitals for the local density matrix. This choice is not convenient in the end, because the resulting basisset depends on the instantaneous electronic structure. Nevertheless the point of view taken allows me to formulate the problem. Later we change it such that we use quasi atomic orbitals instead of the natural orbitals, which are less dependent on the electronic structure.

The one-particle density matrix in this sub-Hilbert space has the form

$$\hat{\rho}_{\mathcal{C}_R} = \sum_{\alpha,\beta} \sum_n |\chi_\alpha\rangle\langle\pi_\alpha|\psi_n\rangle f_n \langle\psi_n|\pi_\beta\rangle\langle\chi_\beta| \tag{1.114}$$

The eigenvalue equation

$$\hat{\rho}|\phi_n\rangle = |\phi_n\rangle f_n$$
$$\sum_{\alpha,\beta} |\chi_\alpha\rangle\langle\pi_\alpha|\hat{\rho}|\pi_\beta\rangle\langle\chi_\beta|\phi_j\rangle = \sum_{\alpha,\beta} |\chi_\alpha\rangle\langle\pi_\alpha|\pi_\beta\rangle\langle\chi_\beta|\phi_j\rangle f_j = \sum_{\alpha,\beta} |\chi_\alpha\rangle S_{\alpha,\beta}^{-1}\langle\chi_\beta|\phi_j\rangle \bar{f}_j \tag{1.115}$$

provides us with a new set of occupations $\bar{f}$ of local natural orbitals and eigenvectors $\langle\chi_\beta|\phi_j\rangle = V_{\beta,j}$.

$$\rho V = S^{-1}V\bar{f} \qquad \text{with} \qquad V^\dagger S^{-1}V = 1 \tag{1.116}$$

The natural orbitals are

$$|\phi_j\rangle = \sum_{\alpha,\beta\in\mathcal{C}_R} \underbrace{|\chi_\alpha\rangle S_{\alpha,\beta}^{-1}\langle\chi_\beta|}_{1_{\mathcal{C}_R}} \phi_j\rangle = \sum_{\alpha\in\mathcal{C}_R} |\chi_\alpha\rangle \underbrace{\left(S^{-1}V\right)_{\alpha,j}}_{V_{\alpha,j}^{\dagger,-1}} \tag{1.117}$$

Remember that the natural orbitals are not the ones used in the calculation! The orbitals chosen are discussed in the following section.

The matrix V is placed into the structure `atomset%natorb%chiphi`, together with the occupations $\bar{f}$ which are in `atomset%natorb%f`. In addition we store $S^{-1}V = V^{\dagger,-1}$ in `atomset%natorb%piphi` All data in `atomset%natorb` are stored in the fully non-collinear model.

Orthonormal orbitals without reference to the density matrix

When approximations are done on the U-tensor, which are not invariant under a unitary transformation of the orbitals, the resulting U-tensor will be itself a functional of the natural orbitals. The approximation of a constant U-tensor in the solver will then lead to uncontrolled results.

For this reason we choose an alternative basisset instead of the local natural orbitals. The main requirement for the basisset is that it is orthonormal. Orthonormality can be obtained from any eigenvalue problem of the form

$$AV = S^{-1}Va \tag{1.118}$$

where A is an arbitrary hermitean matrix, the the matrix V contains the eigenvectors, which obey $V^\dagger S^{-1}V = 1$ and the diagonal matrix a contains the eigenvalues of A.

This eigenvalue equation replaces Eq. 1.116.

As a second criterion, we choose orbitals that closely reflect the shape of the original tight-binding orbitals. In the current implementation the tight-binding orbitals are constructed with a

clear main angular momentum character. If the approximations made by the solver on the U-tensor are not rotationally invariant, one should use here a coordinate system that adapts to the changing local environment.

If one chooses the matrix $\boldsymbol{A}$ to be diagonal, with very different diagonal elements, then the eigenstates will be correspondingly similar to the original orbitals, and they will remain in the original order if the diagonal elements increase with index number.

Therefore, I choose $A_{i,j} = j\delta_{i,j}$. A scale factor is redundant, because it only affects the eigenvalues, but not the eigenvectors.

1.8.7   DMFT_HRHO

Calculate the non-interacting Hamiltonian $\bar{\boldsymbol{h}}$ that produces the specified (k-dependent) density matrix.

$$\bar{h}_{a,b}(\vec{k}) = \mu S_{a,b}(\vec{k}) + \sum_n \langle \chi_a | \psi'_n \rangle \frac{1}{\beta} \ln \left[\frac{1 - f'_n}{f'_n} \right] \langle \psi'_n | \chi_b \rangle \qquad (1.119)$$

where the natural orbitals $|\psi'_n\rangle$ and the occupations f'_n differ from the original natural orbitals.

1. First, we transform onto natural orbitals

$$|\psi'_n\rangle = \sum_a |\chi_a\rangle\langle\pi_a|\psi'_n\rangle \qquad (1.120)$$

These natural orbitals may be slighly different from the original natural orbitals, because they are restricted to the space of local orbitals.

$$\hat{\rho}|\psi'_n\rangle = |\psi'_n\rangle f'_n$$

$$\langle\chi_a| \underbrace{\sum_{b,c} |\chi_b\rangle \overbrace{\left(\sum_m \langle\pi_b|\psi_m\rangle f_m \langle\psi_m|\pi_c\rangle\right)}^{\rho_{b,c}} \langle\chi_c|}_{\hat{\rho}} \underbrace{\sum_d |\chi_d\rangle\langle\pi_d|\psi'_n\rangle}_{|\psi'_n\rangle} = \langle\chi_a| \underbrace{\sum_d |\chi_d\rangle\langle\pi_d|\psi'_n\rangle}_{|\psi'_n\rangle} f'_n$$

$$S_{a,b}\rho_{b,c}S_{c,d}\langle\pi_d|\psi'_n\rangle = S_{a,d}\langle\pi_d|\psi'_n\rangle f'_n$$

$$\boldsymbol{\rho}\left(\boldsymbol{S}\vec{x}_n\right) = \boldsymbol{S}^{-1}\left(\boldsymbol{S}\vec{x}_n\right) f'_n \qquad (1.121)$$

Thus, for each k-point solve the generalized eigenvalue problem

$$\boldsymbol{\rho}(k)\boldsymbol{V}(\vec{k}) = \boldsymbol{S}^{-1}(\vec{k})\boldsymbol{V}(\vec{k})\boldsymbol{f}'(\vec{k})$$

where $\boldsymbol{f}'(\vec{k})$ is a diagonal matrix that contains k-dependent occupations. (They differ from the occupations f_n of the natural orbitals $|\psi_n\rangle$.)

2. Next we evaluate the hamiltonian $\bar{\boldsymbol{h}}$ in the representation of the natural orbitals $|\psi'_n\rangle$.

   The conversion of occupations into energies is done in the routine `DMFT_EOFF`, described in section 1.8.7.

$$\epsilon = \mu + k_B \begin{cases} \ln\left(\frac{1-f}{f}\right) & \text{for } f_0 < f < 1 - f_0 \\ a + b(f - f_0) & \text{for } f < f_0 \\ -a + b(f - (1 - f_0)) & \text{for } f > 1 - f_0 \end{cases} \qquad (1.122)$$

where a and b are determined such that the mapping is differentiable. The value of f_0 is currently set to 10^{-6}.

The energies obtained from `DMFT_EOFF` are still spread over a too large energy interval. Therefore, we limit the energies to the interval $[\mu - zk_BT, \mu + zk_BT]$, where z is a fixed parameter. z should be chosen so that the occupations calculated with the Fermi distribution from $\bar{h}$ are not affected too much.

z	$min(f); max(1-f)$
4.6	10^{-2}
6.9	10^{-3}
9.2	10^{-4}
11.5	10^{-5}
14.8	10^{-6}

3. next we transform this Hamiltonian back into the basis of local orbitals, where the Hamiltonian has the form $\bar{h}_{a,b} = \langle \chi_a | \hat{\bar{h}} | \chi_b \rangle$, respectively $\hat{\bar{j}} = \sum_{a,b} |\pi_a\rangle h_{a,b} \langle \pi_b|$.

$$\hat{\bar{h}} = \sum_n |\psi'_n\rangle \epsilon_n \langle \psi'_n|$$

$$\langle \chi_a | \hat{\bar{h}} | \chi_b \rangle = \sum_n \langle \chi_a | \psi'_n \rangle \epsilon_n \langle \psi'_n | \chi_b \rangle$$

$$= \sum_{n,c,d} \langle \chi_a | \chi_c \rangle \langle \pi_c | \psi'_n \rangle \epsilon_n \langle \psi'_n | \pi_d \rangle \langle \chi_d | \chi_b \rangle = V_{a,n} \epsilon_n V^{\dagger}_{n,b}$$

$$\bar{h}(\vec{k}) = V \epsilon V^{\dagger} \tag{1.123}$$

DMFT_EOFF

The routine `DMFT\_EOFF` constructs the energy relative to the Fermi level $x = \epsilon - \mu$ for a given occupation f. It modifies the Fermi distribution in order to avoid infinities near $f = 0$ and $f = 1$. Furthermore the modified mapping produces energies even for occupations outside the interval $[0, 1]$. The modification is to extend the fermi functions linearly outside the interval $[f_{min}, 1 - f_{min}]$, where f_{min} is a fixed parameter.

Let us first determine the inverted function of the Fermi distribution and calculate its energies.

$$f(x) = \left(1 + e^{\beta x}\right)^{-1} \quad \Rightarrow f + f e^{\beta x} = 1 \quad \Rightarrow e^{\beta x} = \frac{1 - f}{f} \tag{1.124}$$

$$\Rightarrow \quad x(f) = k_B T \ln\left(\frac{1-f}{f}\right) \tag{1.125}$$

$$\Rightarrow \quad \frac{dx}{df} = k_B T \frac{f}{1-f}\left[\frac{-1}{f} - \frac{1-f}{f^2}\right] = k_B T \frac{f}{1-f}\left[\frac{-1}{f} - \frac{1-f}{f^2}\right]$$

$$= -k_B T \frac{1}{f(1-f)} \tag{1.126}$$

- for $f \in [f_{min}, 1 - f_{min}]$ we evaluate

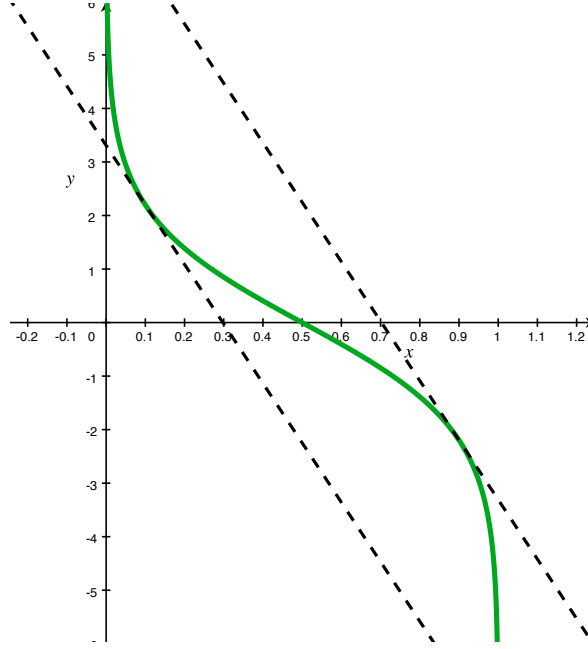$$x(f) = k_B T \ln\left(\frac{1-f}{f}\right) \tag{1.127}$$

Fig. 1.1: Inverted Fermi function (green full line) and linear extensions (dashed) map occupations onto energies in DMFT_EOFF. Here the extensions are at $f_0 = 0.1$ and $f_0 = 0.9$.

- for f outside the interval $f \in [f_{min}, 1 - f_{min}]$, we choose

$$f_0 = \begin{cases} f_{min} & \text{for } f \leq f_{min} \\ 1 - f_{min} & \text{for } f \geq 1 - f_{min} \end{cases} \tag{1.128}$$

and determine

$$x(f) = x(f_0) + \left. \frac{dx}{df} \right|_{f_0} (f - f_0) \tag{1.129}$$

This construction produces a unique mapping from the occupations to the energies $\epsilon = \mu + x$, even for occupations outside $[0, 1]$.

1.8.8   DMFT_CONSTRAINTS

Green's function

The Green's function is calculated as follows

$$\boldsymbol{G}(\vec{k}, i\omega_\nu) = \left[(i\omega_\nu + \mu)\boldsymbol{S}(\vec{k}) - \bar{\boldsymbol{h}}(\vec{k}) + \boldsymbol{\Gamma}(\vec{k}) - \sum_R \boldsymbol{\Sigma}_R^{dyn}(i\omega_\nu) \right]^{-1} \tag{1.130}$$

As described in section B.3.2 on p. 48, the Laurent-expansion coefficients are

$$\mathcal{G}^{(1)}(\vec{k}) = \boldsymbol{S}^{-1}(\vec{k})$$

$$\mathcal{G}^{(2)}(\vec{k}) = \boldsymbol{S}^{-1}(\vec{k})\left(-\mu\boldsymbol{S}(\vec{k}) + \bar{\boldsymbol{h}}(\vec{k}) - \boldsymbol{\Gamma}(\vec{k}) + \mathcal{S}^{(0)}_{dyn}(\vec{k})\right)\boldsymbol{S}^{-1}(\vec{k})$$

$$\mathcal{G}^{(3)}(\vec{k}) = \boldsymbol{S}^{-1}(\vec{k})\left[\mathcal{S}^{(1)}_{dyn}(\vec{k}) + \left(-\mu\boldsymbol{S}(\vec{k}) + \bar{\boldsymbol{h}}(\vec{k}) - \boldsymbol{\Gamma}(\vec{k}) + \mathcal{S}^{(0)}_{dyn}(\vec{k})\right)\right.$$

$$\left.\times\boldsymbol{S}^{-1}(\vec{k})\left(-\mu\boldsymbol{S}(\vec{k}) + \bar{\boldsymbol{h}}(\vec{k}) - \boldsymbol{\Gamma}(\vec{k}) + \mathcal{S}^{(0)}_{dyn}(\vec{k})\right)\right]\boldsymbol{S}^{-1}(\vec{k})$$

$$(1.131)$$

Green's function difference

In order to calculate the constraint, it may be adviseable to directly evaluate the difference of te Green's function from the non-interacting Greens function $\bar{\boldsymbol{G}}$.

$$\Delta\mathcal{G}^{(1)}(\vec{k}) = 0$$

$$\Delta\mathcal{G}^{(2)}(\vec{k}) = \boldsymbol{S}^{-1}(\vec{k})\left(\mathcal{S}^{(0)}_{dyn}(\vec{k}) - \boldsymbol{\Gamma}(\vec{k})\right)\boldsymbol{S}^{-1}(\vec{k})$$

$$\Delta\mathcal{G}^{(3)}(\vec{k}) = \boldsymbol{S}^{-1}(\vec{k})\left[\mathcal{S}^{(1)}_{dyn}(\vec{k}) + \left(-\mu\boldsymbol{S}(\vec{k}) + \bar{\boldsymbol{h}}(\vec{k}) - \boldsymbol{\Gamma}(\vec{k}) + \mathcal{S}^{(0)}_{dyn}(\vec{k})\right)\right.$$

$$\times\boldsymbol{S}^{-1}(\vec{k})\left(-\mu\boldsymbol{S}(\vec{k}) + \bar{\boldsymbol{h}}(\vec{k}) - \boldsymbol{\Gamma}(\vec{k}) + \mathcal{S}^{(0)}_{dyn}(\vec{k})\right)$$

$$\left.-\left(-\mu\boldsymbol{S}(\vec{k}) + \bar{\boldsymbol{h}}(\vec{k})\right)\boldsymbol{S}^{-1}(\vec{k})\left(-\mu\boldsymbol{S}(\vec{k}) + \bar{\boldsymbol{h}}(\vec{k})\right)\right]\boldsymbol{S}^{-1}(\vec{k})\qquad(1.132)$$

Update $\boldsymbol{\Gamma}$

UPDATE $\boldsymbol{\Gamma}$

The following two equations are solved iteratively[a]

$$\delta\boldsymbol{\rho}(\vec{k}) = \left(\frac{1}{\beta}\sum_{\nu}\underbrace{\left[(i\omega_\nu + \mu)\boldsymbol{S}(\vec{k}) - \bar{\boldsymbol{h}}(\vec{k}) + \boldsymbol{\Gamma}(\vec{k}) - \sum_R\boldsymbol{\Sigma}^{dyn}_R(i\omega_\nu)\right]^{-1}}_{\boldsymbol{G}(\vec{k})}\right)]$$

$$-\underbrace{\left[(i\omega_\nu + \mu)\boldsymbol{S}(\vec{k}) - \bar{\boldsymbol{h}}(\vec{k})\right]^{-1}}_{\bar{\boldsymbol{G}}(\vec{k})}\Bigg)$$

$$\boldsymbol{\Gamma}(\vec{k}) = \boldsymbol{\Gamma}(\vec{k}) - \left[\frac{4}{\beta}\boldsymbol{S}(\vec{k})\delta\rho(\vec{k})\boldsymbol{S}(\vec{k})\right]^{\top} \qquad (1.133)$$

until $\delta\boldsymbol{\rho}$ vanishes.[b]

---

[a]Instead of subtracting the density matrix from the Matsubara sum for the Green'sfunction, we subtract the Greens function $\bar{\boldsymbol{G}}$ inside the Matsubara sum to avoid numerical problems due to the finite Matsubara sum.
[b]The transposition in the expression for $\boldsymbol{\Gamma}$ is needed, because $dQ = \text{Tr}(\boldsymbol{\Gamma}\,d\boldsymbol{\rho})$.

This equation is a Newton scheme with the Green's function in the slope estimate replaced by

the non-interacting Green's function with zero potential self energy and chemical potential.

$$\delta\boldsymbol{\rho}(\boldsymbol{\Gamma}) = \delta\boldsymbol{\rho}(\boldsymbol{\Gamma}_0) - \frac{1}{\beta}\sum_\nu \boldsymbol{G}(\boldsymbol{\Gamma} - \boldsymbol{\Gamma}_0)\boldsymbol{G} + \dots \qquad (1.134)$$

Now we approximate $\boldsymbol{G}$ by $(i\hbar\omega_\nu)^{-1}\boldsymbol{S}^{-1}$

$$\delta\boldsymbol{\rho}(\boldsymbol{\Gamma}) = \delta\boldsymbol{\rho}(\boldsymbol{\Gamma}_0) - \frac{1}{\beta}\underbrace{\left[\sum_\nu \frac{1}{(i\hbar\omega_\nu)^2}\right]}_{-\beta/4}\boldsymbol{S}^{-1}(\boldsymbol{\Gamma} - \boldsymbol{\Gamma}_0)\boldsymbol{S}^{-1} + \dots$$

$$= \delta\boldsymbol{\rho}(\boldsymbol{\Gamma}_0) + \frac{1}{4}\beta\boldsymbol{S}^{-1}(\boldsymbol{\Gamma} - \boldsymbol{\Gamma}_0)\boldsymbol{S}^{-1} + \dots$$

$$\Rightarrow \qquad \boldsymbol{\Gamma} = \boldsymbol{\Gamma}_0 + \frac{4}{\beta}\boldsymbol{S}\Big(\underbrace{\delta\boldsymbol{\rho}(\boldsymbol{\Gamma})}_{=0} - \delta\boldsymbol{\rho}(\boldsymbol{\Gamma}_0)\Big)\boldsymbol{S} \qquad (1.135)$$

Should there be convergence problems, it may be improved by using the static Green's function $\boldsymbol{G}_\rho$ instead.

1.8.9   DMFT_SOLVER

The solver first calculates the Hartree-Fock contribution to the Luttinger-Ward functional as defined in Eq. **??** and the corresponding self energy. Because the Hartree-Fock self energy is static and because it does not affect the density matrix constraint, it is added together with the double counting correction to `atomset%denmat%h`.

