The GW Method: Theory and Implementation

July 20, 2016

Contents

Contents 3

I Theory 9

1 Density functional theory 11
1.1 The band gap problem . . . 11
1.1.1 Derivative discontinuity of $E_{\rm xc}$ . . . 11

2 GW Approximation 13
2.1 Summary of GW equations . . . 13
2.2 Energy-only selfconsistent GW . . . 15
2.3 Matrix form of the GW equations . . . 15
2.4 On the k- and q-points grid . . . 16
2.4.1 G_0W_0 based on LDA+U . . . 16

3 Vertex corrections 19

II Implementation 21

4 Symbols and Notation 23
4.1 Normalization schemes used for wavefunctions . . . 23
4.2 Notations used . . . 23
4.3 Programming conventions . . . 25

5 The (L)APW+lo method (WIEN2k) 27
5.1 The (L)APW+lo basis functions . . . 27
5.1.1 Core states . . . 27
5.1.2 Valence and conduction states . . . 28
5.1.2.1 The traditional linearization method: LAPW . . . 28
5.1.2.2 The new linearization method: APW+lo . . . 28
5.1.3 Semi-core states: local orbitals . . . 29
5.1.3.1 SC-LAPW . . . 29
5.1.3.2 SC-APW+lo . . . 30
5.1.4 The Bloch character of the wavefunctions . . . 31

6 Mixed basis 33
6.1 Definition of the basis . . . 33
6.1.1 MB basis functions for MT region . . . 33
6.1.2 Interstitial region . . . 34
6.2 Matrix elements $\mathcal{W}^i_{\mathbf{G}}(\mathbf{q})$ . . . 35
6.3 Matrix elements $M^i_{nm}(\mathbf{k},\mathbf{q})$ . . . 36
6.3.1 $\tilde{\chi}^{\mathbf{q}}_i(\mathbf{r})$ corresponds to functions in the MT-sphere region . . . 36
6.3.1.1 $n,m \in$ band states . . . 37
6.3.1.2 $n \in$ band state, $m \equiv c \in$ core states . . . 37
6.3.1.3 $n \equiv c \in$ core state, $m \in$ band states . . . 37
6.3.1.4 $n \equiv c, m \equiv c' \in$ core state . . . 38
6.3.2 $\tilde{\chi}^{\mathbf{q}}_i(\mathbf{r})$ corresponds to an IPW . . . 38

7 The coulomb matrix **39**
7.1 Case A: χ_i and χ_i belong to different MT spheres . . . 39
7.2 B: Both Interstitial . . . 42
7.3 C: One MT-sphere and one interstitial . . . 42
7.4 The singularity at the Γ point . . . 44
7.4.1 Subtracting the $\mathbf{q} = 0$ component of the wave functions . . . 44
7.4.2 Step by step: The different terms in the matrix elements . . . 45
7.4.2.1 Case 1: $\mathbf{r}_1 \in a$ and $\mathbf{r}_2 \in a'$ . . . 45
7.4.2.2 Case 2: $\mathbf{r}_1 \in a$ and $\mathbf{r}_2 \in a'' \neq a'$ . . . 46
7.4.2.3 Case 3: $\mathbf{r}_1 \in a'' \neq a$ and $\mathbf{r}_2 \in a'$ . . . 46
7.4.2.4 Case 4: $\mathbf{r}_1 \in a'' \neq a$ and $\mathbf{r}_2 \in a''' \neq a'$ . . . 46
7.4.2.5 Case 5: $\mathbf{r}_1 \in a''$ and $\mathbf{r}_2 \in I$ . . . 47
7.4.2.6 Case 6: $\mathbf{r}_1 \in I$ and $\mathbf{r}_2 \in a''$ . . . 47
7.4.2.7 Case 7: $\mathbf{r}_1, \mathbf{r}_2 \in I$ . . . 48
7.4.3 Final expression . . . 48

8 Green's Function **51**

9 The Polarization matrix **53**
9.1 General formalism . . . 53
9.2 Formalism for periodic systems . . . 54

10 The dielectric function **57**
10.1 The symmetrized dielectric matrix . . . 57
10.2 Plane wave expansion of the symmetrized dielectric matrix at the Γ point . . . 57
10.2.1 $M_{nn'}^{\mathbf{G}=0}(\mathbf{k}, \mathbf{q})$ in the limit of $\mathbf{q} \to 0$ . . . 58
10.2.2 The head:$P_{\mathbf{G}=0,\mathbf{G}'=0}(\mathbf{q} \to 0, \omega)$ . . . 58
10.2.3 The Wings:$P_{\mathbf{G}=0,\mathbf{G}'\neq 0}(\mathbf{q} \to 0, \omega)$ . . . 60
10.3 Mixed basis expansion of the dielectric matrix at the Γ point . . . 60
10.3.0.1 Head . . . 61
10.3.0.2 Wing . . . 61
10.3.0.3 Body . . . 62
10.4 Dielectric matrix in the basis of bare Coulomb matrix eigenvectors . . . 62
10.5 Inverse dielectric function at Γ point . . . 63

11 The Dynamically screened potential **65**
11.1 General expressions . . . 65
11.2 Singularity at the Γ point ($\mathbf{q} = 0$) . . . 65
11.3 Formulalism using v-diagonalized basis set . . . 66

12 Evaluation of the sef-energy Σ **67**
12.1 Exchange self-energy . . . 67
12.2 Correlation term . . . 67
12.3 Brillouin-Zone integration of the singular terms . . . 68
12.4 Exchange and correlation selfenergy using v-diagonalized basis set . . . 69
12.4.0.1 Exchange . . . 69
12.4.0.2 Correlation . . . 69
12.5 Combining $\tilde{v}^{\frac{1}{2}}$ and M_{nm}^{i} . . . 70
12.5.0.1 Dielectric matrix . . . 70
12.5.0.2 Exchange self-energy . . . 70
12.5.0.3 Correlation selfenergy . . . 70
12.6 Static COHSEX approximation . . . 71

13 G_0W_0 and GW_0 Approximation **73**
13.1 G_0W_0 approximation . . . 73
13.2 Analytic continuation of correlation selfenergy . . . 73
13.2.1 Multipole fitting method . . . 73
13.2.2 Pade approximant method . . . 74
13.3 Fermi energy shift . . . 74
13.4 GW_0 approach . . . 76

14 G_0W_0 based on LDA+U **77**
14.1 LDA+U method . . . 77
14.2 LDA+U as an approximation to GW . . . 78
14.3 KS equation in LDA+U . . . 80
14.4 Derive LDA+U from GW . . . 81
14.5 LDA+U correction in G_0W_0 . . . 82
14.6 How to calculate U? . . . 83
14.6.1 Constrained DFT method . . . 83
14.6.2 RPA without or with constaint . . . 83

15 SOC-GW **85**

16 Selfconsistent GW **87**
16.1 Full self-consistent GW . . . 87
16.2 Approximate self-consistent GW . . . 88
16.2.1 Faleev-van Schilfgaarde-Kotani scheme . . . 88
16.2.2 Shishkin-Marsman-Kresse scheme . . . 88
16.2.3 self-consistent COHSEX . . . 89
16.2.4 Sakuma-Miyake-Aryasetiawan scheme . . . 89
16.3 Implementation of QSGW . . . 90
16.3.1 General issues . . . 90
16.3.2 Matrix elements in the FB approach . . . 90
16.3.2.1 Bare-exchange $\Sigma^{\mathrm{x}}_{\mu\nu}$ . . . 90
16.3.2.2 COHSEX correlation self-energy . . . 91
16.3.2.3 GW correlation selfenergy in the FvSK scheme . . . 91
16.3.2.4 Hartree potential δV^{H} . . . 92

17 ACFD total energy **95**
17.1 Exact exchange energy . . . 95
17.2 RPA correlation energy . . . 96
17.3 ACFD correlation energy with ALDA f^{xc} . . . 97

18 Constrained RPA **99**
18.1 U-matrix elements . . . 99
18.2 Projection-based disentanglement approach . . . 102
18.2.1 The $\mathbf{q} \to 0$ limit . . . 102
18.3 Construction of the Wannier functions . . . 104
18.3.1 $\mathbf{k}$-summation: Symmetrization . . . 104
18.3.1.1 In the case of two-particle functions . . . 104
18.4 Implementation . . . 105
18.4.1 Data structure . . . 105

19 GW+DMFT **107**
19.1 Theory . . . 107
19.2 Implementation . . . 107

20 The Brillouin-Zone Integration **109**
20.1 The Linear Tetrahedron Method . . . 110
20.1.1 The Isoparametric Transfromation . . . 111
20.1.2 Integrals in One Tetrahedron . . . 112
20.1.3 The Integration Weights . . . 113
20.2 Tetrahedron Method for $\mathbf{q}$-dependent Brillouin-zone Integration . . . 113
20.2.1 Isoparametric Transformation . . . 115
20.2.2 The Integration Region . . . 115
20.2.3 Polarizability . . . 115
20.2.3.1 Polarisability on the Real Frequency Axis . . . 116
20.2.3.2 Polarisability on the Imaginary Frequency Axis . . . 117

21 Speeding up GW calculations **119**
21.1 Using static COHSEX to include static remainder in selfenergy . . . 119
21.2 Core pproximations . . . 120
21.3 Reducing the size of mixed basis set . . . 120
21.4 Using symmetries . . . 120
21.4.1 The LAPW basis functions . . . 120

22 On the calculation of lattice sums **121**
22.1 Ewald's method . . . 121
22.2 Treatment of more general lattice sums . . . 122
22.2.1 Selection of η . . . 125
22.2.2 Determination of the *cutoffs* . . . 125

23 Exchange-correlation **129**
23.1 MT-Sphere integration . . . 129
23.2 Interstitial integration . . . 130
23.3 Final result . . . 130

24 Momentum matrix elements **131**
24.1 Contribution from the MT-sphere . . . 131
24.1.1 $x-$ and $y-$ components . . . 131
24.1.2 $z-$ component . . . 132
24.1.3 Radial integrals . . . 133
24.2 Contribution from the Interstitial . . . 134
24.3 Core states . . . 134
24.3.1 Matrix elements between two core states . . . 134
24.3.2 Matrix elements between a core and a valence state . . . 135

25 Speeding up GW calculations **137**
25.1 Using static COHSEX to include static remainder in selfenergy . . . 137
25.2 Core pproximations . . . 138
25.3 Reducing the size of mixed basis set . . . 138
25.4 Using symmetries . . . 138
25.4.1 The LAPW basis functions . . . 138

A Mathematical Tools **139**
A.1 Fourier series expansion of lattice periodic functions . . . 139
A.1.1 Local functions . . . 139
A.1.2 non-local function . . . 139
A.2 Brillouin-zone integrations of singular functions . . . 140
A.3 The integration in frequency . . . 142
A.3.1 Remove the peak at $\omega' = \omega$ . . . 142
A.3.2 Gaussian quadrature . . . 142
A.3.2.1 Gauss-Legendre quadrature . . . 142
A.3.2.2 Double Gauss-Legendre quadrature . . . 143
A.3.2.3 Generalized Gauss-Laguerre quadrature . . . 143
A.4 Matrix computation . . . 143
A.4.1 Block-wise inversion . . . 143
A.5 Spherical Harmonics . . . 143
A.5.1 Expansion of Plane waves by spherical harmonics . . . 145
A.6 Lattice Harmonics . . . 145
A.6.1 Normalized real spherical harmonics . . . 145
A.6.2 Normalized cubic harmonics . . . 145
A.6.3 Stars . . . 149
A.7 Fourier Transform . . . 149
A.8 Spherical coordinates . . . 149
A.9 Special Functions . . . 150
A.9.1 Complete Gamma Function . . . 150
A.9.2 Incomplete Gamma Function . . . 150
A.9.3 The step function . . . 150

B Programming conventions **151**

Bibliography **153**

Part I

Theory

Chapter 1

Density functional theory

1.1 The band gap problem

1.1.1 Derivative discontinuity of $E_{\rm xc}$

According to the Hohenberg-Kohn theorem

$$\begin{aligned} &\delta\left\{E_v[n(\mathbf{r})]-\mu\left(\int d^3r n(\mathbf{r})-N\right)\right\}=0 \\ \Longrightarrow &\frac{\delta E_v}{\delta n(\mathbf{r})}=\mu \\ &\mu=\frac{\partial E_v}{\partial N} \end{aligned} \tag{1.1}$$

$$\begin{aligned} \Gamma &= \sum_i p_i \left|\Psi_i\right\rangle \left\langle\Psi_i\right| \\ \langle\hat{O}\rangle_\Gamma &= \sum_i p_i \left\langle\Psi_i\right| \hat{O} \left|\Psi_i\right\rangle \end{aligned} \tag{1.2}$$

$$F[n(\mathbf{r})]=\mathrm{Min}_{\Gamma\to n(\mathbf{r})}\langle\hat{T}+\hat{V}_{ee}\rangle_\Gamma \tag{1.3}$$

$$\begin{aligned} &\int n(\mathbf{r})d\mathbf{r}=M+\omega \qquad (0\le\omega<1) \\ \Longrightarrow &n(\mathbf{r})=(1-\omega)n_M(\mathbf{r})+\omega n_{M+1}(\mathbf{r}) \\ &E(M+\omega)=(1-\omega)E_M+\omega E_{M+1} \end{aligned} \tag{1.4}$$

$$\begin{aligned} \frac{\partial E}{\partial N}|_{N_0+\delta} &= E_{N_0+1}-E_{N_0}=-A \\ \frac{\partial E}{\partial N}|_{N_0-\delta} &= E_{N_0}-E_{N_0-1}=-I \end{aligned} \tag{1.5}$$

For non-interacting systems

$$\begin{aligned} E(N) &= \sum_i n_i\varepsilon_i \\ \frac{\partial E}{\partial N}|_{N_0+\delta} &= \varepsilon_{\rm LUMO} \\ \frac{\partial E}{\partial N}|_{N_0-\delta} &= \varepsilon_{\rm HOMO} \end{aligned} \tag{1.6}$$

$$E_{\rm gap}^{\rm integer}=E_v[N_0-1)+E_v[N_0+1]-2E_v[N_0]=I-A \tag{1.7}$$

$$\begin{aligned} E_{\rm gap}^{\rm deriv} &= \lim_{\delta N\to 0}\left\{\frac{\partial E_v}{\partial N}|_{N_0+\delta N}-\frac{\partial E_v}{\partial N}|_{N_0-\delta N}\right\} \\ &= E_{\rm gap}^{\rm KS}+\Delta_{\rm xc} \end{aligned} \tag{1.8}$$

$$\rho_s(\mathbf{r},\mathbf{r}')=\sum_i n_i\phi_i(\mathbf{r})\phi_i^*(\mathbf{r}') \tag{1.9}$$

$$E_{\mathrm{xc}} = E_{\mathrm{xc}}[\rho_s(\mathbf{r}, \mathbf{r}')] \tag{1.10}$$

$$\begin{aligned} E_{\mathrm{gap}}^{\mathrm{deriv}} &= \langle \phi_{N_0+1} | \, \hat{H}_{\mathrm{eff}} \, | \phi_{N_0+1} \rangle - \langle \phi_{N_0} | \, \hat{H}_{\mathrm{eff}} \, | \phi_{N_0} \rangle \\ \hat{H}_{\mathrm{eff}} &= -\frac{1}{2}\nabla^2 + v + v_J + \hat{v}_{\mathrm{xc}} \end{aligned} \tag{1.11}$$

$$\hat{v}_{\mathrm{xc}}(\mathbf{r}, \mathbf{r}') \equiv \frac{\delta E_{\mathrm{xc}}}{\delta \rho_s(\mathbf{r}, \mathbf{r}')} \tag{1.12}$$

$$\begin{aligned} E_{\mathrm{gap}} &= I - A \\ &\equiv [E(N-1) - E(N)] - [E(N) - E(N+1)] \\ &= [-\epsilon_N(N)] - [-\epsilon_{N+1}(N+1)] \\ &= [\epsilon_{N+1}(N) - \epsilon_N(N)] + [\epsilon_{N+1}(N+1) - \epsilon_{N+1}(N)] \\ &= \epsilon_{\mathrm{gap}}^{\mathrm{KS}} + \Delta_{\mathrm{xc}} \end{aligned} \tag{1.13}$$

$$\Delta_{\mathrm{xc}} = \left.\frac{\delta E_{\mathrm{xc}}[\rho]}{\delta \rho(\mathbf{r})}\right|_{N+\delta} - \left.\frac{\delta E_{\mathrm{xc}}[\rho]}{\delta \rho(\mathbf{r})}\right|_{N-\delta} \tag{1.14}$$

Chapter 2

GW Approximation

This chapter is mostly thought as a summary of the equations needed for the application of the GW approximation (GWA) to the Wien2k code. For the derivation of the approximation please refer to the original work of L. Hedin [28],and L. Hedin andS. Lundqvist [29] as well as the extensive reviews of L. Aryasetiawan [8] and L. Aryasetiawan and O. Gunnarsson [9].

2.1 Summary of GW equations

Electronic band structures of a solid as probed by the photoemission (for occupied states) and its inverse process (for unoccupied states) are described by quasi-particle (QP) energies $E_{n\mathbf{k}}^{\mathrm{QP}}$) and wave functions $\Psi_{n\mathbf{k}}(\mathbf{r})$ which are solutions of the following Dyson-type QP equation

$$\left[-\frac{\nabla^2}{2}+V_{\mathrm{ext}}(\mathbf{r})+V_{\mathrm{H}}(\mathbf{r})\right]\Psi_{n\mathbf{k}}(\mathbf{r})+\int\Sigma_{\mathrm{xc}}(\mathbf{r},\mathbf{r}';\mathcal{E}_{n\mathbf{k}})\Psi_{n\mathbf{k}}(\mathbf{r}')d^3\mathbf{r}'=\mathcal{E}_{n\mathbf{k}}\Psi_{n\mathbf{k}}(\mathbf{r}) \tag{2.1}$$

$V_{\mathrm{ext}}(\mathbf{r})$ is the external potential accounting for the interaction between electrons and nuclei. $V_{\mathrm{H}}(\mathbf{r})$ is the Hartree) potential resulted from classical Coulomb repulsion. All non-classical electron-electron interaction effects are included in the non-local energy-dependent exchange-correlation self-energy term $\Sigma^{\mathrm{xc}}(\mathbf{r},\mathbf{r}';\omega)$.

In the G_0W_0 approach the quasiparticle (qp) energy $E_{n\mathbf{k}}$ is calculated from the perturbation theory using the Kohn-Sham orbital energies as the zero-th order approximation

$$\left[-\frac{\nabla^2}{2}+V_{\mathrm{ext}}(\mathbf{r})+V_{\mathrm{H}}(\mathbf{r})\right]\Psi_{n\mathbf{k}}(\mathbf{r})+V_{\mathrm{xc}}(\mathbf{r})\Psi_{n\mathbf{k}}(\mathbf{r})=\epsilon_{n\mathbf{k}}\Psi_{n\mathbf{k}}(\mathbf{r}) \tag{2.2}$$

$$\mathcal{E}_{n\mathbf{k}}=\epsilon_{n\mathbf{k}}+Z_{n\mathbf{k}}\left(\epsilon_{n\mathbf{k}}\right)\left\langle\psi_{n\mathbf{k}}\right|\Sigma(\epsilon_{n\mathbf{k}})-V_{\mathrm{xc}}\left|\psi_{n\mathbf{k}}\right\rangle \tag{2.3}$$

where $\epsilon_{n\mathbf{k}}$ are the DFT eigenvalues,$\psi_{n\mathbf{k}}(\mathbf{r})$ are the DFT eigenfunctions and $V_{\mathrm{xc}}(\mathbf{r})$ is the DFT exchange correlation potential. $Z_{n\mathbf{k}}$ is the qp renormalization factor, defined by:

$$Z_{n\mathbf{k}}\left(\epsilon_{n\mathbf{k}}\right)=\left[1-\left(\frac{\partial}{\partial\omega}\left\langle\psi_{n\mathbf{k}}\right|\Sigma(\epsilon_{n\mathbf{k}})\left|\psi_{n\mathbf{k}}\right\rangle\right)_{\epsilon_{n\mathbf{k}}}\right]^{-1} \tag{2.4}$$

and accounts for the fact that Σ is evaluated at the DFT energy rather that the qp energy. $\Sigma(\mathbf{r}_1,\mathbf{r}_2;\omega)$ is the non-local, energy dependent selfenergy, which in the GW approximation is given by

$$\Sigma(\mathbf{r}_1,\mathbf{r}_2;\omega)=\frac{i}{2\pi}\int G_0(\mathbf{r}_1,\mathbf{r}_2;\omega+\omega')W_0(\mathbf{r}_2,\mathbf{r}_1;\omega')d\omega' \tag{2.5}$$

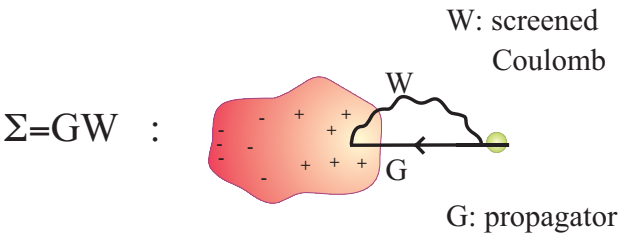

Figure 2.1: Illustration of the GW approximation.

$G_0(\mathbf{r}_1, \mathbf{r}_2; \omega)$ is the DFT Green's function defined by:

$$G_0(\mathbf{r}_1, \mathbf{r}_2; \omega) = \sum_{n\mathbf{k}}^{\text{occ}} \frac{\Psi_{n\mathbf{k}}(\mathbf{r}_1)\Psi^*_{n\mathbf{k}}(\mathbf{r}_2)}{\omega - \epsilon_{nk} - i\eta} + \sum_{n\mathbf{k}}^{\text{unocc}} \frac{\Psi_{n\mathbf{k}}(\mathbf{r}_1)\Psi^*_{n\mathbf{k}}(\mathbf{r}_2)}{\omega - \epsilon_{nk} + i\eta} \tag{2.6}$$

where η is a positive infinitesimal. $W_0(\mathbf{r}_2, \mathbf{r}_1; \omega)$ is the dynamically screened Coulomb potential given by:

$$W_0(\mathbf{r}_1, \mathbf{r}_2; \omega) = \int \varepsilon^{-1}(\mathbf{r}_1, \mathbf{r}_3; \omega) v(\mathbf{r}_3, \mathbf{r}_2) d\mathbf{r}_3 \tag{2.7}$$

$v(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}$ is the bare Coulomb potential and $\varepsilon(\mathbf{r}_1, \mathbf{r}_2; \omega)$ is the dielectric function defined by:

$$\varepsilon(\mathbf{r}_1, \mathbf{r}_2; \omega) = 1 - \int v(\mathbf{r}_1, \mathbf{r}_3) P(\mathbf{r}_3, \mathbf{r}_2; \omega) d\mathbf{r}_3 \tag{2.8}$$

and $P(\mathbf{r}_1, \mathbf{r}_2; \omega)$ is the polarization, which in the random phase approximation (RPA) is written:

$$P(\mathbf{r}_1, \mathbf{r}_2; \omega) = -\frac{i}{2\pi} \int G_0(\mathbf{r}_1, \mathbf{r}_2; \omega + \omega') G_0(\mathbf{r}_2, \mathbf{r}_1; \omega`) d\omega' \tag{2.9}$$

The self energy can be separated into a static and a dynamic part. If we define:

$$W_0^c(\mathbf{r}_1, \mathbf{r}_2; \omega) = W_0(\mathbf{r}_1, \mathbf{r}_2; \omega) - v(\mathbf{r}_1, \mathbf{r}_2) \tag{2.10}$$

then we have the dynamic term:

$$\Sigma^c(\mathbf{r}_1, \mathbf{r}_2; \omega) = \frac{i}{2\pi} \int G_0(\mathbf{r}_1, \mathbf{r}_2; \omega + \omega') W_0^c(\mathbf{r}_2, \mathbf{r}_1; \omega`) d\omega' \tag{2.11}$$

and the static one,

$$\begin{aligned} \Sigma^x(\mathbf{r}_1, \mathbf{r}_2) = & \frac{i}{2\pi} \int G_0(\mathbf{r}_1, \mathbf{r}_2; \omega') v(\mathbf{r}_2, \mathbf{r}_1) d\omega' \\ & - \sum_{n\mathbf{k}}^{\text{occ}} \Psi_{n\mathbf{k}}(\mathbf{r}_1) v(\mathbf{r}_2, \mathbf{r}_1) \Psi^*_{n\mathbf{k}}(\mathbf{r}_2) \end{aligned} \tag{2.12}$$

which clearly corresponds to the Fock or bare exchange operator. Equation 14.39 is then

$$\Sigma(\mathbf{r}_1, \mathbf{r}_2; \omega) = \Sigma^x(\mathbf{r}_1, \mathbf{r}_2) + \Sigma^c(\mathbf{r}_1, \mathbf{r}_2; \omega) \tag{2.13}$$

where Σ^c represents the dynamic correlation of the quasi-particles.