Then the double counting correction is calculated. **At the moment we still subtract out only the exchange part, which is consistent with the hybrid functionals but not as double counting for correlation.**

Finally the data are prepared for the solver in `DMFT_dynamicsolver`. The dynamicsolver transforms all data into a spin-orbital representation of orthonormal states, which may be either natural orbitals derived from the local density matrix or which may be eigenstates of the local overlap matrix.

1.8.10   DMFT_ETOT

When the loop is converged, we evaluate

$$Q^{\hat{W}_2}_{dyn,\beta}[\boldsymbol{\rho}] = \Bigg\{ \Phi^{LW}_\beta[\boldsymbol{G}, \hat{W}_2] - \Phi^{HF,LW}_\beta[\boldsymbol{G}, \hat{W}_2]$$

$$-\frac{1}{\beta}\sum_\nu \mathrm{Tr}\Big\{ \ln\Big[\boldsymbol{1} - \bar{\boldsymbol{G}}(i\omega_\nu)\Big(\boldsymbol{\Sigma}_{dyn}(i\omega_\nu) - \boldsymbol{\Gamma}\Big)\Big]$$

$$+\Big(\boldsymbol{\Sigma}_{dyn}(i\omega_\nu) - \boldsymbol{\Gamma}\Big)\boldsymbol{G}(i\omega_\nu) + \Big[\boldsymbol{G}(i\omega_\nu) - \bar{\boldsymbol{G}}(i\omega_\nu)\Big]\boldsymbol{\Gamma}\Big\}$$

$$(1.136)$$

Evaluation of the logarithm using a power series expansion

We use the Taylor expansion of the logarithm

$$\ln[1-x] = -\sum_{n=1}^{\infty}\frac{1}{n}x^n \qquad \text{for } |x| < 1 \tag{1.137}$$

$$
\begin{aligned}
Q_{dyn,\beta}^{\hat{W}_2}[\boldsymbol{\rho}] &= \Phi_\beta^{LW}[\boldsymbol{G},\hat{W}_2] - \Phi_\beta^{HF,LW}[\boldsymbol{G},\hat{W}_2] \\
&\quad -\frac{1}{\beta}\sum_\nu \text{Tr}\Big\{ -\sum_{n=1}^{\infty}\frac{1}{n}\Big[\bar{\boldsymbol{G}}(i\omega_\nu)\Big(\boldsymbol{\Sigma}_{dyn}(i\omega_\nu)-\boldsymbol{\Gamma}\Big)\Big]^n \\
&\quad +\Big(\boldsymbol{\Sigma}_{dyn}(i\omega_\nu)-\boldsymbol{\Gamma}\Big)\boldsymbol{G}(i\omega_\nu) + \Big[\boldsymbol{G}(i\omega_\nu)-\bar{\boldsymbol{G}}(i\omega_\nu)\Big]\boldsymbol{\Gamma}\Big\} \\
&= \Phi_\beta^{LW}[\boldsymbol{G},\hat{W}_2] - \Phi_\beta^{HF,LW}[\boldsymbol{G},\hat{W}_2] \\
&\quad -\frac{1}{\beta}\sum_\nu \text{Tr}\Big\{ \boldsymbol{\Sigma}_{dyn}(i\omega_\nu)\Big[\boldsymbol{G}(i\omega_\nu)-\bar{\boldsymbol{G}}(i\omega_\nu)\Big] - \sum_{n=2}^{\infty}\frac{1}{n}\Big[\bar{\boldsymbol{G}}(i\omega_\nu)\Big(\boldsymbol{\Sigma}_{dyn}(i\omega_\nu)-\boldsymbol{\Gamma}\Big)\Big]^n\Big\}
\end{aligned}
$$
$$\tag{1.138}$$

Evaluation of the logarithm using Dahlen's trick

The evaluation fo the logarithm is problematic, because Green's function and self energy are not hermitean. In appendix B of their paper[6] Dahlen et al proposed a trick to solve the problem. It is not yet clear to me if this trick is correct.See some relations for non-hermitean matrices appendix C of Bickers et al.[7]

The trick rests on the assumption of the following identity

$$\text{Tr}\ln(\boldsymbol{A}\boldsymbol{A}^\dagger) \overset{?}{=} \text{Tr}\ln(\boldsymbol{A}) + Tr\ln(\boldsymbol{A}^\dagger) \tag{1.139}$$

which should be valid for arbitrary non-hermitean matrices $\boldsymbol{A}$.

Consider the singular value decompostion of $\boldsymbol{A} = \boldsymbol{U}\boldsymbol{\Sigma}\boldsymbol{V}^\dagger$, where $\boldsymbol{U}$ and $\boldsymbol{V}$ are unitary matrices and $\boldsymbol{\Sigma}$ is a diagonal matrix with real, non-negative numbers, the singular values, on the diagonal.

$$
\begin{aligned}
\text{Tr}\ln(\boldsymbol{A}\boldsymbol{A}^\dagger) &= \text{Tr}\ln(\boldsymbol{U}\boldsymbol{\Sigma}\boldsymbol{V}^\dagger\boldsymbol{V}\boldsymbol{\Sigma}^\dagger\boldsymbol{U}^\dagger) = \text{Tr}\ln(\boldsymbol{U}\boldsymbol{\Sigma}\boldsymbol{\Sigma}^\dagger\boldsymbol{U}^\dagger) = \text{Tr}\Big[\boldsymbol{U}\ln(\boldsymbol{\Sigma}\boldsymbol{\Sigma}^\dagger)\boldsymbol{U}^\dagger\Big] \\
&= \text{Tr}\Big[\ln(\boldsymbol{\Sigma}\boldsymbol{\Sigma}^\dagger)\Big] = \sum_i \ln(s_i) + \sum_i \ln(s_i) + = \text{Tr}\ln[\boldsymbol{\Sigma}] + \text{Tr}\ln[\boldsymbol{\Sigma}^\dagger]
\end{aligned}
$$
$$\text{Tr}\ln(\boldsymbol{A}) + Tr\ln(\boldsymbol{A}^\dagger) = \text{Tr}\ln(\boldsymbol{U}\boldsymbol{\Sigma}\boldsymbol{V}^\dagger) + \text{Tr}\ln(\boldsymbol{V}\boldsymbol{\Sigma}^\dagger\boldsymbol{U}^\dagger) \tag{1.140}$$

Unfortunately $\boldsymbol{V}^\dagger\boldsymbol{U} \neq \boldsymbol{1}$ so that we cannot simply convert the power series expansion into one of the singular values.This is the problem.

Instead of the singular value decomposition, we can also simply use the eigenvalue equation

$$\boldsymbol{A}\boldsymbol{V} = \boldsymbol{V}\boldsymbol{\Sigma} \tag{1.141}$$

so that

$$
\begin{aligned}
\boldsymbol{A} &= \boldsymbol{V}\boldsymbol{\Sigma}\boldsymbol{V}^{-1} \\
\boldsymbol{A}^\dagger &= \boldsymbol{V}^{-1,\dagger}\boldsymbol{\Sigma}^*\boldsymbol{V}^\dagger
\end{aligned}
$$
$$\tag{1.142}$$

Unfortunately, the same problem arises, because, in general, $\boldsymbol{V}\boldsymbol{V}^\dagger \neq \boldsymbol{1}$.

Chapter 2

Tests and Numerical problems

- for insulators the Fermi-level is not well defined. It tends to fluctuate insite the band gap.

- in order to limit the number of times the solver has to be called explicitely, one may linearize the Luttinger-Ward functional

$$\Phi^{LW}[\boldsymbol{G}] \approx \Phi^{LW}[\boldsymbol{G}_0] + \frac{1}{\beta}\sum_{\nu}\sum_{a,b}\left[\underbrace{\left.\frac{\beta\delta\Phi^{LW}}{\delta G_{a,b}(i\omega_\nu)}\right|_{\boldsymbol{G}_0}}_{\Sigma_{0,b,a}(i\omega_\nu)}\left(\boldsymbol{G}_{a.b}(i\omega_\nu) - \boldsymbol{G}_{0,a,b}(i\omega_\nu)\right)\right] \quad (2.1)$$

  $\boldsymbol{G}_0$ is the last Greens function for which the Luttinger ward functional and the self energy has been calculated explicitely. The approximate form can be used until convergence of the outer loop is reached. Then the Luttinger Ward functional is updated and the cycle is repeated.

- semi-core states may be a problem, because their occupation is near integer so that large changes in Γ are required to adjust the occupation.

- It may be helpful to diagonalize $\bar{h} - \boldsymbol{Gamma}$ in dmft_constraints in order to make the connection between occupation and eigenlevels more direct.

- there are unknown factors of 0.25 and 2, once in the derivatives of drho^2 and once integrating Γ into the waves object.

Appendix A

Matsubara frequencies

The **Matsubara frequencies** for Fermions are

$$\omega_\nu = (2\nu + 1)\frac{\pi}{\hbar\beta}$$

A **Matsubara sum** has the general form

$$\frac{1}{\beta}\sum_{\nu\in z} g(i\omega_\nu)$$

where $g(i\omega_\nu)$ is a analytic function.

A.1   Evaluation using residual theorem

In order to evaluate the Matsubara sum we introduce a **Matsubara weighting functions**, that has simple poles at $i\omega_\nu$, so that we can exploit the residuum theorem. For Fermions, two such weighting functions are used

$$h^\pm(z) = \frac{\mp\beta\hbar}{1 + e^{\pm\beta\hbar z}} \tag{A.1}$$

The poles of the Matsubara weighting functions obey

$$1 + e^{\pm\beta\hbar z} = 0 \tag{A.2}$$

With the help of

$$e^{\pm\beta\hbar z} = e^{\pm\beta\hbar \mathrm{Re}(z)}e^{\pm i\beta\hbar\mathrm{Im}(z)} = e^{\beta\hbar\mathrm{Re}(z)}\cos(\beta\hbar\mathrm{Im}(z)) \pm ie^{\beta\hbar\mathrm{Re}(z)}\sin(\beta\hbar\mathrm{Im}(z))$$

Eq. A.2 can be rewrfitten in the form

$$\Rightarrow e^{\pm\beta\hbar\mathrm{Re}(z)}\cos(\beta\hbar\mathrm{Im}(z)) = -1 \quad \text{and} \quad e^{\pm\beta\hbar\mathrm{Re}(z)}\sin(\beta\hbar\mathrm{Im}(z)) = 0 \tag{A.3}$$

The second equation is obeyed for

$$\mathrm{Im}(z) = \frac{n\pi}{\hbar\beta} \quad \text{for arbitrary integer } n \tag{A.4}$$

The first equation yields

$$-1 = e^{\pm\beta\hbar\text{Re}(z)}\cos(\beta\hbar\text{Im}(z)) = e^{\pm\beta\hbar\text{Re}(z)}\cos(n\pi) = e^{\pm\beta\hbar\text{Re}(z)}(-1)^n$$
$$\Rightarrow n - 1 = 2\nu \qquad \text{for arbitrary integer } \nu, \text{ and } Re(z) = 0$$
$$\Rightarrow n = 2\nu + 1 \tag{A.5}$$

Thus we obtain that the poles of the Matsubara weighting function lie at the Matsubara frequencies.

$$z_\nu = i(2\nu + 1)\frac{\pi}{\hbar\beta} = i\omega_\nu \tag{A.6}$$

Next we need to show that the weighting function at the poles behaves like $\frac{1}{z-z_0}+O(|z-z_0|^2)$, where x_0 is the position of the pole. For this purpose we expand the inverse

$$\frac{1}{\mp\hbar\beta}(1 + e^{\pm\hbar\beta z}) = \frac{1}{\mp\hbar\beta}(\underbrace{1 + e^{\pm\hbar\beta z_0}}_{=0} \pm\hbar\beta \underbrace{e^{\pm\hbar\beta z_0}}_{-1}(z - z_0) + O(|z - z_0|^2)) \tag{A.7}$$

$$= (z - z_0) + O(|z - z_0|^2) \tag{A.8}$$

With the help of the Matsubara weighting function we can evaluate the Matsubara sum as[1]

$$\frac{1}{\beta}\sum_{nu\in Z} g(i\omega_\nu) = \frac{1}{2\pi i\beta}\oint g(z)h^\pm(z) = -\frac{1}{\beta}\sum_{z_0\in\text{poles of g}} \text{Res}(gh^\pm, z_0) \tag{A.9}$$

The minus sign occurs because the c ounter clockwise integration of the contur in the half plane turns into a clock-wise integration about the pole.
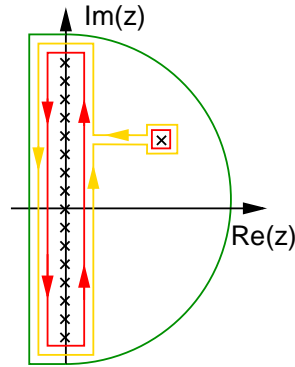
The integration is closed in the half plane with $\pm Re(z) > 0$, because we there the corresponding weighting function $h^\pm$ decays exponentially for $Re(z) \to \pm\infty$.

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[1] Cauchy's Integral formula:

$$Res(f, z_0) = \frac{1}{2\pi i}\oint_\gamma dz\, f(z)$$

where γ is a counter-clockwise countour around a pole z_0 of a function f, that can be expanded into a Laurent series about z_0. The Residuum is the prefactor of the term $1/(z - z_0)$ in the Laurent expansion.

A.1.1 Matsubara sums

From http://en.wikipedia.org/wiki/Matsubara_frequency we obtain the following expression for the **fermionic** summations. In these expressions the Matsubara frequencies are[2]

$$\omega_\nu = (2\nu + 1)\pi/(\hbar\beta) \tag{A.10}$$

$$-k_B T \sum_\nu \ln[-i\hbar\omega_\nu + \epsilon] e^{i\omega_\nu 0^+} = -k_B T \ln[1 + e^{-\beta\epsilon}] \tag{A.11}$$

$$k_B T \sum_\nu \frac{1}{(i\hbar\omega_\nu - \epsilon)} e^{i\omega_\nu 0^+} = (1 + e^{\beta\epsilon})^{-1} \tag{A.12}$$

$$k_B T \sum_\nu \frac{1}{(i\hbar\omega_\nu - \epsilon)^n} = \frac{1}{(k_B T)^{n-1}(n-1)!} \left.\partial_\epsilon^{n-1}\right|_{x=\beta\epsilon} (1 + e^x)^{-1} \tag{A.13}$$

j	1	2	3	4	5	6	7	8	9	10
$\partial_x^{j-1}(1+e^x)^{-1}$	$\frac{1}{2}$	$-\frac{1}{4}$	0	$+\frac{1}{8}$	0	$-\frac{1}{4}$	0	$\frac{17}{16}$	0	$-\frac{31}{4}$
$\partial_x^{j-1}(1+e^x)^{-1}$	0.5	-0.25	0	$+0.125$	0	-0.25	0	$+1.0625$	0	-7.75

j	11	12	13	14	15	16	17	18	19	20
$\partial_x^{j-1}(1+e^x)^{-1}$	0	$\frac{691}{8}$	0	$-\frac{5461}{4}$	0	$\frac{929569}{32}$	0	$-\frac{3202291}{4}$	0	$+\frac{221930581}{8}$
$\partial_x^{j-1}(1+e^x)^{-1}$	0	86.375	0	-1365.25	0	29.0×10^3	0	-800×10^3	0	27.7×10^6

A.1.2 Matsubara sums on finite grids

The finite Matsubara sums result in a Fermi function that does not reach zero or one. In particular, in the limit of e level, that lies far from the chemical potential, the finite Matsubara sum falls off to $\frac{1}{2}$.

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[2]They differ from those of the source by a factor $1/\hbar$.
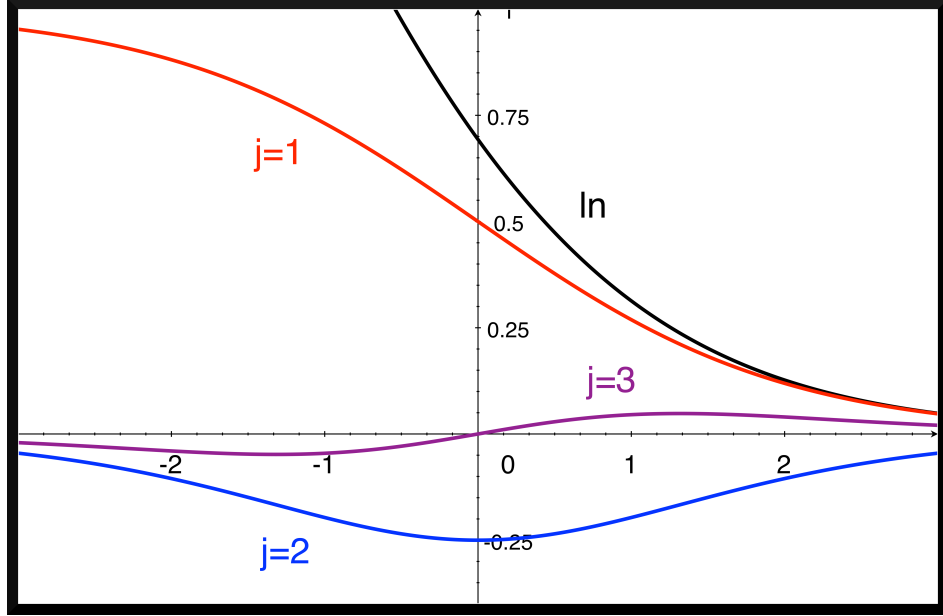
Fig. A.1: The result of Matsubara sums $-k_BT \sum_\nu \ln[-i\hbar\omega_\nu + \epsilon]$, $k_BT \sum_\nu \frac{1}{(i\hbar\omega_\nu - \epsilon)} e^{i\omega_\nu 0^+}$, $k_BT \sum_\nu \frac{1}{(i\hbar\omega_\nu - \epsilon)^2}$ as function of energy ϵ.
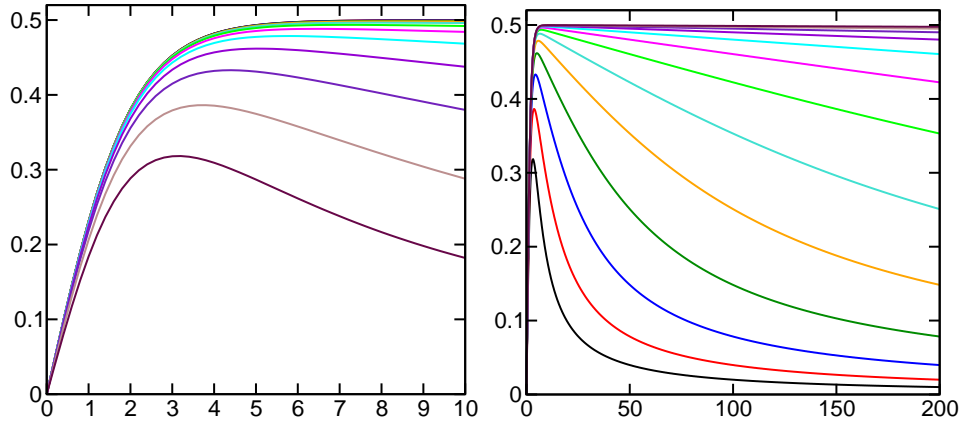

Fig. A.2: Fermi function calculated from a finite Matsubara sum. The function is shifted by $-\frac{1}{2}$ because no relgularization has been done. The sums have been performed with 2^n grid points with $n = 0, \ldots, 12$ for $k_BT = 1$.

Appendix B

The Green function

B.1 Generic properties

B.1.1 Green's function with negative Matsubara frequencies

Green's functions and self energies obey the relation

$$\boldsymbol{G}(-i\omega_\nu) = \boldsymbol{G}^\dagger(i\omega) \tag{B.1}$$

This allows one to store only half of the Green's functions.