To summarize

$$\mathcal{E}_{n\mathbf{k}} = \epsilon_{n\mathbf{k}} + Z_{n\mathbf{k}}\left(\epsilon_{n\mathbf{k}}\right) \Re\left[\left\langle \psi_{n\mathbf{k}} \right| \Sigma(\epsilon_{n\mathbf{k}}) - V_{\text{xc}} \left| \psi_{n\mathbf{k}} \right\rangle\right]$$

$$\begin{aligned} Z_{n\mathbf{k}}\left(\epsilon_{n\mathbf{k}}\right) &= \left[1 - \Re\left(\frac{\partial}{\partial\omega} \left\langle \psi_{n\mathbf{k}} \right| \Sigma(\omega) \left| \psi_{n\mathbf{k}} \right\rangle\right)_{\epsilon_{n\mathbf{k}}}\right]^{-1} \\ \Sigma(\mathbf{r}_1, \mathbf{r}_2; \omega) &= \frac{i}{2\pi} \int G_0(\mathbf{r}_1, \mathbf{r}_2; \omega + \omega') W_0(\mathbf{r}_2, \mathbf{r}_1; \omega') d\omega' \\ G_0(\mathbf{r}_1, \mathbf{r}_2; \omega) &= \sum_{n\mathbf{k}}^{\text{occ}} \frac{\Psi_{n\mathbf{k}}(\mathbf{r}_1)\Psi^*_{n\mathbf{k}}(\mathbf{r}_2)}{\omega - \epsilon_{nk} - i\eta} + \sum_{n\mathbf{k}}^{\text{unocc}} \frac{\Psi_{n\mathbf{k}}(\mathbf{r}_1)\Psi^*_{n\mathbf{k}}(\mathbf{r}_2)}{\omega - \epsilon_{nk} + i\eta} \\ W_0(\mathbf{r}_1, \mathbf{r}_2; \omega) &= \int \varepsilon^{-1}(\mathbf{r}_1, \mathbf{r}_3; \omega) v(\mathbf{r}_3, \mathbf{r}_2) d\mathbf{r}_3 \\ \varepsilon(\mathbf{r}_1, \mathbf{r}_2; \omega) &= 1 - \int v(\mathbf{r}_1, \mathbf{r}_3) P(\mathbf{r}_3, \mathbf{r}_2; \omega) d\mathbf{r}_3 \\ P(\mathbf{r}_1, \mathbf{r}_2; \omega) &= -\frac{i}{2\pi} \int G_0(\mathbf{r}_1, \mathbf{r}_2; \omega + \omega') G_0(\mathbf{r}_2, \mathbf{r}_1; \omega`) d\omega' \end{aligned}$$

$$\mathcal{E}_{n\mathbf{k}} = \epsilon_{n\mathbf{k}} + \Re\left[\left\langle \psi_{n\mathbf{k}} \right| \Sigma(\mathcal{E}_{n\mathbf{k}})) - V_{\text{xc}} \left| \psi_{n\mathbf{k}} \right\rangle\right]$$

$$
\begin{aligned}
\Sigma(\mathbf{r}_1,\mathbf{r}_2;\omega) &= \frac{i}{2\pi}\int G_0(\mathbf{r}_1,\mathbf{r}_2;\omega+\omega')W_0(\mathbf{r}_2,\mathbf{r}_1;\omega')d\omega' \\
W_0(\mathbf{r}_1,\mathbf{r}_2;\omega) &= \int \varepsilon^{-1}(\mathbf{r}_1,\mathbf{r}_3;\omega)v(\mathbf{r}_3,\mathbf{r}_2)d\mathbf{r}_3 \\
\varepsilon(\mathbf{r}_1,\mathbf{r}_2;\omega) &= 1-\int v(\mathbf{r}_1,\mathbf{r}_3)P(\mathbf{r}_3,\mathbf{r}_2;\omega)d\mathbf{r}_3 \\
P(\mathbf{r}_1,\mathbf{r}_2;\omega) &= -\frac{i}{2\pi}\int G_0(\mathbf{r}_1,\mathbf{r}_2;\omega+\omega')G_0(\mathbf{r}_2,\mathbf{r}_1;\omega')d\omega'
\end{aligned}
$$

2.2 Energy-only selfconsistent GW

$$E_{n\mathbf{k}}^{(i+1)} = E_{n\mathbf{k}}^{(i)} + \langle\psi_{n\mathbf{k}}|\,\Sigma^{(i)}(E_{n\mathbf{k}}^{(i)}) - V_{\mathrm{xc}}\,|\psi_{n\mathbf{k}}\rangle \tag{2.14}$$

2.3 Matrix form of the GW equations

Let's suppose we have a complete set of orthonormal basis functions $\{\chi_i^{\mathbf{q}}(\mathbf{r})\}$ which fulfill Bloch's theorem. From Appendix A.1.2, Eq. (A.7), we can write the Coulomb potential in matrix form:

$$v_{ij}(\mathbf{q}) = \int_V\int_V (\chi_i^{\mathbf{q}}(\mathbf{r}_1))^* v(\mathbf{r}_1,\mathbf{r}_2)\chi_j^{\mathbf{q}}(\mathbf{r}_2)d^3r_2d^3r_1 \tag{2.15}$$

If we define the matrix elements

$$M_{nm}^i(\mathbf{k},\mathbf{q}) \equiv \int_V \chi_i^{\mathbf{q}*}(\mathbf{r})\Psi_{n\mathbf{k}}(\mathbf{r})\Psi^*_{m\mathbf{k}-\mathbf{q}}(\mathbf{r})d^3r \tag{2.16}$$

The polarization for imaginary frequencies is given by (see Appendix 9):

$$P_{ij}(\mathbf{q},i\omega) = \sum_{\mathbf{k}}^{BZ}\sum_{n}^{\text{occ}}\sum_{n'}^{\text{unocc}} M_{nn'}^i(\mathbf{k},\mathbf{q})\left[M_{nn'}^j(\mathbf{k},\mathbf{q})\right]^* \frac{-2(\varepsilon_{n'\mathbf{k}-\mathbf{q}}-\varepsilon_{n\mathbf{k}})}{\omega^2+(\varepsilon_{n'\mathbf{k}-\mathbf{q}}-\varepsilon_{n\mathbf{k}})^2} \tag{2.17}$$

The dielectric function defined in Eq. 2.8 diverges at $\mathbf{q}=0$ (See Appendix **??**) thus, we have to resort to the symmetrized dielectric function as defined in Eq. 10.2 obtaining:

$$\tilde{\varepsilon}_{ij}(\mathbf{q},i\omega) = \delta_{ij} - \sum_{lm} v_{il}^{\frac{1}{2}}(\mathbf{q})P_{lm}(\mathbf{q},i\omega)v_{mj}^{\frac{1}{2}}(\mathbf{q}) \tag{2.18}$$

Using Eq. 11.3 we have:

$$W_{ij}^c(\mathbf{q},i\omega) = \sum_{lm} v_{il}^{\frac{1}{2}}(\mathbf{q})\left[\tilde{\varepsilon}_{lm}^{-1}(\mathbf{q},i\omega)-\delta_{lm}\right]v_{mj}^{\frac{1}{2}} \tag{2.19}$$

The correlation term of the self-energy (see Appendix 12.2) is then

$$
\begin{aligned}
\Sigma_{n\mathbf{k}}^c(i\omega) =& \langle\Psi_{n\mathbf{k}}|\Sigma^c(\mathbf{r}_1,\mathbf{r}_2;i\omega)|\Psi_{n\mathbf{k}}\rangle \\
=& \sum_{\mathbf{q}}^{BZ}\sum_{ij}\sum_{n'}\left[M_{nn'}^i(\mathbf{k},\mathbf{q})\right]^*\left\{\frac{1}{\pi}\int_0^\infty W_{ij}^c(\mathbf{q},i\omega')\frac{\epsilon_{n\mathbf{k}+\mathbf{q}}-i\omega}{(\epsilon_{n\mathbf{k}+\mathbf{q}}-i\omega)^2+w'^2}d\omega'\right\}M_{nn'}^j(\mathbf{k},\mathbf{q})
\end{aligned} \tag{2.20}
$$

(For details on the calculation of the frequency integral see Appendix **??**).And the exchange term is (See Appendix **??**):

$$
\begin{aligned}
\Sigma_{n\mathbf{k}}^x =& \langle\Psi_{n\mathbf{k}}|\Sigma^x(\mathbf{r}_1,\mathbf{r}_2)|\Psi_{n\mathbf{k}}\rangle \\
=& -\sum_{\mathbf{q}}^{BZ}\sum_{ij} v_{ij}(\mathbf{q})\sum_{n'}^{\text{occ}}\left[M_{nn'}^i(\mathbf{k},\mathbf{q})\right]^* M_{nn'}^j(\mathbf{k},\mathbf{q})
\end{aligned} \tag{2.21}
$$

For the details on the BZ-Integration of eqs. 2.20 and 2.21 see Section 10. The correlation term is fitted by a function of the form:

$$\tilde{\Sigma}^c_{n\mathbf{k}}(i\omega) = \sum_j^m \frac{a_j}{i\omega + b_j} \tag{2.22}$$

using nonlinear least squares methods and then analytically continued to the real frequency axis. Thus we have:

$$\tilde{\Sigma}^c_{n\mathbf{k}}(\omega) = \sum_j^m \frac{a_j}{\omega + b_j} \tag{2.23}$$

and

$$\frac{\partial}{\partial\omega}\tilde{\Sigma}^c_{n\mathbf{k}}(\omega) = -\sum_j^m \frac{a_j}{(\omega + b_j)^2} \tag{2.24}$$

Finally, the qp energies are obtained from Eq. 2.14 as:

$$E_{n\mathbf{k}} = \epsilon_{n\mathbf{k}} + Z_{n\mathbf{k}}\left[\tilde{\Sigma}^c_{n\mathbf{k}}(\epsilon_{n\mathbf{k}}) + \Sigma^x_{n\mathbf{k}} - \langle\Psi_{n\mathbf{k}}|V^{DFT}_{xc}(\mathbf{r}_1)|\Psi_{n\mathbf{k}}\rangle\right] \tag{2.25}$$

with (as in eq. 13.3):

$$Z_{n\mathbf{k}} = \left[1 - \left(\frac{\partial}{\partial\omega}\tilde{\Sigma}^c_{n\mathbf{k}}(\omega)\right)_{\epsilon_{n\mathbf{k}}}\right]^{-1} \tag{2.26}$$

Note that only equations 2.15 and 2.16 depend on the selection of the basis functions. We will revisit them in the next chapter, after defining the basis set.

2.4 On the k- and q-points grid

In order to calculate the polarization $\hat{P}_{\mathbf{ij}'}(\mathbf{q}, i\tau)$ we need a grid of $\mathbf{k}$-points that allows us the use of the tethraedron method for the integration. On the other side, to calculate the self-energy, the $\mathbf{q}$-points grid should also be suitable for such integration. One way to avoid having to run `lapw1` several times is selecting the set of $\mathbf{q}$-points such that $\{\mathbf{k}\} = \{\mathbf{k} + \mathbf{q}\}$. For the equality to hold, the Γ-point has to be included in the $\{\mathbf{q}\}$-set.

On the other side, the inclusion of the Γ-point has the disadvantage that the dielectric matrix, as well as the bare and screened Coulomb potentials diverge as $\mathbf{q} \to 0$. For the first case, the problem is solved by using the symmetrized dielectric matrix, which does not diverge (See Appendix **??**). The divergence of the Coulomb potential can not be avoided, but it can be integrated... (See Appendix 12.3)

2.4.1 G_0W_0 based on LDA+U

Formally, the only difference between LDA-based and LDA+U-based G_0W_0 is the contribution of $\delta\hat{V}_U$.

$$E_{n\mathbf{k}} = \epsilon_{n\mathbf{k}} + \Re\left[\langle\psi_{n\mathbf{k}}|\,\Sigma(E_{n\mathbf{k}}) - V_{\text{xc}} - \delta\hat{V}_U\,|\psi_{n\mathbf{k}}\rangle\right]$$

To see the relation between LDA and LDA+U based G_0W_0 more explicitly, we notice that the KS eigen-energies obtained from LDA+U, denoted as $\epsilon^{\text{LDA+U}}_{n\mathbf{k}}$, contain a contribution from $\delta\hat{V}_U$ so that

$$\begin{aligned}\epsilon^{\text{LDA+U}}_{n\mathbf{k}} =& \langle\psi_{n\mathbf{k}}| - \frac{1}{2}\nabla^2 + V^{\text{LDA}} + \delta\hat{V}_U\,|\psi_{n\mathbf{k}}\rangle \\ =& \overline{\epsilon}^{\text{LDA}}_{n\mathbf{k}} + \delta\hat{V}_{U\,n\mathbf{k}}\end{aligned} \tag{2.27}$$

where $\overline{\epsilon}^{\text{LDA}}_{n\mathbf{k}}$ are the LDA KS eigen-energies calculated using LDA+U wave functions. If we expand the self-energy around $\overline{\epsilon}^{\text{LDA}}_{n\mathbf{k}}$ instead of $\epsilon^{\text{LDA+U}}_{n\mathbf{k}}$,

$$\begin{aligned}\mathcal{E}_{n\mathbf{k}} =& \epsilon^{\text{LDA+U}}_{n\mathbf{k}} + \delta\Sigma_{n\mathbf{k}}(\mathcal{E}_{n\mathbf{k}}) \\ \simeq& \overline{\epsilon}^{\text{LDA}}_{n\mathbf{k}} + \delta\hat{V}_{U\,n\mathbf{k}} + \delta\Sigma_{n\mathbf{k}}(\overline{\epsilon}^{\text{LDA}}_{n\mathbf{k}}) \\ &+ \delta\Sigma'_{n\mathbf{k}}(\overline{\epsilon}^{\text{LDA}}_{n\mathbf{k}})(\mathcal{E}_{n\mathbf{k}} - \overline{\epsilon}^{\text{LDA}}_{n\mathbf{k}})\end{aligned} \tag{2.28}$$

the final quasi-particle energies can be written as

$$\begin{aligned}\mathcal{E}_{n\mathbf{k}} =& \overline{\epsilon}^{\text{LDA}}_{n\mathbf{k}} + Z_{n\mathbf{k}}\left(\overline{\epsilon}^{\text{LDA}}_{n\mathbf{k}}\right)\left[\delta\Sigma_{n\mathbf{k}}\left(\overline{\epsilon}^{\text{LDA}}_{n\mathbf{k}}\right) + \delta\hat{V}_{U\,n\mathbf{k}}\right] \\ =& \overline{\epsilon}^{\text{LDA}}_{n\mathbf{k}} + Z_{n\mathbf{k}}\left(\overline{\epsilon}^{\text{LDA}}_{n\mathbf{k}}\right)\left[\Sigma_{n\mathbf{k}}\left(\overline{\epsilon}^{\text{LDA}}_{n\mathbf{k}}\right) - V^{\text{XC}}_{n\mathbf{k}}\right].\end{aligned} \tag{2.29}$$

$$\epsilon_{n\mathbf{k}}^{\mathrm{LDA}+U} = \overline{\epsilon}_{n\mathbf{k}}^{\mathrm{LDA}} + \delta\hat{V}_{U\,n\mathbf{k}}$$

$$\begin{aligned}\mathcal{E}_{n\mathbf{k}} &= \epsilon_{n\mathbf{k}}^{\mathrm{LDA}+U} + Z_{n\mathbf{k}}\left(\epsilon_{n\mathbf{k}}^{\mathrm{LDA}+U}\right)\left[\Sigma_{n\mathbf{k}}\left(\epsilon_{n\mathbf{k}}^{\mathrm{LDA}+U}\right) - V_{n\mathbf{k}}^{\mathrm{XC}} - \delta\hat{V}_{U\,n\mathbf{k}}\right] \\ &= \overline{\epsilon}_{n\mathbf{k}}^{\mathrm{LDA}} + Z_{n\mathbf{k}}\left(\overline{\epsilon}_{n\mathbf{k}}^{\mathrm{LDA}}\right)\left[\Sigma_{n\mathbf{k}}\left(\overline{\epsilon}_{n\mathbf{k}}^{\mathrm{LDA}}\right) - V_{n\mathbf{k}}^{\mathrm{XC}}\right]\end{aligned}$$

Under the assumption that $\Sigma_{n\mathbf{k}}^{\mathrm{xc}}(E)$ can be well approximated as a linear function of the energy around $\epsilon_{n\mathbf{k}}^{\mathrm{LDA}}$, there are mainly two origins for the U-dependence of G_0W_0 quasi-particle energies on top of LDA+U: 1) the difference between LDA+U and LDA wave functions, and 2) the change of screened Coulomb interaction W_0 due to the variation of the energy spectrum. The second factor can be exemplified by the clamped-ion static macroscopic dielectric function,

$$\epsilon_{\mathrm{M}}(0) \equiv \left[\lim_{\mathbf{q}\to 0}\epsilon^{-1}(\mathbf{q},\mathbf{q},\omega=0)\right]^{-1} \tag{2.30}$$

calculated from LDA+U wave functions at different U. Since both factors depend on U in an indirect manner, we expect that the band gap from G_0W_0 depends on U in a much weaker way than in case of the LDA+U, where the splitting between occupied and unoccupied d/f-bands is approximately equal to U.

Chapter 3

Vertex corrections

Part II

Implementation

Chapter 4

Symbols and Notation

In this chapter we enumerate the symbols used throughout the text for clarity. Sometimes, within the text, the arguments of the functions are not written, just to shorten the notation. The symbols are enumerated in alphabetical order, first Arabic characters, then Greek ones.

4.1 Normalization schemes used for wavefunctions

To differentiate different normalization schemes for wavefunctions (including basis functions used to expand wave functions), we use the following convention: wave functionsl normalized in the whole crystal volume (V) is denoted as normal sysmbols; wavefunctions normalized in the unit cell volume are denoted by using symbols with a tilde.

$$\begin{aligned} \int_V d\mathbf{r}\chi_i^{\mathbf{q}*}(\mathbf{r})\chi_j^{\mathbf{q}'}(\mathbf{r}) &= \delta_{i,j}\delta_{\mathbf{q},\mathbf{q}'} \\ \int_\Omega d\mathbf{r}\tilde{\chi}_i^{\mathbf{q}*}(\mathbf{r})\tilde{\chi}_j^{\mathbf{q}'}(\mathbf{r}) &= \delta_{i,j}\delta_{\mathbf{q},\mathbf{q}'} \end{aligned} \tag{4.1}$$

Wavefucntions with the two normalization are related by

$$\chi_i^{\mathbf{q}}(\mathbf{r}) = \frac{1}{N_c^{1/2}}\sum_{\mathbf{R}} e^{i\mathbf{q}\cdot\mathbf{R}}\tilde{\chi}_i^{\mathbf{q}}(\mathbf{r}+\mathbf{R}) \tag{4.2}$$

4.2 Notations used

a Index running over atoms in the unit cell

$A_{lm}^a(\mathbf{k}+\mathbf{G})$ Expansion coefficient of the LAPW basis function $\Phi_{\mathbf{G}}^{\mathbf{k}}(\mathbf{r})$ for the function $u_l^a(r)Y_{lm}(\hat{r})$ inside the MT-Sphere of atom s (See equations 5.6, 5.9, 5.12, 5.16 and 5.20).

$\mathcal{A}_{lm}^{na}(\mathbf{k})$ Expansion coefficient of the LAPW eigenfunction function $\Psi_{n\mathbf{k}}(\mathbf{r})$ for the function $u_l^a(r)Y_{lm}(\hat{r})$ inside the MT-Sphere of atom s (See equations 6.30).

$B_{lm}^a(\mathbf{k}+\mathbf{G})$ Expansion coefficient of the LAPW basis function $\Phi_{\mathbf{G}}^{\mathbf{k}}(\mathbf{r})$ for the function $\dot{u}_l^a(r)Y_{lm}(\hat{r})$ inside the MT-Sphere of atom s (See equations 5.6, 5.12 and 5.16).

$\mathcal{B}_{lm}^{na}(\mathbf{k})$ Expansion coefficient of the LAPW eigenfunction function $\Psi_{n\mathbf{k}}(\mathbf{r})$ for the function $\dot{u}_l^a(r)Y_{lm}(\hat{r})$ inside the MT-Sphere of atom s(See equations 6.30).

$C_{lm}^a(\mathbf{k}+\mathbf{G})$ Expansion coefficient of the LAPW basis function $\Phi_{\mathbf{G}}^{\mathbf{k}}(\mathbf{r})$ for the function $u_l^a(r,E_2)Y_{lm}(\hat{r})$ for local orbitals inside the MT-Sphere of atom s (See equations 5.16 and 5.20).

$\mathcal{C}_{lm}^{na}(\mathbf{k})$ Expansion coefficient of the LAPW eigenfunction function $\Psi_{n\mathbf{k}}(\mathbf{r})$ for the function $u_l^a(r,E_2)Y_{lm}(\hat{r})$ for local orbitals inside the MT-Sphere of atom s(See equations 6.30).

$\mathcal{D}_{ll'}^{NL}$ Radial integral of the mixed basis radial function and a product of u_l's. See equation 6.8

$E_{a,l}$ Augmentation energy for the radial function u_l

$\mathcal{G}_{ll',mm'}^{LM}$ Gaunt coefficient, see equation **??**

$\mathbf{G}$ Reciprocal lattice vector

$\mathbf{k}$ Points in the reciprocal space, not belonging to the reciprocal Bravais lattice, usually they belong to the First Brillouin zone, otherwise, it is clearly stated.

$\mathbf{K}$ Reciprocal lattice vector

$\mathcal{I}_{\mathbf{G}}$ Integral of an IPW of wave vector $\mathbf{G}$ over the interstitial region of the unit cell.

l Angular momentum quantum number.

L Angular momentum quantum number of the mixed basis functions.

$\mathcal{L}$ Unified notation for the set of indexes $\{aNLM\}$.

m Quantum number corresponding to the z-component of the angular momentum.

M Quantum number corresponding to the z-component of the angular momentum of the mixed basis function.

$M^i_{nm}(\mathbf{k},\mathbf{q})$ The "overlap" of the i-th. mixed basis function with the product of the n-th. LAPW eigenfunction at $\mathbf{k}$ and the conjugate of the m-th LAPW eigenfunction at $\mathbf{k}-\mathbf{q}$. See equation **??**.

N Principal quantum number of the radial mixed basis functions.

N_c Number of cells in the crystal.

$P^{\mathbf{q}}_{\mathbf{G}}(\mathbf{r})$ IPW of wave vector $\mathbf{q}+\mathbf{G}$

$\tilde{P}^{\mathbf{q}}_{\mathbf{G}}(\vec{r})$ Orthogonalized IPW of wave vector $\mathbf{q}+\mathbf{G}$

$\mathbf{q}$ Points in the reciprocal space, not belonging to the reciprocal Bravais lattice, usually they belong to the First Brillouin zone, otherwise, it is clearly stated.

$\mathbf{R}$ Bravais lattice vector.

R^a_{MT} Muffin-Tin Sphere radius of atom a.

$\mathbf{r}$ Real space vector in general coordinate system

r Length of $\mathbf{r}$.

$\hat{r}$ Unit vector in the direction of $\mathbf{r}$, also used to symbolize angular coordinates of $\mathbf{r}$.

$\mathbf{r}_a$ Position of atom a in the unit cell.

$\mathbf{r}^a$ Real space vector in the local coordinate system of atom a ($\mathbf{r}^a = T_a^{-1}(\mathbf{r}-\mathbf{r}_a)$).

r^a Length of $\mathbf{r}^a$.

$\hat{r}^a$ Unit vector in the direction of $\mathbf{r}^a$, also used to symbolize angular coordinates of $\mathbf{r}^a$.

$S_{\mathbf{G},i}$ Coefficient of the $\mathbf{G}$ component of the i-th orthogonalized IPW.

$\tilde{S}_{\mathbf{G},i}$ Coefficient of the $\mathbf{G}$ component of the i-th orthogonalized IPW normalized to 1.

T_a Rotation operator to the local coordinate system of the atom a.

$u_l(r^a, E_{al})$ The regular solutions of the radial Schrödinger equation in the spherically averaged effective crystal potential around site $\mathbf{r}_a$. (The radial part of the augmentation functions)

$v_{ij}(\mathbf{q})$ The matrix elements of the Bare Coulomb potential in the mixed basis.

V Volume of the crystal.

V^a_{MT} Volume of the Muffin-Tin Sphere of atom a.

$\mathcal{W}^{an}\mathbf{k}, lm(r)$ Radial part of the n-th LAPW eigenfunction at $\mathbf{k}$

$Y_{lm}(\theta,\varphi)$ Spherical Harmonic function of indexes l, m. Usually written a as $Y_{lm}(\hat{r})$. We use always the Condon and Shortley convention.

ε_i i-th eigenvalue of the IPW overlap matrix

$\gamma_{aNLM}(\mathbf{r}^a)$ Muffin Tin Mixed basis function

$\gamma^{\mathbf{q}}_{aNLM}(\mathbf{r}^a)$ Bloch sum of Muffin Tin Mixed basis function

$\Phi^{\mathbf{k}}_{\mathbf{G}}(\mathbf{r})$ The (L)APW+lo basis function.

$\Psi_{n\mathbf{k}}(\mathbf{r})$ The (L)APW+lo eigenfunction of band n and wave vector $\mathbf{k}$

$\upsilon_{aNLM}(r^a)$ The radial part of the Mixed Basis Functions

$\chi^{\mathbf{q}}_i(\mathbf{r})$ Mixed basis function.

$\tilde{\chi}^{\mathbf{q}}_i(\mathbf{r})$ Orthogonalized Mixed basis function.

Ω Volume of the unit cell.

4.3 Programming conventions

i. Strict ANSI Fortran90 should be used. Features marked as obsolescent in F90/95 should be avoided (i.e. assigned format specifiers, labelled do-loops, statement functions).

ii. Modules should be used in place of common blocks for declaring global variables.

iii. `use` statements should include the `only` option and the corresponding list of global variables used by the subroutine, unless all the variables in the module are used.

iv. Any code should be written in lower-case form, starting from column 6. An extra indentation of 2 columns should be added inside each loop level. The length of each line should be kept to fewer than 75 characters using the & character for line continuation.

v. Every function or subroutine, no matter how small, should be in its own file named `routine.f90`, where `routine` is the function or subroutine name. It is recommended that the routines are named so as to make their purpose apparent from the name alone.

vi. Use of `implicit none` is mandatory.

vii. Each passed argument should have its `intent` option defined, and a short description of its purport should be added as comment in the same line.

viii. All called procedures within the subroutine (intrinsic or external) should be explicitly declared.

ix. Declarations of the form `datatype*N`, as well as `doble precision` or `double complex` should be avoided. The form `datatype(N)` should be used.

x. Each variable should be declared separately, and, when possible, its purpose should be described in a short comment on the same line.

xi. Subroutines should be "plentifully" commented. If you are not sure, whether or not a comment should be added here... **do it**.

xii. The use of `goto` statements should be kept to a minimum. Only if it is impossible to avoid it. They should be used for exiting loops only and always point to a `continue` statement.

xiii. Local allocatable arrays must be deallocated on exit of the routine to prevent memory leakage.

xiv. Every function or subroutine must be documented with the `Protex` source code documentation system. This should include a short LaTeX description of the algorithms and methods involved. Equations which need to be referenced should be labeled with `routine1`, `routine2`, etc. The autorship of each new piece of code or modification should be indicated in the REVISION HISTORY part of the header. See the `Protex` documentation for details.

xv. Each routine should terminate the program when given improper input.

xvi. Report errors prior to termination with a short description using the `outerr` subroutine.

xvii. Avoid redundant or repeated code: check to see if the routine you need already exists, before writing a new one.

xviii. All internal units should be atomic. Input and output units should be atomic by default and clearly stated otherwise (with exception of WIEN2k output files used as input, it does not depend on us).

Chapter 5

The (L)APW+lo method (WIEN2k)

"Loving you is a dirty job
but somebody's got to do it."
Bonnie Tyler.

5.1 The (L)APW+lo basis functions

5.1.1 Core states

In the Wien2k code, the core states are calculated by solving numerically the full relativistic Dirac equation within the DFT in the LDA(GGA) approximation. Only the spherically symmetric part of the LDA(GGA) potential is taken into account.

The radial wave functions calculated are defined by the relativistic quantum number $\kappa = -s(j + \frac{1}{2})$ as shown in Table 5.1.1

Thus, the radial wave functions obtained are eigenfunctions of the total angular momentum number j and not of the orbital one l. Since the core states are calculated including spin-orbit coupling, the angular and spin dependence can not be disentangled. Thus, the core wave functions, including angular dependence are:

$$\tilde{\Phi}^{core}_{an,j,m_j}(\mathbf{r}) = u_{an\kappa}(r^a)|jm_j\rangle_l \tag{5.1}$$

where

$$|jm_j\rangle_l \equiv \sum_{\sigma=-\frac{1}{2}}^{\frac{1}{2}} \left(l\ \tfrac{1}{2}\ m_l\ \sigma | j\ m_j\right) Y_{lm_l}\left(\hat{r}^a\right)|\sigma\rangle\delta_{m+\sigma,m_j} \tag{5.2}$$

where $\left(l\ \frac{1}{2}\ m_l\ \sigma | j\ m_j\right)$ is the corresponding Clebsch-Gordon coefficient [47].

In the LAPW calculation, the mixed spin character of the core wave-functions is neglected. Since they only interact with the valence states through the potential, which depends on the density, being this spherically symmetric, there is no need to care about the angular dependence of the core states. In our case, this generates a complication, since usually, for spin-polarized systems, the Green's function as well as the polarization are taken as spin block diagonal. One possible solution to this situation, which we are going to follow by now, is just to take the core wave-functions as:

$$\tilde{\Phi}^{core}_{an,\kappa,l,m}(\mathbf{r}) = \sqrt{\frac{n_\kappa}{2l+1}} u_{an\kappa}(r^a) Y_{lm_l}\left(\hat{r}^a\right) \tag{5.3}$$

where n_κ is the total occupation of the state a, n, κ. In this way, the full angular dependence is taken into account, and the normalization factor ensures the correct number of electrons in each state.

Table 5.1: Relativistic quantum numbers

		$j = l + \frac{s}{2}$		κ		max. occupation	
	l	$s=-1$	$s=+1$	$s=-1$	$s=+1$	$s=-1$	$s=+1$
s	0		1/2		-1		2
p	1	1/2	3/2	1	-2	2	4
d	2	3/2	5/2	2	-3	4	6
f	3	5/2	7/2	3	-4	6	8

5.1.2 Valence and conduction states

The Wien2k code [15] allows the use of two different linearization methods for making the Augmented Plane Wave (APW) basis functions independent of the energy and anyway well suited to the solution of the problem.