    Proof:

$$
\begin{aligned}
G_{\alpha,\beta}(i\omega_n) \quad &= \quad -\frac{1}{\hbar}\int_0^{\hbar\beta} d\tau\; e^{i\omega_n\tau}\left\langle \mathcal{T}\hat{c}_\alpha(\tau)\hat{c}_\beta^\dagger(0)\right\rangle \tag{B.2}\\
\Rightarrow G_{\alpha,\beta}(-i\omega_n) \quad &= \quad -\frac{1}{\hbar}\int_0^{\hbar\beta} d\tau\; e^{-i\omega_n\tau}\left\langle \mathcal{T}\hat{c}_\alpha(\tau)\hat{c}_\beta^\dagger(0)\right\rangle\\
&= \quad \left\{-\frac{1}{\hbar}\int_0^{\hbar\beta} d\tau\; e^{i\omega_n\tau}\left\langle \left(e^{\beta(\hat{H}-\mu\hat{N})}\hat{c}_\alpha e^{-\beta(\hat{H}-\mu\hat{N})}\hat{c}_\beta^\dagger\right)^\dagger\right\rangle\right\}^*\\
&= \quad \left\{-\frac{1}{\hbar}\int_0^{\hbar\beta} d\tau\; e^{i\omega_n\tau}\left\langle \hat{c}_\beta e^{-\beta(\hat{H}-\mu\hat{N})}\hat{c}_\alpha^\dagger e^{\beta(\hat{H}-\mu\hat{N})}\right\rangle\right\}^*\\
&\overset{cycl.perm}{=} \quad \left\{-\frac{1}{\hbar}\int_0^{\hbar\beta} d\tau\; e^{i\omega_n\tau}\left\langle e^{\beta(\hat{H}-\mu\hat{N})}\hat{c}_\beta e^{-\beta(\hat{H}-\mu\hat{N})}\hat{c}_\alpha^\dagger\right\rangle\right\}^*\\
&= \quad \left\{-\frac{1}{\hbar}\int_0^{\hbar\beta} d\tau\; e^{i\omega_n\tau}\left\langle \mathcal{T}\hat{c}_\beta(\tau)\hat{c}_\alpha^\dagger\right\rangle\right\}^*\\
&= \quad G_{\beta,\alpha}^*(i\omega_\nu) \tag{B.3}
\end{aligned}
$$

B.1.2 Density of states

For a system of independent electrons, the number of particles is related to the chemical potential via

$$N(\mu) = \int_{-\infty}^{\infty} d\epsilon\; f_\mu(\epsilon)D(\epsilon)\,, \tag{B.4}$$

where D is the density of states. $f_\mu(\epsilon)$ is the Fermi function.

$$\frac{dN}{d\mu} = \int_{-\infty}^{\infty} d\epsilon \, \frac{\partial f_\mu(\epsilon)}{\partial \mu} D(\epsilon) = \int_{-\infty}^{\infty} d\epsilon \, \underbrace{\frac{\beta}{\cosh^2\left(\frac{1}{2}\beta(\epsilon - \mu)\right)} D(\epsilon)}_{\tilde{D}(\mu)} \tag{B.5}$$

Thus $dN/d\mu$ provides us with a broadened density of states.

Now we generalize the relation obtained for independent Fermions to interacting Fermions. The number of states function $N_{a,b}(\mu)$ can be obtained from the Green's function

$$N_{a,b}(\mu) = \frac{1}{\beta} \sum_\nu G_{a,b}(i\omega_\nu, \mu) e^{i\omega_\nu 0^+} = \frac{1}{\beta} \sum_\nu \left[\left(\boldsymbol{G}(i\omega_\nu, \mu_0)\right)^{-1} + (\mu - \mu_0)\right]_{a,b}^{-1} e^{i\omega_\nu 0^+} \tag{B.6}$$

The smoothened density of states $\tilde{D}_{a,b}(\mu)$ is then obtained as derivative with respect to μ.

$$\tilde{D}_{a,b}(\mu) \overset{\text{def}}{=} \frac{\partial N_{a,b}}{\partial \mu}$$

$$= -\frac{1}{\beta} \sum_\nu \sum_c \left[\left(\boldsymbol{G}(i\omega_\nu, \mu_0)\right)^{-1} + (\mu - \mu_0)\boldsymbol{1}\right]_{a,c}^{-1} \left[\left(\boldsymbol{G}(i\omega_\nu, \mu_0)\right)^{-1} + (\mu - \mu_0)\boldsymbol{1}\right]_{c,b}^{-1}$$

$$\tag{B.7}$$

This relation is however only valid for non-interacting electrons, because a self energy may depend itself on the chemical potential.

B.2   Greens functions between band states and local orbitals

B.2.1   Lattice Greens functions and limited set of band states

We construct the **lattice Green's function** defined as

$$\hat{G}^{lat}(i\omega_\nu) = \left[(i\hbar\omega_\nu + \mu)\hat{1} - \hat{h} - \Delta\hat{\Sigma}(i\omega_\nu)\right]^{-1}$$

$$= \sum_{n,n'}^{\infty} |\psi_n\rangle \underbrace{\left[\langle\psi_{n'}|(i\hbar\omega_\nu + \mu)\hat{1} - \hat{h} - \Delta\hat{\Sigma}(i\omega_\nu)|\psi_n\rangle\right]_{n,n'}^{-1}}_{G_{n,n'}^{lat}} \langle\psi_{n'}|$$

$$\approx \sum_{n,n'}^{N_x} |\psi_n\rangle \underbrace{\left[\langle\psi_{n'}|(i\hbar\omega_\nu + \mu)\hat{1} - \hat{h} - \Delta\hat{\Sigma}(i\omega_\nu)|\psi_n\rangle\right]_{n,n'}^{-1}}_{G_{n,n'}^{lat}} \langle\psi_{n'}| \tag{B.8}$$

This expression is approximate, if the set of band states is not complete. In practice, corrections are required.

In the representation of the band states, the lattice Green's function has the form

$$G_{n,n'}^{lat}(i\omega_\nu) = \left[\langle\psi_{n'}|(i\hbar\omega_\nu + \mu)\hat{1} - \hat{h} - \Delta\hat{\Sigma}(i\omega_\nu)|\psi_n\rangle\right]_{n,n'}^{-1} \tag{B.9}$$

Note, that the matrix to be inverted is not necessarily hermitean!

B.2.2   Green's function on the Hilbert space of correlated orbitals

Here, we define the Green's function as inverse of a Hamiltonian, which is projected onto a sub-Hilbert space of correlated orbitals.

We introduce the projection operator onto the correlated orbitals.

$$\hat{\mathcal{P}}_\chi = \sum_{a,b} |\chi_a\rangle S_{a,b}^{-1}\langle\chi_b| \qquad \text{with} \qquad \sum_c S_{a,c}^{-1}\langle\chi_c|\chi_b\rangle = \delta_{a,b} \tag{B.10}$$

onto the correlated orbitals. The projection operator is idempotent, i.e. $\hat{\mathcal{P}}_\chi^2 = \hat{\mathcal{P}}_\chi$

The Green's function is that operator that acts in the Hilbert space of the correlated orbitals, and that inverts the Hamiltonian projected onto that Hilbert space. Thus the following equation defines the Greens function.

$$\hat{G}\hat{\mathcal{P}}_\chi \left[(i\hbar\omega_\nu + \mu)\hat{1} - \hat{h} - \sum_{c,d} |\pi_c\rangle \Sigma_{c,d}(i\omega_\nu)\langle\pi_d| \right]\hat{\mathcal{P}}_\chi = \hat{\mathcal{P}}_\chi \tag{B.11}$$

We extract the matrix elements of the Green's function $\hat{G} = |\chi\rangle \boldsymbol{G}\langle\chi|$.

$$\underbrace{|\chi\rangle \boldsymbol{G}\langle\chi|}_{\hat{G}}\underbrace{|\chi\rangle \boldsymbol{S}^{-1}\langle\chi|}_{\hat{\mathcal{P}}_\chi} \left[(i\hbar\omega_\nu + \mu)\hat{1} - \hat{h} - \sum_{c,d} |\pi_c\rangle \Sigma_{c,d}(i\omega_\nu)\langle\pi_d| \right]\underbrace{|\chi\rangle \boldsymbol{S}^{-1}\langle\chi|}_{\hat{\mathcal{P}}_\chi} = \underbrace{|\chi\rangle \boldsymbol{S}^{-1}\langle\chi|}_{\hat{\mathcal{P}}_\chi}$$

$$\boldsymbol{G}\langle\chi| \left[(i\hbar\omega_\nu + \mu)\hat{1} - \hat{h} - \sum_{c,d} |\pi_c\rangle \Sigma_{c,d}(i\omega_\nu)\langle\pi_d| \right]|\chi\rangle = \boldsymbol{1}$$

$$\boldsymbol{G}\left[(i\hbar\omega_\nu + \mu)\boldsymbol{S} - \langle\chi|\hat{h}|\chi\rangle - \boldsymbol{\Sigma}(i\omega_\nu) \right] = \boldsymbol{1}$$
$$\tag{B.12}$$

which yields with $\hat{h} = \sum_n |\psi_n\rangle\epsilon_n\langle\chi_n|$

$$\boldsymbol{G} = \left[(i\hbar\omega_\nu + \mu)\boldsymbol{S} - \sum_{n=1}^{\infty} \langle\chi|\psi_n\rangle\epsilon_n\langle\psi_n|\chi\rangle - \boldsymbol{\Sigma}(i\omega_\nu) \right]^{-1} \tag{B.13}$$

This expression involves still an infinite sum over band states, which are not all available in practice. In order to remedy this deficiency without introducing major errors, we modify the spectrum of of the Hamiltonian in an energy region above the partially occupied states. This approximation can be controlled by increasing the number N_x of states that are explicitly included in the sum. Specifically, we change all eigenvalues with a band index higher than N_x of the Hamiltonian to ϵ_x.

This transforms the Hamiltonian into its approximate form

$$\hat{h} \rightarrow \sum_{n=1}^{N_x} |\psi_n\rangle\epsilon_n\langle\psi_n| + \sum_{n=N_x+1}^{\infty} |\psi_n\rangle\epsilon_x\langle\psi_n| \tag{B.14}$$

The approximation allows one to limit the sum over states to a finite sum.

$$\boldsymbol{G} = \left[(i\hbar\omega_\nu + \mu - \epsilon_x)\boldsymbol{S} - \sum_{n=1}^{N_x} \langle\chi|\psi_n\rangle(\epsilon_n - \epsilon_x)\langle\psi_n|\chi\rangle - \boldsymbol{\Sigma}(i\omega_\nu) \right]^{-1} \tag{B.15}$$

After limiting the sum over the states that can be well represented by the correlated orbitals, we use the approximation $|\psi_n\rangle = \sum_a |\chi_a\rangle\langle\pi_a|\psi_n\rangle$, which yields

$$\langle\chi|\psi\rangle = \langle\chi|\chi\rangle\langle\pi|\hat{\mathcal{P}}_\chi|\psi\rangle = S\langle\pi|\hat{\mathcal{P}}_\chi|\psi\rangle \approx S\langle\pi|\psi\rangle \tag{B.16}$$

The results depends on how well the band states are representable by the correlated orbitals. Thus, it is important to limit the sum over band states to those that are well represented by tight-binding orbitals. Furthermore one should always include a as complete as possible set of correlated orbiatals, rather that just limiting oneself to particular atoms. A potential test of this approximation is to evaluate the effect on the orthonormality of the band states in the form

$$\delta_{n,m} = \langle\psi_n|\psi_m\rangle \approx \sum_{a,b}\langle\psi_n|\pi_a\rangle\langle\chi_a|\chi_b\rangle\langle\pi_b|\psi_m\rangle = \sum_{a,b}\langle\psi_n|\pi_a\rangle S_{a,b}\langle\pi_b|\psi_m\rangle \tag{B.17}$$

With this approximation we obtain

GREENS FUNCTION PROJECTED

$$G = \left[(i\hbar\omega_\nu + \mu - \epsilon_x)S - \sum_{n=1}^{N_x} S\langle\pi|\psi_n\rangle(\epsilon_n - \epsilon_x)\langle\psi_n|\pi\rangle S - \Sigma(i\omega_\nu)\right]^{-1} \tag{B.18}$$

This matrix corresponds to

$$G = \left[(i\hbar\omega_\nu + \mu)S - \bar{h} + \Gamma - \Sigma(i\omega_\nu)\right]^{-1} \tag{B.19}$$

which allows one to make the identification (for full selfconsistency)

$$\epsilon_x\left[S - \sum_{n=1}^{N_x} S\langle\pi|\psi_n\rangle\langle\psi_n|\pi\rangle S\right] - \underbrace{\sum_{n=1}^{N_x} S\langle\pi|\psi_n\rangle\epsilon_n\langle\psi_n|\pi\rangle S}_{\rightarrow \frac{\hat{\bar{p}}^2}{2m} + v_{ext} + v_H + v_{xc}} = -\bar{h} + \Gamma$$

$$\Rightarrow \quad \bar{h} = \underbrace{\sum_{n=1}^{N_x} S\langle\pi|\psi_n\rangle\epsilon_n\langle\psi_n|\pi\rangle S}_{\rightarrow \frac{\hat{\bar{p}}^2}{2m} + v_{ext} + v_H + v_{xc}} - \epsilon_x\left[S - \sum_{n=1}^{N_x} S\langle\pi|\psi_n\rangle\langle\psi_n|\pi\rangle S\right] + \Gamma \tag{B.20}$$

B.3   Project Green's function onto local orbitals

For a Hamiltonian $\hat{h} = \sum_{a,b}|\pi_a\rangle h_{a,b}\langle\pi_b|$ and a self energy $\hat{\Sigma}(i\omega_\nu) = \sum_{a,b}|\pi_a\rangle\Sigma_{a,b}(i\omega_\nu)\langle\pi_b|$ acting on the local orbitals, the Green's function can be expressed as

$$\hat{G}(i\omega_\nu) = \sum_{a,b}|\chi_a\rangle\left\{\sum_{n,n'}\langle\pi_a|\psi_n\rangle\left[(i\hbar\omega_\nu + \mu)\delta_{n,n'}\right.\right.$$

$$\left.\left. - \sum_{c,d}\langle\psi_n|\pi_c\rangle\left(h_{c,d} + \Sigma_{c,d}(i\omega_\nu)\right)\langle\pi_d|\psi_{n'}\rangle\right]_{n,n'}^{-1}\langle\psi_{n'}|\pi_b\rangle\right\}\langle\chi_b| \tag{B.21}$$

We converted Eq. (B.8) into a basis of local orbitals $|\chi_a\rangle$ using $|\psi_n\rangle = \sum_a |\chi_a\rangle\langle\pi_a|\psi_n\rangle$.

In order to evaluate the Green's function, we still need to refer to the band states. The Green's function can, however, also be expressed without making direct use of the band states, namely as

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GREEN'S FUNCTION IN MATRIX FORM

For a hamiltonian $\hat{h}$ and a self energy $\hat{\Sigma}$ that can be expressed entirely in terms of projector functions, the Green's function in the approximate form of Eq. B.8 has the form

$$\hat{G}(i\omega_\nu) = \sum_{a,b} |\chi_a\rangle G_{a,b}(i\omega_\nu)\langle\chi_b| \tag{B.22}$$

with

$$G_{a,b}(i\omega_\nu)$$
$$= \left\{ \sum_{n,n'} \langle\pi_a|\psi_n\rangle \left[(i\hbar\omega_\nu + \mu)\delta_{n,n'} - \sum_{c,d}\langle\psi_n|\pi_c\rangle\Big(h_{c,d} + \Sigma_{c,d}(i\omega_\nu)\Big)\langle\pi_d|\psi_{n'}\rangle \right]_{n,n'}^{-1} \langle\psi_{n'}|\pi_b\rangle \right\}$$
$$= \left[(i\hbar\omega_\nu + \mu)\boldsymbol{S} - \boldsymbol{h} - \boldsymbol{\Sigma}(i\omega_\nu) \right]^{-1} \tag{B.23}$$

where[a]

$$S_{a,b}^{-1} = \langle\pi_a|\psi_n\rangle\langle\psi_n|\pi_b\rangle \tag{B.24}$$

---

[a]in a representation of Bloch states the inverse overlap calculation is calculated for each k-point and inverted.

Proof: Here, I will show that the Green's function matrix

$$\boldsymbol{G}_{a,b}(i\omega_\nu) = \sum_n \langle\pi_a|\psi_n\rangle \left[(i\hbar\omega_\nu + \mu)\delta_{n,n'} - \sum_{c,d}\langle\psi_n|\pi_c\rangle\Big(\boldsymbol{h}_{c,d} + \boldsymbol{\Sigma}_{c,d}(i\omega_\nu)\Big)\langle\pi_d|\psi_{n'}\rangle \right]_{n,n'}^{-1} \langle\psi_{n'}|\pi_b\rangle$$

$$\tag{B.25}$$

can be expressed in the form of Eq. B.23.

In order to simplify the proof, I will not write out the self energy, nor the chemical potential. This is possible because the proof works for each Matsubara frequency independently, so that

both can be absorbed in the non-interacting Hamiltonian.

$$
\begin{aligned}
G_{a,b}(i\omega_\nu) &= \sum_{n,n'} \langle \pi_a | \psi_n \rangle \left(i\hbar\omega_\nu \delta_{n,n'} - \langle \psi_n | \pi \rangle \boldsymbol{h} \langle \pi | \psi_{n'} \rangle \right)^{-1}_{n,n'} \langle \psi_{n'} | \pi_b \rangle \\
&= \sum_{n,n'} \langle \pi_a | \psi_n \rangle \left[\sum_{j=0}^{\infty} \frac{1}{(i\hbar\omega_\nu)^{j+1}} \left(\langle \psi | \pi \rangle \boldsymbol{h} \langle \pi | \psi \rangle \right)^j \right]_{n,n'} \langle \psi_{n'} | \pi_b \rangle \\
&= \sum_{n,n'} \langle \pi_a | \psi_n \rangle \left[\sum_{j=0}^{\infty} \frac{1}{(i\hbar\omega_\nu)^{j+1}} \left(\sum_{n_2,\ldots,n_j} \langle \psi_n | \pi \rangle \boldsymbol{h} \langle \pi | \psi_{n_2} \rangle \langle \psi_{n_2} | \pi \rangle \ldots \boldsymbol{h} \langle \pi | \psi_{n'} \rangle \right) \right] \langle \psi_{n'} | \pi_b \rangle \\
&= \sum_{j=0}^{\infty} \frac{1}{(i\hbar\omega_\nu)^{j+1}} \left(\sum_{n_1,\ldots,n_{j+1}} \underbrace{\langle \pi | \psi_{n_1} \rangle \langle \psi_{n_1} | \pi \rangle}_{\boldsymbol{S}^{-1}} \boldsymbol{h} \underbrace{\langle \pi | \psi_{n_2} \rangle \langle \psi_{n_2} | \pi \rangle}_{\boldsymbol{S}^{-1}} \ldots \boldsymbol{h} \underbrace{\langle \pi | \psi_{n_{j+1}} \rangle \langle \psi_{n_{j+1}} | \pi \rangle}_{\boldsymbol{S}^{-1}} \right)_{a,b} \\
&= \left(\sum_{j=0}^{\infty} \frac{1}{(i\hbar\omega_\nu)^{j+1}} \left(\boldsymbol{S}^{-1} \boldsymbol{h} \right)^j \boldsymbol{S}^{-1} \right)_{a,b} \\
&= \left[i\hbar\omega_\nu \boldsymbol{S} \left(1 - \frac{1}{i\hbar\omega_\nu} \boldsymbol{S}^{-1} \boldsymbol{h} \right) \right]^{-1}_{a,b} \\
&= \left[i\hbar\omega_\nu \boldsymbol{S} - \boldsymbol{h} \right]^{-1}_{a,b}
\end{aligned}
\tag{B.26}
$$

q.e.d.