5.1.2.1 The traditional linearization method: LAPW

The first linearized APW method, LAPW, was developed by O. K. Andersen [3] in the mid 70's. A detailed description of this method can also be found in Ref. [54]. The LAPW basis functions are defined by:

$$\tilde{\Phi}^{\mathbf{k}}_{\mathbf{G}}(\mathbf{r}) = \begin{cases} \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} & \mathbf{r} \in I \\ \sum_{l=0}^{l_{max}} \sum_{m=-l}^{+l} \left[A^a_{lm}(\mathbf{k}+\mathbf{G}) u_l(r^a, E_l) + B^a_{lm}(\mathbf{k}+\mathbf{G}) \dot{u}_l(r^a, E_l)\right] Y_{lm}(\hat{r}^a) & \mathbf{r} \in MT_a \end{cases} \tag{5.4}$$

where $\mathbf{r}^{\,a} = T_a^{-1}(\mathbf{r} - \mathbf{r}_a)$, being $\mathbf{r}_a$ the position of atom a in the cell and T_a a rotation to the local coordinate system of atom a, $\dot{u}_l$ is the energy derivative $\frac{\partial u_l}{\partial E}$ evaluated at the linearization energy E_l. The radial wave functions $u_l(r^a, E_l)$ and its energy derivatives are determined from a numerical integration of the radial part of the Schrödinger equation and its energy derivative (see [44, 54]), and fulfill the conditions:

$$\int_0^{R^a_{MT}} r^2 u_l^2(r) dr = 1, \tag{5.5a}$$

$$\int_0^{R^a_{MT}} r^2 u_l(r) \dot{u}_l(r) dr = 0. \tag{5.5b}$$

The coefficients $A^a_{lm}(\mathbf{k}+\mathbf{G})$ and $B^a_{lm}(\mathbf{k}+\mathbf{G})$ in equation 5.4 are determined by the condition that the basis functions are continuous up to the first derivative at the sphere boundaries. Their expression is:

$$A^a_{lm}(\mathbf{k}+\mathbf{G}) = \frac{4\pi}{\sqrt{\Omega}} i^l Y^*_{lm}(T_a^{-1}(\widehat{\mathbf{k}+\mathbf{G}})) c^a_l(\mathbf{k}+\mathbf{G}) \left[R^a_{MT}\right]^2 e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}_a} \tag{5.6a}$$

$$B^a_{lm}(\mathbf{k}+\mathbf{G}) = \frac{4\pi}{\sqrt{\Omega}} i^l Y^*_{lm}(T_a^{-1}(\widehat{\mathbf{k}+\mathbf{G}})) d^a_l(\mathbf{k}+\mathbf{G}) \left[R^a_{MT}\right]^2 e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}_a} \tag{5.6b}$$

with the abreviations

$$\begin{aligned} c^a_l(\mathbf{k}+\mathbf{G}) =& \left(\tfrac{\partial j_l(|\mathbf{k}+\mathbf{G}|r)}{\partial r}\right)_{R^a_{MT}} \dot{u}_l(R^a_{MT}, E_l) - j_l(|\mathbf{k}+\mathbf{G}|R^a_{MT}) \dot{u}'_l(R^a_{MT}, E_l) \\ =& |\mathbf{k}+\mathbf{G}| j'_l(|\mathbf{k}+\mathbf{G}|R^a_{MT}) \dot{u}_l(R^a_{MT}, E_l) - j_l(|\mathbf{k}+\mathbf{G}|R^a_{MT}) \dot{u}'_l(R^a_{MT}, E_l), \end{aligned} \tag{5.7a}$$

$$\begin{aligned} d^a_l(\mathbf{k}+\mathbf{G}) =& j_l(|\mathbf{k}+\mathbf{G}|R^a_{MT}) u'_l(R^a_{MT}, E_l) - \left(\tfrac{\partial j_l(|\mathbf{k}+\mathbf{G}|r)}{\partial r}\right)_{R^a_{MT}} u_l(R^a_{MT}, E_l) \\ =& j_l(|\mathbf{k}+\mathbf{G}|R^a_{MT}) u'_l(R^a_{MT}, E_l) - |\mathbf{k}+\mathbf{G}| r j'_l(|\mathbf{k}+\mathbf{G}|R^a_{MT}) u_l(R^a_{MT}, E_l). \end{aligned} \tag{5.7b}$$

Here, j_l is the spherical Bessel function, the dots denote partial derivatives with respect to the expansion energy E_l and the primes with respect to the first variable.

5.1.2.2 The new linearization method: APW+lo

As we saw in the previous section, the LAPW method replaces the exact solutions u_l of the muffin tin potential by linear combinations of u_l and $\dot{u}_l$, matched to the planewaves in value and slope at the sphere boundaries. As a consequence, the LAPW basis set size must be increased as compared to that of the original APW method [57]. In [56] and [55] an alternative way of linearizing the APW method is presented, which does not change the shape of the original augmenting functions. As indicated by the name, the basis functions of the APW+lo method consists of:

i. The original APW basis functions

$$\tilde{\Phi}^{\mathbf{k}}_{\mathbf{G}}(\mathbf{r}) = \begin{cases} \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} & \mathbf{r} \in I \\ \sum_{l=0}^{l_{max}} \sum_{m=-l}^{+l} A^a_{lm}(\mathbf{k}+\mathbf{G}) u_l(r^a, E_l) Y_{lm}(\hat{r}^a) & \mathbf{r} \in MT_a \end{cases} \tag{5.8}$$

The coefficients $A^a_{lm}(\mathbf{k}+\mathbf{G})$ are obtained by requiring the wave function to be continuous at the sphere boundaries. This yields:

$$A^a_{lm}(\mathbf{k}+\mathbf{G}) = \frac{4\pi}{\sqrt{\Omega}} i^l Y^*_{lm}(T_a^{-1}(\widehat{\mathbf{k}+\mathbf{G}})) \frac{j_l(|\mathbf{k}+\mathbf{G}|R^a_{MT})}{u_l(R^a_{MT}, E_l)} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}_a}. \tag{5.9}$$

ii. A set of local orbitals of the form:

$$\tilde{\Phi}^{lo}_{APW}(\mathbf{r}) = \begin{cases} 0 & \mathbf{r} \in I \\ \left[A^a_{lm} u_l(r^a, E_l) + B^a_{lm} \dot{u}_l(r^a, E_l)\right] Y_{lm}(\hat{r}^a) & \mathbf{r} \in MT_a \end{cases} \tag{5.10}$$

Each local orbital is matched to zero at the sphere boundary, thus

$$\frac{A^a_{lm}}{B^a_{lm}} = -\frac{\dot{u}_l(R^a_{MT}, E_l)}{u_l(R^a_{MT}, E_l)} \tag{5.11}$$

The undetermined coefficient is determined by associating it to a fictitious plane wave $e^{i(\mathbf{k}+\mathbf{G}_{lo})\cdot\mathbf{r}}$ (see section 5.9.2 in Ref. [54] or section 3.1.1 in [55]), ending up with:

$$A^a_{lm}(\mathbf{k}+\mathbf{G}_{lo}) = \frac{4\pi}{\sqrt{\Omega}} i^l Y^*_{lm}(T_a^{-1}(\widehat{\mathbf{k}+\mathbf{G}_{lo}})) c^a_l(\mathbf{k}+\mathbf{G}_{lo}) \left[R^a_{MT}\right]^2 e^{i(\mathbf{k}+\mathbf{G}_{lo})\cdot\mathbf{r}_a} \tag{5.12a}$$

$$B^a_{lm}(\mathbf{k}+\mathbf{G}_{lo}) = \frac{4\pi}{\sqrt{\Omega}} i^l Y^*_{lm}(T_a^{-1}(\widehat{\mathbf{k}+\mathbf{G}_{lo}})) d^a_l(\mathbf{k}+\mathbf{G}_{lo}) \left[R^a_{MT}\right]^2 e^{i(\mathbf{k}+\mathbf{G}_{lo})\cdot\mathbf{r}_a} \tag{5.12b}$$

with

$$c^a_l(\mathbf{k}+\mathbf{G}_{lo}) = \frac{\dot{u}_l(R^a_{MT})}{\sqrt{\dot{u}^2_l(R^a_{MT}) + u^2_l(R^a_{MT})|\dot{u}_l|^2}} \tag{5.13a}$$

$$d^a_l(\mathbf{k}+\mathbf{G}_{lo}) = -\frac{u_l(R^a_{MT})}{\sqrt{\dot{u}^2_l(R^a_{MT}) + u^2_l(R^a_{MT})|\dot{u}_l|^2}} \tag{5.13b}$$

$$\tag{5.13c}$$

and

$$|\dot{u}_l|^2 = \int_0^{R^a_{MT}} |\dot{u}_l(r)|^2 r^2 dr \tag{5.14}$$

The use of this basis has the following advantages:

- a smaller number of planewaves is needed for convergence, thus the matrix sizes are smaller
- the eigenfunctions close to E_l are better described
- the setup of matrix elements is faster than in for LAPW's since the majority of the basis functions include only u_l.

A major drawback of the APW+lo method comes from the fact that, as can be seen from equations 5.8 and 5.11, the radial derivative of the wavefunction is discontinuous at the sphere boundary, thus there appears a surface term in the kinetic energy. For a discussion on the subject see [56].

5.1.3 Semi-core states: local orbitals

5.1.3.1 SC-LAPW

Local orbitals were introduced into the LAPW method to treat semi-core states [53, 54].

While each augmented planewave is connected to a vector $\mathbf{k}$ and has and augmenting part summed over atoms and l, m-characters, a local orbital is independent of $\mathbf{k}$ and $\mathbf{G}$. It belongs only ot one atom and has a specific l, m-character. The local orbital of the LAPW method involves an additional radial function, evaluated at a new linearization energy E_{l2}.

$$\tilde{\Phi}^{LO}_{LAPW}(\mathbf{r}) = \begin{cases} 0 & \mathbf{r} \in I \\ \left[A^a_{lm} u_l(r^a, E_l) + B^a_{lm} \dot{u}_l(r^a, E_l) + C^a_{lm} u^{(2)}_l(r^a)\right] Y_{lm}(\hat{r}^a) & \mathbf{r} \in MT_a \end{cases} \tag{5.15}$$

The local orbitals are local in the sense that they are identically zero outside the MT-sphere, and two of the coefficients of equation 5.15 are set to match the value and the first derivative to zero at the sphere boundary. The third parameter is set by associating it to a fictitious planewave as in the previous section.

The coefficients are:

$$A^a_{lm}(\mathbf{k}+\mathbf{G}_{LO}) = \frac{4\pi}{\sqrt{\Omega}} i^l Y^*_{lm}(T_a^{-1}(\widehat{\mathbf{k}+\mathbf{G}_{LO}})) c^a_l(\mathbf{k}+\mathbf{G}_{LO}) \left[R^a_{MT}\right]^2 e^{i(\mathbf{k}+\mathbf{G}_{LO})\cdot\mathbf{r}_a} \tag{5.16a}$$

$$B^a_{lm}(\mathbf{k}+\mathbf{G}_{LO}) = \frac{4\pi}{\sqrt{\Omega}} i^l Y^*_{lm}(T_a^{-1}(\widehat{\mathbf{k}+\mathbf{G}_{LO}})) d^a_l(\mathbf{k}+\mathbf{G}_{LO}) \left[R^a_{MT}\right]^2 e^{i(\mathbf{k}+\mathbf{G}_{LO})\cdot\mathbf{r}_a} \tag{5.16b}$$

$$C^a_{lm}(\mathbf{k}+\mathbf{G}_{LO}) = \frac{4\pi}{\sqrt{\Omega}} i^l Y^*_{lm}(T_a^{-1}(\widehat{\mathbf{k}+\mathbf{G}_{LO}})) e^a_l(\mathbf{k}+\mathbf{G}_{LO}) \left[R^a_{MT}\right]^2 e^{i(\mathbf{k}+\mathbf{G}_{LO})\cdot\mathbf{r}_a} \tag{5.16c}$$

with

$$c^a_l(\mathbf{k}+\mathbf{G}_{LO}) = \frac{\mathbf{a}_l}{\sqrt{\mathbf{a}_l(\mathbf{a}_l + 2\langle u_l u_l^{(2)}\rangle) + \mathbf{b}_l(\mathbf{b}_l + 2\langle \dot{u}_l u_l^{(2)}\rangle) + 1}} \tag{5.17a}$$

$$d^a_l(\mathbf{k}+\mathbf{G}_{LO}) = \frac{\mathbf{b}_l}{\sqrt{\mathbf{a}_l(\mathbf{a}_l + 2\langle u_l u_l^{(2)}\rangle) + \mathbf{b}_l(\mathbf{b}_l + 2\langle \dot{u}_l u_l^{(2)}\rangle) + 1}} \tag{5.17b}$$

$$e^a_l(\mathbf{k}+\mathbf{G}_{LO}) = \frac{1}{\sqrt{\mathbf{a}_l(\mathbf{a}_l + 2\langle u_l u_l^{(2)}\rangle) + \mathbf{b}_l(\mathbf{b}_l + 2\langle \dot{u}_l u_l^{(2)}\rangle) + 1}} \tag{5.17c}$$

$$\tag{5.17d}$$

where

$$\mathbf{a}_l = (u_l^{(2)}(R^a_{MT})\dot{u}'_l(R^a_{MT}) - u_l'^{(2)}(R^a_{MT})\dot{u}_l(R^a_{MT}))\left[R^a_{MT}\right]^2 \tag{5.18a}$$

$$\mathbf{b}_l = (u_l^{(2)}(R^a_{MT})u'_l(R^a_{MT}) - u_l'^{(2)}(R^a_{MT})u_l(R^a_{MT}))\left[R^a_{MT}\right]^2 \tag{5.18b}$$

$$\langle u_l u_l^{(2)}\rangle = \int_0^{R^a_{MT}} u_l(r)u_l^{(2)}(r)r^2 dr \tag{5.18c}$$

$$\langle \dot{u}_l u_l^{(2)}\rangle = \int_0^{R^a_{MT}} \dot{u}_l(r)u_l^{(2)}(r)r^2 dr \tag{5.18d}$$

5.1.3.2 SC-APW+lo

In this case the semi-core states are obtained by adding a *second* set of local orbitals of the form:

$$\tilde{\Phi}^{LO}_{APW}(\mathbf{r}) = \begin{cases} 0 & \mathbf{r} \in I \\ \left[A^a_{lm}u_l(r^a, E_l) + C^a_{lm}u_l^{(2)}(r^a)\right] Y_{lm}(\hat{r}^a) & \mathbf{r} \in MT_a \end{cases} \tag{5.19}$$

These local orbitals are matched to zero value at R^a_{MT}, with no condition on the first derivative.

The coefficients are:

$$A^a_{lm}(\mathbf{k}+\mathbf{G}_{LO}) = \frac{4\pi}{\sqrt{\Omega}} i^l Y^*_{lm}(T_a^{-1}(\widehat{\mathbf{k}+\mathbf{G}_{LO}})) c^a_l(\mathbf{k}+\mathbf{G}_{LO}) \left[R^a_{MT}\right]^2 e^{i(\mathbf{k}+\mathbf{G}_{LO})\cdot\mathbf{r}_a} \tag{5.20a}$$

$$C^a_{lm}(\mathbf{k}+\mathbf{G}_{LO}) = \frac{4\pi}{\sqrt{\Omega}} i^l Y^*_{lm}(T_a^{-1}(\widehat{\mathbf{k}+\mathbf{G}_{LO}})) e^a_l(\mathbf{k}+\mathbf{G}_{LO}) \left[R^a_{MT}\right]^2 e^{i(\mathbf{k}+\mathbf{G}_{LO})\cdot\mathbf{r}_a} \tag{5.20b}$$

with

$$c^a_l(\mathbf{k}+\mathbf{G}_{LO}) = \frac{u_l^{(2)}(R^a_{MT})}{\sqrt{\left[u_l^{(2)}(R^a_{MT})\right]^2 + \left[u_l(R^a_{MT})\right]^2 - u_l(R^a_{MT})u_l^{(2)}(R^a_{MT})\langle u_l u_l^{(2)}\rangle}} \tag{5.21a}$$

$$e^a_l(\mathbf{k}+\mathbf{G}_{LO}) = -\frac{u_l(R^a_{MT})}{\sqrt{\left[u_l^{(2)}(R^a_{MT})\right]^2 + \left[u_l(R^a_{MT})\right]^2 - u_l(R^a_{MT})u_l^{(2)}(R^a_{MT})\langle u_l u_l^{(2)}\rangle}} \tag{5.21b}$$

5.1.4 The Bloch character of the wavefunctions

In Section 5.1, the basis functions where defined within the Wigner-Seitz cell. To extend them to the whole volume of the crystal, so that they fulfil Bloch's theorem we just extend the definition as follows:

$$\Phi^{\mathbf{k}}_{\mathbf{G}}(\mathbf{r}) = \frac{1}{\sqrt{N_c}} \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \tilde{\Phi}^{\mathbf{k}}_{\mathbf{G}}(\mathbf{r}') \tag{5.22}$$

Where $\mathbf{r}'$ belongs to the Wigner-Seitz cell at the origin and $\mathbf{r} = \mathbf{r}' + \mathbf{R}$. Note that with this definition, the basis function in the interstitial part are just changed to $\frac{1}{\sqrt{V}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$ where $\mathbf{r}$ now runs on the whole crystal volume V and the function is also normalized to it.

Chapter 6

Mixed basis

In this chapter we define an optimized set of basis functions for the expansion of the non-local operators.

6.1 Definition of the basis

In the (L)APW+lo method, the space is divided into the MT-sphere regions and the interstitial region. As we have seen, the wavefunction for valence and conduction states is expanded as

$$\tilde{\psi}_{n\mathbf{k}}(\mathbf{r}) = \sum_{a\nu lm} A^{n\mathbf{k}}_{a\nu lm} u_{a\nu l}(r^a) Y_{lm}(\hat{r}^a) + \sum_{\mathbf{G}} Z^{n\mathbf{k}}_{\mathbf{G}} \tilde{P}^{\mathbf{k}}_{\mathbf{G}}(\mathbf{r}) \tag{6.1}$$

where the radial function $u_{a\nu l}(r^a)$ can be $u_{al}(r^a, E_l)$, $\dot{u}_{al}(r^a, E_l)$ or $u_{al}(r^a, E_{l2})$. The interstitial planewave(IPW) $\tilde{P}^{\mathbf{q}}_{\mathbf{G}}(\mathbf{r})$ is defined by

$$\tilde{P}^{\mathbf{k}}_{\mathbf{G}}(\mathbf{r}) = \begin{cases} 0 & \text{in the MT-sphere regions} \\ \dfrac{1}{\sqrt{\Omega}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} & \text{in the interstitial region} \end{cases} \tag{6.2}$$

Core states can be written as a special form of Eq. (6.1) with the second part taken out.

The interactions, *v* and *W*, are well expressed by the product of two eigenfunctions in our perturbative treatment. The product $\psi_{n\mathbf{k}}(\mathbf{r})\psi^*_{n'\mathbf{k}'}(\mathbf{r})$ is expanded by the products of two local functions, $\Lambda_{a\nu lm}(\mathbf{r})A_{a\nu' l' m'}(\mathbf{r})$, in the MT-sphere regions, and by IPW's $P^{\mathbf{k}}_{\mathbf{G}}(\mathbf{r})$, in the interstitial region (since the product of IPW's is also a IPW in the interstitial region.

6.1.1 MB basis functions for MT region

In the a-atom MT-sphere region, we define a product function by

$$\beta_{\nu lm;\nu' l' m'}(\mathbf{r}) \equiv \Lambda_{\nu lm}(\mathbf{r})\Lambda_{\nu' l' m'}(\mathbf{r}) \tag{6.3}$$

with $\Lambda_{a\nu lm}(\mathbf{r}^a) := u_{a\nu l}(r^a)Y_{lm}(\hat{r}^a)$. As it is, this basis is non-orthogonal and overcomplete. On the other side, it's dependence on a product of spherical harmonics makes their computational treatment quite cumbersome. Thus we will define a set of basis functions of the form:

$$\gamma_{aNLM}(\mathbf{r}^a) \equiv \upsilon_{NL}(r^a)Y_{LM}(\hat{r}^a) \tag{6.4}$$

To obtain an optimal set of radial functions $\upsilon_{NL}(r)$ we proceed as follows:

- For each L, take the product of radial functions $u_{\nu l}(r)u_{\nu' l'}(r)$ which fullfil the condition $|l-l'| \leq L \leq l+l'$.
- calculate the overlap matrix of the products of radial functions:

$$\mathbb{O}_{(\nu l,\nu' l');(\nu_1 l_1,\nu'_1 l'_1)} = \int_0^{R^a_{MT}} u_{\nu_1 l}(r^a)u_{\nu' l'}(r^a)u_{\nu_1 l_1}(r^a)u_{\nu'_1 l'_1}(r^a)(r^a)^2 dr^a \tag{6.5}$$

- Diagonalize the matrix $\mathbb{O}$
- Discard the eigenvectors corresponding to eigenvalues with absolute value lower than a given tolerance (usually 10^{-5}).

- The rest of the eigenvectors are normalized and stored for a grid of $\mathbf{r}$ that constitute the new basis $\{\upsilon_{NL}\}$

So defined the set of functions $\{\gamma_{aNLM}\}$ constitute and orthonormal basis set, that is:

$$\int_{V_{MT}^a} \gamma_{aNLM}(\mathbf{r})\gamma_{aN'L'M'}(\mathbf{r})d^3r = \delta_{N,N'}\delta_{L,L'}\delta_{M,M'} \tag{6.6}$$

and the set of functions $\beta_{alm;l'm'}(\mathbf{r})$ can be expanded as:

$$\beta_{\nu lm;\nu' l'm'}(\mathbf{r}) = \sum_N \sum_{L=|l-l'|}^{l+l'} \sum_{M=-L}^{L} D^{NL}_{\nu l,\nu' l'} G^{LM}_{ll',mm'} \gamma_{aNLM}(\mathbf{r}) \tag{6.7}$$

where the coefficients $D^{NL}_{ll'}$ are defined by:

$$\mathcal{D}^{NL}_{\nu l,\nu' l'} = \int_0^{R^a_{MT}} \upsilon_{aNL}(r) u_{\nu l}(r) u_{\nu' l'}(r) r^2 dr \tag{6.8}$$

and $\mathcal{G}^{LM}_{ll',mm'}$ are the Gaunt coefficients defined in equation A.39.

For the electrons in a perfect crystal, we need a Bloch basis for the periodic system. Thus we make the Bloch sum:

$$\gamma^{\mathbf{q}}_{aNLM}(\mathbf{r}) = \frac{1}{\sqrt{N_c}} \sum_{\vec{R}} e^{i\mathbf{q}\cdot(\vec{R}+\mathbf{r}_a)} \gamma_{aNLM}(\mathbf{r}^{\,a}). \tag{6.9}$$

where $\mathbf{r}_a$ is the position of atom a in the unit cell.

6.1.2 Interstitial region

Because of the nonorthogonality of IPW's, the overlap integral $\mathbb{O}^{\mathbf{q}}_{\mathbf{G};\mathbf{G}'} \equiv \langle P^{\mathbf{q}}_{\mathbf{G}} | P^{\mathbf{q}}_{\mathbf{G}'} \rangle$, is nonvanishing for $\mathbf{G} \neq \mathbf{G}'$. the overlap matrix is:

$$\mathbb{O}^{\mathbf{q}}_{\mathbf{G};\mathbf{G}'} = \int_V \left[P^{\mathbf{q}}_{\mathbf{G}}(\mathbf{r})\right]^* P^{\mathbf{q}}_{\mathbf{G}'}(\mathbf{r}) d^3r \tag{6.10}$$

which using equation 6.2 can be written:

$$\begin{aligned} \mathbb{O}^{\mathbf{q}}_{\mathbf{G};\mathbf{G}'} &= \frac{1}{V}\int_I e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}} d^3r \\ &= \frac{1}{V}\int_I e^{-i(\mathbf{G}-\mathbf{G}')\cdot\mathbf{r}} d^3r = \frac{1}{\Omega}\int_{I_\Omega} e^{-i(\mathbf{G}-\mathbf{G}')\cdot\mathbf{r}} d^3r \end{aligned} \tag{6.11}$$

Thus, we can write $\mathbb{O}^{\mathbf{q}}_{\mathbf{G};\mathbf{G}'} \equiv \mathbb{O}_{\mathbf{G};\mathbf{G}'}$ since it has no $\mathbf{q}$ dependence. The advantage is that it only needs to be calculated once. The integral over the interstitial region is carried out by integrating over the whole unit cell and subtracting the contribution from the atomic spheres. That is

$$\mathcal{I}_{\mathbf{G}} \equiv \int_{I_\Omega} e^{i\mathbf{G}\cdot\mathbf{r}} d^3r = \int_{\Omega} e^{i\mathbf{G}\cdot\mathbf{r}} d^3r - \sum_a \int_{MT_a} e^{i\mathbf{G}\cdot\mathbf{r}} d^3r \tag{6.12}$$

The integral over the unit cell is:

$$\int_{\Omega} e^{i\mathbf{G}\cdot\mathbf{r}} d^3r = \Omega\delta_{\mathbf{G},0} \tag{6.13}$$

while the integral over the muffin tin sphere is equal to the volume of the muffin tin sphere (V^a_{MT}) if $\mathbf{G} = 0$. For the case $\mathbf{G} \neq 0$ the integral can be done using thee Rayleig-expansion for a plane wave in terms of spherical harmonics.

$$e^{i\mathbf{G}\cdot\mathbf{r}} = 4\pi e^{i\mathbf{G}\cdot\mathbf{r}_a} \sum_{\lambda\mu} i^\lambda j_\lambda(r^a G) Y^*_{\lambda\mu}(\hat{G}) Y_{\lambda\mu}(\hat{r}^a) \tag{6.14}$$

which when substituted in the last term of eq. 6.12 gives:

$$\begin{aligned}
\int_{MT_a} e^{i\mathbf{G}\cdot\mathbf{r}} d^3r =& 4\pi e^{i\mathbf{G}\cdot\mathbf{r}_a} \sum_{\lambda\mu} Y^*_{\lambda\mu}(\hat{G}) i^\lambda \int_{MT_a} j_\lambda(r^a G) Y_{\lambda\mu}(\hat{r}^a) d^3r^a \\
=& 4\pi e^{i\mathbf{G}\cdot\mathbf{r}_a} \sum_{\lambda\mu} Y^*_{\lambda\mu}(\hat{G}) i^\lambda \int_0^{R^a_{MT}} j_\lambda(r^a G) \left(r^a\right)^2 dr^a \int Y_{\lambda\mu}(\hat{r}^a) d\hat{r}^a \\
=& 4\pi e^{i\mathbf{G}\cdot\mathbf{r}_a} \sum_{\lambda\mu} Y^*_{\lambda\mu}(\hat{G}) i^\lambda \int_0^{R^a_{MT}} j_\lambda(r^a G) \left(r^a\right)^2 dr^a \sqrt{4\pi}\delta_{\lambda,0}\delta_{\mu,0} \\
=& 4\pi e^{i\mathbf{G}\cdot\mathbf{r}_a} \int_0^{R^a_{MT}} j_0(r^a G) \left(r^a\right)^2 dr^a \\
=& 4\pi e^{i\mathbf{G}\cdot\mathbf{r}_a} \left[\frac{\sin(GR^a_{MT}) - (GR^a_{MT})\cos(GR^a_{MT})}{G^3}\right] \\
=& 3V^a_{MT} e^{i\mathbf{G}\cdot\mathbf{r}_a} \left[\frac{\sin(GR^a_{MT}) - (GR^a_{MT})\cos(GR^a_{MT})}{(GR^a_{MT})^3}\right]
\end{aligned} \tag{6.15}$$

Thus we have:

$$\mathcal{I}_{\mathbf{G}} = \begin{cases} \Omega - \sum_a V^a_{MT} & \mathbf{G} = 0 \\ -3\sum_a V^a_{MT} e^{i\mathbf{G}\cdot\mathbf{r}_a} \left[\frac{\sin(GR^a_{MT}) - (GR^a_{MT})\cos(GR^a_{MT})}{(GR^a_{MT})^3}\right] & \mathbf{G} \neq 0 \end{cases} \tag{6.16}$$

Using this result (eq. 6.16) the overlap matrix can be writen:

$$\boxed{\mathbb{O}_{\mathbf{G};\mathbf{G}'} = \frac{1}{\Omega}\mathcal{I}_{\mathbf{G}'-\mathbf{G}}} \tag{6.17}$$

We therefore diagonalize the overlap matrix by solving the set of equations:[1]

$$\sum_{\mathbf{G}'} \mathbb{O}_{\mathbf{G};\mathbf{G}'} S_{\mathbf{G}',i} = \varepsilon_i S_{\mathbf{G},i} \tag{6.18}$$

And define the orthogonal IPW function:

$$\tilde{P}^{\mathbf{q}}_i(\mathbf{r}) \equiv \sum_{\mathbf{G}} \tilde{S}_{\mathbf{G},i} P^{\mathbf{q}}_{\mathbf{G}}(\mathbf{r}). \tag{6.19}$$

where $\tilde{S}_{\mathbf{G},i} = \frac{1}{\sqrt{\varepsilon_i}} S_{\mathbf{G},i}$ so that the orthogonal IPW's are normalized within a unit cell.

We therefore obtain a orthonormal mixed basis

$$\left\{\chi^{\mathbf{q}}_j(\mathbf{r})\right\} \equiv \left\{\gamma^{\mathbf{q}}_{aNLM}(\mathbf{r}), P^{\mathbf{q}}_i(\mathbf{r})\right\}, \tag{6.20}$$

which is suitable for expansions of v and W. The index j specifies a member of the basis and runs through $\mathbf{G}$ and $aNLM$.

6.2 Matrix elements $\mathcal{W}^i_{\mathbf{G}}(\mathbf{q})$

In this section we calculate the matrix elements

$$\mathcal{W}^i_{\mathbf{G}}(\mathbf{q}) = \langle \chi^{\mathbf{q}}_i | \mathbf{q}+\mathbf{G}\rangle = \frac{1}{\sqrt{V}} \int_V \left[\chi^{\mathbf{q}}_i(\mathbf{r})\right]^* e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} d^3r \tag{6.21}$$

Inside the MT-sphere we have, using equation 6.9:

[1] The overlap matrix of the IPW's is $\mathbf{q}$ independent, see Appendix **??**

$$\begin{aligned}\mathcal{W}^{\mathcal{L}}_{\mathbf{G}}(\mathbf{q}) =& \frac{1}{\sqrt{V}}\int_V \left[\gamma^{\mathbf{q}}_{aNLM}(\mathbf{r})\right]^* e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} d^3r \\ =& \frac{1}{\sqrt{N_cV}}\sum_{\vec{R}} e^{-i\mathbf{q}\cdot(\vec{R}+\mathbf{r}_a)} e^{i(\mathbf{q}+\mathbf{G})\cdot(\vec{R}+\mathbf{r}_a)} \int_{MT} \gamma^*_{aNLM}(\mathbf{r}^a) e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}^a} d^3r^a \\ =& \frac{1}{\sqrt{N_cV}}\sum_{\vec{R}} e^{i\mathbf{G}\cdot(\vec{R}+\mathbf{r}_a)} \int_{MT} \upsilon_{NL}(r^a) Y^*_{LM}(T^{-1}\hat{r}^a) e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}^a} d^3r^a\end{aligned} \tag{6.22}$$

Using $\mathbf{G}\cdot\vec{R} = 2n\pi$ and the Rayleigh expansion (eq. A.40) we obtain:

$$\begin{aligned}\mathcal{W}^{\mathcal{L}}_{\mathbf{G}}(\mathbf{q}) =& 4\pi\sqrt{\frac{N_c}{V}} e^{i\mathbf{G}\cdot\mathbf{r}_a} \sum_{\lambda\mu} i^\lambda Y^*_{\lambda\mu}(T^{-1}\widehat{\mathbf{q}+\mathbf{G}}) \int_{MT} \upsilon_{NL}(r^a) Y^*_{LM}(T^{-1}\hat{r}^a) j_\lambda(|\mathbf{q}+\mathbf{G}|r^a) Y_{\lambda\mu}(T^{-1}\hat{r}^a) d^3r^a \\ =& \frac{4\pi}{\sqrt{\Omega}} e^{i\mathbf{G}\cdot\mathbf{r}_a} \sum_{\lambda\mu} i^\lambda Y^*_{\lambda\mu}(T^{-1}\widehat{\mathbf{q}+\mathbf{G}}) \int_0^{R^a_{MT}} \upsilon_{NL}(r) j_\lambda(|\mathbf{q}+\mathbf{G}|r) r^2 dr \delta_{\lambda,L}\delta_{\mu,M} \\ =& \frac{4\pi}{\sqrt{\Omega}} e^{i\mathbf{G}\cdot\mathbf{r}_a} i^L Y^*_{LM}(T^{-1}\widehat{\mathbf{q}+\mathbf{G}}) \int_0^{R^a_{MT}} \upsilon_{NL}(r) j_L(|\mathbf{q}+\mathbf{G}|r) r^2 dr\end{aligned} \tag{6.23}$$

Thus, according to eq. 7.44 we end up with:

$$\boxed{\mathcal{W}^{\mathcal{L}}_{\mathbf{G}}(\mathbf{q}) = \frac{4\pi}{\sqrt{\Omega}} e^{i\mathbf{G}\cdot\mathbf{r}_a} i^L Y^*_{LM}(T^{-1}\widehat{\mathbf{q}+\mathbf{G}}) \left\langle j_\lambda^{|\mathbf{G}+\mathbf{q}|}\right\rangle_{aNL}} \tag{6.24}$$

In the interstitial region we have, using equation 6.19:

$$\begin{aligned}\mathcal{W}^{\rangle}_{\mathbf{G}}(\mathbf{q}) =& \frac{1}{V}\sum_{\mathbf{G}'} \tilde{\mathbb{S}}^*_{\mathbf{G}',i} \int_I e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}} e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} d^3r \\ =& \frac{1}{\Omega}\sum_{\mathbf{G}'} \tilde{\mathbb{S}}^*_{\mathbf{G}',i} \int_I^{WZ} e^{i(\mathbf{G}-\mathbf{G}')\cdot\mathbf{r}} d^3r\end{aligned} \tag{6.25}$$

which according to equation 6.12 is:

$$\boxed{\mathcal{W}^i_{\mathbf{G}}(\mathbf{q}) = \frac{1}{\Omega}\sum_{\mathbf{G}'} \tilde{\mathbb{S}}^*_{\mathbf{G}',i} \mathcal{I}_{\mathbf{G}-\mathbf{G}'}} \tag{6.26}$$

6.3 Matrix elements $M^i_{nm}(\mathbf{k},\mathbf{q})$

The matrix elements $M^i_{nm}(\mathbf{k},\mathbf{q})$ are defined as

$$M^i_{nm}(\mathbf{k},\mathbf{q}) \equiv \int_\Omega \left[\tilde{\chi}^{\mathbf{q}}_i(\mathbf{r})\tilde{\psi}_{m,\mathbf{k}-\mathbf{q}}(\mathbf{r})\right]^* \tilde{\psi}_{n\mathbf{k}}(\mathbf{r}) d\mathbf{r} \tag{6.27}$$

Since our basis functions describe separately the two regions of space, the calculation of the brackets depends on wether *i* corresponds to a function in the sphere or an IPW.

6.3.1 $\tilde{\chi}^{\mathbf{q}}_i(\mathbf{r})$ corresponds to functions in the MT-sphere region

In this case, the mixed basis function, normalized in the unit cell, reads

$$\tilde{\chi}^{\mathbf{q}}_i(\mathbf{r}) \equiv e^{i\mathbf{q}\cdot\mathbf{r}_a}\gamma_{aNLM}(\mathbf{r}^a) = e^{i\mathbf{q}\cdot\mathbf{r}_a} v_{aNL}(r^a) Y_{LM}(\hat{\mathbf{r}}^a) \tag{6.28}$$

where $\mathbf{r}_a$ is the position vector of a-th atom in the unit cell.

KS wave functions in the a-th MT sphere can be written in a general form as

$$\begin{aligned}\tilde{\psi}_{n\mathbf{k}}(\mathbf{r}) &= \sum_{lm}\left[\mathcal{A}^{n\mathbf{k}}_{alm}u_{al}(r^a,E_l)+\mathcal{B}^{n\mathbf{k}}_{alm}\dot{u}_{al}(r^a,E_l)+\mathcal{C}^{n\mathbf{k}}_{alm}u_{al}(r^a,E_{l_2})\right]Y_{lm}(\hat{r}^a)\\ &= \sum_{\nu lm}\mathcal{A}^{n\mathbf{k}}_{a\nu lm}u_{a\nu l}(r^a)Y_{lm}(\hat{r}^a)\end{aligned} \tag{6.29}$$

For normal LAPW states, we have:

$$\mathcal{A}^{n\mathbf{k}}_{alm} \equiv \sum_{\mathbf{G}} Z^{n\mathbf{k}}_{\mathbf{G}} A^a_{lm}(\mathbf{k}+\mathbf{G}) \tag{6.30a}$$

$$\mathcal{B}^{n\mathbf{k}}_{alm} \equiv \sum_{\mathbf{G}} Z^{n\mathbf{k}}_{\mathbf{G}} B^a_{lm}(\mathbf{k}+\mathbf{G}) \tag{6.30b}$$

$$\mathcal{C}^{n\mathbf{k}}_{alm} \equiv \sum_{\mathbf{G}} Z^{n\mathbf{k}}_{\mathbf{G}} C^a_{lm}(\mathbf{k}+\mathbf{G}) \tag{6.30c}$$

For core states,

$$\tilde{\psi}_{c\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}_a}u_c(r^a)Y_{lm}(\hat{\mathbf{r}}^a) \tag{6.31}$$

Now we consider different combinations of n and m.

6.3.1.1 $n,m \in$ band states

$$\begin{aligned}M^i_{nm}(\mathbf{k},\mathbf{q}) &= \int_\Omega \tilde{\chi}^{\mathbf{q}*}_i(\mathbf{r})\tilde{\psi}_{n\mathbf{k}}(\mathbf{r})\tilde{\psi}^*_{m\mathbf{k}-\mathbf{q}}(\mathbf{r})\\ &= e^{-i\mathbf{q}\cdot\mathbf{r}_a}\sum_{\nu_1 l_1 m_1}\sum_{\nu_2 l_2 m_2}\mathcal{A}^{n\mathbf{k}}_{a\nu_1 l_1 m_1}\left[\mathcal{A}^{m\mathbf{k}-\mathbf{q}}_{a\nu_2 l_2 m_2}\right]^*\int_0^{R^a_{\mathrm{MT}}}drr^2 v_{aNL}(r)u_{a\nu_1 l_1}(r)u_{a\nu_2 l_2}(r)\\ &\times\int d\hat{\mathbf{r}}Y^*_{LM}(\hat{\mathbf{r}})Y_{l_1 m_1}(\hat{\mathbf{r}})Y^*_{l_2 m_2}(\hat{\mathbf{r}})\\ &\equiv e^{-i\mathbf{q}\cdot\mathbf{r}_a}\sum_{\nu_1 l_1 m_1}\sum_{\nu_2 l_2 m_2}\mathcal{A}^{n\mathbf{k}}_{a\nu l_1 m_1}\left[\mathcal{A}^{m\mathbf{k}-\mathbf{q}}_{a\nu_2 l_2 m_2}\right]^* I^a_{NL,\nu_1 l_1,\nu_2 l_2}\left[\mathcal{G}^{l_1 m_1}_{LM,l_2 m_2}\right]^*\end{aligned} \tag{6.32}$$

where $\mathcal{G}^{lm}_{LM,l'm'}$ are Gaunt's coefficients and

$$I^a_{NL,\nu l,\nu' l'} \equiv \int_0^{R^a_{\mathrm{MT}}} drr^2 v_{aNL}(r)u_{a\nu l}(r)u_{a\nu' l'}(r) \tag{6.33}$$

6.3.1.2 $n \in$ band state, $m \equiv c \in$ core states

$$\begin{aligned}M^i_{nc}(\mathbf{k},\mathbf{q}) &= \int_\Omega \tilde{\chi}^{\mathbf{q}*}_i(\mathbf{r})\tilde{\psi}_{n\mathbf{k}}(\mathbf{r})\tilde{\psi}^*_{c\mathbf{k}-\mathbf{q}}(\mathbf{r})\\ &= e^{-i\mathbf{k}\cdot\mathbf{r}_a}\sum_{\nu lm}\mathcal{A}^{n\mathbf{k}}_{a\nu lm}\int_0^{R^a_{\mathrm{MT}}}drr^2 v_{aNL}(r)u_{a\nu l}(r)u_{an_c l_c}(r)\\ &\times\int d\hat{\mathbf{r}}Y^*_{LM}(\hat{\mathbf{r}})Y_{lm}(\hat{\mathbf{r}})Y^*_{l_c m_c}(\hat{\mathbf{r}})\\ &\equiv e^{-i\mathbf{k}\cdot\mathbf{r}_a}\sum_{\nu lm}\mathcal{A}^{n\mathbf{k}}_{a\nu lm}I^a_{NL,\nu l,n_c l_c}\left[\mathcal{G}^{lm}_{LM,l_c m_c}\right]^*\end{aligned} \tag{6.34}$$

6.3.1.3 $n \equiv c \in$ core state, $m \in$ band states

$$\begin{aligned}M^i_{cm}(\mathbf{k},\mathbf{q}) &= \int_\Omega \tilde{\chi}^{\mathbf{q}*}_i(\mathbf{r})\tilde{\psi}_{n\mathbf{k}}(\mathbf{r})\tilde{\psi}^*_{c\mathbf{k}-\mathbf{q}}(\mathbf{r})\\ &= e^{i(\mathbf{k}-\mathbf{q})\cdot\mathbf{r}_a}\sum_{\nu lm}\mathcal{A}^{n\mathbf{k}}_{a\nu lm}\int_0^{R^a_{\mathrm{MT}}}drr^2 v_{aNL}(r)u_{an_c l_c}(r)u_{a\nu l}(r)\\ &\times\int d\hat{\mathbf{r}}Y^*_{LM}(\hat{\mathbf{r}})Y_{l_c m_c}(\hat{\mathbf{r}})Y^*_{lm}(\hat{\mathbf{r}})\\ &\equiv e^{i(\mathbf{k}-\mathbf{q})\cdot\mathbf{r}_a}\sum_{\nu lm}\mathcal{A}^{n\mathbf{k}}_{a\nu lm}I^a_{NL,n_c l_c,\nu l}\left[\mathcal{G}^{l_c m_c}_{LM,lm}\right]^*\end{aligned} \tag{6.35}$$

6.3.1.4 $n \equiv c, m \equiv c' \in$ core state

$$\begin{aligned} M^i_{cc'}(\mathbf{k},\mathbf{q}) &= \int_\Omega \tilde{\chi}^{\mathbf{q}*}_i(\mathbf{r})\tilde{\psi}_{c\mathbf{k}}(\mathbf{r})\tilde{\psi}^*_{c'\mathbf{k}-\mathbf{q}}(\mathbf{r}) \\ &= \int_0^{R^a_{\mathrm{MT}}} dr r^2 v_{aNL}(r) u_{an_cl_c}(r) u_{an_{c'}l_{c'}}(r) \\ &\times \int d\hat{\mathbf{r}} Y^*_{LM}(\hat{\mathbf{r}}) Y_{l_cm_c}(\hat{\mathbf{r}}) Y^*_{l_{c'}m_{c'}}(\hat{\mathbf{r}}) \\ &\equiv I^a_{NL,n_cl_c,n_{c'}l_{c'}} \left[\mathcal{G}^{l_cm_c}_{LM,l_{c'}m_{c'}}\right]^* \end{aligned} \tag{6.36}$$

6.3.2 $\tilde{\chi}^{\mathbf{q}}_i(\mathbf{r})$ corresponds to an IPW

In this case, one starts from the expression for the eigenvectors $\tilde{\psi}_{n\mathbf{k}}(\mathbf{r})$ of equation 8.6, that is:

$$\tilde{\psi}_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} Z^{n\mathbf{k}}_{\mathbf{G}} \tilde{\Phi}^{\mathbf{k}}_{\mathbf{G}}(\mathbf{r}) \tag{6.37}$$

Equation 6.27 is converted to:

$$\begin{aligned} M^i_{nm}(\mathbf{k},\mathbf{q}) &= \sum_{\mathbf{G}\mathbf{G}'} Z^{n\mathbf{k}}_{\mathbf{G}} \left[Z^{m\mathbf{k}-\mathbf{q}}_{\mathbf{G}'}\right]^* \int_\Omega \left[\tilde{\chi}^{\mathbf{q}}_i(\mathbf{r})\tilde{\Phi}^{\mathbf{k}-\mathbf{q}}_{\mathbf{G}'}(\mathbf{r})\right]^* \tilde{\Phi}^{\mathbf{k}}_{\mathbf{G}}(\mathbf{r}) d^3r \\ &\equiv \sum_{\mathbf{G}\mathbf{G}'} Z^{n\mathbf{k}}_{\mathbf{G}} \left[Z^{m\mathbf{k}-\mathbf{q}}_{\mathbf{G}'}\right]^* \left\langle \tilde{\chi}^{\mathbf{q}}_i \tilde{\Phi}^{(\mathbf{k}-\mathbf{q})}_{\mathbf{K}'} | \Phi^{\mathbf{k}}_{\mathbf{G}} \right\rangle \end{aligned} \tag{6.38}$$

Using the definition within one unit cell:

$$\tilde{\chi}^{\mathbf{q}}_i(\mathbf{r}) \equiv \sum_{i'} \chi^{\mathbf{q}}_{i'}(\mathbf{r}) S^{-1}_{i'i} = \sum_{\mathbf{G}} P^{\mathbf{q}}_{\mathbf{G}}(\mathbf{r}) S^{-1}_{\mathbf{G}} \tag{6.39}$$

and

$$\Phi^{\mathbf{k}}_{\mathbf{G}}(\mathbf{r}) \equiv P^{\mathbf{k}}_{\mathbf{G}}(\mathbf{r}) \equiv \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \tag{6.40}$$

inserting equations 6.39 and 6.40 into equation **??** we have:

$$\begin{aligned} \left\langle \tilde{\chi}^{\mathbf{q}}_i \Phi^{(\mathbf{k}-\mathbf{q})}_{\mathbf{K}'} | \Phi^{\mathbf{k}}_{\vec{K}} \right\rangle &= \frac{1}{\Omega^{\frac{3}{2}}} \sum_{\mathbf{G}_1} \left[S^{-1}_{\mathbf{G}_1 i}\right]^* \int_{I_\Omega} e^{-i(\mathbf{q}+\mathbf{G}_1)\cdot\mathbf{r}} e^{-i\left(\mathbf{k}-\mathbf{q}+\mathbf{K}'\right)\cdot\mathbf{r}} e^{i\left(\mathbf{k}+\vec{K}\right)\cdot\mathbf{r}} d^3r \\ &= \frac{1}{\Omega^{\frac{3}{2}}} \sum_{\mathbf{G}_1} \left[S^{-1}_{\mathbf{G}_1 i}\right]^* \int_{I_\Omega} e^{i\left(\vec{K}-\mathbf{G}_1-\mathbf{K}'\right)\cdot\mathbf{r}} d^3r \end{aligned} \tag{6.41}$$

Making use of equation 6.16, we get:

$$\boxed{\left\langle \tilde{\chi}^{\mathbf{q}}_i \Phi^{(\mathbf{k}-\mathbf{q})}_{\mathbf{K}'} | \Phi^{\mathbf{k}}_{\vec{K}} \right\rangle = \frac{1}{\Omega^{\frac{3}{2}}} \sum_{\mathbf{G}_1} \mathcal{I}_{\vec{K}-\mathbf{G}_1-\mathbf{K}'} \left[S^{-1}_{\mathbf{G}_1 i}\right]^*} \tag{6.42}$$

Chapter 7

The coulomb matrix

The coulomb matrix $v_{ij}(\mathbf{q})$ is given by:

$$v_{ij}(\mathbf{q}) = \int_V \int_V \chi_i^{\mathbf{q}}(\mathbf{r}_1))^* v(\mathbf{r}_1, \mathbf{r}_2) \chi_j^{\mathbf{q}}(\mathbf{r}_2) d^3 r_2 d^3 r_1 \tag{7.1}$$

which, using the mixed basis functions normalized in the unit cell, can be written as:

$$v_{ij}(\mathbf{q}) = N_c \int_\Omega \int_\Omega (\tilde{\chi}_i^{\mathbf{q}}(\mathbf{r}_1))^* \sum_{\mathbf{R}} v(\mathbf{r}_1, \mathbf{r}_2 - \mathbf{R}) e^{-i\mathbf{q}\cdot\mathbf{R}} \tilde{\chi}_j^{\mathbf{q}}(\mathbf{r}_2) d^3 r_2 d^3 r_1 \tag{7.2}$$

The mixed basis functions are partitioned in those in the MT spheres and those in the interstitial region, and the two groups of MB functions do not overlap. In addition, the basis functions belonging different MT spheres do not overlap either. We can therefore distinguish four different cases and we analyze them separately in the following sections:

7.1 Case A: χ_i and χ_i belong to different MT spheres

In this case equation 7.2 can be writen as:

$$v_{i,j}(\mathbf{q}) = \int_{V^a} \int_{V^{a'}} [\tilde{\gamma}_{aNLM}^{\mathbf{q}}(\mathbf{r}_1))]^* \sum_{\mathbf{R}} v(\mathbf{r}_1, \mathbf{r}_2 - \mathbf{R}) e^{-i\mathbf{q}\cdot\mathbf{R}} \tilde{\gamma}_{a'N'L'M'}^{\mathbf{q}}(\mathbf{r}_2) d^3 r_2 d^3 r_1 \tag{7.3}$$

where $i \equiv aNLM$ and $j \equiv a'N'L'M'$. Writing the bare Coulomb potential, and the basis functions explicitly, equation 7.3 becomes:

$$v_{ij}(\mathbf{q}) = e^{i\mathbf{q}\cdot(\mathbf{r}_{a'} - \mathbf{r}_a)} \iint_{V^a} v_{aNL}(r^a) Y_{LM}^*(\hat{r}^a) \sum_{\mathbf{R}} \frac{e^{-i\mathbf{q}\cdot\mathbf{R}}}{|\mathbf{r}_1^a - \mathbf{r}_2^{a'} + \mathbf{R}_{aa'}|} v_{a'N'L'}(r_2^{a'}) Y_{L'M'}(\hat{r}_2^{a'}) d^3 r_2 d^3 r_1 \tag{7.4}$$

where $\mathbf{R}_{aa'} = \mathbf{R} + \mathbf{r}_a - \mathbf{r}_{a'}$ and $\mathbf{r}_1^{\,a} \equiv \mathbf{r}_1 - \mathbf{r}_a$. We now make use of the Laplace expansion for the Coulomb potential in terms of spherical harmonics:

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{4\pi}{2l+1} \frac{r_<^l}{r_>^{l+1}} Y_{lm}^*(\hat{r}_1) Y_{lm}(\hat{r}_2) \tag{7.5}$$

where $r_< = \min(r_1, r_2)$ and $r_> = \max(r_1, r_2)$.

Since in LAPW the MT-spheres do not overlap, if $a \neq a'$ we have $r_< = |\mathbf{r}_2^a - \mathbf{r}_1^a|$ and $r_> = |\mathbf{R}_{aa'}|$ and equation 7.5 aplied to the electron-electron interaction in equation 7.4 becomes:

$$\frac{1}{|\mathbf{r}_1^{\,a} - \mathbf{r}_2^{\,a'} + \mathbf{R}_{aa'}|} = \sum_{lm} \frac{4\pi}{2l+1} \frac{|\mathbf{r}_2^{\,a} - \mathbf{r}_1^{\,a}|^l}{R_{aa'}^{l+1}} Y_{lm}^*(\widehat{\mathbf{r}_2^{\,a} - \mathbf{r}_1^{\,a}}) Y_{lm}(\hat{R}_{aa'}) \tag{7.6}$$

Using the Addition Theorem for Solid Harmonics of reference [48] we can write it as:

$$\frac{1}{|\mathbf{r}_1^{\,a} - \mathbf{r}_2^{\,a'} + \mathbf{R}_{aa'}|} = (4\pi)^{\frac{3}{2}} \sum_{lm} \sum_{l'm'} \tilde{g}_{lm,l'm'} \frac{(\mathbf{r}_1^a)^l \, (\mathbf{r}_2^a)^{l'}}{R_{aa'}^{l+l'+1}} Y_{lm}^*(\hat{\mathbf{r}}_1^a) Y_{l'm'}^*(\hat{\mathbf{r}}_2^a) Y_{(l+l')(m+m')}(\hat{R}_{aa'}) \tag{7.7}$$

where, according to [47][1],

$$\begin{aligned}\tilde{g}_{lm,l'm'} =& \frac{(-1)^l\sqrt{[2(l+l')]!}(ll'mm'|l+l',m+m')}{\sqrt{(2l'+1)!(2l+1)!(2l+2l'+1)!}} \\ =&(-1)^l\sqrt{\frac{(l+l'+m+m')!(l+l'-m-m')!}{(2l+1)(2l'+1)[2(l+l')+1](l+m)!(l-m)!(l'+m')!(l'-m')!}}\end{aligned} \tag{7.8}$$

where $(ll'mm'|l+l'm+m')$ is the corresponding Clebsch-Gordan coefficient[2]. Including equation 7.7 into equation 7.4, and using the definition of $\mathbf{R}_{aa'} = \mathbf{R} + \mathbf{r}_a - \mathbf{r}_{a'}$ we have

$$\begin{aligned}v_{\mathcal{L},\mathcal{L}'}(\mathbf{q}) =& \sum_{\mathbf{R}}\sum_{\lambda=0}^{\infty}\sum_{\mu=-\lambda}^{\lambda}\sum_{\lambda_1=0}^{\infty}\sum_{\mu_1=-\lambda_1}^{\lambda_1}\int_{V_{MT}^a}\int_{V_{MT}^{a'}} v_{aNL}(r_1^a)Y_{LM}^*(\hat{r}_1^a)e^{-i\mathbf{q}\cdot\mathbf{R}_{aa'}}(4\pi)^{\frac{3}{2}}\tilde{g}_{\lambda\mu,\lambda_1\mu_1}\times \\ &\frac{(\mathbf{r}_1^a)^{\lambda}(\mathbf{r}_2^a)^{\lambda_1}}{R_{aa'}^{\lambda+\lambda_1+1}}Y_{\lambda\mu}^*(\hat{\mathbf{r}}_1^a)Y_{\lambda_1\mu_1}^*(\hat{\mathbf{r}}_2^a)Y_{(\lambda+\lambda_1)(\mu+\mu_1)}(\hat{R}_{aa'})v_{a'N'L'}(r_2^{a'})Y_{L'M'}(\hat{r}_2^{a'})d^3r_2d^3r_1\end{aligned} \tag{7.9}$$

which can be reorganized as

$$\begin{aligned}v_{\mathcal{L},\mathcal{L}'}(\mathbf{q}) =& \sum_{\lambda=0}^{\infty}\sum_{\mu=-\lambda}^{\lambda}\sum_{\lambda_1=0}^{\infty}\sum_{\mu_1=-\lambda_1}^{\lambda_1}(4\pi)^{\frac{3}{2}}\tilde{g}_{\lambda\mu,\lambda_1\mu_1}\sum_{\mathbf{R}}\frac{e^{-i\mathbf{q}\cdot\mathbf{R}_{aa'}}}{R_{aa'}^{\lambda+\lambda_1+1}}Y_{(\lambda+\lambda_1)(\mu+\mu_1)}(\hat{R}_{aa'})\times \\ &\int_{V_{MT}^a} v_{aNL}(r_1^a)Y_{LM}^*(\hat{r}_1^a)\,(\mathbf{r}_1^a)^{\lambda}\,Y_{\lambda\mu}^*(\hat{\mathbf{r}}_1^a)d^3r_1\times \\ &\int_{V_{MT}^{a'}}(\mathbf{r}_2^a)^{\lambda_1}\,Y_{\lambda_1\mu_1}^*(\hat{\mathbf{r}}_2^a)v_{a'N'L'}(r_2^{a'})Y_{L'M'}(\hat{r}_2^{a'})d^3r_2\end{aligned} \tag{7.10}$$

Defining the structure constants

$$\boxed{\mathbb{S}_{l'm',lm}^{a,a'}(\mathbf{q}) = (4\pi)^{\frac{3}{2}}\tilde{g}_{l'm',lm}\Sigma_{l'+l,m'+m}^{a,a'}(-\vec{q})} \tag{7.11}$$

with

$$\boxed{\Sigma_{\lambda,\mu}^{a,a'}(\mathbf{q}) = \sum_{\mathbf{R}}\frac{e^{i\mathbf{q}\cdot\mathbf{R}_{aa'}}}{R_{aa'}^{(\lambda+1)}}Y_{\lambda\mu}\left(\hat{R}_{aa'}\right)} \tag{7.12}$$

and separating the integrals over the MT-sphere into radial[3] and angular parts we have:

$$\begin{aligned}v_{\mathcal{L},\mathcal{L}'}(\mathbf{q}) =& \sum_{\lambda\mu}\sum_{\lambda_1\mu_1}\mathbb{S}_{\lambda\mu,\lambda_1\mu_1}^{a,a'}(\mathbf{q})\left(\int_0^{R_{MT}^a}(r_1^a)^{\lambda}\,v_{aNL}(r_1^a)\,(r_1^a)^2\,dr_1^a\right)\times \\ &\left(\int Y_{LM}^*(\hat{r}_1^a)Y_{\lambda\mu}^*(\hat{\mathbf{r}}_1^a)d\hat{r}_1^a\right)\times \\ &\left(\int_0^{R_{MT}^{a'}}\left(r_2^{a'}\right)^{\lambda_1}v_{a'N'L'}(r_2^{a'})\left(r_2^{a'}\right)^2dr_2^{a'}\right)\left(\int Y_{\lambda_1\mu_1}^*(\hat{\mathbf{r}}_2^{a'})Y_{L'M'}(\hat{r}_2^{a'})d\hat{r}_2^{a'}\right)\end{aligned} \tag{7.13}$$

To solve the angular integrals we use:

$$Y_{LM}(\hat{r}^a) = Y_{LM}(T_a^{-1}\hat{\mathbf{r}}^a) = T_aY_{LM}(\hat{\mathbf{r}}^a) \tag{7.14}$$

Now using equation 4.8 in [47] we have:

$$T_aY_{LM}(\hat{\mathbf{r}}^a) = \sum_{M_1=-L}^{L}D_{M_1M}^{aL}Y_{LM_1}(\hat{\mathbf{r}}^a) \tag{7.15}$$

together with the orthogonality of the spherical harmonics and the relation $Y_{lm}^* = (-1)^mY_{l-m}$, and defining

[1] The factor $\sqrt{4\pi}$ appearing in the referenced text is taken out in our definition of $\tilde{g}$ to simplify the algebra.