B.3.1   Laurent expansion of the non-interacting Green's function

We determine the Laurent expansion terms of $\bar{\boldsymbol{G}}$

$$
\bar{\boldsymbol{G}} = \left[i\hbar\omega_\nu \boldsymbol{S} - \left(\bar{\boldsymbol{h}} - \mu \boldsymbol{S} \right) \right]^{-1} = \sum_{j=1}^{\infty} \frac{1}{(i\hbar\omega_\nu)^j} \bar{\mathcal{G}}^{(j)}
\tag{B.27}
$$

and therefore

$$
\begin{aligned}
\boldsymbol{1} &= \sum_{j=1} \frac{1}{(i\hbar\omega_\nu)^j} \bar{\mathcal{G}}^{(j)} \left[i\hbar\omega_\nu \boldsymbol{S} - \left(\bar{\boldsymbol{h}} - \mu \boldsymbol{S} \right) \right] \\
&= \sum_{j=0} \frac{1}{(i\hbar\omega_\nu)^j} \bar{\mathcal{G}}^{(j+1)} \boldsymbol{S} - \sum_{j=1} \frac{1}{(i\hbar\omega_\nu)^j} \bar{\mathcal{G}}^{(j)} \left(\bar{\boldsymbol{h}} - \mu \boldsymbol{S} \right) \\
\bar{\mathcal{G}}^{(1)} &= \boldsymbol{S}^{-1} \\
\bar{\mathcal{G}}^{(j+1)} &= \bar{\mathcal{G}}^{(j)} \left(\bar{\boldsymbol{h}} - \mu \boldsymbol{S} \right) \boldsymbol{S}^{-1} \qquad \text{for } j > 1 \\
\bar{\mathcal{G}}^j &= \boldsymbol{S}^{-1} \left[\left(\bar{\boldsymbol{h}} - \mu \boldsymbol{S} \right) \boldsymbol{S}^{-1} \right]^{j-1}
\end{aligned}
\tag{B.28}
$$

The first term in the Laurent expansion of $\boldsymbol{G} - \bar{\boldsymbol{G}}$ vanishes

$$
\mathcal{G}^{(1)} - \bar{\mathcal{G}}^{(1)} = 0
\tag{B.29}
$$

B.3.2   Laurent expansion of the Green's function (new)

In order to regularize the Matsubara sums, respectively, to limit the extent of the Matsubara sum evaluated numerically, we need to represent the Green's function for high frequencies in terms of Matsubara sums.

Here, we extract the Laurent expansion of the Green's function in the form

$$\boldsymbol{G} = \Big[(i\hbar\omega_\nu + \mu)\boldsymbol{S} - \boldsymbol{h} - \boldsymbol{\Sigma}(i\omega_\nu)\Big]^{-1} \tag{B.30}$$

where the self energy has the Laurent expansion

$$\boldsymbol{\Sigma}(i\omega_\nu) = \sum_{j=0}^{\infty} \frac{1}{(i\hbar\omega_\nu)^j}\mathcal{S}^{(j)} \tag{B.31}$$

Thus the numerical representation of the Green's function is

$$\boldsymbol{G}(i\omega_\nu) = \begin{cases} \Big[(i\hbar\omega_\nu + \mu)\boldsymbol{S} - \boldsymbol{h} - \boldsymbol{\Sigma}(i\omega_\nu)\Big]^{-1} & \text{for } |\nu| \leq \nu_x \\ \Big[(i\hbar\omega_\nu + \mu)\boldsymbol{S} - \boldsymbol{h} - \sum_{j'=0}^{j'_x} \mathcal{S}^{(j')}\frac{1}{(i\hbar\omega_\nu)^{j'}}\Big]^{-1} & \text{for } |\nu| > \nu_x \end{cases} \tag{B.32}$$

The high-frequency representation of the Green's function shall itself be represented by a Laurent expansion

$$\boldsymbol{G}(i\omega_\nu) = \sum_{j=1}^{\infty} \mathcal{G}^{(j)}\frac{1}{(i\hbar\omega_\nu)^j} \tag{B.33}$$

The identity

$$\sum_{j=1}^{\infty} \mathcal{G}^{(j)}\frac{1}{(i\hbar\omega_\nu)^j} = \Big[(i\hbar\omega_\nu + \mu)\boldsymbol{S} - \boldsymbol{h} - \sum_{j'=0}^{j'_x} \mathcal{S}^{(j')}\frac{1}{(i\hbar\omega_\nu)^{j'}}\Big]^{-1} \tag{B.34}$$

yields

$$\sum_{j=1}^{\infty} \mathcal{G}^{(j)}\frac{1}{(i\hbar\omega_\nu)^j}\Big[(i\hbar\omega_\nu + \mu)\boldsymbol{S} - \boldsymbol{h} - \sum_{j'=0}^{j'_x} \mathcal{S}^{(j')}\frac{1}{(i\hbar\omega_\nu)^{j'}}\Big] = \boldsymbol{1} \tag{B.35}$$

which we can be arranged in orders of inverse Matsubara frequencies

$$\sum_{j=0}^{\infty} \mathcal{G}^{(j+1)}\boldsymbol{S}\frac{1}{(i\hbar\omega_\nu)^j} + \sum_{j=1}^{\infty} \mathcal{G}^{(j)}\Big[\mu\boldsymbol{S} - \boldsymbol{h} - \mathcal{S}^{(0)}\Big]\frac{1}{(i\hbar\omega_\nu)^j}$$

$$-\sum_{j=2}^{\infty}\sum_{n=1}^{j'_x} \mathcal{G}^{(j-n)}\mathcal{S}^{(n)}\frac{1}{(i\hbar\omega_\nu)^j} = \boldsymbol{1} \tag{B.36}$$

Thus, the expansion coefficients are

$$\mathcal{G}^{(1)} = \boldsymbol{S}^{-1}$$

$$\mathcal{G}^{(j+1)} = -\mathcal{G}^{(j)}\Big[\mu\boldsymbol{S} - \boldsymbol{h} - \mathcal{S}^{(0)}\Big]\boldsymbol{S}^{-1} + \sum_{n=1}^{min(j'_x, j-1)} \mathcal{G}^{(j-n)}\mathcal{S}^{(n)}\boldsymbol{S}^{-1} \qquad \text{for } j > 0 \quad \text{(B.37)}$$

Let us make the higher-order terms more explicit

$$\mathcal{G}^{(1)} = \boldsymbol{S}^{-1}$$

$$\mathcal{G}^{(2)} = -\mathcal{G}^{(1)}\Big[\mu\boldsymbol{S} - \boldsymbol{h} - \mathcal{S}^{(0)}\Big]\boldsymbol{S}^{-1} = -\boldsymbol{S}^{-1}\Big[\mu\boldsymbol{S} - \boldsymbol{h} - \mathcal{S}^{(0)}\Big]\boldsymbol{S}^{-1}$$

$$\mathcal{G}^{(3)} = -\mathcal{G}^{(2)}\Big[\mu\boldsymbol{S} - \boldsymbol{h} - \mathcal{S}^{(0)}\Big]\boldsymbol{S}^{-1} + \mathcal{G}^{(1)}\mathcal{S}^{(1)}\boldsymbol{S}^{-1}$$

$$= \boldsymbol{S}^{-1}\Big[\mu\boldsymbol{S} - \boldsymbol{h} - \mathcal{S}^{(0)}\Big]\boldsymbol{S}^{-1}\Big[\mu\boldsymbol{S} - \boldsymbol{h} - \mathcal{S}^{(0)}\Big]\boldsymbol{S}^{-1} + \boldsymbol{S}^{-1}\mathcal{S}^{(1)}\boldsymbol{S}^{-1} \qquad \text{(B.38)}$$

In practice, we expand the Green's function up to $\mathcal{G}^{(3)}$ and the self energy up to $\mathcal{S}^{(1)}$.

Thus the Green's function will be represented in the form

$$\boldsymbol{G}(i\omega_\nu) = \begin{cases} \Big[(i\hbar\omega_\nu + \mu)\boldsymbol{S} - \boldsymbol{h} - \boldsymbol{\Sigma}(i\omega_\nu)\Big]^{-1} & \text{for } |\nu| \leq \nu_x \\ \sum_{j=1}^{3} \mathcal{G}^{(j)}\frac{1}{(i\hbar\omega_\nu)^j} & \text{for } |\nu| > \nu_x \end{cases} \qquad \text{(B.39)}$$

where the Laurent-expansion coefficients of the Green's function are defined in eqeq:Lauenttermsgreenappendix. The variational degrees of freedom for the Greens functrion is the Green's function for $0 < \omega_\nu \leq \omega_x$ and the first two Laurent-expansion terms $\mathcal{S}^{(0)}$ and $\mathcal{S}^{(1)}$ of the self energy. The Green's functiuon for negative Matsubara frequencies are obtained by Eq. B.1, $\boldsymbol{G}(-\text{ß}\omega_\nu) = \boldsymbol{G}^\dagger(\text{ß}\omega_\nu)$.

Laurent-expansion coefficients are Hermitean

The expansion coefficients for the Laurent expansion are hermitian. We exploit that $\boldsymbol{G}(-i\omega_\nu) = \boldsymbol{G}^\dagger(i\omega_\nu)$

$$\sum_{j=1}^{\infty} \frac{1}{(-i\hbar\omega_\nu)^j}\mathcal{G}^{(j)} = \boldsymbol{G}(-i\omega_\nu) = \boldsymbol{G}^\dagger(i\omega_\nu) = \sum_{j=1}^{\infty} \frac{1}{(-i\hbar\omega_\nu)^j}\left(\mathcal{G}^{(j)}\right)^\dagger$$

$$\Rightarrow \qquad \mathcal{G}^{(j)} = \left(\mathcal{G}^{(j)}\right)^\dagger \qquad \text{(B.40)}$$

From this requirement we can derive that $\boldsymbol{S}$, $\boldsymbol{h}$, $\mathcal{S}^{(0)}$ and $\mathcal{S}^{(0)}$ are hermitian as well.

Difference of Green's functions

The difference of two Green's function with different self energies has the form

$$\Delta\mathcal{G}^{(1)} = 0 \qquad \text{(B.41)}$$

$$\Delta\mathcal{G}^{(2)} = \boldsymbol{S}^{-1}\mathcal{S}^{(0)}\boldsymbol{S}^{-1} \qquad \text{(B.42)}$$

$$\Delta\mathcal{G}^{(3)} = -\boldsymbol{S}^{-1}\Big[\mu\boldsymbol{S} - \boldsymbol{h}\Big]\boldsymbol{S}^{-1}\mathcal{S}^{(0)}\boldsymbol{S}^{-1} - \boldsymbol{S}^{-1}\mathcal{S}^{(0)}\boldsymbol{S}^{-1}\Big[\mu\boldsymbol{S} - \boldsymbol{h}\Big]\boldsymbol{S}^{-1}$$

$$+ \boldsymbol{S}^{-1}\mathcal{S}^{(0)}\boldsymbol{S}^{-1}\mathcal{S}^{(0)}\boldsymbol{S}^{-1} + \boldsymbol{S}^{-1}\mathcal{S}^{(1)}\boldsymbol{S}^{-1} \qquad \text{(B.43)}$$

Laurent expansion for the density matrix

With this expression, we obtain the Matsubara sum required for the density matrix as

$$\frac{1}{\beta}\sum_{\nu}\boldsymbol{G}e^{i\omega_{\nu}0^{+}} = \sum_{j=1}^{\infty}\mathcal{G}^{(j)}\frac{1}{(j-1)!}\partial_{\epsilon}^{j-1}\Big|_{\epsilon=0}(1+e^{\beta\epsilon})^{-1}$$

$$= \frac{1}{2}\mathcal{G}^{(1)} - \frac{1}{4}\beta\mathcal{G}^{(2)} - 0\cdot\beta^{2}\mathcal{G}^{(3)} + \underbrace{\left(\frac{1}{3!}\frac{1}{8}\beta^{3}\mathcal{G}^{(4)} - \frac{1}{5!}\frac{1}{4}\beta^{5}\mathcal{G}^{(6)} + \frac{1}{7!}1.0?\beta^{7}\mathcal{G}^{(8)}\right)}_{\text{from grapher}} + O(\beta^{9})$$

$$= \frac{1}{2}\mathcal{G}^{(1)} - \frac{1}{4}\beta\mathcal{G}^{(2)} + \underbrace{\left(\frac{1}{48}\beta^{3}\mathcal{G}^{(4)} - \frac{1}{480}\beta^{5}\mathcal{G}^{(6)} + \frac{1.0?}{4320}\beta^{7}\mathcal{G}^{(8)}\right)}_{\text{from grapher}} + O(\beta^{9})$$

Derivative of the Luttinger Ward functional

For $j' \in \{0,1\}$

$$\frac{\partial\Phi_{\beta}^{LW}}{\partial\mathcal{S}^{(j')}} = \sum_{j=1}^{3}\frac{1}{\beta}\sum_{\nu;|\nu|>\nu_{x}}\frac{\beta\partial\Phi_{\beta}^{LW}}{\partial\boldsymbol{G}(i\omega_{\nu})}\frac{\partial\boldsymbol{G}(i\omega_{\nu})}{\partial\mathcal{G}^{(j)}}\frac{\partial\mathcal{G}^{(j)}}{\partial\mathcal{S}^{(j')}}$$

$$= \sum_{j=1}^{3}\left[\frac{1}{\beta}\sum_{\nu;|\nu|>\nu_{x}}\frac{\beta\partial\Phi_{\beta}^{LW}}{\partial\boldsymbol{G}(i\omega_{\nu})}\frac{1}{(i\hbar\omega_{\nu})^{j}}\right]\frac{\partial\mathcal{G}^{(j)}}{\partial\mathcal{S}^{(j')}}$$

$$\frac{\partial\Phi_{\beta}^{LW}}{\partial\mathcal{S}^{(0)}} = \boldsymbol{S}^{-1}\underbrace{\left[\frac{1}{\beta}\sum_{\nu;|\nu|>\nu_{x}}\frac{\beta\partial\Phi_{\beta}^{LW}}{\partial\boldsymbol{G}(i\omega_{\nu})}\frac{1}{(i\hbar\omega_{\nu})^{2}}\right]}_{\delta\Phi_{\beta,dyn}^{LW}/\delta\mathcal{G}^{(2)}}\boldsymbol{S}^{-1}$$

$$- \boldsymbol{S}^{-1}\underbrace{\left[\frac{1}{\beta}\sum_{\nu;|\nu|>\nu_{x}}\frac{\beta\partial\Phi_{\beta}^{LW}}{\partial\boldsymbol{G}(i\omega_{\nu})}\frac{1}{(i\hbar\omega_{\nu})^{3}}\right]}_{\delta\Phi_{\beta,dyn}^{LW}/\delta\mathcal{G}^{(3)}}\boldsymbol{S}^{-1}\left[\mu\boldsymbol{S} - \boldsymbol{h} - \mathcal{S}^{(0)}\right]\boldsymbol{S}^{-1}$$

$$- \boldsymbol{S}^{-1}\left[\mu\boldsymbol{S} - \boldsymbol{h} - \mathcal{S}^{(0)}\right]\boldsymbol{S}^{-1}\underbrace{\left[\frac{1}{\beta}\sum_{\nu;|\nu|>\nu_{x}}\frac{\beta\partial\Phi_{\beta}^{LW}}{\partial\boldsymbol{G}(i\omega_{\nu})}\frac{1}{(i\hbar\omega_{\nu})^{3}}\right]}_{\delta\Phi_{\beta,dyn}^{LW}/\delta\mathcal{G}^{(3)}}\boldsymbol{S}^{-1}$$

$$\frac{\partial\mathcal{G}^{(j)}}{\partial\mathcal{S}^{(1)}} = \boldsymbol{S}^{-1}\underbrace{\left[\frac{1}{\beta}\sum_{\nu;|\nu|>\nu_{x}}\frac{\beta\partial\Phi_{\beta}^{LW}}{\partial\boldsymbol{G}(i\omega_{\nu})}\frac{1}{(i\hbar\omega_{\nu})^{3}}\right]}_{\delta\Phi_{\beta,dyn}^{LW}/\delta\mathcal{G}^{(3)}}\boldsymbol{S}^{-1} \tag{B.44}$$

Appendix C

in progress: Green function in matrix form

In the previous section we have shown the expression for the Green's function in the form Eq. B.23, albeit under the strong condition that the hamiltonian can exactly be expressed in terms of the projector functions. The goal of this section is to perform the proof under weaker conditions.

The Green function of the non-interacting system has the form

$$G_{a,b}(i\omega_\nu) = \sum_n \langle \pi_a | \psi_n \rangle \frac{1}{i\hbar\omega_\nu + \mu - \epsilon_n} \langle \psi_n | \pi_b \rangle \tag{C.1}$$

Note, that the sum over n includes the sum over k-points, and that the orbital indices may refer to orbitals from different unit cells. In practice the Green's function is calculated for each k-point individually, with orbitals only from one unit cell. The full Green's function can then be recovered from those k- projected Green's functions by a summation and using the corresponding phase factors.

The density matrix is defined by

$$\rho_{a,b} = \sum_n \langle \pi_a | \psi_n \rangle f(\epsilon_n) \langle \psi_n | \pi_b \rangle \tag{C.2}$$

If (1) the Matsubara sum is complete and (2) the sum in the Green's function is perfomed over all states with non-zero occupations, the density matrix has the form

$$\begin{aligned} \rho_{a,b} &= \sum_n \langle \pi_a | \psi_n \rangle \left(\frac{1}{\beta} \sum_\nu e^{i\hbar\omega\beta 0^+} \frac{1}{i\hbar\omega_\nu + \mu - \epsilon_n} \right) \langle \psi_n | \pi_b \rangle \\ &= \frac{1}{\beta} \sum_\nu e^{i\hbar\omega\beta 0^+} \boldsymbol{G}(i\omega_\nu) \end{aligned} \tag{C.3}$$

Let us rewrite the Green's function in terms of a matrix equation that does not involve a sum over all states, but with matrices on the space of local orbitals. As shown below, the result is

The Green's function matrix of the form

$$G_{a,b}(i\omega_\nu) = \sum_n^{N_x} \langle \pi_a|\psi_n\rangle \frac{1}{i\hbar\omega_\nu + \mu - \epsilon_n} \langle \psi_n|\pi_b\rangle \tag{C.4}$$

can be expressed as

$$G_{a,b}(i\omega_\nu) = \sum_{n,n'}^{N_x} \langle \pi_a|\psi_n\rangle \left((i\hbar\omega_\nu + \mu)\delta_{n,n'} - \sum_{c,d} \langle \psi_n|\pi_c\rangle h_{c,d} \langle \pi_d|\psi_{n'}\rangle - \Delta_{n,n'} \right)^{-1}_{n,n'} \langle \psi_{n'}|\pi_b\rangle \tag{C.5}$$

with[a]

$$h_{c,d} \stackrel{\text{def}}{=} \sum_{a,b} \left(\sum_m^{N_x} \langle \pi_a|\psi_m\rangle\langle \psi_m|\pi_c\rangle \right)^{-1}_{c,a} \left(\sum_n^{N_x} \langle \pi_a|\psi_n\rangle\epsilon_n\langle \psi_n|\pi_b\rangle \right) \left(\sum_{m'}^{N_x} \langle \pi_d|\psi_{m'}\rangle\langle \psi_{m'}|\pi_b\rangle \right)^{-1}_{b,d} \tag{C.6}$$

$$P_{n,n'} \stackrel{\text{def}}{=} \sum_{a,b} \langle \psi_n|\pi_a\rangle \left(\sum_m^{N_x} \langle \pi_b|\psi_m\rangle\langle \psi_m|\pi_a\rangle \right)^{-1}_{a,b} \langle \pi_b|\psi_{n'}\rangle \tag{C.7}$$

$$\boldsymbol{\Delta} \stackrel{\text{def}}{=} \boldsymbol{\epsilon} - \boldsymbol{P}\boldsymbol{\epsilon}\boldsymbol{P} \tag{C.8}$$

All vectors and matrices with band indices are considered to be objects in a N_x-dimensional space.

It is shown that $\boldsymbol{P}$ is a projection operator in the space of band states, namely $\boldsymbol{P}^2 = \boldsymbol{P}$, while $\boldsymbol{P} \neq \boldsymbol{1}$.