[2] In the special case of $(ll'mm'|l+l',m+m')$ its value is given by (See Appendix C of [41]): $(ll'mm'|l+l',m+m') = \sqrt{\frac{(2l)!(2l')!}{[2(l+l')]!}}\sqrt{\frac{(l+l'+m+m')!(l+l'-m-m')!}{(l+m)!(l-m)!(l'+m')!(l'-m')!}}$ which, when replaced in the second term of equation 7.8 gives the third one.

[3] Since the only difference between $\mathbf{r}^a$ and $\mathbf{r}^a$ is a rotation, we have that $r^a = \mathbf{r}^a$ and use only the first one in the radial integrals

$$\boxed{\langle r^{\lambda}\rangle_{aNL} \equiv \int_0^{R^a_{MT}} (r^a)^{\lambda+2}\, \upsilon_{aNL}(r^a) dr^a} \tag{7.16}$$

equation 7.10 becomes:

$$\begin{aligned} \upsilon_{\mathcal{L},\mathcal{L}'}(\mathbf{q}) = &\sum_{\lambda\mu}\sum_{\lambda_1\mu_1}\sum_{M_1M_2} \mathbb{S}^{a,a'}_{\lambda\mu,\lambda_1\mu_1}(\mathbf{q})\langle r^{\lambda}\rangle_{aNL} \\ &(-1)^{\mu} D^{aL*}_{M_1M}\delta_{L,\lambda}\delta_{M_1,-\mu}\langle r^{\lambda_1}\rangle_{a'N'L'} D^{a'L'}_{M_2M'}\delta_{L',\lambda_1}\delta_{M_2,\mu_1} \end{aligned} \tag{7.17}$$

Leading to the final expression:

$$\boxed{\upsilon_{\mathcal{L},\mathcal{L}'}(\mathbf{q}) = \sum_{\mu\mu_1} \mathbb{S}^{a,a'}_{L\mu,L'\mu_1}(\mathbf{q})\langle r^{L}\rangle_{aNL}(-1)^{\mu}\langle r^{L'}\rangle_{aN'L'} D^{aL*}_{-\mu M} D^{a'L'}_{\mu_1 M'}} \tag{7.18}$$

We still have to analyze the case $a = a'$. In this case, $\mathbf{R}_{aa'} = \mathbf{R}$ and the same equations are obtained with the restriction that $\mathbf{R} \neq 0$. When $\mathbf{R} = 0$ and $a = a'$, the application of equation 7.5 into equation 7.4 leads to:

$$\begin{aligned} \upsilon_{\mathcal{L},\mathcal{L}'}(\mathbf{q}) = \sum_{\lambda} \frac{4\pi}{2\lambda+1} &\left(\iint_0^{R^a_{MT}} \upsilon_{aNLM}(r^a_1) \frac{r^{\lambda}_<}{r^{(\lambda+1)}_>} \upsilon_{aN'L'M'}(r^a_2)\,(r^a_1)^2\, dr^a_1\,(r^a_2)^2\, dr^a_2 \right) \times \\ &\sum_{\mu} \left(\int Y_{\lambda\mu}(\hat{\mathbf{r}}^a_1) Y^*_{LM}(\hat{r}^a_1) d\hat{r}^a_1 \right) \left(\int Y^*_{\lambda\mu}(\hat{\mathbf{r}}^a_2) Y_{L'M'}(\hat{r}^a_2) d\hat{r}^a_2 \right) \end{aligned} \tag{7.19}$$

The double radial integrals in this case can not be separated . Defining:

$$\boxed{\left\langle \begin{array}{c} r^{\lambda}_< \\ r^{\lambda+1}_> \end{array} \right\rangle_{aNL,N'L'} = \iint_0^{R^a_{MT}} \upsilon_{aNL}(r^a_1) \frac{r^{\lambda}_<}{r^{(\lambda+1)}_>} \upsilon_{aN'L'}(r^a_2)\,(r^a_1)^2\, dr^a_1\,(r^a_2)^2\, dr^a_2} \tag{7.20}$$

Using again equations 7.14 and 7.15, equation 7.19 gives:

$$\upsilon_{\mathcal{L},\mathcal{L}'}(\mathbf{q}) = \frac{4\pi}{2L+1} \left\langle \begin{array}{c} r^{L}_< \\ r^{L+1}_> \end{array} \right\rangle_{aNL,N'L} \sum_{M_1M_2} D^{aL*}_{M_1M} D^{aL'}_{M_2M'}\delta_{L,L'}\delta_{M_1,M_2} \tag{7.21}$$

The sum in the second term of eq. 7.21 can be transformed to

$$\sum_{M_1M_2} D^{aL*}_{M_1M} D^{aL'}_{M_2M'}\delta_{L,L'}\delta_{M_1,M_2} = \sum_{M_1} D^{aL}_{M_1M} D^{aL}_{M_1M'} = \delta_{M,M'} \tag{7.22}$$

Where the last equality holds from the orthogonality of the rotation matrices (see [47].

Then, for $a = a'$ we have

$$\begin{aligned} \boxed{\upsilon_{\mathcal{L},\mathcal{L}'}(\mathbf{q}) = &\sum_{M_1M_2} \mathbb{S}^{a,a}_{LM_1,L'M_2}(\mathbf{q})\langle r^{L}\rangle_{aNL}(-1)^{M_1}\langle r^{L'}\rangle_{aN'L'} D^{aL*}_{-M_1M} D^{aL'}_{M_2M'} \\ &+ \frac{4\pi}{2L+1} \left\langle \begin{array}{c} r^{L}_< \\ r^{L+1}_> \end{array} \right\rangle_{aNL,N'L} \delta_{L,L'}\delta_{M,M'}} \end{aligned} \tag{7.23}$$

where

$$\mathbb{S}^{a,a}_{l'm',lm}(\mathbf{q}) = (4\pi)^{\frac{3}{2}} \tilde{g}_{l'm',lm} \Sigma^{a,a}_{l'+l,m'+m}(\mathbf{q}) \tag{7.24}$$

$\tilde{g}_{l'm',lm}$ is defined in equation 7.8 and

$$\Sigma^{a,a}_{\lambda,\mu}(\mathbf{q}) = \sum_{\mathbf{R}\neq 0} \frac{e^{i\mathbf{q}\cdot\mathbf{R}}}{R^{(\lambda+1)}} Y_{\lambda\mu}\left(\hat{R}\right) \tag{7.25}$$

7.2 Case B: Both $\mathbf{r}_1$ and $\mathbf{r}_2$ belong to the interstitial region

In this case, it is better to use expression 7.1, which can be written as:

$$v_{ij}(\mathbf{q}) = \int_V \int_V \left[\tilde{P}_i^{\mathbf{q}}(\mathbf{r}_1)\right]^* \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \tilde{P}_j^{\mathbf{q}}(\mathbf{r}_2) d^3r_2 d^3r_1 \tag{7.26}$$

taking the Fourier expansion of the Coulomb interaction[44].

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \frac{1}{V} \sum_{\mathbf{q}\vec{G}} e^{i(\mathbf{q}+\vec{G})\mathbf{r}_1} \frac{4\pi}{|\mathbf{q}+\vec{G}|^2} e^{-i(\mathbf{q}+\vec{G})\mathbf{r}_2} \tag{7.27}$$

we can rewrite equation 7.26 as:

$$v_{ij}(\mathbf{q}) = \int_V \int_V \left[\tilde{P}_i^{\mathbf{q}}(\mathbf{r}_1)\right]^* \frac{1}{V} \sum_{\vec{G}} e^{i(\mathbf{q}+\vec{G})\mathbf{r}_1} \frac{4\pi}{|\mathbf{q}+\vec{G}|^2} e^{-i(\mathbf{q}+\vec{G})\mathbf{r}_2} \tilde{P}_j^{\mathbf{q}}(\mathbf{r}_2) d^3r_2 d^3r_1 \tag{7.28}$$

which can be reorganized as:

$$v_{ij}(\mathbf{q}) = \sum_{\vec{G}} \left(\frac{1}{\sqrt{V}} \int_V \left[\tilde{P}_i^{\mathbf{q}}(\mathbf{r}_1)\right]^* e^{i(\mathbf{q}+\vec{G})\mathbf{r}_1} d^3r_1 \right) \frac{4\pi}{|\mathbf{q}+\vec{G}|^2} \left(\frac{1}{\sqrt{V}} \int_V e^{-i(\mathbf{q}+\vec{G})\mathbf{r}_2} \tilde{P}_j^{\mathbf{q}}(\mathbf{r}_2) d^3r_2 \right) \tag{7.29}$$

But the two integrals correspond to the matrix elements $\mathcal{W}_{\vec{G}}^i(\mathbf{q})$ defined in 6.25 and 6.26, thus we end up with:

$$\boxed{v_{ij}(\mathbf{q}) = \sum_{\vec{G}} \mathcal{W}_{\vec{G}}^i(\mathbf{q}) \frac{4\pi}{|\mathbf{q}+\vec{G}|^2} \mathcal{W}_{\vec{G}}^{*j}(\mathbf{q})} \tag{7.30}$$

7.3 Case C: Either $\mathbf{r}_1$ or $\mathbf{r}_2$ belong to the interstitial region, the other to a MT-sphere

Starting again from equation 7.2, if we suppose that $\mathbf{r}_1$ is in the interstitial region, and $\mathbf{r}_2$ belongs to the a-atom MT-sphere we can write:

$$v_{i,\mathcal{L}}(\mathbf{q}) = N_c \int_\Omega \int_\Omega \left[\tilde{P}_i^{\mathbf{q}}(\mathbf{r}_1)\right]^* \sum_{\mathbf{R}} \frac{e^{-i\mathbf{q}\cdot\mathbf{R}}}{|\mathbf{r}_1 - \mathbf{r}_2 + \mathbf{R}|} \gamma_{aNLM}^{\mathbf{q}}(\mathbf{r}_2) d^3r_2 d^3r_1 \tag{7.31}$$

Making use of equation 7.27 this equation can be written as

$$v_{i,\mathcal{L}}(\mathbf{q}) = \frac{N_c}{V} \int_\Omega \int_\Omega \left[\tilde{P}_i^{\mathbf{q}}(\mathbf{r}_1)\right]^* \sum_{\vec{q}'} \sum_{\vec{G}'} \sum_{\mathbf{r}_1} \frac{4\pi e^{i(\vec{q}'+\vec{G}')\cdot(\mathbf{r}_1-\mathbf{r}_2+\mathbf{R})}}{\left|\vec{q}'+\vec{G}'\right|^2} e^{-i\mathbf{q}\cdot\mathbf{R}} \gamma_{aNLM}^{\mathbf{q}}(\mathbf{r}_2) d^3r_2 d^3r \tag{7.32}$$

The integrations in the variables $\mathbf{r}_1$ and $\mathbf{r}_2$ can now be separated, giving:

$$\begin{aligned} v_{i,\mathcal{L}}(\mathbf{q}) =& \frac{1}{\Omega} \sum_{\vec{q}'} \sum_{\vec{G}'} \frac{4\pi}{\left|\vec{q}'+\vec{G}'\right|^2} \sum_{\mathbf{R}} e^{-i(\mathbf{q}-\vec{q}')\cdot\mathbf{R}} \left(\int_\Omega \left[\tilde{P}_i^{\mathbf{q}}(\mathbf{r}_1)\right]^* e^{i(\vec{q}'+\vec{G}')\cdot\mathbf{r}_1} d^3r \right) \times \\ & \left(\int_\Omega e^{-i(\vec{q}'+\vec{G}')\cdot\mathbf{r}_2} \gamma_{aNLM}^{\mathbf{q}}(\mathbf{r}_2) d^3r_2 \right) \end{aligned} \tag{7.33}$$

Where we made use of the condition $e^{-i\vec{G}'\cdot\mathbf{R}} = 1$. Furthermore, since we have[11]:

$$\sum_{\mathbf{R}} e^{i\mathbf{q}\cdot\mathbf{R}} = N_c \delta_{\mathbf{q},0} \tag{7.34}$$

we can eliminate the sums over $\mathbf{R}$ and $\vec{q}'$ in equation 7.33 to obtain:

$$\begin{aligned} v_{i,\mathcal{L}}(\mathbf{q}) =& \frac{N_c}{\Omega} \sum_{\vec{G}'} \frac{4\pi}{\left|\mathbf{q}+\vec{G}'\right|^2} \left(\int_\Omega \left[\tilde{P}_i^{\mathbf{q}}(\mathbf{r}_1)\right]^* e^{i(\mathbf{q}+\vec{G}')\cdot\mathbf{r}_1} d^3r_1 \right) \times \\ & \left(\int_\Omega e^{-i(\mathbf{q}+\vec{G}')\cdot\mathbf{r}_2} \gamma_{aNLM}^{\mathbf{q}}(\mathbf{r}_2) d^3r_2 \right) \end{aligned} \tag{7.35}$$

We now solve for the integral on $\mathbf{r}_1$. From equation 6.19, we have:

$$\tilde{P}_i^{\mathbf{q}} \equiv \sum_{\vec{G}} P_{\vec{G}}^{\mathbf{q}} \tilde{S}_{\vec{G},i} \tag{7.36}$$

thus the integral is:

$$\int_\Omega \left[\tilde{P}_i^{\mathbf{q}}(\mathbf{r}_1)\right]^* e^{i(\mathbf{q}+\vec{G}')\cdot\mathbf{r}_1} d^3r_1 = \sum_{\vec{G}} S^*_{\vec{G},i} \int_\Omega \left[P_{\vec{G}}^{\mathbf{q}}(\mathbf{r}_1)\right]^* e^{i(\mathbf{q}+\vec{G}')\cdot\mathbf{r}_1} d^3r_1 \tag{7.37}$$

and we can make use of equation 6.16 and write:

$$\begin{aligned}
\int_\Omega \left[\tilde{P}_i^{\mathbf{q}}(\mathbf{r}_1)\right]^* e^{i(\mathbf{q}+\vec{G}')\cdot\mathbf{r}_1} d^3r &= \frac{1}{\sqrt{V}} \sum_{\vec{G}} S^*_{\vec{G},i} \int_I e^{-i(\mathbf{q}+\vec{G})\cdot\mathbf{r}_1} e^{i(\mathbf{q}+\vec{G}')\cdot\mathbf{r}_1} d^3r_1 \\
&= \frac{1}{\sqrt{V}} \sum_{\vec{G}} S^*_{\vec{G},i} \int_I e^{-i(\vec{G}-\vec{G}')\cdot\mathbf{r}_1} d^3r_1 \\
&= \frac{1}{\sqrt{V}} \sum_{\vec{G}} S^*_{\vec{G},i} \mathcal{I}_{\vec{G}-\vec{G}'} \\
&= \frac{\Omega}{\sqrt{V}} \sum_{\vec{G}} S^*_{\vec{G},i} \mathbb{O}_{\vec{G},\vec{G}'} = \frac{\sqrt{\Omega}}{\sqrt{N_c}} S^*_{\vec{G}',i}
\end{aligned} \tag{7.38}$$

To solve the integral on $\mathbf{r}_2$ we substitute equation 6.9 into the second factor of eq. 7.37:

$$\int_\Omega e^{-i(\mathbf{q}+\vec{G}')\cdot\mathbf{r}_2} \gamma_{aNLM}^{\mathbf{q}}(\mathbf{r}_2) d^3r_2 = \frac{e^{i\mathbf{q}\cdot\mathbf{r}_a}}{\sqrt{N_c}} \int_{V_{MT}^a} e^{-i(\mathbf{q}+\vec{G}')\cdot\mathbf{r}_2} \gamma_{aNLM}(\mathbf{r}_2^a) d^3r_2 \tag{7.39}$$

Taking into account that $\mathbf{r}_2^a = \mathbf{r}_2 - \mathbf{r}_a$ and replacing variables it transforms to:

$$\int_\Omega e^{-i(\mathbf{q}+\vec{G}')\cdot\mathbf{r}_2} \gamma_{aNLM}^{\mathbf{q}}(\mathbf{r}_2) d^3r_2 = \frac{1}{\sqrt{N_c}} \int_{V_{MT}^a} e^{-i(\mathbf{q}+\vec{G}')\cdot\mathbf{r}_2^a} \gamma_{aNLM}(\mathbf{r}_2^a) d^3r_2^a \tag{7.40}$$

Using equation 6.4 to replace γ we get

$$\int_\Omega e^{-i(\mathbf{q}+\vec{G}')\cdot\mathbf{r}_2} \gamma_{aNLM}^{\mathbf{q}}(\mathbf{r}_2) d^3r_2 = \frac{1}{\sqrt{N_c}} \int_{V_{MT}^a} e^{-i(\mathbf{q}+\vec{G}')\cdot\mathbf{r}_2^a} \upsilon_{aNL}(r_2^a) Y_{LM}(\hat{r}_2^a) d^3r_2^a \tag{7.41}$$

In order to further evaluate this integral we expand the plane wave in spherical harmonics and Bessel functions using the Rayleigh expansion (Equation A.40).

Inserting the second equality in equation A.40 into the plane wave of equation 7.41, and taking into account that $\hat{\mathbf{r}}^a = T_a^{-1}\hat{r}^a$ we get:

$$\begin{aligned}
\int_\Omega e^{-i(\mathbf{q}+\vec{G}')\cdot\mathbf{r}_2} \gamma_{aNLM}^{\mathbf{q}}(\mathbf{r}_2) d^3r_2 = \frac{4\pi}{\sqrt{N_c}} \sum_{\lambda\mu} \int_{V_{MT}^a} i^\lambda j_\lambda \left(\left|\vec{G}'+\mathbf{q}\right| r_2^a\right) \times \\
Y_{\lambda\mu}(T_a^{-1}(\widehat{\vec{G}'+\mathbf{q}})) Y^*_{\lambda\mu}(\hat{r}_2^a) \upsilon_{aLM}(r_2^a) Y_{LM}(\hat{r}_2^a) d^3r_2^a
\end{aligned} \tag{7.42}$$

We can now separate the radial and angular integrals, leading to:

$$\begin{aligned}
\int_\Omega e^{-i(\mathbf{q}+\vec{G}')\cdot\mathbf{r}_2} \gamma_{aNLM}^{\mathbf{q}}(\mathbf{r}_2) d^3r_2 = \frac{4\pi}{\sqrt{N_c}} \sum_{\lambda\mu} i^\lambda Y_{\lambda\mu}(T_a^{-1}(\widehat{\vec{G}'+\mathbf{q}})) \times \\
\left(\int_0^{R_{MT}^a} j_\lambda \left(\left|\vec{G}'+\mathbf{q}\right| r_2^a\right) \upsilon_{aNL}(r_2^a) (r_2^a)^2 dr_2^a\right) \times \\
\left(\int Y^*_{\lambda\mu}(\hat{r}_2^a) Y_{LM}(\hat{r}_2^a) d\hat{r}_2^a\right)
\end{aligned} \tag{7.43}$$

Defining

$$\left\langle j_\lambda^{|\vec{G}+\mathbf{q}|} \right\rangle_{aNL} \equiv \int_0^{R_{MT}^a} j_\lambda \left(\left|\vec{G}+\mathbf{q}\right| r^a\right) \upsilon_{aNL}(r^a) (r^a)^2 dr^a \tag{7.44}$$

and taking into account the orthogonality of the spherical harmonics we have:

$$\int_\Omega e^{-i(\mathbf{q}+\vec{G}')\cdot\mathbf{r}_2}\gamma^{\mathbf{q}}_{aNLM}(\mathbf{r}_2)d^3r_2 = \frac{4\pi}{\sqrt{N_c}} i^L Y_{LM}(T_a^{-1}(\widehat{\vec{G}'+\mathbf{q}}))\left\langle j_L^{|\vec{G}'+\mathbf{q}|}\right\rangle_{aLM} \tag{7.45}$$

Finally, inserting equations 7.45 and 7.38 into equation 7.35 we obtain:

$$\boxed{v_{i,\mathcal{L}}(\mathbf{q}) = \frac{(4\pi)^2}{\sqrt{\Omega}}\sum_{\vec{G}'}\frac{1}{\left|\mathbf{q}+\vec{G}'\right|^2} S^*_{\vec{G}',i} i^L Y_{LM}(T_a^{-1}(\widehat{\vec{G}'+\mathbf{q}}))\left\langle j_L^{|\vec{G}'+\mathbf{q}|}\right\rangle_{aLM}} \tag{7.46}$$

7.4 The singularity at the Γ point

We have already obtained a general expression for the Coulomb matrix elements in the general case 7. In the case of $\mathbf{q}=0$ the bare Coulomb potential diverges. It can be easily seen if one makes a plane wave expansion:

$$v_{\vec{G}\vec{G}'}(\mathbf{q}) = \frac{4\pi}{|\mathbf{q}+\vec{G}|^2}\delta_{\vec{G}\vec{G}'} \tag{7.47}$$

with the advantage that one can clearly separate the divergence from the rest by writing:

$$v_{\vec{G}\vec{G}'}(\mathbf{q}\to 0) = \lim_{\mathbf{q}\to 0}\left(\frac{1}{|\mathbf{q}|^2}\right) v^s_{\vec{G}\vec{G}'} + \tilde{v}_{\vec{G}\vec{G}'} \tag{7.48}$$

with

$$\begin{aligned} v^s_{\vec{G}\vec{G}'} =& 4\pi\delta_{\vec{G}\vec{G}'}\delta_{\vec{G}0} \\ \tilde{v}_{\vec{G}\vec{G}'} =& \frac{4\pi}{|\vec{G}|^2}\delta_{\vec{G}\vec{G}'}(1-\delta_{\vec{G}0}) \end{aligned} \tag{7.49}$$

The same separation can be done when expanding the Coulomb matrix in the mixed basis, and write:

$$v_{ij}(\mathbf{q}\to 0) = \lim_{\mathbf{q}\to 0}\left(\frac{1}{|\mathbf{q}|^2}\right) v^s_{ij} + \tilde{v}_{ij} \tag{7.50}$$

the singular term can easily be obtained from 7.49 transforming to the mixed basis using Eq. 6.21

$$v^s_{ij} = 4\pi \mathcal{W}^i_0(0)\left[\mathcal{W}^j_0(0)\right]^* \tag{7.51}$$

We still need to obtain the coulomb matrix elements without the divergent terms. This is trivial in the cases B and C (sections 7.2 and 7.3), since in both cases the Coulomb interaction is expanded in plane waves, it suffices with taking only terms with $\vec{G}\neq 0$ in eqs. 7.30 and 7.46. The interaction between two functions within the spheres is more complicated, and what we analyze in the following sections.

7.4.1 Subtracting the $\mathbf{q}=0$ component of the wave functions

The first thing to do is eliminate the fourier component corresponding to $\mathbf{q}=0$ from the basis functions: From eq. 6.9, for $\mathbf{q}=0$ the basis functions are:

$$\gamma^0_{aNLM}(\mathbf{r}) = \frac{1}{\sqrt{N_c}}\sum_{\mathbf{R}}\gamma_{aNLM}(\mathbf{r}^{\,a}). \tag{7.52}$$

To extract the $\mathbf{q}=0$ component we have to calculate the integral;

$$\int_V \gamma^0_{aNLM}(\mathbf{r})\frac{1}{\sqrt{V}}d^3r = \frac{1}{N_c\sqrt{\Omega}}\sum_{\mathbf{R}}\int_\Omega \gamma_{aNLM}(\mathbf{r}^{\,a})d^3r^{\,a} = \frac{1}{\sqrt{\Omega}}\int_\Omega \gamma_{aNLM}(\mathbf{r}^{\,a})d^3r^{\,a} \tag{7.53}$$

using expression 6.4 we have:

$$\int_\Omega \gamma_{aNLM}(\mathbf{r}^{\,a})d^3r^{\,a} = \int_\Omega v_{NL}(r^a)Y_{LM}(\hat{r}^a)d^3r^{\,a} = \sqrt{4\pi}\int_0^{R^a_{MT}} v_{NL}(r)r^2dr\delta_{L,0} = \sqrt{4\pi}\langle r^L\rangle_{aN0}\delta_{L,0} \tag{7.54}$$

where, for the last equality we have used the definition 7.16.

We can then define the functions $\tilde{\gamma}^0_{aNLM}$, which have no $\mathbf{q}=0$ component as:

$$\tilde{\gamma}^0_{aNLM}(\mathbf{r}) = \frac{1}{\sqrt{N_c}}\left\{\sum_{\mathbf{R}} \upsilon_{NL}(r^a)Y_{LM}(\hat{r}^a)\Theta(R^a_{MT}-r^a) - \frac{\sqrt{4\pi}\langle r^L\rangle_{aNL}}{\Omega}\delta_{L,0}\right\}. \tag{7.55}$$

In a more useful way, one can write it as:

$$\tilde{\gamma}^0_{aNLM}(\mathbf{r}) = \begin{cases} \frac{1}{\sqrt{N_c}}\left\{\sum_{\mathbf{R}}\left(\upsilon_{NL}(r^a) - \frac{4\pi}{\Omega}\langle r^L\rangle_{aNL}\delta_{L,0}\right)Y_{LM}(\hat{r}^a)\right\} & \mathbf{r}\in MT_a \\ -\frac{4\pi}{\sqrt{N_c}\Omega}\langle r^L\rangle_{aNL}\left\{\sum_{\mathbf{R}} Y_{LM}(\hat{r}^{a'})\delta_{L,0}\right\} & \mathbf{r}\in MT_{a'\neq a} \\ -\frac{\sqrt{4\pi}}{\sqrt{N_c}\Omega}\langle r^L\rangle_{aNL} & \mathbf{r}\in I \end{cases} \tag{7.56}$$

For calculating the matrix elements $\upsilon_{\mathcal{L},\mathcal{L}'}$ we have to analyze separately the different cases as follows:

7.4.2 Step by step: The different terms in the matrix elements

In this subsection we are not doing a detailed deduction of the result. Since the procedure is the same as in chapter 7 we just use them and refer the reader to this chapter for more details. A supraindex is used to indicate each term, the q-dependence is suppressed since this is valid only for the $\mathbf{q}=0$ point.

7.4.2.1 Case 1: $\mathbf{r}_1 \in a$ and $\mathbf{r}_2 \in a'$

In this case we can take equation 7.23 with the modified function. The first term is straightforward, for the second, we have to calculate:

$$\begin{aligned}
&\iint_0^{R^a_{MT}}\left(\upsilon_{aNL}(r^a_1) - \frac{4\pi}{\Omega}\langle r^L\rangle_{aNL}\delta_{L,0}\right)\frac{r^L_<}{r^{(L+1)}_>}\left(\upsilon_{aN'L}(r^a_2) - \frac{4\pi}{\Omega}\langle r^L\rangle_{aN'L}\delta_{L,0}\right)(r^a_1)^2\,dr^a_1\,(r^a_2)^2\,dr^a_2 = \\
&\qquad \iint_0^{R^a_{MT}}\upsilon_{aNL}(r^a_1)\frac{r^L_<}{r^{(L+1)}_>}\upsilon_{aN'L}(r^a_2)\,(r^a_1)^2\,dr^a_1\,(r^a_2)^2\,dr^a_2 \\
&\qquad -\frac{4\pi}{\Omega}\langle r^L\rangle_{aNL}\delta_{L,0}\iint_0^{R^a_{MT}}\frac{1}{r_>}\upsilon_{aN'L}(r^a_2)\,(r^a_1)^2\,dr^a_1\,(r^a_2)^2\,dr^a_2 \\
&\qquad -\frac{4\pi}{\Omega}\langle r^L\rangle_{aN'L}\delta_{L,0}\iint_0^{R^a_{MT}}\frac{1}{r_>}\upsilon_{aNL}(r^a_1)\,(r^a_1)^2\,dr^a_1\,(r^a_2)^2\,dr^a_2 \\
&\qquad +\left(\frac{4\pi}{\Omega}\right)^2\langle r^L\rangle_{aN'L}\langle r^L\rangle_{aNL}\delta_{L,0}\iint_0^{R^a_{MT}}\frac{1}{r_>}(r^a_1)^2\,dr^a_1\,(r^a_2)^2\,dr^a_2
\end{aligned} \tag{7.57}$$

According to eq. 7.20 the first term on the right is just the definition of $\left\langle \begin{smallmatrix} r^L_< \\ r^{L+1}_> \end{smallmatrix} \right\rangle_{aNL,N'L}$. For the others we have:

$$\begin{aligned}
\iint_0^{R^a_{MT}}\frac{1}{r_>}\upsilon_{aNL}(r^a_2)\,(r^a_1)^2\,dr^a_1\,(r^a_2)^2\,dr^a_2 &= \int_0^{R^a_{MT}}\upsilon_{aNL}(r_2)\left[\frac{1}{r_2}\int_0^{r_2}(r_1)^2\,dr_1 + \int_{r_2}^{R^a_{MT}} r_1 dr_1\right](r_2)^2\,dr_2 \\
&= \int_0^{R^a_{MT}}\upsilon_{aNL}(r_2)\left[\frac{1}{r_2}\frac{1}{3}{r_2}^3 + \frac{1}{2}\left({R^a_{MT}}^2 - {r_2}^2\right)\right](r_2)^2\,dr_2 \\
&= -\frac{1}{6}\int_0^{R^a_{MT}}\upsilon_{aNL}(r_2){r_2}^4 dr_2 + \frac{1}{2}{R^a_{MT}}^2\int_0^{R^a_{MT}}\upsilon_{aNL}(r_2)\,(r_2)^2\,dr_2 \\
&= \frac{1}{2}{R^a_{MT}}^2\langle r^L\rangle_{aNL} - \frac{1}{6}\langle r^{L+2}\rangle_{aNL}
\end{aligned} \tag{7.58}$$

where in the last line we took into account that $L=0$ and used the definition of eq. 7.16. For the fourth term we can replace υ_{aNL} by 1 in eq. 7.58 to obtain:

$$\iint_0^{R^a_{MT}}\frac{1}{r_>}(r^a_1)^2\,dr^a_1\,(r^a_2)^2\,dr^a_2 = \frac{2}{15}{R^a_{MT}}^5 \tag{7.59}$$

Using these results we have:

$$\begin{aligned}\tilde{v}^{(1)}_{\mathcal{L},\mathcal{L}'} =&\langle r^L\rangle_{aNL}\langle r^{L'}\rangle_{a'N'L'}\left(1-\frac{V^a_{MT}}{\Omega}\delta_{L,0}\right)\left(1-\frac{V^{a'}_{MT}}{\Omega}\delta_{L',0}\right)\sum_{M_1M_2}\mathbb{S}^{a,a'}_{LM_1,L'M_2}(-1)^{M_1}D^{aL*}_{-M_1M}D^{a'L'}_{M_2M'}\\
&+\frac{4\pi}{2L+1}\left\langle\begin{array}{c} r^L_< \\ r^{L+1}_>\end{array}\right\rangle_{aNL,N'L}\delta_{a,a'}\delta_{L,L'}\delta_{M,M'}\\
&-\frac{(4\pi)^2}{\Omega}\left[\langle r^L\rangle_{aNL}\langle r^L\rangle_{aN'L}\left({R^a_{MT}}^2-\frac{8\pi}{15\Omega}{R^a_{MT}}^5\right)-\frac{1}{6}\left(\langle r^L\rangle_{aNL}\langle r^{L+2}\rangle_{aN'L}+\langle r^L\rangle_{aN'L}\langle r^{L+2}\rangle_{aNL}\right)\right]\\
&\delta_{L,0}\delta_{a,a'}\delta_{L,L'}\delta_{M,M'}\end{aligned} \tag{7.60}$$

where $V^a_{MT}=\frac{4\pi}{3}{R^a_{MT}}^3$ is the volume of the MT-Sphere surrounding atom a.

7.4.2.2 Case 2: $\mathbf{r}_1\in a$ and $\mathbf{r}_2\in a''\neq a'$

In this case, for the wave functions we have:

$$\begin{aligned}\tilde{\gamma}^0_{\mathcal{L}}(\mathbf{r}_1)=&\frac{1}{\sqrt{N_c}}\left\{\sum_{\mathbf{R}}\left(\upsilon_{NL}(r^a_1)-\frac{4\pi}{\Omega}\langle r^L\rangle_{aNL}\delta_{L,0}\right)Y_{LM}(\hat{r}^a_1)\right\}\\
\tilde{\gamma}^0_{\mathcal{L}'}(\mathbf{r}_2)=&-\frac{4\pi}{\sqrt{N_c}\Omega}\langle r^{L'}\rangle_{a'N'L'}\left\{\sum_{\mathbf{R}}Y_{L'M'}(\hat{r}^{a''}_2)\delta_{L',0}\right\}\end{aligned} \tag{7.61}$$

We can follow the same steps as in case A of subsection 7, and for the particular case of $a''=a$ the results of equation 7.58 to obtain:

$$\begin{aligned}\tilde{v}^{(2)}_{\mathcal{L},\mathcal{L}'} =&\langle r^L\rangle_{aNL}\langle r^{L'}\rangle_{a'N'L'}\left(1-\frac{V^a_{MT}}{\Omega}\delta_{L,0}\right)\left(-\frac{V^{a''}_{MT}}{\Omega}\delta_{L',0}\right)\sum_{M_1M_2}\mathbb{S}^{a,a''}_{LM_1,L'M_2}(-1)^{M_1}D^{aL*}_{-M_1M}D^{a''L'}_{M_2M'}\\
&-\frac{(4\pi)^2}{\Omega}\langle r^{L'}\rangle_{a'N'L'}\left[\langle r^L\rangle_{aNL}\left({R^a_{MT}}^2-\frac{8\pi}{15\Omega}{R^a_{MT}}^5\right)-\frac{1}{6}\langle r^{L+2}\rangle_{aNL}\right]\delta_{L',0}\delta_{a,a''}\delta_{L,L'}\delta_{M,M'}\end{aligned} \tag{7.62}$$

7.4.2.3 Case 3: $\mathbf{r}_1\in a''\neq a$ and $\mathbf{r}_2\in a'$

Just by inverting the indexes and taking complex conjugate of equation 7.62 we have:

$$\begin{aligned}\tilde{v}^{(3)}_{\mathcal{L},\mathcal{L}'} =&\langle r^L\rangle_{aNL}\langle r^{L'}\rangle_{a'N'L'}\left(1-\frac{V^{a'}_{MT}}{\Omega}\delta_{L',0}\right)\left(-\frac{V^{a''}_{MT}}{\Omega}\delta_{L,0}\right)\sum_{M_1M_2}\mathbb{S}^{a'',a'}_{LM_1,L'M_2}(-1)^{M_1}D^{a''L*}_{-M_1M}D^{a'L'}_{M_2M'}\\
&-\frac{(4\pi)^2}{\Omega}\langle r^L\rangle_{aNL}\left[\langle r^{L'}\rangle_{a'N'L'}\left({R^{a'}_{MT}}^2-\frac{8\pi}{15\Omega}{R^{a'}_{MT}}^5\right)-\frac{1}{6}\langle r^{L'+2}\rangle_{a'N'L'}\right]\delta_{L,0}\delta_{a',a''}\delta_{L,L'}\delta_{M,M'}\end{aligned} \tag{7.63}$$

7.4.2.4 Case 4: $\mathbf{r}_1\in a''\neq a$ and $\mathbf{r}_2\in a'''\neq a'$

In this case, for the wave functions we have:

$$\begin{aligned}\tilde{\gamma}^0_{\mathcal{L}}(\mathbf{r}_1)=&-\frac{4\pi}{\sqrt{N_c}\Omega}\langle r^L\rangle_{aNL}\left\{\sum_{\mathbf{R}}Y_{LM}(\hat{r}^{a''}_1)\delta_{L,0}\right\}\\
\tilde{\gamma}^0_{\mathcal{L}'}(\mathbf{r}_2)=&-\frac{4\pi}{\sqrt{N_c}\Omega}\langle r^{L'}\rangle_{a'N'L'}\left\{\sum_{\mathbf{R}}Y_{L'M'}(\hat{r}^{a'''}_2)\delta_{L',0}\right\}\end{aligned} \tag{7.64}$$

Again we can follow the same steps as in case A of subsection 7, and for the particular case of $a''=a'''$ the results of equation 7.59 to obtain:

$$\begin{aligned}\tilde{v}^{(4)}_{\mathcal{L},\mathcal{L}'} =&\langle r^L\rangle_{aNL}\langle r^{L'}\rangle_{a'N'L'}\frac{V^{a'''}_{MT}}{\Omega}\delta_{L',0}\frac{V^{a''}_{MT}}{\Omega}\delta_{L,0}\sum_{M_1M_2}\mathbb{S}^{a'',a'''}_{LM_1,L'M_2}(-1)^{M_1}D^{a''L*}_{-M_1M}D^{a'''L'}_{M_2M'}\\
&+\frac{(4\pi)^2}{\Omega}\langle r^L\rangle_{aNL}\langle r^{L'}\rangle_{a'N'L'}\frac{8\pi}{15\Omega}{R^{a''}_{MT}}^5\delta_{L,0}\delta_{a''',a''}\delta_{L,L'}\delta_{M,M'}\end{aligned} \tag{7.65}$$

7.4.2.5 Case 5: $\mathbf{r}_1 \in a''$ and $\mathbf{r}_2 \in I$

In this case the wave functions are:

$$\begin{aligned}\tilde{\gamma}^0_{\mathcal{L}}(\mathbf{r}_1) =& \frac{1}{\sqrt{N_c}}\left\{\sum_{\mathbf{R}}\left(\upsilon_{NL}(r_1^{a''})\delta_{a'',a} - \frac{4\pi}{\Omega}\langle r^L\rangle_{aNL}\delta_{L,0}\right)Y_{LM}(\hat{r}_1^{a''})\right\}\\ \tilde{\gamma}^0_{\mathcal{L}'}(\mathbf{r}_2) =& -\frac{\sqrt{4\pi}}{\sqrt{N_c}\Omega}\langle r^{L'}\rangle_{a'N'L'}\end{aligned} \tag{7.66}$$

Following the procedure of case C in subsection 7 we have to expand in planewaves. As in equation 7.35 we have

$$\tilde{v}^{(5)}_{\mathcal{L},\mathcal{L}'} = \frac{N_c}{\Omega}\sum_{\vec{G}}\frac{4\pi}{\left|\vec{G}\right|^2}\left(\int_{MT_{a''}}\left[\tilde{\gamma}^0_{\mathcal{L}}(\mathbf{r}_1)\right]^* e^{i\vec{G}\cdot\mathbf{r}_1}d^3r_1\right)\left(\int_I e^{-i\vec{G}\cdot\mathbf{r}_2}\tilde{\gamma}^0_{\mathcal{L}'}(\mathbf{r}_2)d^3r_2\right) \tag{7.67}$$

The second integral on the righthand side is just:

$$\int_I e^{-i\vec{G}\cdot\mathbf{r}_2}\tilde{\gamma}^0_{\mathcal{L}'}(\mathbf{r}_2)d^3r_2 = -\frac{\sqrt{4\pi}}{\sqrt{N_c}\Omega}\langle r^{L'}\rangle_{a'N'L'}\mathcal{I}^*_{\vec{G}} \tag{7.68}$$

By writing:

$$\tilde{\gamma}^0_{\mathcal{L}}(\mathbf{r}_1) = \gamma^0_{\mathcal{L}}(\mathbf{r}_1)\delta_{a'',a} - \frac{1}{\sqrt{N_c}}\sum_{\mathbf{R}}\left(\frac{4\pi}{\Omega}\langle r^L\rangle_{aNL}\delta_{L,0}\right)Y_{LM}(\hat{r}_1^{a''}) \tag{7.69}$$

The first integral can be separated in two terms:

$$\int_\Omega\left[\tilde{\gamma}^0_{\mathcal{L}}(\mathbf{r}_1)\right]^* e^{i\vec{G}\cdot\mathbf{r}_1}d^3r_1 = \int_{MT_{a''}}\left[\gamma^0_{\mathcal{L}}(\mathbf{r}_1)\right]^* e^{i\vec{G}\cdot\mathbf{r}_1}d^3r_1\delta_{a'',a} - \frac{1}{\sqrt{N_c}}\frac{\sqrt{4\pi}}{\Omega}\langle r^L\rangle_{aNL}\delta_{L,0}\int_{MT_{a''}} e^{i\vec{G}\cdot\mathbf{r}_1}d^3r_1 \tag{7.70}$$

The first term is just the definition of $\mathcal{W}^{\mathcal{L}}_{\vec{G}}$ according to equation 6.21. Let's define:

$$\bar{\mathcal{I}}^a_{\vec{G}} = \int_{MT_a} e^{i\vec{G}\cdot\mathbf{r}_1}d^3r_1 \tag{7.71}$$

Then, equation 7.70 can be written as:

$$\int_\Omega\left[\tilde{\gamma}^0_{\mathcal{L}}(\mathbf{r}_1)\right]^* e^{i\vec{G}\cdot\mathbf{r}_1}d^3r_1 = \mathcal{W}^{\mathcal{L}}_{\vec{G}}\delta_{a'',a} - \frac{1}{\sqrt{N_c}}\frac{\sqrt{4\pi}}{\Omega}\langle r^L\rangle_{aNL}\bar{\mathcal{I}}^{a''}_{\vec{G}}\delta_{L,0} \tag{7.72}$$

Inserting eqs. 7.68 and 7.72 into eq. 7.67 we have:

$$\tilde{v}^{(5)}_{\mathcal{L},\mathcal{L}'} = -\frac{(4\pi)^{\frac{3}{2}}}{\Omega^2}\langle r^{L'}\rangle_{a'N'L'}\delta_{L',0}\left[\delta_{a'',a}\sum_{\vec{G}}\mathcal{W}^{\mathcal{L}}_{\vec{G}}\frac{1}{|\vec{G}|^2}\mathcal{I}^*_{\vec{G}} - \frac{(4\pi)^{\frac{1}{2}}}{\Omega^2}\langle r^L\rangle_{aNL}\delta_{L,0}\sum_{\vec{G}}\frac{\bar{\mathcal{I}}^{a''}_{\vec{G}}\mathcal{I}^*_{\vec{G}}}{|\vec{G}|^2}\right] \tag{7.73}$$

7.4.2.6 Case 6: $\mathbf{r}_1 \in I$ and $\mathbf{r}_2 \in a''$

Following the same steps as those used to obtain equation 7.73 we obtain:

$$\tilde{v}^{(6)}_{\mathcal{L},\mathcal{L}'} = -\frac{(4\pi)^{\frac{3}{2}}}{\Omega}\langle r^L\rangle_{aNL}\delta_{L,0}\left[\delta_{a'',a'}\sum_{\vec{G}}\mathcal{W}^{\mathcal{L}'*}_{\vec{G}}\frac{1}{|\vec{G}|^2}\mathcal{I}_{\vec{G}} - \frac{(4\pi)^{\frac{1}{2}}}{\Omega^2}\langle r^{L'}\rangle_{a'N'L'}\delta_{L,0}\sum_{\vec{G}}\frac{\left(\bar{\mathcal{I}}^{a''}_{\vec{G}}\right)^*\mathcal{I}_{\vec{G}}}{|\vec{G}|^2}\right] \tag{7.74}$$

7.4.2.7 Case 7: $\mathbf{r}_1, \mathbf{r}_2 \in I$

In this case the wave functions are:

$$\begin{aligned}\tilde{\gamma}^0_{\mathcal{L}}(\mathbf{r}_1) &= -\frac{\sqrt{4\pi}}{\sqrt{N_c}\Omega}\langle r^L\rangle_{aNL}\\ \tilde{\gamma}^0_{\mathcal{L}'}(\mathbf{r}_2) &= -\frac{\sqrt{4\pi}}{\sqrt{N_c}\Omega}\langle r^{L'}\rangle_{a'N'L'}\end{aligned} \tag{7.75}$$

Following the procedure of case B in subsection 7 we have to expand in planewaves. As in equation 7.29 we have

$$\tilde{v}^{(7)}_{\mathcal{L},\mathcal{L}'} = \frac{4\pi}{\Omega^2}\langle r^L\rangle_{aNL}\langle r^{L'}\rangle_{a'N'L'}\sum_{\vec{G}}\left(\frac{1}{\sqrt{V}}\int_I e^{i\vec{G}\cdot\mathbf{r}_1}d^3r_1\right)\frac{4\pi}{|\vec{G}|^2}\left(\frac{1}{\sqrt{V}}\int_I e^{-i\vec{G}\cdot\mathbf{r}_2}d^3r_2\right) \tag{7.76}$$

Using the diefinition 6.16 we obtain:

$$\tilde{v}^{(7)}_{\mathcal{L},\mathcal{L}'} = \frac{(4\pi)^2}{\Omega^3}\langle r^L\rangle_{aNL}\delta_{L,0}\langle r^{L'}\rangle_{a'N'L'}\delta_{L',0}\sum_{\vec{G}}\frac{|\mathcal{I}_{\vec{G}}|^2}{|\vec{G}|^2} \tag{7.77}$$

7.4.3 Final expression

To obtain the final expression we sum up all the terms (Eqs. 7.60, 7.62, 7.64, 7.65, 7.73, 7.74 and 7.77), taking into account that eqs. 7.62, 7.64, 7.65, 7.73 and 7.74 have to be summed over all the atoms in the unit cell, we get:

$$\begin{aligned}\tilde{v}_{\mathcal{L},\mathcal{L}'} =&\langle r^L\rangle_{aNL}\langle r^{L'}\rangle_{a'N'L'}\sum_{M_1M_2}\mathbb{S}^{a,a'}_{LM_1,L'M_2}(-1)^{M_1}D^{aL*}_{-M_1M}D^{a'L'}_{M_2M'}\\
&+\frac{4\pi}{2L+1}\left\langle\begin{matrix} r^L_< \\ r^{L+1}_>\end{matrix}\right\rangle_{aNL,N'L}\delta_{a,a'}\delta_{L,L'}\delta_{M,M'}\\
&-\delta_{L,0}\Bigg[\langle r^L\rangle_{aNL}\langle r^{L'}\rangle_{a'N'L'}\sum_{a''}\frac{V^{a''}_{MT}}{\Omega}\sum_{M_1M_2}\mathbb{S}^{a'',a'}_{LM_1,L'M_2}(-1)^{M_1}D^{a''L*}_{-M_1M}D^{a'L'}_{M_2M'}\\
&-\frac{(4\pi)^{\frac{3}{2}}}{\Omega^2}\langle r^L\rangle_{aNL}\sum_{\vec{G}}\mathcal{W}^{\mathcal{L}'*}_{\vec{G}}\frac{1}{|\vec{G}|^2}\mathcal{I}_{\vec{G}}\Bigg]\\
&-\delta_{L',0}\Bigg[\langle r^L\rangle_{aNL}\langle r^{L'}\rangle_{a'N'L'}\sum_{a''}\frac{V^{a''}_{MT}}{\Omega}\sum_{M_1M_2}\mathbb{S}^{a,a''}_{LM_1,L'M_2}(-1)^{M_1}D^{aL*}_{-M_1M}D^{a''L'}_{M_2M'}\\
&-\frac{(4\pi)^{\frac{3}{2}}}{\Omega^2}\langle r^{L'}\rangle_{a'N'L'}\sum_{\vec{G}}\mathcal{W}^{\mathcal{L}}_{\vec{G}}\frac{1}{|\vec{G}|^2}\mathcal{I}^*_{\vec{G}}\Bigg]\\
&+\delta_{L',0}\delta_{L,0}\Bigg\{\langle r^L\rangle_{aNL}\langle r^{L'}\rangle_{a'N'L'}\sum_{a'',a'''}\frac{V^{a''}_{MT}V^{a'''}_{MT}}{\Omega^2}\sum_{M_1M_2}\mathbb{S}^{a'',a'''}_{LM_1,L'M_2}(-1)^{M_1}D^{a''L*}_{-M_1M}D^{a'''L'}_{M_2M'}\\
&-\frac{(4\pi)^2}{\Omega}\Bigg[\langle r^L\rangle_{aNL}\langle r^L\rangle_{aN'L}\frac{1}{2}\left({R^a_{MT}}^2+{R^{a'}_{MT}}^2\right)-\frac{1}{6}(\langle r^L\rangle_{aNL}\langle r^{L+2}\rangle_{aN'L}\\
&+\langle r^L\rangle_{aN'L}\langle r^{L+2}\rangle_{aNL})\Bigg]+\frac{(4\pi)^2}{\Omega}\langle r^L\rangle_{aNL}\langle r^{L'}\rangle_{a'N'L'}\frac{8\pi}{15\Omega}\sum_{a''}{R^{a''}_{MT}}^5\\
&+\frac{(4\pi)^2}{\Omega^3}\langle r^L\rangle_{aNL}\langle r^{L'}\rangle_{a'N'L'}\sum_{\vec{G}}\frac{1}{|\vec{G}|^2}\left[|\mathcal{I}_{\vec{G}}|^2+\sum_{a''}\left(\bar{\mathcal{I}}^{a''}_{\vec{G}}\mathcal{I}^*_{\vec{G}}+\left(\bar{\mathcal{I}}^{a''}_{\vec{G}}\right)^*\mathcal{I}_{\vec{G}}\right)\right]\Bigg\}\end{aligned} \tag{7.78}$$

From equations 6.12 and 6.13 it is obvious that:

$$\sum_a\bar{\mathcal{I}}^a_{\vec{G}} = \Omega\delta_{\vec{G},0}-\mathcal{I}_{\vec{G}} \tag{7.79}$$

Since in all the sums, the terms $\vec{G}=0$ is discarded we have:

$$\sum_{\vec{G}}\frac{1}{|\vec{G}|^2}\left[|\mathcal{I}_{\vec{G}}|^2+\sum_{a''}\left(\bar{\mathcal{I}}^{a''}_{\vec{G}}\mathcal{I}^*_{\vec{G}}+\left(\bar{\mathcal{I}}^{a''}_{\vec{G}}\right)^*\mathcal{I}_{\vec{G}}\right)\right] = -\sum_{\vec{G}}\frac{|\mathcal{I}_{\vec{G}}|^2}{|\vec{G}|^2} \tag{7.80}$$

Furthermore, taking the case $L' \neq 0$ and $L = 0$ the second term is just the interaction of the function with L' with a constant background, expanding the Coulomb potential in planewaves and taking into account that atomic functions with $L \neq 0$ are orthogonal with a constant function. Since v is diagonal in planewaves, this term is identically zero. Thus we have:

$$\begin{aligned}
\tilde{v}_{\mathcal{L},\mathcal{L}'} =& \langle r^L \rangle_{aNL} \langle r^{L'} \rangle_{a'N'L'} \sum_{M_1 M_2} \mathbb{S}^{a,a'}_{LM_1,L'M_2} (-1)^{M_1} D^{aL*}_{-M_1 M} D^{a'L'}_{M_2 M'} \\
&+ \frac{4\pi}{2L+1} \left\langle \begin{array}{c} r_<^L \\ r_>^{L+1} \end{array} \right\rangle_{aNL,N'L} \delta_{a,a'} \delta_{L,L'} \delta_{M,M'} \\
&- \delta_{L,0}\delta_{L',0} \Bigg\{ \langle r^L \rangle_{aNL} \langle r^{L'} \rangle_{a'N'L'} \sum_{a''} \frac{V^{a''}_{MT}}{\Omega} \sum_{M_1 M_2} \mathbb{S}^{a'',a'}_{LM_1,L'M_2} (-1)^{M_1} D^{a''L*}_{-M_1 M} D^{a'L'}_{M_2 M'} \\
&- \frac{(4\pi)^{\frac{3}{2}}}{\Omega^2} \langle r^L \rangle_{aNL} \sum_{\vec{G}} \mathcal{W}^{\mathcal{L}'*}_{\vec{G}} \frac{1}{|\vec{G}|^2} \mathcal{I}_{\vec{G}} \\
&+ \langle r^L \rangle_{aNL} \langle r^{L'} \rangle_{a'N'L'} \sum_{a''} \frac{V^{a''}_{MT}}{\Omega} \sum_{M_1 M_2} \mathbb{S}^{a,a''}_{LM_1,L'M_2} (-1)^{M_1} D^{aL*}_{-M_1 M} D^{a''L'}_{M_2 M'} \\
&- \frac{(4\pi)^{\frac{3}{2}}}{\Omega^2} \langle r^{L'} \rangle_{a'N'L'} \sum_{\vec{G}} \mathcal{W}^{\mathcal{L}}_{\vec{G}} \frac{1}{|\vec{G}|^2} \mathcal{I}^*_{\vec{G}} \\
&- \langle r^L \rangle_{aNL} \langle r^{L'} \rangle_{a'N'L'} \sum_{a'',a'''} \frac{V^{a''}_{MT} V^{a'''}_{MT}}{\Omega^2} \sum_{M_1 M_2} \mathbb{S}^{a'',a'''}_{LM_1,L'M_2} (-1)^{M_1} D^{a''L*}_{-M_1 M} D^{a'''L'}_{M_2 M'} \\
&+ \frac{(4\pi)^2}{\Omega} \Bigg[\langle r^L \rangle_{aNL} \langle r^L \rangle_{aN'L} \frac{1}{2} \left({R^a_{MT}}^2 + {R^{a'}_{MT}}^2 \right) - \frac{1}{6} (\langle r^L \rangle_{aNL} \langle r^{L+2} \rangle_{aN'L} \\
&+ \langle r^L \rangle_{aN'L} \langle r^{L+2} \rangle_{aNL}) \Bigg] - \frac{(4\pi)^2}{\Omega} \langle r^L \rangle_{aNL} \langle r^{L'} \rangle_{a'N'L'} \frac{8\pi}{15\Omega} \sum_{a''} {R^{a''}_{MT}}^5 \\
&- \frac{(4\pi)^2}{\Omega^3} \langle r^L \rangle_{aNL} \langle r^{L'} \rangle_{a'N'L'} \sum_{\vec{G}} \frac{|\mathcal{I}_{\vec{G}}|^2}{|\vec{G}|^2} \Bigg\}
\end{aligned} \tag{7.81}$$

Now we can use the fact that for $L = 0$ the rotation matrices are just the identity to further simplify the expression, and reordering a little bit...

$$\begin{aligned}
\tilde{v}_{\mathcal{L},\mathcal{L}'} =& \langle r^L \rangle_{aNL} \langle r^{L'} \rangle_{a'N'L'} \Bigg\{ \sum_{M_1 M_2} \mathbb{S}^{a,a'}_{LM_1,L'M_2} (-1)^{M_1} D^{aL*}_{-M_1 M} D^{a'L'}_{M_2 M'} \\
&- \delta_{L,0}\delta_{L',0} \Bigg[\sum_{a''} \frac{V^{a''}_{MT}}{\Omega} \mathbb{S}^{a'',a'}_{LM,L'M'} + \sum_{a''} \frac{V^{a''}_{MT}}{\Omega} \mathbb{S}^{a,a''}_{LM,L'M'} - \sum_{a'',a'''} \frac{V^{a''}_{MT} V^{a'''}_{MT}}{\Omega^2} \mathbb{S}^{a'',a'''}_{LM,L'M'} \\
&- \frac{(4\pi)^2}{\Omega^2} \frac{2}{5} \sum_{a''} V^{a''}_{MT} {R^{a''}_{MT}}^2 + \frac{(4\pi)^2}{\Omega} \frac{1}{2} \left({R^a_{MT}}^2 + {R^{a'}_{MT}}^2 \right) - \frac{(4\pi)^2}{\Omega^3} \sum_{\vec{G}} \frac{|\mathcal{I}_{\vec{G}}|^2}{|\vec{G}|^2} \Bigg] \Bigg\} \\
&+ \frac{4\pi}{2L+1} \left\langle \begin{array}{c} r_<^L \\ r_>^{L+1} \end{array} \right\rangle_{aNL,N'L} \delta_{a,a'} \delta_{L,L'} \delta_{M,M'} \\
&+ \delta_{L,0}\delta_{L',0} \Bigg\{ \langle r^L \rangle_{aNL} \left[\frac{(4\pi)^{\frac{3}{2}}}{\Omega^2} \sum_{\vec{G}} \mathcal{W}^{\mathcal{L}'*}_{\vec{G}} \frac{1}{|\vec{G}|^2} \mathcal{I}_{\vec{G}} + \frac{(4\pi)^2}{6\Omega} \langle r^{L'+2} \rangle_{a'N'L'} \right] \\
&+ \langle r^{L'} \rangle_{a'N'L'} \left[\frac{(4\pi)^{\frac{3}{2}}}{\Omega^2} \sum_{\vec{G}} \mathcal{W}^{\mathcal{L}}_{\vec{G}} \frac{1}{|\vec{G}|^2} \mathcal{I}^*_{\vec{G}} + \frac{(4\pi)^2}{6\Omega} \langle r^{L+2} \rangle_{aNL} \right] \Bigg\}
\end{aligned} \tag{7.82}$$

Chapter 8

Green's Function

The zeroth-order Green's function constructed in real space and frequency is:

$$G_0(\vec{r}_1, \vec{r}_2; \omega) = \sum_{n\vec{k}} \frac{\Psi_{n\vec{k}}(\vec{r}_1)\Psi^*_{n\vec{k}}(\vec{r}_2)}{\omega - \varepsilon_{n\vec{k}} - i\eta_{n\vec{k}}} \tag{8.1}$$

where

$$\eta_{n\vec{k}} = \text{sign}(\varepsilon_F - \varepsilon_{n\vec{k}})\eta \tag{8.2}$$

η is a positive infinitesimal. The wavefunctions $\Psi_{n\vec{k}}$ are eigenfunctions, with eigenvalues $\varepsilon_{n\vec{k}}$, determined from the self-consistent LDA calculation for the system under consideration.