---

[a]To motivate the form for $\boldsymbol{h}$, equate the denominator of both expressions for the Greens function, which gives

$$\epsilon_n\delta_{n,n'} = \sum_{c,d} \langle \psi_n|\pi_c\rangle h_{c,d} \langle \pi_d|\psi_{n'}\rangle + \Delta_{n,n'}$$

$$\Rightarrow \quad \sum_{n,n'} \langle \pi_a|\psi_n\rangle \left(\epsilon_n\delta_{n,n'} - \Delta_{n,n'} \right) \langle \psi_{n'}|\pi_b\rangle = \sum_{n,n'} \sum_{c,d} \langle \pi_a|\psi_n\rangle\langle \psi_n|\pi_c\rangle h_{c,d} \langle \pi_d|\psi_{n'}\rangle\langle \psi_{n'}|\pi_b\rangle$$

$$\Leftrightarrow \quad h_{c,d} = \sum_{a,b} \left(\sum_m \langle \pi_a|\psi_m\rangle\langle \psi_m|\pi_c\rangle \right)^{-1}_{c,a} \left(\sum_{n,n'} \langle \pi_a|\psi_n\rangle \left(\epsilon_n\delta_{n,n'} - \Delta_{n,n'} \right) \langle \psi_{n'}|\pi_b\rangle \right) \left(\sum_{m'} \langle \pi_d|\psi_{m'}\rangle\langle \psi_{m'}|\pi_b\rangle \right)^{-1}_{b,d}$$

If we set $\Delta = 0$, we obtain our choice for $\boldsymbol{h}$.

The presence of $\boldsymbol{\Delta}$ in Eq. C.5 demonstrates an important limitation of Eq. B.23 given on p. 46.

$\boldsymbol{\Delta}$ and projection

For $\boldsymbol{P}$ defined through Eq. C.7, the identity

$$\boldsymbol{P}\langle \psi|\pi\rangle = \langle \psi|\pi\rangle \tag{C.9}$$

holds. This is shown as follows

$$\sum_{n'}^{N_x} P_{n,n'} \langle \psi_{n'} | \pi_c \rangle \overset{\text{Eq. } C.7}{=} \underbrace{\sum_{n'}^{N_x} \sum_{a,b} \langle \psi_n | \pi_a \rangle \Big(\sum_m^{N_x} \langle \pi_b | \psi_m \rangle \langle \psi_m | \pi_a \rangle \Big)_{a,b}^{-1} \langle \pi_b | \psi_{n'} \rangle \langle \psi_{n'} | \pi_c \rangle}_{P_{n,n'}}$$

$$= \sum_{a,b} \langle \psi_n | \pi_a \rangle \Big(\sum_m^{N_x} \langle \pi_b | \psi_m \rangle \langle \psi_m | \pi_a \rangle \Big)_{a,b}^{-1} \underbrace{\Big(\sum_{n'}^{N_x} \langle \pi_b | \psi_{n'} \rangle \langle \psi_{n'} | \pi_c \rangle \Big)}_{\delta_{a,c}} = \langle \psi_n | \pi_c \rangle$$

which proves Eq. C.7.

With Eq. C.7, we obtain

$$\langle \pi | \psi \rangle \mathbf{\Delta} \langle \psi | \pi \rangle = 0 \tag{C.10}$$

which is shown as follows:

$$\langle \pi | \psi \rangle \mathbf{\Delta} \langle \psi | \pi \rangle \overset{\text{Eq. } C.8}{=} \langle \pi | \psi \rangle \Big(\boldsymbol{\epsilon} - \boldsymbol{P} \boldsymbol{\epsilon} \boldsymbol{P} \Big) \langle \psi | \pi \rangle \overset{\text{Eq. } C.7}{=} 0$$

Hamilton matrix and projection

A useful relation is

$$\sum_{c,d} \langle \psi_n | \pi_c \rangle h_{c,d} \langle \pi_d | \psi_{n'} \rangle = \sum_m P_{n,m} \epsilon_m P_{m,n'} \tag{C.11}$$

which is shown by insertion

$$\sum_{c,d} \langle \psi_n | \pi_c \rangle h_{c,d} \langle \pi_d | \psi_{n'} \rangle$$

$$\overset{\text{Eq. } C.6}{=} \sum_{c,d} \langle \psi_n | \pi_c \rangle \times$$

$$\overbrace{\sum_{a,b} \Big(\sum_m \langle \pi_a | \psi_m \rangle \langle \psi_m | \pi_c \rangle \Big)_{c,a}^{-1} \Big(\sum_{n''} \langle \pi_a | \psi_{n''} \rangle \epsilon_{n''} \langle \psi_{n''} | \pi_b \rangle \Big) \Big(\sum_{m'} \langle \pi_d | \psi_{m'} \rangle \langle \psi_{m'} | \pi_b \rangle \Big)_{b,d}^{-1}}^{h_{cd}} \langle \pi_d | \psi_{n'} \rangle$$

$$= \sum_{n''} \underbrace{\Big[\sum_{c,a} \langle \psi_n | \pi_c \rangle \Big(\sum_m \langle \pi_a | \psi_m \rangle \langle \psi_m | \pi_c \rangle \Big)_{c,a}^{-1} \langle \pi_a | \psi_{n''} \rangle \Big]}_{P_{n,n''}} \epsilon_{n''}$$

$$\times \underbrace{\Big[\sum_{b,d} \langle \psi_{n''} | \pi_b \rangle \Big(\sum_{m'} \langle \pi_d | \psi_{m'} \rangle \langle \psi_{m'} | \pi_b \rangle \Big)_{b,d}^{-1} \langle \pi_d | \psi_{n'} \rangle \Big]}_{P_{n'',n'}}$$

$$\overset{\text{Eq. } C.7}{=} \Big(\sum_m P_{n,m} \epsilon_m P_{m,n} \Big)$$

which proves Eq. C.11

Proof of the identity between Eq. C.1 and Eq. C.5.

The identity between Eq. C.1 and Eq. C.5 is exact irrespective of the completeness of the band states or the local orbitals. This can be shown with the help of Eq. C.11. It is sufficient to show that the denominators are identical, namely that

$$
\epsilon_n \delta_{n,n'} \quad = \quad \underbrace{\left(\sum_m P_{n,m} \epsilon_m P_{m,n'} \right)}_{\sum_{c,d} \langle \psi_n | \pi_c \rangle h_{c,d} \langle \pi_d | \psi_{n'} \rangle} + \underbrace{\left(\epsilon_n \delta_{n,n'} - \sum_m P_{n,m} \epsilon_m P_{m,n'} \right)}_{\Delta_{n,n'}}
$$

$$
\overset{Eqs.\ C.11,C.8}{=} \sum_{c,d} \langle \psi_n | \pi_c \rangle h_{c,d} \langle \pi_d | \psi_{n'} \rangle + \Delta_{n,n'}
$$

When this identity is inserted into Eq. C.1, we arrive directly at Eq. C.5. This completes the proof of the identity between Eq. C.1 and Eq. C.5.

Self energy from the uncorrelated orbitals

We define the Green's function without the additional term $\boldsymbol{\Delta}$ as unperturbed (by the uncorrelated orbitals) Green's function. With the help of Eq. B.23 from p. 46 it can be expressed in matrix form without reference to the natural orbitals.

$$
\boldsymbol{G}_{0,a,b}^{-1}(i\omega_\nu) \quad \overset{def}{=} \quad \sum_{n,n'} \langle \pi_a | \psi_n \rangle \left((i\hbar\omega_\nu + \mu)\delta_{n,n'} - \sum_{c,d} \langle \psi_n | \pi_c \rangle h_{c,d} \langle \pi_d | \psi_{n'} \rangle \right)_{n,n'}^{-1} \langle \psi_{n'} | \pi_b \rangle
$$

$$
\overset{Eq.\ B.23}{=} \left[(i\hbar\omega_\nu + \mu)\boldsymbol{S} - \boldsymbol{h} \right]_{a,b}^{-1} \tag{C.12}
$$

with

$$
\boldsymbol{S}^{-1} = \langle \pi_a | \psi_n \rangle \langle \psi_n | \pi_b \rangle \tag{C.13}
$$

We can derive a self energy, which connects this Green function to the full Green's function by a Dyson's equation.

$$
\boldsymbol{G}^{-1} = \boldsymbol{G}_0^{-1} - \boldsymbol{\Sigma}
$$

$$
\boldsymbol{\Sigma} = \left[(i\hbar\omega_\nu + \mu)\boldsymbol{S} - \boldsymbol{h} \right] - \boldsymbol{G}^{-1}
$$

$$
= \underbrace{\boldsymbol{P}(\boldsymbol{\epsilon} - \boldsymbol{\mu})(\boldsymbol{1} - \boldsymbol{P})}_{H_{AB}} \underbrace{\left((\boldsymbol{1} - \boldsymbol{P})\left((i\hbar\omega_\nu + \mu)\boldsymbol{1} - \boldsymbol{\epsilon} \right)(\boldsymbol{1} - \boldsymbol{P}) \right)^{-1}}_{G_{BB}(i\omega_\nu)} \underbrace{(\boldsymbol{1} - \boldsymbol{P})(\boldsymbol{\epsilon} - \boldsymbol{\mu})\boldsymbol{P}}_{H_{BA}}
$$

$$
\tag{C.14}
$$

Partitioning

The introduction of the projection operator $\boldsymbol{P}$ allows one to break up the Hamiltonian into a part related to the correlated orbitals, a part outside and the hopping between correlated orbitals and the others.

Let me first review the partitioning of Green's functions

$$-\boldsymbol{H}_{BA}\boldsymbol{G}_{AB} + (x\boldsymbol{1}_{BB} - \boldsymbol{H}_{BB})\boldsymbol{G}_{BA} = \boldsymbol{0}_{BA}$$

$$\Rightarrow \quad \boldsymbol{G}_{BA} = (x\boldsymbol{1}_{BB} - \boldsymbol{H}_{BB})^{-1}\boldsymbol{H}_{BA}\boldsymbol{G}_{AB} \tag{C.15}$$

$$\left(x\boldsymbol{1}_{AA} - \boldsymbol{H}_{AA}\right)\boldsymbol{G}_{AA} - \boldsymbol{H}_{AB}\boldsymbol{G}_{BA} = \boldsymbol{1}_{AA}$$

$$\overset{\text{Eq. C.15}}{\Rightarrow} \quad \left(x\boldsymbol{1}_{AA} - \boldsymbol{H}_{AA} - \boldsymbol{H}_{AB}(x\boldsymbol{1}_{BB} - \boldsymbol{H}_{BB})^{-1}\boldsymbol{H}_{BA}\right)\boldsymbol{G}_{AA} = \boldsymbol{1}_{AA}$$

$$\Rightarrow \quad \boldsymbol{G}_{AA} = \Big[x\boldsymbol{1}_{AA} - \boldsymbol{H}_{AA} - \underbrace{\boldsymbol{H}_{AB}(x\boldsymbol{1}_{BB} - \boldsymbol{H}_{BB})^{-1}\boldsymbol{H}_{BA}}_{\Sigma(x)}\Big]^{-1} \tag{C.16}$$

The relation between these subblocks and the projected quantities is non-trivial, which can be seen as follows:

$$\boldsymbol{P}\Big[(i\hbar\omega_\nu + \mu)\boldsymbol{1} - \boldsymbol{\epsilon}\Big]^{-1}\boldsymbol{P} = \langle\psi|\pi\rangle\boldsymbol{S}\boldsymbol{G}(i\omega_\nu)\boldsymbol{S}\langle\pi|\psi\rangle \tag{C.17}$$

==================following is unchecked========================
The diagonal matrix of the eigenvalues of the band states can be partitioned in the form

$$\boldsymbol{\epsilon} = \boldsymbol{P}\boldsymbol{\epsilon}\boldsymbol{P} + \underbrace{\boldsymbol{\epsilon} - \boldsymbol{P}\boldsymbol{\epsilon}\boldsymbol{P}}_{\Delta}$$

$$= \boldsymbol{P}\boldsymbol{\epsilon}\boldsymbol{P} + \boldsymbol{P}\boldsymbol{\epsilon}\Big(\boldsymbol{1} - \boldsymbol{P}\Big) + \Big(\boldsymbol{1} - \boldsymbol{P}\Big)\boldsymbol{\epsilon}\boldsymbol{P} + \Big(\boldsymbol{1} - \boldsymbol{P}\Big)\boldsymbol{\epsilon}\Big(\boldsymbol{1} - \boldsymbol{P}\Big) \tag{C.18}$$

This suggests to do the following definitions

$$\boldsymbol{G}_{AA} = \boldsymbol{P}\boldsymbol{G}\boldsymbol{P}$$
$$\boldsymbol{G}_{AB} = \boldsymbol{P}\boldsymbol{G}(\boldsymbol{1} - \boldsymbol{P})$$
$$\boldsymbol{1}_{AA} = \boldsymbol{P}^2$$
$$\boldsymbol{0}_{AB} = \boldsymbol{P}(\boldsymbol{1} - \boldsymbol{P})$$
$$\boldsymbol{H}_{AA} = \boldsymbol{P}(\boldsymbol{\epsilon} - \mu\boldsymbol{1})\boldsymbol{P} \tag{C.19}$$

Next we partition the Green's function

$$\begin{pmatrix} x\boldsymbol{1}_{AA} - \boldsymbol{H}_{AA} & -\boldsymbol{H}_{AB} \\ -\boldsymbol{H}_{BA} & x\boldsymbol{1}_{BB} - \boldsymbol{H}_{BB} \end{pmatrix}\begin{pmatrix} \boldsymbol{G}_{AA}(x) & \boldsymbol{G}_{AB}(x) \\ \boldsymbol{G}_{BA}(x) & \boldsymbol{G}_{BB}(x) \end{pmatrix} = \begin{pmatrix} \boldsymbol{1}_{AA} & \boldsymbol{0}_{AB} \\ \boldsymbol{0}_{BA} & \boldsymbol{1}_{BB} \end{pmatrix} \tag{C.20}$$

Our goal is to find the Green's function $\boldsymbol{G}_{AA}$ for the correlated orbitals.

This can now be written in the form

$$\boldsymbol{G}_{AA}(x) = \Big[x\underbrace{\boldsymbol{P}}_{\boldsymbol{1}_{AA}} - \underbrace{\boldsymbol{P}(\boldsymbol{\epsilon} - \mu)\boldsymbol{P}}_{\boldsymbol{H}_{AA}}$$

$$- \underbrace{\boldsymbol{P}(\boldsymbol{\epsilon} - \mu)(\boldsymbol{1} - \boldsymbol{P})}_{\boldsymbol{H}_{AB}}\Big((\boldsymbol{1} - \boldsymbol{P})(x\boldsymbol{1} - \boldsymbol{\epsilon} + \mu)(\boldsymbol{1} - \boldsymbol{P})\Big)^{-1}\underbrace{(\boldsymbol{1} - \boldsymbol{P})(\boldsymbol{\epsilon} - \mu)\boldsymbol{P}}_{\boldsymbol{H}_{BA}}\Big]^{-1} \tag{C.21}$$

Determine

$$\sum_n \langle \pi_a | \psi_n \rangle \langle \psi_n | \pi_b \rangle = \sum_c U_{a,c} \lambda_c U_{c,b}^\dagger \qquad \text{(C.22)}$$

with $UU^\dagger = \mathbf{1}$.

$$\left(\sum_n \langle \pi_a | \psi_n \rangle \langle \psi_n | \pi_b \rangle \right)^{-1}_{a,b} = \sum_c U_{a,c} \frac{1}{\lambda_c} U_{c,b}^\dagger$$

$$\mathbf{P} = \sum_{a,b} \langle \psi_n | \pi_a \rangle \left(\sum_m \langle \pi | \psi_m \rangle \langle \psi_m | \pi \rangle \right)^{-1}_{a,b} \langle \pi_b | \psi_n \rangle$$

$$= \sum_c \left(\sum_a \langle \psi_n | \pi_a \rangle U_{a,c} \right) \frac{1}{\lambda_c} \left(U_{c,b}^\dagger \langle \pi_b | \psi_n \rangle \right) \qquad \text{(C.23)}$$

Appendix D

Dividing the correlation contribution into a static and a dynamic part

We will divide the correlation contribution $Q_\beta^{\hat{W}}$ in Eq. 1.7 on p. 4 into two separate terms. This principle will allow us to divide $Q[\boldsymbol{\rho}]$ according to Eq. 1.9 on p. 5.

It seems that division is only possible if only one of the terms has a frequency-dependent self energy.

For this purpose, we express the Luttinger-Ward functional as a sum of two terms $\Phi_\beta^{LW} = \Phi_\beta^{LW,2} + \Phi_\beta^{LW,2}$, of which only the second has the frequency dependent self energy.

$$
\begin{aligned}
Q_\beta^{\hat{W}}[\boldsymbol{\rho}] \overset{\text{Eq.}\,1.7}{=} \underset{\boldsymbol{h'}}{\text{stat}}\,\underset{\boldsymbol{G},\boldsymbol{\Sigma}}{\text{stat}} \Big\{ &\Phi_\beta^{LW,1}[\boldsymbol{G}, \hat{W}_1] + \Phi_\beta^{LW,2}[\boldsymbol{G}, \hat{W}_2] \\
&- \frac{1}{\beta} \sum_\nu \text{Tr}\Big\{ \ln\Big[\mathbf{1} - \underbrace{\big(i\hbar\omega_\nu + \mu)\mathbf{1} - \bar{\boldsymbol{h}}\big)^{-1}}_{\bar{\boldsymbol{G}}} \big(\boldsymbol{h'} + \boldsymbol{\Sigma}(i\omega_\nu) - \bar{\boldsymbol{h}}\big) \Big] \\
&+ (\boldsymbol{h'} + \boldsymbol{\Sigma}(i\omega_\nu) - \bar{\boldsymbol{h}})\boldsymbol{G}(i\omega_\nu) - \Big[\boldsymbol{G}(i\omega_\nu) - \underbrace{\big(i\hbar\omega_\nu + \mu)\mathbf{1} - \bar{\boldsymbol{h}}\big)^{-1}}_{\bar{\boldsymbol{G}}} \Big]\big(\boldsymbol{h'} - \bar{\boldsymbol{h}}\big) \Big\} \Big\}
\end{aligned}
$$

$$(\text{D.1})$$

As usual, $\bar{\boldsymbol{h}}$ is an explicit functional of the density matrix $\boldsymbol{\rho}$ as defined in Eq. 1.5 and $\bar{\boldsymbol{G}}$ is the non-interacting Green's function with the hamiltonian $\bar{\boldsymbol{h}}$.