For real times, the Green function 8.1 becomes:

$$G_0(\vec{r}_1, \vec{r}_2; t) = \begin{cases} i\sum_{n\vec{k}}^{\text{occ}} \Psi_{n\vec{k}}(\vec{r}_1)\Psi^*_{n\vec{k}}(\vec{r}_2)e^{-i\varepsilon_{n\vec{k}}t}, & t < 0 \\ -i\sum_{n\vec{k}}^{\text{unocc}} \Psi_{n\vec{k}}(\vec{r}_1)\Psi^*_{n\vec{k}}(\vec{r}_2)e^{-i\varepsilon_{n\vec{k}}t}, & t > 0 \end{cases} \tag{8.3}$$

For imaginary times the expression for G_0 corresponds to analytically continuing the $t < 0$ form (the retarded Green function) to the positive imaginary time axis, and the $t > 0$ form (the advanced Green function) to the negative imaginary axis. This yields (see references [45] and [60])

$$G_0(\vec{r}_1, \vec{r}_2; i\tau) = \begin{cases} i\sum_{n\vec{k}}^{\text{occ}} \Psi_{n\vec{k}}(\vec{r}_1)\Psi^*_{n\vec{k}}(\vec{r}_2)e^{\varepsilon_{n\vec{k}}\tau}, & \tau > 0 \\ -i\sum_{n\vec{k}}^{\text{unocc}} \Psi_{n\vec{k}}(\vec{r}_1)\Psi^*_{n\vec{k}}(\vec{r}_2)e^{\varepsilon_{n\vec{k}}\tau}, & \tau < 0 \end{cases} \tag{8.4}$$

Taking the Fourier transform between complex axes (Eq. A.52) we obtain:

$$G_0(\vec{r}_1, \vec{r}_2; i\omega) = \sum_{n\vec{k}} \frac{\Psi_{n\vec{k}}(\vec{r}_1)\Psi^*_{n\vec{k}}(\vec{r}_2)}{i\omega - \varepsilon_{n\vec{k}}} \tag{8.5}$$

which corresponds to the analytical continuation of Eq. 8.1 to the imaginary axis.

The eigenfunctions can be written as a linear combination of the basis functions

$$\Psi^*_{n\vec{k}}(\vec{r}) = \sum_{\vec{G}} Z^n_{\vec{k}+\vec{G}}\Phi_{\vec{k}+\vec{G}}(\vec{r}) \tag{8.6}$$

Thus, the Green function of equation 8.4 can be writen:

$$G_0(\vec{r}_1, \vec{r}_2; i\tau) = \begin{cases} i\sum_{n\vec{k}}^{\text{occ}} \sum_{\vec{G},\vec{G}'} \mathbb{C}^{n\vec{k}}_{\vec{G},\vec{G}'}\Phi_{\vec{k}+\vec{G}}(\vec{r}_1)\Phi^*_{\vec{k}+\vec{G}'}(\vec{r}_2)e^{\varepsilon_{n\vec{k}}\tau}, & \tau > 0 \\ -i\sum_{n\vec{k}}^{\text{unocc}} \sum_{\vec{G},\vec{G}'} \mathbb{C}^{n\vec{k}}_{\vec{G},\vec{G}'}\Phi_{\vec{k}+\vec{G}}(\vec{r}_1)\Phi^*_{\vec{k}+\vec{G}'}(\vec{r}_2)e^{\varepsilon_{n\vec{k}}\tau}, & \tau < 0 \end{cases} \tag{8.7}$$

where

$$\mathbb{C}^{n\vec{k}}_{\vec{G},\vec{G}'} \equiv Z^n_{\vec{k}+\vec{G}} \left[Z^n_{\vec{k}+\vec{G}'} \right]^* \tag{8.8}$$

Chapter 9

The Polarization matrix

9.1 General formalism

The polarization function in the space-time representation is written as

$$P(1,2) = -iG_0(1,2)G_0(2,1^+) \tag{9.1}$$

where we use the abbrievation $1 \equiv (\mathbf{x}_1, t_1)$ with $\mathbf{x} \equiv (\mathbf{r}, \sigma)$. The Green's function in space-time representation can be represented by its Fourier transform

$$G(\mathbf{x}_1 t_1, \mathbf{x}_2 t_2) = \frac{1}{2\pi}\int d\omega G(\mathbf{x}_1, \mathbf{x}_2; \omega) e^{-i\omega(t_1 - t_2)} \tag{9.2}$$

and the Green's function in frequency space is a summation over states

$$G(\mathbf{x}_1, \mathbf{x}_2; \omega) = \sum_k \frac{\psi_n(\mathbf{x}_1)\psi_n(\mathbf{x}_2)^*}{\omega - \tilde{\epsilon}_n} \tag{9.3}$$

where we have used the notation $\tilde{\epsilon}_n \equiv \epsilon_n + i\eta \mathrm{sgn}(\epsilon_F - \epsilon_n)$.

$$\begin{aligned}
P(\mathbf{x}_1, \mathbf{x}_2; \omega) =& \int d(t_1 - t_2) e^{i\omega(t_1 - t_2)} P(\mathbf{x}_1 t_1, \mathbf{x}_2 t_2) \\
=& (-i)\int d(t_1 - t_2) \frac{1}{2\pi}\int d\omega' G(\mathbf{x}_1, \mathbf{x}_2; \omega') e^{-i\omega'(t_1 - t_2)} \\
& \times \frac{1}{2\pi}\int d\omega'' G(\mathbf{x}_2, \mathbf{x}_1; \omega'') e^{-i\omega''(t_2 - t_1 - \eta)} \\
=& \frac{-i}{2\pi}\int d\omega' \int d\omega'' G(\mathbf{x}_1, \mathbf{x}_2; \omega') G(\mathbf{x}_2, \mathbf{x}_1; \omega'') \\
& \times \frac{1}{2\pi}\int d\tau e^{i(\omega - \omega' + \omega'')\tau} e^{i\omega''\eta} \\
=& \frac{-i}{2\pi}\int d\omega'' e^{i\omega''\eta} G(\mathbf{x}_1, \mathbf{x}_2; \omega'' + \omega) G(\mathbf{x}_2, \mathbf{x}_1; \omega'')
\end{aligned} \tag{9.4}$$

Therefore the polarization function in the frequency space is the convolution of two Green's functions with a phase factor

$$P(\mathbf{x}_1, \mathbf{x}_2, \omega) = \frac{1}{2\pi i}\int_{-\infty}^{\infty} e^{i\omega'\eta} G(\mathbf{x}_1, \mathbf{x}_2, \omega' + \omega) G(\mathbf{x}_2, \mathbf{x}_1, \omega') d\omega' \tag{9.5}$$

Using the expression for Green's function, one can carry out the convolution analytically

$$\begin{aligned}
P(\mathbf{x}_1, \mathbf{x}_2, \omega) =& \frac{1}{2\pi i}\int_{-\infty}^{\infty} e^{i\omega'\eta} \sum_n \frac{\psi_n(\mathbf{x}_1)\psi_n(\mathbf{x}_2)^*}{\omega + \omega' - \tilde{\epsilon}_n} \sum_m \frac{\psi_m(\mathbf{x}_2)\psi_m(\mathbf{x}_1)^*}{\omega' - \tilde{\epsilon}_m} \\
=& \sum_{n,m} \psi_n(\mathbf{x}_1)\psi_m(\mathbf{x}_1)^* \psi_n(\mathbf{x}_2)^* \psi_m(\mathbf{x}_2) I_{nm}(\omega)
\end{aligned} \tag{9.6}$$

with

$$I_{nm}(\omega) \equiv \frac{1}{2\pi i}\int_{-\infty}^{\infty} \frac{e^{i\omega'\eta}}{(\omega + \omega' - \tilde{\epsilon}_n)(\omega' - \tilde{\epsilon}_m)} \tag{9.7}$$

Due to the presence of the phase factor in the integrand above, the integration can be replace by a contour integral over the upder-half plane. The integrand is singular at $\omega' = \tilde{\epsilon}_n - \omega$ and $\omega' = \tilde{\epsilon}_m$, if both poles fall into the upper half plane, i.e. both n and m are occupied, the integral vanishes. We have therefore have

$$I_{nm}(\omega) = \frac{f_n(1-f_m)}{\tilde{\epsilon}_n - \omega - \tilde{\epsilon}_m} + \frac{f_m(1-f_n)}{\omega + \tilde{\epsilon}_m - \tilde{\epsilon}_n} = \frac{f_m - f_n}{\omega + \tilde{\epsilon}_m - \tilde{\epsilon}_n} \tag{9.8}$$

Now we have

$$\begin{aligned} P(\mathbf{x}_1, \mathbf{x}_2, \omega) =& \sum_{n,m} \psi_n(\mathbf{x}_1)\psi_m(\mathbf{x}_1)^*\psi_n(\mathbf{x}_2)^*\psi_m(\mathbf{x}_2)\frac{f_m - f_n}{\omega + \tilde{\epsilon}_m - \tilde{\epsilon}_n} \\ =& \sum_{n,m} \frac{f_n(1-f_m)}{-\omega - \omega_{nm} + i\eta}\Phi_{nm}(\mathbf{x}_1)\Phi_{nm}(\mathbf{x}_2)^* \\ &+ \sum_{n,m} \frac{f_m(1-f_n)}{\omega + \omega_{nm} + i\eta}\Phi_{nm}(\mathbf{x}_1)\Phi_{nm}(\mathbf{x}_2)^* \end{aligned} \tag{9.9}$$

Above we have introduced the notation

$$\begin{aligned} \Phi_{nm}(\mathbf{x}) &\equiv \psi_n(\mathbf{x})\psi_m(\mathbf{x})^* \\ \omega_{nm} &\equiv \epsilon_m - \epsilon_n \end{aligned} \tag{9.10}$$

Note $\Phi_{nm}(\mathbf{x}) = \Phi_{mn}(\mathbf{x})^*$. Now switch the dummy index n and m in the second term we obtain

$$P(\mathbf{x}_1, \mathbf{x}_2; \omega) = \sum_{n,m} f_n(1-f_m)\left\{\frac{\Phi_{nm}(\mathbf{x}_1)\Phi_{nm}(\mathbf{x}_2)^*}{-\omega - \omega_{nm} + i\eta} + \frac{\Phi_{nm}(\mathbf{x}_1)^*\Phi_{nm}(\mathbf{x}_2)}{\omega - \omega_{nm} + i\eta}\right\} \tag{9.11}$$

From the equation above one can see that $P(\mathbf{x}_1, \mathbf{x}_2, \omega)$ has the following symmetry property

$$P(\mathbf{x}_1, \mathbf{x}_2; \omega) = P(\mathbf{x}_2, \mathbf{x}_1; -\omega) \tag{9.12}$$

In imaginary frequency $\omega = iu$,

$$\begin{aligned} P(\mathbf{x}_1, \mathbf{x}_2; iu) &= \sum_{n,m} f_n(1-f_m)\left\{\frac{\Phi_{nm}(\mathbf{x}_1)^*\Phi_{nm}(\mathbf{x}_2)}{iu - \omega_{nm}} + \frac{\Phi_{nm}(\mathbf{x}_1)\Phi_{nm}(\mathbf{x}_2)^*}{-iu - \omega_{nm}}\right\} \\ &= \sum_{n,m} f_n(1-f_m)\left\{\frac{\Phi_{nm}(\mathbf{x}_1)^*\Phi_{nm}(\mathbf{x}_2)}{iu - \omega_{nm}} + c.c.\right\} \end{aligned} \tag{9.13}$$

9.2 Formalism for periodic systems

For extended systems, we can write the $\mathbf{k}$-dependence of KS eigenstates explicitly

$$P(\mathbf{x}_1, \mathbf{x}_2; \omega) = \sum_{n,m}\sum_{\mathbf{k},\mathbf{k}'} f_{n\mathbf{k}}(1-f_{m\mathbf{k}'})\left\{\frac{\Phi_{n\mathbf{k},m\mathbf{k}'}(\mathbf{x}_1)\Phi_{n\mathbf{k},m\mathbf{k}'}(\mathbf{x}_2)^*}{-\omega - \omega_{n\mathbf{k},m\mathbf{k}'} + i\eta} + \frac{\Phi_{n\mathbf{k},m\mathbf{k}'}(\mathbf{x}_1)^*\Phi_{n\mathbf{k},m\mathbf{k}'}(\mathbf{x}_2)}{\omega - \omega_{n\mathbf{k},m\mathbf{k}'} + i\eta}\right\} \tag{9.14}$$

For systems with time-reversal symmetry (without spin-orbit coupling (SOC)), for every $\psi_{n\mathbf{k}}$ there is a $\psi^*_{n-\mathbf{k}}$ with the same eigenenergy, therefore the second term in$P(\mathbf{x}_1, \mathbf{x}_2; \omega)$

$$\begin{aligned} &\sum_{n,m}\sum_{\mathbf{k},\mathbf{k}'} f_{n\mathbf{k}}(1-f_{m\mathbf{k}'})\frac{\Phi_{n\mathbf{k},m\mathbf{k}'}(\mathbf{x}_1)^*\Phi_{n\mathbf{k},m\mathbf{k}'}(\mathbf{x}_2)}{\omega - \omega_{n\mathbf{k},m\mathbf{k}'} + i\eta} \\ =& \sum_{n,m}\sum_{\mathbf{k},\mathbf{k}'} f_{n\mathbf{k}}(1-f_{m\mathbf{k}'})\frac{\psi_{n\mathbf{k}}(\mathbf{x}_1)^*\psi_{m\mathbf{k}'}(\mathbf{x}_1)\psi_{n\mathbf{k}}(\mathbf{x}_2)\psi_{m\mathbf{k}'}(\mathbf{x}_2)^*}{\omega - \omega_{n\mathbf{k},m\mathbf{k}'} + i\eta} \\ =& \sum_{n,m}\sum_{\mathbf{k},\mathbf{k}'} f_{n\mathbf{k}}(1-f_{m\mathbf{k}'})\frac{\psi_{n-\mathbf{k}}(\mathbf{x}_1)\psi_{m-\mathbf{k}'}(\mathbf{x}_1)^*\psi_{n-\mathbf{k}}(\mathbf{x}_2)^*\psi_{m-\mathbf{k}'}(\mathbf{x}_2)}{\omega - \omega_{n-\mathbf{k},m-\mathbf{k}'} + i\eta} \\ =& \sum_{n,m}\sum_{\mathbf{k},\mathbf{k}'} f_{n\mathbf{k}}(1-f_{m\mathbf{k}'})\frac{\psi_{n\mathbf{k}}(\mathbf{x}_1)\psi_{m\mathbf{k}'}(\mathbf{x}_1)^*\psi_{n\mathbf{k}}(\mathbf{x}_2)^*\psi_{m\mathbf{k}'}(\mathbf{x}_2)}{\omega - \omega_{n\mathbf{k},m\mathbf{k}'} + i\eta} \\ =& \sum_{n,m}\sum_{\mathbf{k},\mathbf{k}'} f_{n\mathbf{k}}(1-f_{m\mathbf{k}'})\frac{\Phi_{n\mathbf{k},m\mathbf{k}'}(\mathbf{x}_1)\Phi_{n\mathbf{k},m\mathbf{k}'}(\mathbf{x}_2)^*}{\omega - \omega_{n\mathbf{k},m\mathbf{k}'} + i\eta} \end{aligned} \tag{9.15}$$

Then one has

$$\begin{aligned} P(\mathbf{x}_1,\mathbf{x}_2;\omega) =& \sum_{n,m}\sum_{\mathbf{k},\mathbf{k}'} f_{n\mathbf{k}}(1-f_{m\mathbf{k}'})\Phi_{n\mathbf{k},m\mathbf{k}'}(\mathbf{x}_1)\Phi_{n\mathbf{k},m\mathbf{k}'}(\mathbf{x}_2)^* \\ &\times\left\{\frac{1}{\omega-\omega_{n\mathbf{k},m\mathbf{k}'}+i\eta}-\frac{1}{\omega+\omega_{n\mathbf{k},m\mathbf{k}'}-i\eta}\right\} \end{aligned} \tag{9.16}$$

or equivalently

$$\begin{aligned} P(\mathbf{x}_1,\mathbf{x}_2;\omega) =& \sum_{n,m}\sum_{\mathbf{k},\mathbf{k}'} f_{n\mathbf{k}}(1-f_{m\mathbf{k}'})\Phi_{n\mathbf{k},m\mathbf{k}'}(\mathbf{x}_1)^*\Phi_{n\mathbf{k},m\mathbf{k}'}(\mathbf{x}_2) \\ &\times\left\{\frac{1}{\omega-\omega_{n\mathbf{k},m\mathbf{k}'}+i\eta}-\frac{1}{\omega+\omega_{n\mathbf{k},m\mathbf{k}'}-i\eta}\right\} \end{aligned} \tag{9.17}$$

In other words, for systems with time-reveral symmetry we have

$$P(\mathbf{x}_1,\mathbf{x}_2;\omega) = P(\mathbf{x}_2,\mathbf{x}_1;\omega). \tag{9.18}$$

or combining the previous symmetry relation

$$P(\mathbf{x}_1,\mathbf{x}_2;-\omega) = P(\mathbf{x}_1,\mathbf{x}_2;\omega). \tag{9.19}$$

In imaginary frequency, in the general case

$$\begin{aligned} P(\mathbf{x}_1,\mathbf{x}_2;iu) &= \sum_{n,m}\sum_{\mathbf{k},\mathbf{k}'} f_{n\mathbf{k}}(1-f_{m\mathbf{k}'})\left\{\frac{\Phi_{n\mathbf{k},m\mathbf{k}'}(\mathbf{x}_1)\Phi_{n\mathbf{k},m\mathbf{k}'}(\mathbf{x}_2)^*}{-iu-\omega_{n\mathbf{k},m\mathbf{k}'}}+\frac{\Phi_{n\mathbf{k},m\mathbf{k}'}(\mathbf{x}_1)^*\Phi_{n\mathbf{k},m\mathbf{k}'}(\mathbf{x}_2)}{iu-\omega_{n\mathbf{k},m\mathbf{k}'}}\right\} \\ &= \sum_{n,m}\sum_{\mathbf{k},\mathbf{k}'} f_{n\mathbf{k}}(1-f_{m\mathbf{k}'})\left\{\frac{\Phi_{n\mathbf{k},m\mathbf{k}'}(\mathbf{x}_1)\Phi_{n\mathbf{k},m\mathbf{k}'}(\mathbf{x}_2)^*}{-iu-\omega_{n\mathbf{k},m\mathbf{k}'}}+c.c.\right\} \end{aligned} \tag{9.20}$$

For systems with time-reversal symmetry, it can be further simplified as

$$P(\mathbf{x}_1,\mathbf{x}_2;iu) = \sum_{n\mathbf{k}}^{\text{occ}}\sum_{m\mathbf{k}'}^{\text{unocc}} \Phi_{n\mathbf{k},m\mathbf{k}'}(\mathbf{x}_1)\Phi_{n\mathbf{k},m\mathbf{k}'}(\mathbf{x}_2)^*\frac{-2\omega_{n\mathbf{k},m\mathbf{k}'}}{u^2+\omega_{n\mathbf{k},m\mathbf{k}'}^2} \tag{9.21}$$

Now to obtain the matrix representation of P, we can expand$\Phi_{n\mathbf{k},m\mathbf{k}'}(\mathbf{x})$ by a general basis se. First we note that $\Phi_{n\mathbf{k},m\mathbf{k}'}(\mathbf{x})$ is a Bloch function with a wave vector of $\mathbf{k}-\mathbf{k}'$

$$\begin{aligned} \Phi_{n\mathbf{k},m\mathbf{k}'}(\mathbf{r}+\mathbf{R}) &= \psi_{n\mathbf{k}}(\mathbf{r}+\mathbf{R})\psi_{m\mathbf{k}'}(\mathbf{r}+\mathbf{R})^* \\ &= e^{i\mathbf{k}\cdot\mathbf{R}}\psi_{n\mathbf{k}}(\mathbf{r})e^{-i\mathbf{k}'\cdot\mathbf{R}}\psi_{m\mathbf{k}'}(\mathbf{r})^* \\ &= e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}}\Phi_{n\mathbf{k},m\mathbf{k}'}(\mathbf{r}) \end{aligned} \tag{9.22}$$

therefore $\Phi_{n\mathbf{k},m\mathbf{k}'}(\mathbf{r}+\mathbf{R})$ can be expanded by the basis set $\chi_i^{\mathbf{q}}(\mathbf{r})$ with $\mathbf{q}=\mathbf{k}-\mathbf{k}'$.

$$\Phi_{n\mathbf{k},m\mathbf{k}'}(\mathbf{x}) = \delta_{\mathbf{k}',\mathbf{k}-\mathbf{q}}\sum_i C_i^{n\mathbf{k},m\mathbf{k}-\mathbf{q}}\chi_i^{\mathbf{q}}(\mathbf{x}) \tag{9.23}$$

where the expansion coefficients can be obtained from

$$\begin{aligned} C_i^{n\mathbf{k},m\mathbf{k}-\mathbf{q}} &= \int_V d\mathbf{x}\chi_i^{\mathbf{q}}(\mathbf{x})^*\Phi_{n\mathbf{k},m\mathbf{k}-\mathbf{q}}(\mathbf{x}) \\ &= \sum_R\int_\Omega d\mathbf{r}\chi_i^{\mathbf{q}}(\mathbf{r}-\mathbf{R})^*\Phi_{n\mathbf{k},m\mathbf{k}-\mathbf{q}}(\mathbf{r}-\mathbf{R}) \\ &= \sum_R\int_\Omega d\mathbf{r}e^{i\mathbf{q}\mathbf{R}}\chi_i^{\mathbf{q}}(\mathbf{r})^*e^{-i\mathbf{q}\mathbf{R}}\Phi_{n\mathbf{k},m\mathbf{k}-\mathbf{q}}(\mathbf{r}) \\ &= \sum_R\int_\Omega d\mathbf{r}\chi_i^{\mathbf{q}}(\mathbf{r})^*\Phi_{n\mathbf{k},m\mathbf{k}-\mathbf{q}}(\mathbf{r}) \\ &= N_c\int_\Omega d\mathbf{r}\chi_i^{\mathbf{q}}(\mathbf{r})^*\Phi_{n\mathbf{k},m\mathbf{k}-\mathbf{q}}(\mathbf{r}) \\ &= N_c^{-1/2}\int_\Omega d\mathbf{r}\tilde{\chi}_i^{\mathbf{q}}(\mathbf{r})^*\tilde{\Phi}_{n\mathbf{k},m\mathbf{k}-\mathbf{q}}(\mathbf{r}) \\ &\equiv N_c^{-1/2}M_{nm}^i(\mathbf{k},\mathbf{q}) \end{aligned} \tag{9.24}$$

where we have introduced

$$\begin{aligned} M^i_{nm}(\mathbf{k},\mathbf{q}) &\equiv \int_\Omega d\mathbf{r}\tilde{\chi}^{\mathbf{q}}_i(\mathbf{r})^*\tilde{\Phi}_{n\mathbf{k},m\mathbf{k}-\mathbf{q}}(\mathbf{r}) \\ &= N_c^{1/2}\int_V d\mathbf{x}\chi^{\mathbf{q}}_i(\mathbf{x})^*\Phi_{n\mathbf{k},m\mathbf{k}-\mathbf{q}}(\mathbf{x}) \end{aligned} \tag{9.25}$$

Here the subscript V and Ω for the integrals represent integration over the whole space and the primitive unit cell, recpectively, and $\tilde{\chi}^{\mathbf{q}}_i(\mathbf{r})$ and $\tilde{\Phi}_{n\mathbf{k},m\mathbf{k}-\mathbf{q}}(\mathbf{r})$ defined in the Ω-normalized scheme.

We finally obtain

$$\begin{aligned} P_{ij}(\mathbf{q},\omega) &= \int_V d\mathbf{r}_1\int_V d\mathbf{r}_2\left[\chi^{\mathbf{q}}_i(\mathbf{r}_1)\right]^* P(\mathbf{r}_1,\mathbf{r}_2,\omega)\chi^{\mathbf{q}}_j(\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2 \\ &= N_c^{-1}\sum_{\mathbf{k}}^{BZ}\sum_n^{\text{occ}}\sum_m^{\text{unocc}} M^i_{nm}(\mathbf{k},\mathbf{q})\left[M^j_{nm}(\mathbf{k},\mathbf{q})\right]^* F_{nm\mathbf{k}}(\mathbf{q},\omega) \end{aligned} \tag{9.26}$$

We have introduce the notation

$$F_{nm\mathbf{k}}(\mathbf{q},\omega) \equiv \frac{1}{\omega-\omega_{n\mathbf{k},m\mathbf{k}-\mathbf{q}}+i\eta} - \frac{1}{\omega+\omega_{n\mathbf{k},m\mathbf{k}-\mathbf{q}}-i\eta} \tag{9.27}$$

and for imaginary frequency

$$F_{nm\mathbf{k}}(\mathbf{q},iu) \equiv \frac{-2\omega_{n\mathbf{k},m\mathbf{k}-\mathbf{q}}}{u^2+\omega^2_{n\mathbf{k},m\mathbf{k}-\mathbf{q}}} \tag{9.28}$$

Chapter 10

The dielectric function

10.1 The symmetrized dielectric matrix

In frequency space the *dielectric matrix* $\epsilon(\mathbf{q}, i\omega)$ can be calculated via:

$$\boxed{\epsilon(\mathbf{q},\omega) = 1 - \mathbf{v}(\mathbf{q})\mathbf{P}(\mathbf{q},\omega)} \tag{10.1}$$

To treat the singularity at the Γ point, it is more convenient to make use of the symmertized dielectric matrix, denoted as ε, which is defined as:

$$\varepsilon_{ij}(\mathbf{q},\omega) = \sum_{lm} v_{il}^{-\frac{1}{2}}(\mathbf{q})\epsilon_{lm}(\mathbf{q},\omega)v_{mj}^{\frac{1}{2}}(\mathbf{q}) \tag{10.2}$$

which has no divergences, and is hermitian. It can be easily shown, from eq. 10.2 that:

$$\varepsilon_{ij}^{-1}(\mathbf{q},\omega) = \sum_{lm} v_{il}^{-\frac{1}{2}}(\mathbf{q})\epsilon_{lm}^{-1}(\mathbf{q},\omega)v_{mj}^{\frac{1}{2}}(\mathbf{q}) \tag{10.3}$$

It has also been shown that $\epsilon(\mathbf{q},\omega)$ and $\varepsilon(\mathbf{q},\omega)$ have the same eigenvalues (See [12]). Inserting Eq. 10.1 into 10.2 we have

$$\boxed{\varepsilon_{ij}(\mathbf{q},i\omega) = \delta_{ij} - \sum_{lm} v_{il}^{\frac{1}{2}}(\mathbf{q})P_{lm}(\mathbf{q},i\omega)v_{mj}^{\frac{1}{2}}(\mathbf{q})} \tag{10.4}$$

In the matrix notation

$$\boxed{\varepsilon(\mathbf{q},\omega) = \mathbf{1} - \mathbf{v}^{\frac{1}{2}}(\mathbf{q})\mathbf{P}(\mathbf{q},\omega)\mathbf{v}^{\frac{1}{2}}(\mathbf{q})} \tag{10.5}$$

In the next section we calculate the symmetrized dielectric matrix at the Γ point, and show that it does not diverge.