The stationary conditions are

$$0 = \frac{\partial \mathcal{Q}_\beta^{\hat{W}}}{\partial \boldsymbol{G}} = -\frac{\beta \delta \Phi^{LW,1}}{\delta \boldsymbol{G}(i\omega_\nu)} - \frac{\beta \delta \Phi^{LW,2}}{\delta \boldsymbol{G}(i\omega_\nu)} + \left(\boldsymbol{h}' + \boldsymbol{\Sigma}(i\omega_\nu) - \bar{\boldsymbol{h}}\right) - \left(\boldsymbol{h}' - \bar{\boldsymbol{h}}\right)$$

$$\Rightarrow \qquad \boldsymbol{\Sigma}(i\omega_\nu) = \frac{\beta \delta \Phi^{LW,1}}{\delta \boldsymbol{G}(i\omega_\nu)} + \frac{\beta \delta \Phi^{LW,2}}{\delta \boldsymbol{G}(i\omega_\nu)}$$

$$0 = \frac{\partial \mathcal{Q}_\beta^{\hat{W}}}{\partial \boldsymbol{\Sigma}} = \left[\mathbf{1} - \bar{\boldsymbol{G}}(i\omega_\nu)\left(\boldsymbol{h}' + \boldsymbol{\Sigma}(i\omega_\nu) - \bar{\boldsymbol{h}}\right)\right]^{-1}\left(-\bar{\boldsymbol{G}}(i\omega_\nu)\right) + \boldsymbol{G}(i\omega_\nu) \tag{D.2}$$

$$\Rightarrow \qquad \boldsymbol{G}(i\omega_\nu) = \left[\mathbf{1} - \bar{\boldsymbol{G}}(i\omega_\nu)\left(\boldsymbol{h}' + \boldsymbol{\Sigma}(i\omega_\nu) - \bar{\boldsymbol{h}}\right)\right]^{-1}\bar{\boldsymbol{G}}(i\omega_\nu)$$

$$0 = \frac{\partial \mathcal{Q}_\beta^{\hat{W}}}{\partial \boldsymbol{h}'}$$

$$= -\frac{1}{\beta}\sum_\nu \left\{ \underbrace{\left[\mathbf{1} - \bar{\boldsymbol{G}}(i\omega_\nu)\left(\boldsymbol{h}' + \boldsymbol{\Sigma}(i\omega_\nu) - \bar{\boldsymbol{h}}\right)\right]^{-1}\left(-\bar{\boldsymbol{G}}(i\omega_\nu)\right) + \boldsymbol{G}(i\omega_\nu)}_{=0 \quad \text{Eq. D.2}} - \left(\boldsymbol{G}(i\omega_\nu) - \bar{\boldsymbol{G}}(i\omega_\nu)\right) \right\}$$

$$\Rightarrow \qquad \frac{1}{\beta}\sum_\nu \boldsymbol{G}(i\omega_\nu)e^{i\hbar\omega_\nu\beta0^+} = \frac{1}{\beta}\sum_\nu \bar{\boldsymbol{G}}(i\omega_\nu)e^{i\hbar\omega_\nu\beta0^+} = \boldsymbol{\rho} \tag{D.3}$$

Whenever the Luttinger-Ward functional can be expressed directly by the density matrix, the self energy is independent of the Matsubara frequencies. In this case the Luttinger-Ward functional depends on the Green'sfunction only via the integral $\boldsymbol{\rho} = \frac{1}{\beta}\sum_\nu \boldsymbol{G}(i\omega_\nu)e^{i\hbar\omega_\nu\beta0^+}$. This is the case for the Hartree-Fock approximation and it is the case for the density-functional theory.

In the following, we assume that $\Phi_\beta^{LW,1}$ has this form, i.e. that it depends on the Green's function only via the density matrix.

Divided form

We rewrite the expression as

$$Q_\beta^{\hat{W}}[\boldsymbol{\rho}] = \Phi_\beta^{LW,1}[\bar{\boldsymbol{G}}, \hat{W}_1] + \underset{h_2'}{\text{stat}}\,\underset{\boldsymbol{G},\boldsymbol{\Sigma}_2}{\text{stat}}\left\{\Phi_\beta^{LW,2}[\boldsymbol{G}, \hat{W}_2]\right.$$

$$-\frac{1}{\beta}\sum_\nu \text{Tr}\left\{\ln\left[\mathbf{1} - \left(i\hbar\omega_\nu + \mu\right)\mathbf{1} - \bar{\boldsymbol{h}}\right)^{-1}\left(\boldsymbol{h}_2' + \boldsymbol{\Sigma}_2(i\omega_\nu) - \bar{\boldsymbol{h}}\right)\right]$$

$$\left. +(\boldsymbol{h}_2' + \boldsymbol{\Sigma}_2(i\omega_\nu) - \bar{\boldsymbol{h}})\boldsymbol{G}(i\omega_\nu) - \left[\boldsymbol{G}(i\omega_\nu) - \left(i\hbar\omega_\nu + \mu\right)\mathbf{1} - \bar{\boldsymbol{h}}\right)^{-1}\right]\left(\boldsymbol{h}_2' - \bar{\boldsymbol{h}}\right)\right\}\right\} \tag{D.4}$$

The stationary conditions are

$$\boldsymbol{\Sigma}_2(i\omega_\nu) = \frac{\beta \delta \Phi^{LW,2}}{\delta \boldsymbol{G}(i\omega_\nu)}$$

$$\boldsymbol{G}(i\omega_\nu) = \left[\mathbf{1} - \bar{\boldsymbol{G}}(i\omega_\nu)\left(\boldsymbol{h}_2' + \boldsymbol{\Sigma}_2(i\omega_\nu) - \bar{\boldsymbol{h}}\right)\right]^{-1}\bar{\boldsymbol{G}}(i\omega_\nu) \tag{D.5}$$

We see that

$$h' = h'_2 + \frac{\beta \delta \Phi^{LW,1}}{\delta G(i\omega_\nu)} \tag{D.6}$$

leads to the same Green's function as in the former case. That is, both forms, i.e. Eq. D.1 and Eq. D.4, have the same stationary state. At the stationary state, both forms have furthermore the same value.

No Matsubara sum with a stationary self energy

Here, I show that $Q_\beta^{\hat{W}}[\boldsymbol{\rho}] = \Phi_\beta^{LW}[\bar{G}, \hat{W}]$, if the Luttinger Ward functional only depends on the Greens function via the density matrix.

In that case, the self energy is frequency independent. All stationary conditions can be fulfilled by choosing

$$h' + \boldsymbol{\Sigma} = \bar{h}$$
$$G(i\omega_\nu) = \bar{G}(i\omega_\nu) \tag{D.7}$$

Thus we may decompose the correlation contribution into several terms of which only one has a frequency dependent self energy

Appendix E

Hartree-Fock energy

. The Hartree-Fock term $Q^{\hat{W}}_{X,\beta}$ is equal to $Q^{\hat{W}}_{\beta}$ when only the first-order term of the Luttinger-Ward functional in the interaction is considered. It is obtained as (BPP-Eq.43)

$$Q^{\hat{W}}_{X,\beta}[\boldsymbol{\rho}] = \frac{1}{2} \sum_{a,b,c,d} U_{a,b,d,c} \left[\rho_{d,a}\rho_{c,b} - \rho_{c,a}\rho_{d,b} \right] \tag{E.1}$$

The interpretation of this term is subtle because it is formulated in non-orthonormal orbitals.

- We consider the expansion of Kohn-Sham orbitals in local orbitals

$$Q^{\hat{W}}_{X,\beta}[\boldsymbol{\rho}] = \frac{1}{2} \sum_{m,n} f_m f_n \int d^3r \int d^3r' \frac{e^2 \left(\phi_m^*(\vec{r})\phi_n^*(\vec{r'})\phi_n(\vec{r'})\phi_m(\vec{r}) - \phi_m^*(\vec{r})\phi_n^*(\vec{r'})\phi_m(\vec{r'})\phi_n(\vec{r}) \right)}{4\pi\epsilon_0 |\vec{r} - \vec{r'}|}$$

$$= \frac{1}{2} \sum_{a,b,c,d} \underbrace{\left(\sum_m \langle \pi_a | \phi_m \rangle f_m \langle \phi_m | \pi_b \rangle \right)}_{\rho_{a,b}} \underbrace{\left(\sum_n \langle \pi_c | \phi_n \rangle f_n \langle \phi_n | \pi_d \rangle \right)}_{\rho_{c,d}}$$

$$\times \int d^3r \int d^3r' \frac{e^2 \left(\chi_b^*(\vec{r})\chi_d^*(\vec{r'})\chi_c(\vec{r'})\chi_a(\vec{r}) - \chi_b^*(\vec{r})\chi_d^*(\vec{r'})\chi_a(\vec{r'})\chi_c(\vec{r}) \right)}{4\pi\epsilon_0 |\vec{r} - \vec{r'}|} \tag{E.2}$$

$$= \frac{1}{2} \sum_{a,b,c,d} \rho_{a,b}\rho_{c,d} \left(U_{b,d,a,c} - U_{b,d,c,a} \right) \tag{E.3}$$

$$= \frac{1}{2} \sum_{a,b,c,d} U_{a,b,d,c} \left(\rho_{d,a}\rho_{c,b} - \rho_{c,a}\rho_{d,b} \right) \tag{E.4}$$

- Consider expectation valiue of a Slater determinant expressed in terms of non-orthonormal local orbitals. The Slater determinant has the form

$$\Psi(\vec{x}_1, \ldots, \vec{x}_n) = C \det |\boldsymbol{M}| = C \sum_{i_1,\ldots,i_N=1}^{N} \epsilon_{i_1,\ldots,i_N} \chi_{i_1}(\vec{x}_1) \cdots \chi_{i_N}(\vec{x}_N) \tag{E.5}$$

with $M_{i,j} = \chi_i(\vec{x}_j)$ and the normalization constant C. $\epsilon_{i_1,\ldots,i_N}$ is the fully antisymmetric tensor defined by $\epsilon_{1,2,\ldots,N} = 1$, by the fact that it changes sign under permutation of two indices, and that it vanishes whenever two indices are identical.

This argument needs to be completed. Probably we obtain the same result as in the first case. This needs to be shown by performing a transformation onto orthogonal one-particle states, that span the same Hilbert space.

Appendix F

Mixing of the self energy

F.1 Structure of the self-consistency

The self-consisten scheme has the following structure

$$\mathbf{\Sigma}_{dyn}(+) = \mathbf{\Sigma}_{dyn}(0) + \alpha \left[\left. \frac{\beta \delta \Phi^{LW,dyn}}{\delta \mathbf{G}} \right|_{\mathbf{G}[\mathbf{\Sigma}_{dyn}(0)]} - \mathbf{\Sigma}_{dyn}(0) \right] \tag{F.1}$$

and we search for the fixed point of this dynamics. $\mathbf{G}[\mathbf{\Sigma}_{dyn}]$ is given by Dyson's equation, that is by the stationary condition of the dynamic-correlation correction with respect to the self energy.

This problem is equivalent to the search of a zero of $\frac{\beta \delta \Phi_{\beta}^{LW,dyn}}{\delta \mathbf{G}} - \mathbf{\Sigma}_{dyn}$. More precisely, we search $\delta \mathbf{\Sigma}_{dyn}$ so that

$$\left. \frac{\beta \delta \Phi_{\beta}^{LW,dyn}}{\delta \mathbf{G}} \right|_{\mathbf{G}[\mathbf{\Sigma}_{dyn} + \delta \mathbf{\Sigma}_{dyn}]} - \mathbf{\Sigma}_{dyn} - \delta \mathbf{\Sigma}_{dyn} = 0 \tag{F.2}$$

This yields to first order in $\delta \Sigma_{dyn}$

$$\left[\left. \frac{\beta \delta \Phi_{\beta}^{LW,dyn}}{\delta \mathbf{G}} \right|_{\mathbf{G}[\mathbf{\Sigma}_{dyn}]} - \mathbf{\Sigma}_{dyn} \right] + \left. \frac{\beta \delta^2 \Phi_{\beta}^{LW,dyn}}{\delta \mathbf{G} \delta \mathbf{G}'} \right|_{\mathbf{G}[\mathbf{\Sigma}_{dyn}]} \frac{\delta \mathbf{G}'}{\delta \mathbf{\Sigma}_{dyn}} \delta \mathbf{\Sigma}_{dyn} - \delta \mathbf{\Sigma}_{dyn} = 0 \tag{F.3}$$

I write out the indices

$$\left[\left. \frac{\beta \delta \Phi_{\beta}^{LW,dyn}}{\delta G_{b,a}} \right|_{\mathbf{G}[\mathbf{\Sigma}_{dyn}]} - \Sigma_{dyn,a,b} \right] + \sum_{e,f} \left\{ \left[\sum_{c,d} \left. \frac{\beta \delta^2 \Phi_{\beta}^{LW,dyn}}{\delta G_{b,a} \delta G_{d,c}} \right|_{\mathbf{G}[\mathbf{\Sigma}_{dyn}]} \frac{\delta G_{d,c}}{\delta \Sigma_{dyn,e,f}} \right] - \delta_{a,e} \delta_{b,f} \right\} \delta \Sigma_{dyn,e,f} = 0 \tag{F.4}$$

We can now evaluate the derivative of the Green's function with respect to the self energy.

$$\mathbf{G} = \left[(i\hbar \omega_\nu + \mu) \mathbf{S} - \bar{\mathbf{h}} - \left(\mathbf{\Sigma}_{dyn} - \mathbf{\Gamma} \right) \right]^{-1}$$

$$\Rightarrow \quad \delta \mathbf{G} = \mathbf{G} \left(\delta \mathbf{\Sigma}_{dyn} - \delta \mathbf{\Gamma} \right) \mathbf{G}$$

$$\Rightarrow \quad \delta G_{d,c} = G_{d,e} \left(\delta \Sigma_{dyn,e,f} - \delta \Gamma_{e,f} \right) \mathbf{G}_{f,c} \tag{F.5}$$

and obtain

$$\left[\frac{\beta\delta\Phi_\beta^{LW,dyn}}{\delta G_{b,a}}\bigg|_{\boldsymbol{G}[\boldsymbol{\Sigma}_{dyn}]} - \Sigma_{dyn,a,b}\right] + \sum_{e,f}\left\{\left[\sum_{c,d}G_{c,e}\frac{\beta\delta^2\Phi_\beta^{LW,dyn}}{\delta G_{b,a}\delta G_{c,d}}\bigg|_{\boldsymbol{G}[\boldsymbol{\Sigma}_{dyn}]}G_{f,d}\right] - \delta_{a,e}\delta_{b,f}\right\}\delta\Sigma_{dyn,e,f} = 0$$

(F.6)

In order to devise an efficient preconditioning scheme, we need a model Green's function and a model dynamical Luttinger-Ward functional. A model Green's function is developed below in section F.3 on p. 64.

$$G_{a,b}(i\omega_\nu)G_{c,d}(i\omega_\nu) \approx -\boldsymbol{S}_{a,b}^{-1}\boldsymbol{S}_{c,d}^{-1}\frac{1}{A + B(\hbar\omega_\nu)^2}$$

(F.7)

Without a good approximation for the Luttinger Ward functional, we make the following simple approximation

$$\sum_{c,d}G_{c,e}\frac{\beta\delta^2\Phi_\beta^{LW,dyn}}{\delta G_{b,a}\delta G_{c,d}}\bigg|_{\boldsymbol{G}[\boldsymbol{\Sigma}_{dyn}]}G_{f,d} \approx -\delta_{a,e}\delta_{b,f}\frac{1}{A + B(\hbar\omega_\nu)^2}$$

(F.8)

With this approximation, I obtain the prediction for $\delta\boldsymbol{\Sigma}_{dyn}$ as

$$\left[\frac{\beta\delta\Phi_\beta^{LW,dyn}}{\delta G_{b,a}}\bigg|_{\boldsymbol{G}[\boldsymbol{\Sigma}_{dyn}]} - \Sigma_{dyn,a,b}\right] - \sum_{e,f}\left\{\delta_{a,e}\delta_{b,f}\frac{1}{A + B(\hbar\omega_\nu)^2} + \delta_{a,e}\delta_{b,f}\right\}\delta\Sigma_{dyn,e,f} = 0$$

$$\left[\frac{\beta\delta\Phi_\beta^{LW,dyn}}{\delta G_{b,a}}\bigg|_{\boldsymbol{G}[\boldsymbol{\Sigma}_{dyn}]} - \Sigma_{dyn,a,b}\right] + \left\{1 + \frac{1}{A + B(\hbar\omega_\nu)^2}\right\}\delta\Sigma_{dyn,a,b} = 0 \quad \text{(F.9)}$$

so that

$$\delta\Sigma_{dyn,a,b} \approx \frac{1}{1 + \frac{1}{A+B(\hbar\omega_\nu)^2}}\left[\frac{\beta\delta\Phi_\beta^{LW,dyn}}{\delta G_{b,a}}\bigg|_{\boldsymbol{G}[\boldsymbol{\Sigma}_{dyn}]} - \Sigma_{dyn,a,b}\right]$$

(F.10)

Thus, in the high-frequency limit, it seems that a mixing factor equal to one seems to be ideal, while the low frequency limit should have an independent mixing.

A more intuitive set of parameters that A, B is to specify the mixing α for $\omega = 0$ and the Matsubara frequency ω_h for which the mixing is halfway between α and one.

$$\boldsymbol{\Sigma}_{dyn}(+) = \boldsymbol{\Sigma}_{dyn}(0) + \frac{1}{1 + \frac{1-\alpha}{\alpha} + \left(\frac{\omega_\nu}{\omega_h}\right)^2}\left[\frac{\beta\delta\Phi_\beta^{LW,dyn}}{\delta G_{b,a}}\bigg|_{\boldsymbol{G}[\boldsymbol{\Sigma}_{dyn}(0)]} - \Sigma_{dyn,a,b}(0)\right] \quad \text{(F.11)}$$

The Laurent expansions are mixed with a mixing factor equal to unity consistent with the high-frequency mixing.

F.2   Euler-Lagrange equations

In order to arrive at a reasonable mixing scheme, we explore a dynamics from a Lagrangian formalism. It is however important to note that this dynamics is useless, because there is no minimum prinicple, so that applying a friction will not lead to a stationary state.

$$m_\Sigma(\omega_\nu)\ddot{\Sigma}_{a,b}(i\omega_\nu) = -\beta\frac{\partial E}{\partial \Sigma^\dagger_{a,b}(i\omega_\nu)}$$

The equation for the self energy is a little complicated. Therefore we obtain it directly from the action principle.

$$\mathcal{L} = \frac{1}{\beta}\sum_\nu m_\Sigma \sum_{a,b}\left\{\dot{\Sigma}_{a,b}(i\omega_\nu)\dot{\Sigma}^\dagger_{b,a}(i\omega_\nu)\right\} - \Phi(\boldsymbol{G})$$

$$0 = \frac{1}{\beta}\sum_\nu m_\Sigma \sum_{a,b}\left\{\dot{\Sigma}^\dagger_{a,b}(i\omega_\nu)\delta\dot{\Sigma}_{b,a}(i\omega_\nu) + \dot{\Sigma}_{a,b}(i\omega_\nu)\delta\dot{\Sigma}^\dagger_{b,a}(i\omega_\nu)\right\}$$

$$-\frac{1}{\beta}\sum_\nu \sum_{a,b,c,d}\left[\frac{\beta\partial\Phi}{\partial G_{a,b}(i\omega_\nu)}\frac{\partial G_{a,b}(i\omega_\nu)}{\partial\Sigma_{c,d}(i\omega_\nu)}\delta\Sigma_{c,d}(i\omega_\nu) + \frac{\beta\partial\Phi}{\partial G^\dagger_{a,b}(i\omega_\nu)}\frac{\partial G^\dagger_{a,b}(i\omega_\nu)}{\partial\Sigma^\dagger_{c,d}(i\omega_\nu)}\delta\Sigma^\dagger_{c,d}(i\omega_\nu)\right]$$

$$= \frac{1}{\beta}\sum_\nu m_\Sigma \sum_{a,b}\left\{-\ddot{\Sigma}^\dagger_{a,b}(i\omega_\nu)\delta\Sigma_{b,a}(i\omega_\nu) - \ddot{\Sigma}_{a,b}(i\omega_\nu)\delta\Sigma^\dagger_{b,a}(i\omega_\nu)\right\}$$

$$-\frac{1}{\beta}\sum_\nu \sum_{a,b,c,d}\frac{\beta\partial\Phi}{\partial G_{a,b}(i\omega_\nu)}G_{a,c}(i\omega_\nu)\delta\Sigma_{c,d}(i\omega_\nu)G_{d,b}(i\omega_\nu)$$

$$-\frac{1}{\beta}\sum_\nu \sum_{a,b,c,d}\frac{\beta\partial\Phi}{\partial G^\dagger_{a,b}(i\omega_\nu)}G^\dagger_{a,c}(i\omega_\nu)\delta\Sigma^\dagger_{c,d}(i\omega_\nu)G^\dagger_{d,b}(i\omega_\nu) + \text{boundary terms at } t_1, t_2$$

$$= -\frac{1}{\beta}\sum_\nu\left[\sum_{a,b}m_\Sigma\ddot{\Sigma}_{a,b}(i\omega_\nu)\delta\Sigma^\dagger_{b,a}(i\omega_\nu) + \sum_{c,d}\left(\sum_{a,b}G^\dagger_{d,b}(i\omega_\nu)\frac{\beta\partial\Phi}{\partial G^\dagger_{a,b}(i\omega_\nu)}G^\dagger_{a,c}(i\omega_\nu)\right)\delta\Sigma^\dagger_{c,d}(i\omega_\nu)\right] + \text{c.c.}$$

$$= -\frac{1}{\beta}\sum_\nu\sum_{a,b}\left[m_\Sigma\ddot{\Sigma}_{a,b}(i\omega_\nu) + \sum_{c,d}G^\dagger_{a,c}(i\omega_\nu)\frac{\beta\partial\Phi}{\partial G^\dagger_{d,c}(i\omega_\nu)}G^\dagger_{d,b}(i\omega_\nu)\right]\delta\Sigma^\dagger_{b,a}(i\omega_\nu) + \text{c.c.}$$

Thus the equation of motion has the form

$$m_\Sigma\ddot{\Sigma}_{a,b}(i\omega_\nu) = -\sum_{c,d}G^\dagger_{a,c}(i\omega_\nu)\frac{\beta\partial\Phi}{\partial G^\dagger_{d,c}(i\omega_\nu)}G^\dagger_{d,b}(i\omega_\nu)$$

With $G(i\omega) = G^\dagger(-i\omega)$ and $\Sigma(i\omega) = \Sigma^\dagger(-i\omega)$, I obtain

$$m_\Sigma\ddot{\Sigma}^\dagger_{a,b}(i\omega_\nu) = -\sum_{c,d}G_{a,c}(i\omega_\nu)\frac{\beta\partial\Phi}{\partial G_{d,c}(i\omega_\nu)}G_{d,b}(i\omega_\nu)$$

F.3   Model Green's function

In order to analyze the equations it is often useful to have a model Green's function that has an analytical form but reflects the qualitative properties of the Green's function.

We start with the expression for a non-interacting Green's function in terms of Matsubara frequencies

$$G_{a,b}(i\omega_\nu) = \sum_n \frac{\langle\pi_a|\psi_n\rangle\langle\psi_n|\pi_b\rangle}{i\hbar\omega_\nu + \mu - \epsilon_n} = \int d\epsilon\, \frac{D_{a,b}(\epsilon)}{i\hbar\omega_\nu + \mu - \epsilon} \tag{F.12}$$

Now we introduce a model density of states that is diagonal in the orbital index and which has a constant density of states of width W centered at the energy E

$$D_{a,b}(\epsilon) = S_{a,b}^{-1} \frac{1}{W} \cdot \underbrace{\theta \left(\epsilon - \left(E - \frac{W}{2} \right) \right)}_{=1 \quad \text{above lower bound}} \cdot \underbrace{\theta \left(\left(E + \frac{W}{2} \right) - \epsilon \right)}_{=1 \quad \text{below upper bound}} \qquad \text{(F.13)}$$

The density of states is normalized so that the total weight of each index equals unity. The Heaviside function $\theta(x)$ is defined such that it vanishes for negative arguments and is equal to one for positive arguments.

We calculate the green's function for $\mu = 0$. The relative position of chemicall potential and the band can be changed easily by adapting the position of the band, i.e. by changing E. Keeping E flexible rather than μ allo expand the argument to multi-band situations. The resulting Green's function has the form

$$
\begin{aligned}
G_{a,b}(i\omega_\nu) &= \int_{E-W/2}^{E+W/2} d\epsilon \, \frac{\frac{1}{W} S_{a,b}^{-1}}{i\hbar\omega_\nu - \epsilon} \\
&= \frac{S_{a,b}^{-1}}{W} \int_{E-W/2}^{E+W/2} d\epsilon \, \frac{-\epsilon - i\hbar\omega_\nu}{(\hbar\omega)^2 + \epsilon^2} \\
&= -\frac{S_{a,b}^{-1}}{W} \int_{E-W/2}^{E+W/2} d\epsilon \, \frac{\epsilon + i\hbar\omega_\nu}{(\hbar\omega)^2 + \epsilon^2} \\
&= -\frac{S_{a,b}^{-1}}{W} \int_{E-W/2}^{E+W/2} dx \, \frac{x + i\hbar\omega_\nu}{(\hbar\omega)^2 + x^2} \\
&= -\frac{S_{a,b}^{-1}}{W} \left\{ \int_{E-W/2}^{E+W/2} dx \, \frac{x}{(\hbar\omega)^2 + x^2} + i\hbar\omega_\nu \int_{E-W/2}^{E+W/2} dx \, \frac{1}{(\hbar\omega)^2 + x^2} \right\} \\
&= -\frac{S_{a,b}^{-1}}{W} \left\{ \frac{1}{2} \ln \left[(\hbar\omega)^2 + (E + W/2)^2 \right] - \frac{1}{2} \ln \left[(\hbar\omega)^2 + (E - W/2)^2 \right] \right. \\
&\qquad \left. + i\hbar\omega_\nu \left[\frac{1}{\hbar\omega} \mathrm{atan} \left(\frac{E + W/2}{\hbar\omega} \right) - \frac{1}{\hbar\omega} \mathrm{atan} \left(\frac{E - W/2}{\hbar\omega} \right) \right] \right\} \\
&= \frac{S_{a,b}^{-1}}{W} \left\{ + \frac{1}{2} \ln \left[\frac{(\hbar\omega)^2 + (E - W/2)^2}{(\hbar\omega)^2 + (E + W/2)^2} \right] - i \left[\mathrm{atan} \left(\frac{E + W/2}{\hbar\omega} \right) - \mathrm{atan} \left(\frac{E - W/2}{\hbar\omega} \right) \right] \right\}
\end{aligned}
$$
$$\text{(F.14)}$$

We used the integral formula's from Bronstein[1]

The result as function of ω is shown in Fig. F.1 The real part is symmetric about the origin, while the imaginary part is antisymmetric. This is consistent with $\boldsymbol{G}(-i\omega_\nu) = \boldsymbol{G}^\dagger(-i\omega_\nu)$.

The imaginary part exhibits a step at the origin from π/W to π/W for metallic systems, that is for a finite density of states at the origin. For an insulating system the imaginary part of the Green's function is smooth and has a finite slope at the origin.

---

[1] Integral formula's:

$$\int dx \, \frac{1}{a^2 + x^2} = \frac{1}{a} \mathrm{atan} \left(\frac{x}{a} \right)$$

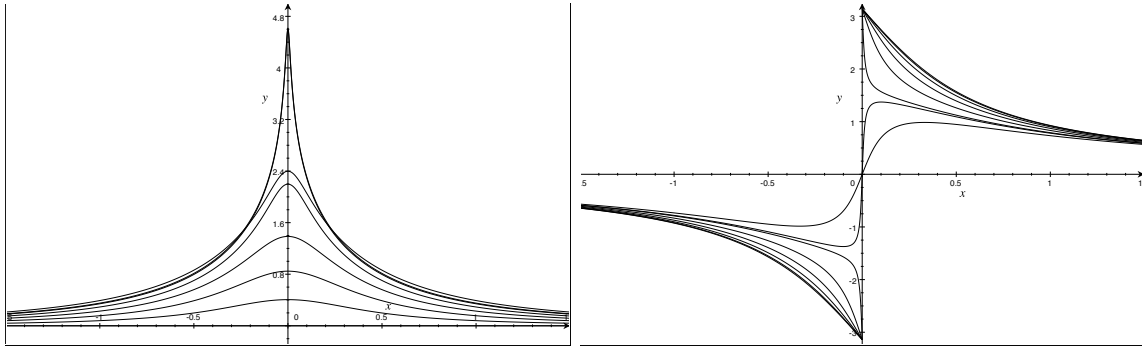$$\int dx \, \frac{x}{a^2 + x^2} = \frac{1}{2} \ln \left(a^2 + x^2 \right) \qquad \text{(F.15)}$$

Fig. F.1: Negative real part (left) and negative imaginary part (right) of the Greens function with a constant density of states of width $W = 1$, centered at $E = \{0, 0.1, 0.2, 0.3, 0.49, 0.51, 0.6\}$.

The real part is positive if the band is centered above the chemical potential and it is negative if it is centered below. The real part vanishes if the density of states at the Fermi level. The real part becomes spiky exactly when the band touches the Fermi level. As the density of states shifts further to positive energies, the Greens function grows further in the tails, but it shrinks in the central region.

The following is not correct! Please check!

Limiting cases

- $\hbar\omega \to 0$:

We use the expansion of the arcus tangens [2] and the expansion of the logarithm [3].

$$
\begin{aligned}
G_{a,b}(i\omega_\nu) &= \frac{S_{a,b}^{-1}}{W}\left\{+\frac{1}{2}\ln\left[\frac{(\hbar\omega)^2+(E-W/2)^2}{(\hbar\omega)^2+(E+W/2)^2}\right]-i\left[\mathrm{atan}\left(\frac{E+W/2}{\hbar\omega}\right)-\mathrm{atan}\left(\frac{E-W/2}{\hbar\omega}\right)\right]\right\} \\
&\approx \frac{S_{a,b}^{-1}}{W}\left\{+\frac{1}{2}\ln\left[\left(\frac{(E-W/2)}{(E+W/2)}\right)^2\right]+\frac{1}{2}\left[\frac{1}{(E-W/2)^2}-\frac{1}{(E+W/2)^2}\right]\hbar\omega^2\right. \\
&\qquad\left. -i\left[\underbrace{\frac{\pi}{2}-\frac{\hbar\omega}{E+W/2}}_{}\underbrace{-\frac{\pi}{2}+\frac{\hbar\omega}{E-W/2}}_{\text{times -1 for insulators}}\right]\right\} \\
&\approx \frac{S_{a,b}^{-1}}{W}\left\{+\ln\left[\frac{(E-W/2)}{(E+W/2)}\right]+\frac{EW}{\left(E^2-\left(\frac{W}{2}\right)^2\right)^2}\hbar\omega^2-i\begin{cases}\frac{W}{E^2-\left(\frac{W}{2}\right)^2}\hbar\omega & \text{for insulators}\\ \pm\pi-\frac{4|E|}{E^2-\left(\frac{W}{2}\right)^2}\hbar\omega & \text{for metals}\end{cases}\right\}
\end{aligned}
$$

$$\text{(F.18)}$$

- $\hbar\omega \to \infty$:

$$
\begin{aligned}
G_{a,b}(i\omega_\nu) &= \frac{S_{a,b}^{-1}}{W}\left\{+\frac{1}{2}\ln\left[\frac{(\hbar\omega)^2+(E-W/2)^2}{(\hbar\omega)^2+(E+W/2)^2}\right]-i\left[\mathrm{atan}\left(\frac{E+W/2}{\hbar\omega}\right)-\mathrm{atan}\left(\frac{E-W/2}{\hbar\omega}\right)\right]\right\} \\
&\approx \frac{S_{a,b}^{-1}}{W}\left\{-EW(\hbar\omega)^{-2}-iW(\hbar\omega)^{-1}\right\} \\
&\approx S_{a,b}^{-1}\left\{-E(\hbar\omega)^{-2}-i(\hbar\omega)^{-1}\right\}
\end{aligned}
$$

$$\text{(F.19)}$$

---

[2]

$$
\mathrm{atan}(x)=y \quad\Rightarrow\quad y=\tan(x)=\frac{\sin(x)}{\cos(x)}
$$

$$
x=\frac{1}{\frac{\pi}{2}-y}+O(y-\frac{\pi}{2})^2 \quad\Rightarrow\quad y\approx\frac{\pi}{2}-\frac{1}{x} \quad\text{for } x\to+\infty
$$

$$
x=\frac{1}{y+\frac{\pi}{2}}+O(y+\frac{\pi}{2})^2 \quad\Rightarrow\quad y\approx-\frac{\pi}{2}+\frac{1}{x} \quad\text{for } x\to-\infty \tag{F.16}
$$

[3]

$$
\ln\left[\frac{a+x}{b+x}\right]\approx\ln\left[\frac{a}{b}\right]+\left(\frac{1}{a}+\frac{1}{b}\right)x+O(x^2) \tag{F.17}
$$

F.4 Enforce constraints by minimizing deviation from the density matrix

$$F = \sqrt{\sum_{a,b} \Delta\rho_{a,b}\Delta\rho_{b,a}} \tag{F.20}$$

$$
\begin{aligned}
dF &= \frac{1}{2F}\sum_{a,b}\left[\frac{\partial\Delta\rho_{a,b}}{\partial\Gamma_{\gamma,\delta}}\Delta\rho_{b,a} + \Delta\rho_{a,b}\frac{\partial\Delta\rho_{b,a}}{\partial\Gamma_{\gamma,\delta}}\right]d\Gamma_{\gamma,\delta}\\
&= \frac{1}{2F}2\sum_{\gamma,\delta}\sum_{a,b}\left[\frac{\partial\Delta\rho_{a,b}}{\partial\Gamma_{\gamma,\delta}}\Delta\rho_{b,a}\right]d\Gamma_{\gamma,\delta}
\end{aligned} \tag{F.21}
$$

Now we make use of the definition of $\Delta\boldsymbol{\rho}$

$$\Delta\boldsymbol{\rho} = k_B T\sum_{\nu}e^{i\hbar\omega\beta0^+}\left[\underbrace{\left((i\hbar\omega_\nu + \mu)\boldsymbol{S} - \bar{\boldsymbol{h}} + \boldsymbol{\Gamma} - \boldsymbol{\Sigma}(i\omega_\nu)\right)^{-1}}_{\boldsymbol{G}(i\omega_\nu)} - \underbrace{\left((i\hbar\omega_\nu + \mu)\boldsymbol{S} - \bar{\boldsymbol{h}}\right)^{-1}}_{\bar{\boldsymbol{G}}(i\omega_\nu)}\right]$$

$$d(\Delta\boldsymbol{\rho}) = k_B T\sum_{\nu}e^{i\hbar\omega\beta0^+}\left[-\boldsymbol{G}\,d\boldsymbol{\Gamma}\,\boldsymbol{G}\right] = -k_B T\sum_{\nu}\boldsymbol{G}(i\omega_\nu)d\boldsymbol{\Gamma}\boldsymbol{G}(i\omega_\nu) \tag{F.22}$$

$$
\begin{aligned}
dF &= \frac{1}{F}\sum_{a,b,\gamma,\delta}\left[-k_B T\sum_{\nu}G_{a,\gamma}(i\omega_\nu)d\Gamma_{\gamma,\delta}G_{\delta,b}(i\omega_\nu)\Delta\rho_{b,a}\right]\\
&= \sum_{\gamma,\delta}\left[-\frac{1}{F}\sum_{a,b}\left[k_B T\sum_{\nu}G_{\delta,b}(i\omega_\nu)\Delta\rho_{b,a}G_{a,\gamma}(i\omega_\nu)\right]\right]d\Gamma_{\gamma,\delta}
\end{aligned} \tag{F.23}
$$

The "optimum" search direction is the one with the largest (negative) projection on the gradient.

$$d\boldsymbol{\Gamma}^{opt} = +\left[\frac{1}{F}k_B T\sum_{\nu}\boldsymbol{G}(i\omega_\nu)\Delta\boldsymbol{\rho}\,\boldsymbol{G}(i\omega_\nu)\right]^{\dagger} \tag{F.24}$$

Appendix G

Usage

G.0.1 Control file

A typical control file looks as follows. The DMFT object is activated by the block `!NTBO` with the value `MODUS='DMFT'`. The DMFT interface requires a finite temperature calculation, which is specified by the `!MERMIN` block, where the temperature is specified. A finite temperature calculation requires `SAFEORTHO=T`, so that the wave function dynamics converges to eigenstates of the Hamiltonian.

```
!CONTROL
  !GENERIC NSTEP=500  DT=5. START=F  !END
  !FOURIER EPWPSI=30. CDUAL=2.0 !END
  !DFT TYPE=10
     !NTBO MODUS='DMFT' !END
  !END
  !PSIDYN STOP=T FRIC=.05 SAFEORTHO=F
    !AUTO FRIC(-)=0.3 FACT(-)=0.97 FRIC(+)=0.3 FACT(+)=1.0 MINFRIC=0.05 !END
  !END
  !MERMIN T[K]=4000. ADIABATIC=T RETARD=10. !END
!end
!EOB
```

G.0.2 Structure file

A typical structure file may look as follows. New are the `!NTBO` subblocks.

```
!STRUCTURE
  !GENERIC  LUNIT[AA]=  3.8   EUNIT[EV]=T !END
  !OCCUPATIONS EMPTY=10 NSPIN=2 SPIN[HBAR]=1.5 !END
  !KPOINTS DIV=1 1 1 SHIFT=1 1 1 !END
  !SPECIES NAME='CA' ID='CA_HBS_SC' NPRO=2 2 1
    !NTBO NOFL=1 0 0 RAUG/RCOV=0.8 RTAIL/RCOV=1.4 TAILLAMBDA=2. 1.
        CV=F FOCKSETUP=F  !END
  !END
  !SPECIES NAME='MN' ID='MN_HBS' NPRO=1 1 1
```

```
      !NTBO NOFL=1 0 1 RAUG/RCOV=1.2 RTAIL/RCOV=1.4 TAILLAMBDA=2. 1.
            LHFWeiGHT=0.25 CV=F FOCKSETUP=F !END
    !END
    !SPECIES NAME='O_' ID='O_.75_6.0'  NPRO=1 1 0
      !NTBO NOFL=1 1  RAUG/RCOV=1.2 RTAIL/RCOV=1.4 TAILLAMBDA=2. 1.
            CV=F FOCKSETUP=F !END
    !END
    !LATTICE T=  1.0000         0.0000         0.0000000000
                 0.0000         1.0000         0.0000000000
                 0.0000         0.0000         1.0000000000 !END
    !ATOM NAME= 'CA1'   R=   0.0  0.0 0.0 !END
    !ATOM NAME= 'MN1'   R=   0.5  0.5 0.5 !END
    !ATOM NAME= 'O_1'   R=   0.0  0.5 0.5 !END
    !ATOM NAME= 'O_2'   R=   0.5  0.0 0.5 !END
    !ATOM NAME= 'O_3'   R=   0.5  0.5 0.0 !END
    !ORBPOT_X
      !POT ATOM='MN(UP)1' VALUE=+.2 TYPE='D' RC=1.5 S=1 !END
    !END
!END
!EOB
```

Appendix H

Bloch representation

Appendix I

Traditional formulation of the dynamical mean-field theory

The loop of solver takes as input a local Greens function and a U-tensor. It produces the value of the Luttinger-Ward functional, and its derivatives of the Luttinger-Ward functional with respect to Greens function and U-tensor.

The algorithm is the following

1. choose a hybridization function $\Delta^{in}(i\omega_\nu)$

2. calculate an output Greens function $\boldsymbol{G}^{out}$ as follows[1]: Caution, I generalized Dieter's Equations without checking. Signs, factors, indices, etc. may be wrong!

$$G^{out}_{\alpha,\beta}(i\omega_\nu) := -\frac{1}{Z} \int \prod_\gamma Dc^*_\gamma Dc_\gamma \; c_\alpha(i\omega_\nu) c^*_\beta(i\omega_\nu) \mathrm{e}^{-S_{loc}}$$

$$Z = \int \prod_\gamma Dc^*_\gamma Dc_\gamma \; \mathrm{e}^{-S_{loc}}$$

$$S_{loc} = -\int_0^\beta d\tau_1 \int_0^\beta d\tau_2 \sum_{\alpha,\beta} c^*_\alpha(\tau_1) \Big[i\hbar\omega_\nu \delta_{\alpha,\beta} - \Delta^{in}_{\alpha,\beta}(i\omega_\nu) \Big] c_\beta(\tau_2)$$

$$- \int_0^\beta d\tau \sum_{\alpha,\beta,\gamma,\delta} U_{\alpha,\beta,\delta,\gamma} c^*_\alpha c^*_\beta c_\gamma c_\delta$$

Note, that only the hybridization function $\boldsymbol{\Delta}^{in}$ and the U-tensor enter in this calculation. The only result is the output Greens function $\boldsymbol{G}^{out}$.

3. Convert the Green's function into a self energy $\boldsymbol{\Sigma}^{out}$ using Dyson's equation

$$\Sigma^{out}_{\alpha,\beta}(i\omega_\nu) := -\Big(G^{out}(i\omega_\nu) \Big)^{-1}_{\alpha,\beta} + i\hbar\omega_\nu \delta_{\alpha,\beta} - \Delta^{in}_{\alpha,\beta}(i\omega_\nu) \tag{I.1}$$

---

[1](D. Vollhardt *Dynamical Mean Field Theory for Strongly Correlated Materials* in *The LDA+DMFT Approach to Strongly Correlated Materials'* E. Pavarini, E. Koch, D. Vollhardt and A. Lichtenstein Eds, Forschungszentrum Juelich 2011. Eq. 23.ff)

4. Use the Greens function $\mathbf{G}$ passed to the solver as input argument (not $\mathbf{G}^{out}$!) to extract a new hybridization function $\mathbf{\Delta}^{out}$

$$\Delta_{\alpha,\beta}^{out}(i\omega_\nu) := -\left(G(i\omega_\nu)\right)^{-1}_{\alpha,\beta} + i\hbar\omega_\nu\delta_{\alpha,\beta} - \Sigma_{\alpha,\beta}^{out}(i\omega_\nu) \tag{I.2}$$

The steps given above yield a unique mapping from Δ^{in} to Δ^{out}. In other words the output hybridization function is a unique functional of the input hybridization function, the input Greens function and the U-tensor.

$$\mathbf{\Delta}^{out} = F[\mathbf{\Delta}^{in}, \mathbf{G}, \mathbf{U}] \tag{I.3}$$

The mapping depends on exactly two quantities, namely the input Green's function and the U-tensor. Self-consistency yields the fixed point $\Delta^{out} = \Delta^{in}$ of this mapping. At this fixed point, Eq. I.2 and Eq. I.1 yield

$$G_{\alpha,\beta}^{out}(i\omega_\nu) = G_{\alpha,\beta}(i\omega_\nu) \tag{I.4}$$

and

$$G_{\alpha,\beta}(i\omega_\nu) = \left[i\hbar\omega_\nu\mathbf{1} - \mathbf{\Sigma}^{out}(i\omega_\nu) - \mathbf{\Delta}^{in}(i\omega_\nu)\right]^{-1}_{\alpha,\beta}. \tag{I.5}$$

Appendix J

Conjugate-gradient method

The conjugate-gradient method is used to determine the constraints.

J.0.3 Wirtinger Calculus

Here, we re-derive it for a real function of a complex vector, because this is not usually written down explicitely. We make use of the **Wirtinger calculus** in that we express the variation of a real function F of a complex argument $z = a + ib$ in the form

$$
\begin{aligned}
dF(a, b) &= \frac{dF}{da} da + \frac{dF}{db} db \\
&= \frac{1}{2}\Big(\frac{dF}{da} - i\frac{dF}{db}\Big)\Big(da + ib\Big) + \frac{1}{2}\Big(\frac{dF}{da} + i\frac{dF}{db}\Big)\Big(da - ib\Big) \\
&= \frac{dF}{dz} dz + \frac{dF}{dz^*} dz^* = dF(z, z^*)
\end{aligned}
\tag{J.1}
$$

which defines the **Wirtinger derivatives**

$$
\begin{aligned}
\frac{dF}{dz} &= \frac{1}{2}\Big(\frac{dF}{da} - i\frac{dF}{db}\Big) \\
\frac{dF}{dz^*} &= \frac{1}{2}\Big(\frac{dF}{da} + i\frac{dF}{db}\Big)
\end{aligned}
\tag{J.2}
$$

We define the force in the Wirtinger calculus as

$$
f = -\frac{dF}{dz}
\tag{J.3}
$$

so that

$$
dF = -f^* dz - dz^* f
\tag{J.4}
$$

J.0.4 Definition of the problem

The goal is to determine the minimum of a real quadratic function $F(\vec{x})$ of a complex vector $\vec{x}$

$$
F(\vec{x}) = \vec{x}^* \boldsymbol{A} \vec{x} - \vec{b}^* \vec{x} - \vec{x}^* \vec{b}
\tag{J.5}
$$

where $\boldsymbol{A}$ is a positive definite, hermitean matrix.

The condition for a minimum is

$$dF(\vec{x}, \vec{x}^*) = d\vec{x}^*\left(\boldsymbol{A}\vec{x} - \vec{b}\right) + \left(\vec{x}^*\boldsymbol{A} - \vec{b}^*\right)d\vec{x} \overset{!}{=} 0$$

$$\Rightarrow \quad \boldsymbol{A}\vec{x} - \vec{b} = 0 \quad \text{and} \quad \vec{x}^*\boldsymbol{A} - \vec{b}^* = 0 \tag{J.6}$$

Because the function F is real, the two equations obtained from the variation of $\vec{x}$ and $\vec{x}^*$ are not indepependent, but both equations are complex conjugate of each other.

J.0.5 Minimization on a hyperplane

Given is a k-dimensional hyperplane $\mathcal{D}_k = span\{\vec{d}_1, \ldots, \vec{d}_k\}$, which is spanned by a set of search directions $\vec{d}_i$. The search directions shall furthermore be conjugate to each other, i.e.

$$\vec{d}_i^*\boldsymbol{A}\vec{d}_j = 0 \qquad \text{for } i \neq j \tag{J.7}$$

All points on the hyperplane can be expressed by

$$\vec{x}(\alpha_1, \ldots, \vec{\alpha}_k) = \sum_{i=1}^{k} \vec{d}_i \alpha_i \tag{J.8}$$

The function F can be mapped onto the hyperplane, yielding F_k

$$F_k(\vec{\alpha}, \vec{\alpha}^*) = \sum_{i,j} \alpha_i^* \vec{d}_i^* \boldsymbol{A} \vec{d}_j \alpha_j - \sum_j \vec{b}^* \vec{d}_j \alpha_j - \sum_i \alpha_i^* \vec{d}_i^* \vec{b} \tag{J.9}$$

The minimum condition of F_k on the hyperplane is

$$dF_k = \sum_i d\alpha_i^* \left(\sum_j \vec{d}_i^* \boldsymbol{A} \vec{d}_j \alpha_j - \vec{d}_i^* \vec{b}\right) + \sum_j \left(\sum_i \alpha_i^* \vec{d}_i^* \boldsymbol{A} \vec{d}_j - \vec{b}^* \vec{d}_j\right) d\alpha_j$$

$$\overset{\text{Eq. } J.7}{=} \sum_i d\alpha_i^* \left(\vec{d}_i^* \boldsymbol{A} \vec{d}_i \alpha_i - \vec{d}_i^* \vec{b}\right) + \sum_i \left(\alpha_i^* \vec{d}_i^* \boldsymbol{A} \vec{d}_i - \vec{b}^* \vec{d}_i\right) d\alpha_i$$

$$dF_k \overset{!}{=} 0 \quad \Rightarrow \quad \alpha_i = \frac{\vec{d}_i^* \vec{b}}{\vec{d}_i^* \boldsymbol{A} \vec{d}_i} \tag{J.10}$$

Thus, we obtain the minimum in the hyperplane as

$$\vec{x}_k \overset{Eq. \ J.8, J.10}{=} \sum_{i=1}^{k} \vec{d}_i \frac{\vec{d}_i^* \vec{b}}{\vec{d}_i^* \boldsymbol{A} \vec{d}_i} \tag{J.11}$$

We can also determine the minima in hyperplanes with successivly higher dimensions in the form

$$\vec{x}_k = \vec{x}_{k-1} + \vec{d}_k \alpha_k = \vec{x}_{k-1} + \vec{d}_k \frac{\vec{d}_k^* \vec{b}}{\vec{d}_k^* \boldsymbol{A} \vec{d}_k} \tag{J.12}$$

In practice we do not wish to use $\vec{b}$ and $\boldsymbol{A}$, but only the values of F and its derivatives at specific points. For this purpose, I exploit that the force $\vec{f} = -\vec{\nabla}_{\vec{x}^*} F$, also called the **residuum**, is orthogonal to the previous search direction.

$$\vec{f}_k = -\vec{\nabla}_{\vec{x}^*}\big|_{\vec{x}_k, \vec{x}_k^*} F = \vec{b} - \boldsymbol{A}\vec{x}_k \tag{J.13}$$

Because

$$dF_k = -\sum_i d\alpha_i^* \vec{d}_i^* \vec{f}_k - \sum_i \vec{f}_k^* \vec{d}_i d\alpha_i \tag{J.14}$$

any component of $\vec{f}_k$ on $\vec{d}_i^*$, i.e. any finite value of $\vec{d}_i^* \vec{f}_k$, would allow one to lower the value of F_k by changing α_k. This, however, would contradict the assumption that $\vec{x}_k$ is the minimum of F_k.

Therefore, we conclude that the force is orthogonal to all "previous" search directions

$$\vec{d}_i^* \vec{f}_k = \vec{f}_k^* \vec{d}_i = 0 \quad \text{for } i \leq k \tag{J.15}$$

In particular, we can determine $\vec{x}_k$ and α_k from

$$\vec{x}_k = \vec{x}_{k-1} + \vec{d}_k \alpha_k \tag{J.16}$$
$$\vec{f}_k^* \vec{d}_k = 0 \rightsquigarrow \alpha_k \tag{J.17}$$

J.0.6   Determine next search direction

The next search direction shall include the last force. Furthermore, it must obey the conjugacy condition to all previous search directions. This can be accomplished by mixing in the previous search directions

$$\vec{d}_{k+1} = \vec{f}_k + \sum_{j=1}^{k} \vec{d}_j \beta_j \tag{J.18}$$

where the coefficients β_j are determined so that

$$\vec{d}_i^* \boldsymbol{A} \vec{d}_{k+1} = 0 \quad \text{for } i \leq k \tag{J.19}$$

$$\vec{d}_i^* \boldsymbol{A} \vec{d}_{k+1} \stackrel{\text{Eq. } J.18}{=} \vec{d}_i^* \boldsymbol{A} \vec{f}_k + \sum_{j=1}^{k} \vec{d}_i^* \boldsymbol{A} \vec{d}_j \beta_j \stackrel{\text{Eq. } J.7}{=} \vec{d}_i^* \boldsymbol{A} \vec{f}_k + \vec{d}_i^* \boldsymbol{A} \vec{d}_i \beta_i \stackrel{!}{=} 0$$

$$\Rightarrow \quad \beta_i \quad = \quad -\frac{\vec{d}_i^* \boldsymbol{A} \vec{f}_k}{\vec{d}_i^* \boldsymbol{A} \vec{d}_i} \tag{J.20}$$

$$\vec{d}_{k+1} \stackrel{\text{Eq. } J.18, J.20}{=} \vec{f}_k - \sum_{j=1}^{k} \vec{d}_j \frac{\vec{d}_j^* \boldsymbol{A} \vec{f}_k}{\vec{d}_j^* \boldsymbol{A} \vec{d}_j} \tag{J.21}$$

It is our goal to express the new search direction without direct reference to the matrix $\boldsymbol{A}$. Therefore, we represent $\vec{d}_j^* \boldsymbol{A}$ by two subsequent forces.

$$\vec{f}_j - \vec{f}_{j-1} \overset{\text{Eq. } J.13}{=} \vec{b} - \boldsymbol{A}\vec{x}_j - \vec{b} + \boldsymbol{A}\vec{x}_{j-1} = -\boldsymbol{A}(\vec{x}_j - \vec{x}_{j-1}) \overset{\text{Eq. } J.16}{=} -\boldsymbol{A}\vec{d}_j \alpha_j \tag{J.22}$$

$$\vec{d}_{k+1} \overset{\text{Eq. } J.21}{=} \vec{f}_k - \sum_{j=1}^{k} \vec{d}_j \frac{\left(\vec{f}_j^* - \vec{f}_{j-1}^*\right) \vec{f}_k}{\left(\vec{f}_j^* - \vec{f}_{j-1}^*\right) \vec{d}_j} \tag{J.23}$$

Next, I show that the forces $\vec{f}_k$ are orthogonal to each other, i.e. $\vec{f}_i^* \vec{f}_j = 0$, which will simplify Eq. J.23 by limiting the sum to the last term.

Because the search directions are built up, via Eq. J.18, from the forces, the forces and search directions span the same hyperplane.

$$\text{span}\{\vec{d}_1, \ldots, \vec{d}_k\} = \text{span}\{\vec{f}_0, \ldots, \vec{f}_{k-1}\} \tag{J.24}$$

Because $\vec{f}_k$ is orthogonal to the search directions $\vec{d}_1, \ldots, \vec{d}_k$, it is also orthogonal to the forces $\vec{f}_0, \ldots, \vec{f}_{k-1}$. Hence, the forces are orthogonal to each other.

$$\vec{f}_i^* \vec{f}_j = 0 \quad \text{for } i \neq j \tag{J.25}$$

With the orthogonality conditions Eq. J.25, we can limit the expression for the new search direction to the last term

$$\vec{d}_{k+1} \overset{\text{Eq. } J.23}{=} \vec{f}_k - \vec{d}_k \frac{\left(\vec{f}_k^* - \vec{f}_{k-1}^*\right) \vec{f}_k}{\left(\vec{f}_k^* - \vec{f}_{k-1}^*\right) \vec{d}_k} \tag{J.26}$$

This is the final expression of **Heestenes and Stiefel**.

Using the orthogonality conditions we can also determine variants of the above equation. We can go a step further and use

$$\vec{d}_k \overset{\text{Eq. } J.26}{=} \vec{f}_{k-1} + \vec{d}_{k-1}\beta \tag{J.27}$$

to transform

$$\left(\vec{f}_k^* - \vec{f}_{k-1}^*\right)\vec{d}_k \overset{\vec{f}_k^* \vec{d}_k = 0}{=} -\vec{f}_{k-1}^* \vec{d}_k \overset{\text{Eq. } J.27}{=} -\vec{f}_{k-1}^*\left(\vec{f}_{k-1} + \vec{d}_{k-1}\beta\right) \overset{\vec{f}_{k-1}^* \vec{d}_{k-1} = 0}{=} -\vec{f}_{k-1}^* \vec{f}_{k-1} \tag{J.28}$$

With this expression we arrive at the formula of **Polak and Ribiere** .

$$\vec{d}_{k+1} \overset{\text{Eqs. } J.26, J.28}{=} \vec{f}_k + \vec{d}_k \frac{\left(\vec{f}_k^* - \vec{f}_{k-1}^*\right) \vec{f}_k}{\vec{f}_{k-1}^* \vec{f}_{k-1}} \tag{J.29}$$

The sequence of Polak and Ribiere shall be restarted, when the $\left(\vec{f}_k^* - \vec{f}_{k-1}^*\right)\vec{f}_k < 0$

Using the orthogonality of the forces again, we arrive at the expression of **Fletcher and Reeves**.

$$\vec{d}_{k+1} \overset{\text{Eq. } J.29}{=} \vec{f}_k + \vec{d}_k \frac{\vec{f}_k^* \vec{f}_k}{\vec{f}_{k-1}^* \vec{f}_{k-1}} \tag{J.30}$$

All three expressions are equivalent, if the problem is purely parabolic. If the problem is nonlinear they provide different convergence.

Most importantly, the sequence must be restarted, whenever the denominator vanishes! The sequence can be restarted by removing the admixture of the previous search direction, i.e. by setting $\beta = 0$.

J.0.7 Nonlinear Conjugate Gradient Method

The nonlinear conjugate gradient method is the same method, just applied to a general real function $F(\vec{x})$ instead of a quadratic function. For a general function, the orthogonality of the forces is no more strictly valid.

The equation of Heestenes-Stiefel and the one of Pollak Ribiere are strictly identical, because they only require the orthogonality $\vec{f}_j^* \vec{d}_j$ between search directions and forces in the same iteration. This is imposed also in the general case.

The equation of Fletcher and Reeves differs from the ones of Heestenes-Stiefel and Polak-Ribiere, because they assume also that $\vec{f}_{k-1} \vec{f}_k$, which is not obeyed in the nonlinear case.

J.0.8   Recipe

CONJUGATE GRADIENT SCHEME

1. Start-up: The conjugate gradient iteration is started from an arbitrary point, $\vec{x}_0$. At this point the force $\vec{f}_0$ is evaluated. The force also defines the first search direction

$$\vec{d}_1 = \vec{f}_0 \tag{J.31}$$

2. Line search for next point $\vec{x}_k$.

$$\vec{x}_k = \vec{x}_{k-1} + \vec{d}_k \alpha_k \tag{J.32}$$
$$\vec{f}_k^* \vec{d}_k = 0 \rightsquigarrow \alpha_k \tag{J.33}$$

3. determine new search direction $\vec{d}_{k+1}$

$$\vec{d}_{k+1} \overset{\text{Eq. } J.21}{=} \vec{f}_k + \vec{d}_k \beta_k \tag{J.34}$$

with one of the expressions

- Fletcher-Reeves

$$\beta_k \overset{\text{Eq. } J.30}{=} + \frac{\vec{f}_k^* \vec{f}_k}{\vec{f}_{k-1}^* \vec{f}_{k-1}} \tag{J.35}$$

- Polak-Ribiere

$$\beta_k \overset{\text{Eq. } J.29}{=} \max \left(0, + \frac{\left(\vec{f}_k^* - \vec{f}_{k-1}^* \right) \vec{f}_k}{\vec{f}_{k-1}^* \vec{f}_{k-1}} \right) \tag{J.36}$$

The condition that $\beta > 0$ has been mentioned by Shewchuk[8].
- Heestenes-Stiefel

$$\beta_k \overset{\text{Eq. } J.26}{=} - \frac{\left(\vec{f}_k^* - \vec{f}_{k-1}^* \right) \vec{f}_k}{\left(\vec{f}_k^* - \vec{f}_{k-1}^* \right) \vec{d}_k} \tag{J.37}$$

Restart the CG iteration (set $\beta_k = 0$) if the denominator vanishes, or if $\beta_k > 0$.

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Bibliography

[1] Peter E. Blöchl, Thomas Pruschke, and Michael Potthoff. Density-matrix functionals from green's functions. Phys. Rev. B, 88:205139, Nov 2013. doi: $10.1103/\mathrm{PhysRevB}.88.205139$. URL http://link.aps.org/doi/10.1103/PhysRevB.88.205139.

[2] J. M. Luttinger and J. C. Ward. Ground-state energy of a many-fermion system ii. Phys. Rev., 118:1417, 1960. doi: $10.1103/\mathrm{PhysRev}.118.1417$. URL http://link.aps.org/doi/10.1103/PhysRev.118.1417.

[3] N.D. Mermin. Thermal properties of the inhomogeneous electron gas. Physical Review, 137:A1441, 1965. doi: $10.1103/\mathrm{PhysRev}.137.\mathrm{A}1441$. URL http://link.aps.org/doi/10.1103/PhysRev.137.A1441.

[4] P. E. Blöchl, C. F. J. Walther, and Th. Pruschke. Method to include explicit correlations into density-functional calculations based on density-matrix functional theory. Phys. Rev. B, 84:205101, 2011. doi: $10.1103/\mathrm{PhysRevB}.84.205101$. URL http://link.aps.org/doi/10.1103/PhysRevB.84.205101.

[5] qian (not done). Xiaofeng qian and ju li and liang qi and cai-zhuang wang and tzu-liang chan and yong-xin yao and kai-ming ho and sidney yip. Phys. Rev. B, 78:245112, 2008.

[6] Nils Erik Dahlen, Robert van Leeuwen, and Ulf von Barth. Variational energy functionals of the green function and of the density tested on molecules. Phys. Rev. A, 73:012511, Jan 2006. doi: $10.1103/\mathrm{PhysRevA}.73.012511$. URL http://link.aps.org/doi/10.1103/PhysRevA.73.012511.

[7] N. E. Bickers and D.J. Scalapino. Conserving approximations for strongly fluctuating electron systems. i. formalism and calculational approach. Ann. Phys., 193:206, 1989. doi: 10.1016/0003-4916(89)90359-X.

[8] J.R. Shewchuk. An introduction to the conjugate gradient method without the agonizing pain. http://www.cs.cmu.edu/~quake-papers/painless-conjugate-gradient.pdf, School of Computer Science, Carnegie Mellon University, Pittsburg, PA, USA, 1994.