10.2 Plane wave expansion of the symmetrized dielectric matrix at the Γ point

The big advantage of the plane wave expansion is that the bare Coulomb potential is diagonal,

$$v_{\mathbf{GG}'}(\mathbf{q}) = \delta_{\mathbf{GG}'}\frac{4\pi}{|\mathbf{q}+\mathbf{G}|^2} \tag{10.6}$$

so that

$$v_{\mathbf{GG}'}^{\frac{1}{2}}(\mathbf{q}) = \delta_{\mathbf{GG}'}\frac{\sqrt{4\pi}}{|\mathbf{q}+\mathbf{G}|} \tag{10.7}$$

much simplifying all the algegra. Expanded in plane waves, the expression for the matrix elements of the symmetrized dielectric function is:

$$\varepsilon_{\mathbf{GG}'}(\mathbf{q},\omega) = \delta_{\mathbf{GG}'} - \frac{4\pi}{|\mathbf{q}+\mathbf{G}||\mathbf{q}+\mathbf{G}'|}P_{\mathbf{GG}'}(\mathbf{q},\omega), \tag{10.8}$$

where $P_{\mathbf{GG}'}(\mathbf{q},\omega)$ is given by:

$$P_{\mathbf{GG}'}(\mathbf{q},\omega) = N_c^{-1}\sum_{\mathbf{k}}^{BZ}\sum_{n,n'} M_{nn'}^{\mathbf{G}}(\mathbf{k},\mathbf{q})\left[M_{nn'}^{\mathbf{G}'}(\mathbf{k},\mathbf{q})\right]^* F_{nn'\mathbf{k}}(\mathbf{q},\omega) \tag{10.9}$$

where now:

$$M^{\mathbf{G}}_{nn'}(\mathbf{k},\mathbf{q}) = \int_{\Omega} \tilde{\chi}^{\mathbf{q}}_{\mathbf{G}}(\mathbf{r})^* \tilde{\Phi}_{n\mathbf{k},n'\mathbf{k}-\mathbf{q}}(\mathbf{r}) \tag{10.10}$$

with

$$\tilde{\chi}^{\mathbf{q}}_{G}(\mathbf{r}) = \frac{1}{\Omega^{1/2}} e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} \tag{10.11}$$

being the plane wave basis functions.

We can see that the possible divergences are located in the head, namely ε_{00} and the wings $\varepsilon_{0\mathbf{G}'}$ and $\varepsilon_{\mathbf{G}0}$.

For the screened potential we obtain:

$$W_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) = 4\pi \frac{1}{|\mathbf{q}+\mathbf{G}|} \varepsilon^{-1}_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) \frac{1}{|\mathbf{q}+\mathbf{G}'|} \tag{10.12}$$

10.2.1 $M^{\mathbf{G}=0}_{nn'}(\mathbf{k},\mathbf{q})$ in the limit of $\mathbf{q} \to 0$

Expressions for the limit $|\mathbf{q}| \to 0$ can be obtained by using the $\mathbf{k}\cdot\mathbf{p}$ perturbation theory.(see [2]). Taking into account the Bloch character of the eigenfunctions we can write:

$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}) \tag{10.13}$$

and according to the results of the $\mathbf{k}\cdot\mathbf{p}$ perturbation theory one can write:

$$\begin{aligned} u_{n\mathbf{k}+\mathbf{q}}(\mathbf{r}) =& u_{n\mathbf{k}}(\mathbf{r}) - \sum_{n'\neq n} \frac{\mathbf{p}_{n'n\mathbf{k}}\cdot\mathbf{q}}{\epsilon_{n'\mathbf{k}} - \epsilon_{n\mathbf{k}}} u_{n'\mathbf{k}}(\mathbf{r}) \\ \epsilon_{n\mathbf{k}+\mathbf{q}} =& \epsilon_{n\mathbf{k}} + \mathbf{p}_{nn\mathbf{k}}\cdot\mathbf{q} \end{aligned} \tag{10.14}$$

where $\mathbf{p}_{nn'\mathbf{k}}$ is the momentum matrix elements

$$\begin{aligned} \mathbf{p}_{nn'\mathbf{k}} &\equiv \langle \psi_{n\mathbf{k}} | \, \hat{\mathbf{p}} \, | \psi_{n'\mathbf{k}} \rangle \\ &= \langle u_{n\mathbf{k}} | \, \hat{\mathbf{p}} + \mathbf{k} \, | u_{n'\mathbf{k}} \rangle \end{aligned} \tag{10.15}$$

The matrix elements $M^{\mathbf{G}}_{nn'}(\mathbf{k},\mathbf{q})$ for $\mathbf{G}=0$ can be writen as:

$$\begin{aligned} M^{\mathbf{G}=0}_{nn'}(\mathbf{k},\mathbf{q}) &= \frac{1}{\Omega^{1/2}} \int_{\Omega} \psi^*_{n'\mathbf{k}-\mathbf{q}}(\mathbf{r}) e^{-i\mathbf{q}\cdot\mathbf{r}} \psi_{n\mathbf{k}}(\mathbf{r}) d^3r \\ &= \frac{1}{\Omega^{1/2}} \int_{\Omega} u^*_{n'\mathbf{k}-\mathbf{q}}(\mathbf{r}) u_{n\mathbf{k}}(\mathbf{r}) d^3r \end{aligned} \tag{10.16}$$

applying equation 10.14 we have:

$$\begin{aligned} M^{0}_{nn'}(\mathbf{k},\mathbf{q}) &= \frac{1}{\Omega^{1/2}} \int_{\Omega} d^3r \left\{ u^*_{n'\mathbf{k}}(\mathbf{r}) + \sum_{n''\neq n'} \frac{\mathbf{p}^*_{n''n'\mathbf{k}}\cdot\mathbf{q}}{\epsilon_{n''\mathbf{k}} - \epsilon_{n'\mathbf{k}}} u^*_{n''\mathbf{k}}(\mathbf{r}) \right\} u_{n\mathbf{k}}(\mathbf{r}) \\ &= \frac{1}{\Omega^{1/2}} \left\{ \delta_{nn'} + \sum_{n''} (1-\delta_{n''n'}) \frac{\mathbf{p}^*_{n''n'\mathbf{k}}\cdot\mathbf{q}}{\epsilon_{n''\mathbf{k}} - \epsilon_{n'\mathbf{k}}} \delta_{nn''} \right\} \\ &= \frac{1}{\Omega^{1/2}} \left\{ \delta_{nn'} + (1-\delta_{nn'}) \frac{\mathbf{p}^*_{nn'\mathbf{k}}\cdot\mathbf{q}}{\epsilon_{n\mathbf{k}} - \epsilon_{n'\mathbf{k}}} \right\} \end{aligned} \tag{10.17}$$

10.2.2 The head: $P_{\mathbf{G}=0,\mathbf{G}'=0}(\mathbf{q}\to 0,\omega)$

Inserting equation 10.17 into 10.9 we have

$$\begin{aligned} P_{00}(\mathbf{q}\to 0,\omega) =& N_c^{-1} \sum_{\mathbf{k}}^{BZ} \sum_{nn'} M^{\mathbf{G}=0}_{nn'}(\mathbf{k},\mathbf{q}\to 0) \left[M^{\mathbf{G}'=0}_{nn'}(\mathbf{k},\mathbf{q}\to 0) \right]^* F_{nn'\mathbf{k}}(\mathbf{q}\to 0,\omega) \\ =& \frac{1}{N_c\Omega} \sum_{\mathbf{k}}^{BZ} \sum_{nn'} \left[\delta_{nn'} + (1-\delta_{nn'}) \frac{\mathbf{p}^*_{nn'\mathbf{k}}\cdot\mathbf{q}}{\epsilon_{n\mathbf{k}} - \epsilon_{n'\mathbf{k}}} \right] \left[\delta_{nn'} + (1-\delta_{nn'}) \frac{\mathbf{p}_{nn'\mathbf{k}}\cdot\mathbf{q}}{\epsilon_{n\mathbf{k}} - \epsilon_{n'\mathbf{k}}} \right] F_{nn'\mathbf{k}}(\mathbf{q},\omega) \\ =& \frac{1}{N_c\Omega} \sum_{\mathbf{k}}^{BZ} \sum_{n,n'} \left[\delta_{nn'} + (1-\delta_{nn'}) \left| \frac{\mathbf{p}_{nn'\mathbf{k}}\cdot\mathbf{q}}{\epsilon_{n\mathbf{k}} - \epsilon_{n'\mathbf{k}}} \right|^2 \right] F_{nn'\mathbf{k}}(\mathbf{q},\omega) \end{aligned} \tag{10.18}$$

Thus we can separate it into intra-band and inter-band contributions as:

$$P_{00}(\mathbf{q}\to 0,\omega)=\frac{1}{N_c\Omega}\sum_{\mathbf{k}}^{BZ}\left[\sum_n F_{nn\mathbf{k}}(\mathbf{q}\to 0,\omega)+\sum_{n'\neq n}|\frac{\mathbf{p}_{nn'\mathbf{k}}\cdot\mathbf{q}}{\epsilon_{n\mathbf{k}}-\epsilon_{n'\mathbf{k}}}|^2F_{nn'\mathbf{k}}(0,\omega)\right] \tag{10.19}$$

The interband part, second summation, is already proportional to q^2. For the intraband term we use $\epsilon_{n\mathbf{k}-\mathbf{q}}=\epsilon_{n\mathbf{k}}-\mathbf{p}_{nn\mathbf{k}}\cdot\mathbf{q}=\epsilon_{n\mathbf{k}}+\Delta$ with $\Delta\equiv-\mathbf{p}_{nn\mathbf{k}}\cdot\mathbf{q}$:

$$\begin{aligned}F_{nn\mathbf{k}}(\mathbf{q}\to 0,\omega)=&f(\epsilon_{n\mathbf{k}})\left[1-f(\epsilon_{n\mathbf{k}}+\Delta)\right]\left[\frac{1}{\omega-\Delta+i\eta}-\frac{1}{\omega+\Delta-i\eta}\right]\\ \simeq&f(\epsilon_{n\mathbf{k}})\left[1-f(\epsilon_{n\mathbf{k}})-f'(\epsilon_{n\mathbf{k}})\Delta\right]\left\{\left[\frac{1}{\omega+i\eta}+\frac{\Delta}{(\omega+i\eta)^2}+\frac{\Delta^2}{(\omega+i\eta)^2}+\cdots\right]\right.\\ &\left.-\left[\frac{1}{\omega-i\eta}-\frac{\Delta}{(\omega-i\eta)^2}+\frac{\Delta^2}{(\omega-i\eta)^2}+\cdots\right]\right\}\\ \simeq&-f(\epsilon_{n\mathbf{k}})f'(\epsilon_{n\mathbf{k}})\left[\frac{1}{(\omega+i\eta)^2}+\frac{1}{(\omega-i\eta)^2}\right]|\mathbf{p}_{nn\mathbf{k}}\cdot\mathbf{q}|^2\end{aligned} \tag{10.20}$$

where we have used the fact that we are considering zero-temperature cases so that

$$f(\epsilon_{n\mathbf{k}})\left[1-f(\epsilon_{n\mathbf{k}}+\Delta)\right]\equiv 0 \tag{10.21}$$

and that η is infinitesimal, and

$$-f(\epsilon_{n\mathbf{k}})f'(\epsilon_{n\mathbf{k}})\to\theta(\epsilon_{\mathrm{F}}-\epsilon_{n\mathbf{k}})\delta(\epsilon_{\mathrm{F}}-\epsilon_{n\mathbf{k}})=\frac{1}{2}\delta(\epsilon_{\mathrm{F}}-\epsilon_{n\mathbf{k}}) \tag{10.22}$$

We therefore have

$$\begin{aligned}P_{00}(\mathbf{q}\to 0,\omega)=&\frac{1}{N_c\Omega}\sum_{\mathbf{k}}^{BZ}\left\{\sum_n\frac{1}{2}\delta(\epsilon_{\mathrm{F}}-\epsilon_{n\mathbf{k}})\left[\frac{1}{(\omega+i\eta)^2}+\frac{1}{(\omega-i\eta)^2}\right]|\mathbf{p}_{nn\mathbf{k}}\cdot\mathbf{q}|^2\right.\\ &\left.+\sum_{n'\neq n}F_{nn'\mathbf{k}}(0,\omega)|\frac{\mathbf{p}_{nn'\mathbf{k}}\cdot\mathbf{q}}{\epsilon_{n\mathbf{k}}-\epsilon_{n'\mathbf{k}}}|^2\right\}\end{aligned} \tag{10.23}$$

Now can obtain the head of dielectric function

$$\begin{aligned}\varepsilon_{00}(\mathbf{q}\to 0,\omega)=&1-\frac{4\pi}{q^2}P_{00}(\mathbf{q}\to 0,\omega)\\ =&1-\frac{4\pi}{N_c\Omega}\sum_{\mathbf{k}}^{BZ}\left\{\sum_n\frac{1}{2}\delta(\epsilon_{\mathrm{F}}-\epsilon_{n\mathbf{k}})\left[\frac{1}{(\omega+i\eta)^2}+\frac{1}{(\omega-i\eta)^2}\right]|\mathbf{p}_{nn\mathbf{k}}\cdot\hat{\mathbf{q}}|^2\right.\\ &\left.+\sum_{n'\neq n}F_{nn'\mathbf{k}}(0,\omega)|\frac{\mathbf{p}_{nn'\mathbf{k}}\cdot\hat{\mathbf{q}}}{\epsilon_{n\mathbf{k}}-\epsilon_{n'\mathbf{k}}}|^2\right\}\\ =&\sum_{\alpha,\beta}\frac{q_\alpha q_\beta}{q^2}F_{\alpha,\beta}(\omega)\end{aligned} \tag{10.24}$$

where

$$\begin{aligned}F_{\alpha,\beta}(\omega)(=&\delta_{\alpha,\beta}+\frac{1}{N_c\Omega}\sum_{\mathbf{k}}^{BZ}\left\{\sum_n\frac{1}{2}\delta(\epsilon_{\mathrm{F}}-\epsilon_{n\mathbf{k}})\left[\frac{1}{(\omega+i\eta)^2}+\frac{1}{(\omega-i\eta)^2}\right]\mathbf{p}^{\alpha*}_{nn\mathbf{k}}\mathbf{p}^{\beta}_{nn\mathbf{k}}\right.\\ &\left.+\sum_{n'\neq n}F_{nn'\mathbf{k}}(0,\omega)\frac{\mathbf{p}^{\alpha*}_{nn'\mathbf{k}}\mathbf{p}^{\beta}_{nn'\mathbf{k}}}{(\epsilon_{n\mathbf{k}}-\epsilon_{n'\mathbf{k}})^2}\right\}\end{aligned} \tag{10.25}$$

with $\alpha,\beta=(x,y,z)$.

10.2.3 The Wings: $P_{\mathbf{G}=0,\mathbf{G}'\neq 0}(\mathbf{q}\to 0,\omega)$

$$\begin{aligned}
P_{0\mathbf{G}'}(\mathbf{q}\to 0,\omega) &= \Omega^{-1/2}N_c^{-1}\sum_{\mathbf{k}}^{BZ}\sum_{n,n'}\left(\delta_{nn'}-(1-\delta_{nn'})\frac{\mathbf{p}^*_{nn'\mathbf{k}}\cdot\mathbf{q}}{\epsilon_{n\mathbf{k}}-\epsilon_{n'\mathbf{k}}}\right)\left[M^{\mathbf{G}'}_{nn'}(\mathbf{k},0)\right]^* F_{nn'\mathbf{k}}(\mathbf{q}\to 0,\omega)\\
&= \Omega^{-1/2}N_c^{-1}\sum_{\mathbf{k}}^{BZ}\left\{\sum_{n}\left[M^{\mathbf{G}'}_{nn'}(\mathbf{k},0)\right]^* F_{nn'\mathbf{k}}(\mathbf{q}\to 0,\omega)\right.\\
&\left.+\sum_{n,n'}F_{nn'\mathbf{k}}(0,\omega)\frac{\mathbf{p}^*_{nn'\mathbf{k}}\cdot\mathbf{q}}{\epsilon_{n\mathbf{k}}-\epsilon_{n'\mathbf{k}}}\left[M^{\mathbf{G}'}_{nn'}(\mathbf{k},0)\right]^*\right\}\\
&= \Omega^{-1/2}N_c^{-1}\sum_{\mathbf{k}}^{BZ}\sum_{n\neq n'}F_{nn'\mathbf{k}}(0,\omega)\frac{\mathbf{p}^*_{nn'\mathbf{k}}\cdot\mathbf{q}}{\epsilon_{n\mathbf{k}}-\epsilon_{n'\mathbf{k}}}\left[M^{\mathbf{G}'}_{nn'}(\mathbf{k},0)\right]^*
\end{aligned} \tag{10.26}$$

Where we have used the fact that the intraband term (the first one) goes to zero as q^2, compared to q of the interband term, so we only need to consider the interband term. From we can the wing of the dielectric function

$$\varepsilon_{0\mathbf{G}'}(\mathbf{q}\to 0,\omega) = -\frac{4\pi N_c^{-1}\Omega^{-1/2}}{|\mathbf{G}'|}\sum_{\mathbf{k}}^{BZ}\sum_{n'\neq n}F_{nn'\mathbf{k}}(0,\omega)\frac{\mathbf{p}^*_{nn'\mathbf{k}}\cdot\hat{\mathbf{q}}}{\epsilon_{n\mathbf{k}}-\epsilon_{n'\mathbf{k}}}\left[M^{\mathbf{G}'}_{nn'}(\mathbf{k},0)\right]^* \tag{10.27}$$

Similarly we have

$$\varepsilon_{\mathbf{G}0}(\mathbf{q}\to 0,\omega) = -\frac{4\pi N_c^{-1}\Omega^{-1/2}}{|\mathbf{G}|}\sum_{\mathbf{k}}^{BZ}\sum_{n'\neq n}F_{nn'\mathbf{k}}(0,\omega)\frac{\mathbf{p}_{nn'\mathbf{k}}\cdot\hat{\mathbf{q}}}{\epsilon_{n\mathbf{k}}-\epsilon_{n'\mathbf{k}}}M^{\mathbf{G}}_{nn'}(\mathbf{k},0) \tag{10.28}$$

For imaginary frequency, the two wings are related by the hermiticity relation, but for real frequency, the relation is more complicated, but still closely related.

10.3 Mixed basis expansion of the dielectric matrix at the Γ point

The use of the symmetrized dielectric matrix expanded in other basis set than plane waves presents several difficulties:

- The divergences for $|\mathbf{q}|\to 0$ are not necessarily located in particular matrix elements of the bare Coulomb potential, the same is, as a consequence, true for the dielectric matrix.
- The bare Coulomb potential is no longer diagonal.

From the second item, we can see that already the calculation of the matrix elements $v^{\frac{1}{2}}_{ij}$ is no longer simple. The simplest option for the expansion of the symmetrized dielectric matrix in our mixed basis is to perform the calculation in a plane wave basis and then make the corresponding matrix multiplications to change the basis.

It is then straightforward to show that:

$$\varepsilon_{ij}(\mathbf{q}\to 0,\omega) = \sum_{\mathbf{G}\mathbf{G}'}\mathcal{W}^i_{\mathbf{G}}\varepsilon_{\mathbf{G}\mathbf{G}'}(\mathbf{q}\to 0,\omega)\mathcal{W}^{j*}_{\mathbf{G}'} \tag{10.29}$$

$$\begin{aligned}
v^{\frac{1}{2}}_{ij}(\mathbf{q}\to 0) &= \sqrt{4\pi}\sum_{\mathbf{G}}\frac{\mathcal{W}^i_{\mathbf{G}}\mathcal{W}^{j*}_{\mathbf{G}}}{|\mathbf{q}+\mathbf{G}|}\\
&= \frac{\sqrt{4\pi}}{q}\mathcal{W}^i_0\mathcal{W}^{j*}_0+\sum_{\mathbf{G}\neq 0}\frac{\sqrt{4\pi}}{|\mathbf{G}|}\mathcal{W}^i_{\mathbf{G}}\mathcal{W}^{j*}_{\mathbf{G}}\\
&= \frac{\sqrt{4\pi}}{q}\mathcal{W}^i_0\mathcal{W}^{j*}_0+\sum_{\mathbf{G}}\tilde{v}^{\frac{1}{2}}_{\mathbf{G}}\mathcal{W}^i_{\mathbf{G}}\mathcal{W}^{j*}_{\mathbf{G}}
\end{aligned} \tag{10.30}$$

where the matrix elements $\mathcal{W}^i_{\mathbf{G}}\equiv\left\langle\chi^{\mathbf{q}=0}_i|\chi^{\mathbf{q}=0}_{\mathbf{G}}\right\rangle$. We have introduced the regularized bare Coulomb interaction at $\mathbf{q}=0$, $\tilde{v}$, which is diagonal in the plane-wave representation, $\tilde{v}_{\mathbf{G}\neq 0}=\frac{4\pi}{|\mathbf{G}|^2}$ and $\tilde{v}_{\mathbf{G}=0}=0$.

First of all let's rewrite Eq. 10.29 in the following way:

$$\begin{aligned}\varepsilon_{ij}(\mathbf{q}\to 0,\omega) &= \mathcal{W}_0^i\varepsilon_{00}(\mathbf{q}\to 0,\omega)\mathcal{W}_0^{j*} \\ &+ \sum_{\mathbf{G}\neq 0}\left\{\mathcal{W}_{\mathbf{G}}^i\varepsilon_{\mathbf{G}0}(\mathbf{q}\to 0,\omega)\mathcal{W}_0^{j*} + \mathcal{W}_0^i\varepsilon_{0\mathbf{G}}(\mathbf{q}\to 0,\omega)\mathcal{W}_{\mathbf{G}}^{j*}\right\} \\ &+ \sum_{\mathbf{G}\mathbf{G}'\neq 0}\mathcal{W}_{\mathbf{G}}^i\varepsilon_{\mathbf{G}\mathbf{G}'}(\mathbf{q}\to 0,\omega)\mathcal{W}_{\mathbf{G}'}^{j*} \\ &= \varepsilon_{ij}^{\mathrm{H}}(\omega)+\varepsilon_{ij}^{\mathrm{W}}(\omega)+\varepsilon_{ij}^{B}(\omega)\end{aligned} \tag{10.31}$$

10.3.0.1 Head

$$\begin{aligned}\varepsilon_{ij}^{H}(\omega) =& \mathcal{W}_0^i\varepsilon_{00}(\mathbf{q}\to 0,\omega)\mathcal{W}_0^{j*} \\ =& \mathcal{W}_0^i\left[1-4\pi P^H(\omega)\right]\mathcal{W}_0^{j*} \\ =& \mathcal{W}_0^i\mathcal{W}_0^{j*} - 4\pi P^H(\omega)\mathcal{W}_0^i\mathcal{W}_0^{j*}\end{aligned} \tag{10.32}$$

10.3.0.2 Wing

Now we consider the second wing term ε_{ij}^{W2} the rest, let us take the second term of the wings (**??**) as an example.

$$\begin{aligned}\varepsilon_{ij}^{W2}(\omega) =& \sum_{\mathbf{G}\neq 0}\mathcal{W}_0^i\varepsilon_{0\mathbf{G}}(\mathbf{q}\to 0,\omega)\mathcal{W}_{\mathbf{G}}^{j*} \\ =& \mathcal{W}_0^i\left(-\frac{4\pi}{\Omega^{1/2}}\right)N_c^{-1}\sum_{\mathbf{k}}^{BZ}\sum_{n'\neq n}F_{nn'\mathbf{k}}(0,\omega)\frac{\mathbf{p}_{nn'\mathbf{k}}^*\cdot\hat{\mathbf{q}}}{\epsilon_{n\mathbf{k}}-\epsilon_{n'\mathbf{k}}}\sum_{\mathbf{G}\neq 0}\frac{\left[M_{nn'}^{\mathbf{G}}(\mathbf{k},0)\right]^*}{|\mathbf{G}|}\mathcal{W}_{\mathbf{G}}^{j*} \\ =& \mathcal{W}_0^i\left(-\sqrt{\frac{4\pi}{\Omega}}\right)N_c^{-1}\sum_{\mathbf{k}}^{BZ}\sum_{n'\neq n}F_{nn'\mathbf{k}}(0,\omega)\frac{\mathbf{p}_{nn'\mathbf{k}}^*\cdot\hat{\mathbf{q}}}{\epsilon_{n\mathbf{k}}-\epsilon_{n'\mathbf{k}}}\left[\sum_{\mathbf{G}}\tilde{v}_{\mathbf{G}}^{\frac{1}{2}}M_{nn'}^{\mathbf{G}}(\mathbf{k},0)\mathcal{W}_{\mathbf{G}}^{j}\right]^*\end{aligned} \tag{10.33}$$

Let's look at the summation in the equation above

$$\begin{aligned}&\sum_{\mathbf{G}}\tilde{v}_{\mathbf{G}}^{\frac{1}{2}}M_{nn'}^{\mathbf{G}}(\mathbf{k},0)\mathcal{W}_{\mathbf{G}}^{j} \\ =&\sum_{\mathbf{G},\mathbf{G}'}\mathcal{W}_{\mathbf{G}'}^{j}\tilde{v}_{\mathbf{G}',\mathbf{G}}^{\frac{1}{2}}M_{nn'}^{\mathbf{G}}(\mathbf{k},0) \\ =&\sum_{\mathbf{G},\mathbf{G}'}\left\langle\chi_j^{\mathbf{q}=0}|\chi_{\mathbf{G}'}^{\mathbf{q}=0}\right\rangle\left\langle\chi_{\mathbf{G}'}^{\mathbf{q}=0}\right|\tilde{v}^{\frac{1}{2}}\left|\chi_{\mathbf{G}}^{\mathbf{q}=0}\right\rangle\left\langle\chi_{\mathbf{G}}^{\mathbf{q}=0}|\Phi_{n\mathbf{k},n'\mathbf{k}}\right\rangle \\ =&\left\langle\chi_j^{\mathbf{q}=0}\right|\tilde{v}^{\frac{1}{2}}\left|\Phi_{n\mathbf{k},n'\mathbf{k}}\right\rangle \\ =&\sum_{p}\left\langle\chi_j^{\mathbf{q}=0}\right|\tilde{v}^{\frac{1}{2}}\left|\chi_p^{\mathbf{q}=0}\right\rangle\left\langle\chi_p^{\mathbf{q}=0}|\Phi_{n\mathbf{k},n'\mathbf{k}}\right\rangle \\ =&\sum_{p}\tilde{v}_{jp}^{\frac{1}{2}}M_{nn'}^{p}(\mathbf{k},0)\end{aligned} \tag{10.34}$$

So finally we have

$$\varepsilon_{ij}^{W2}(\omega) = \left(-\sqrt{\frac{4\pi}{\Omega}}\right)N_c^{-1}\sum_{\mathbf{k}}^{BZ}\sum_{n'\neq n}F_{nn'\mathbf{k}}(0,\omega)\frac{\mathbf{p}_{nn'\mathbf{k}}^*\cdot\hat{\mathbf{q}}}{\epsilon_{n\mathbf{k}}-\epsilon_{n'\mathbf{k}}}\mathcal{W}_0^i\left[\sum_{p}\tilde{v}_{jp}^{\frac{1}{2}}M_{nn'}^{p}(\mathbf{k},0)\right]^* \tag{10.35}$$

Similarly we have

$$\varepsilon_{ij}^{W1}(\omega) = \left(-\sqrt{\frac{4\pi}{\Omega}}\right)N_c^{-1}\sum_{\mathbf{k}}^{BZ}\sum_{n'\neq n}F_{nn'\mathbf{k}}(0,\omega)\frac{\mathbf{p}_{nn'\mathbf{k}}\cdot\hat{\mathbf{q}}}{\epsilon_{n\mathbf{k}}-\epsilon_{n'\mathbf{k}}}\sum_{p}\tilde{v}_{ip}^{\frac{1}{2}}M_{nn'}^{p}(\mathbf{k},0)\mathcal{W}_0^{j*} \tag{10.36}$$

10.3.0.3 Body

For the body part,

$$\begin{aligned}
\varepsilon^B_{ij}(\omega) =& \sum_{\mathbf{G}\mathbf{G}'\neq 0} \mathcal{W}^i_{\mathbf{G}} \varepsilon_{\mathbf{G}\mathbf{G}'}(0,\omega) \mathcal{W}^{j*}_{\mathbf{G}'} \\
=& \sum_{\mathbf{G}\mathbf{G}'\neq 0} \mathcal{W}^i_{\mathbf{G}} \left[\delta_{\mathbf{G},\mathbf{G}'} - \frac{4\pi}{|\mathbf{G}||\mathbf{G}'|} P_{\mathbf{G}\mathbf{G}'}(0,\omega) \right] \mathcal{W}^{j*}_{\mathbf{G}'} \\
=& \sum_{\mathbf{G}\neq 0} \mathcal{W}^i_{\mathbf{G}} \mathcal{W}^{j*}_{\mathbf{G}} - \sum_{\mathbf{G}\mathbf{G}'\neq 0} \mathcal{W}^i_{\mathbf{G}} \frac{4\pi}{|\mathbf{G}||\mathbf{G}'|} P_{\mathbf{G}\mathbf{G}'}(0,\omega) \mathcal{W}^{j*}_{\mathbf{G}'} \\
=& \delta_{ij} - \mathcal{W}^i_0 \mathcal{W}^{j*}_0 - \sum_{\mathbf{G}\mathbf{G}'\neq 0} \mathcal{W}^i_{\mathbf{G}} \tilde{v}^{\frac{1}{2}}_{\mathbf{G}} P_{\mathbf{G}\mathbf{G}'}(0,\omega) \tilde{v}^{\frac{1}{2}}_{\mathbf{G}'} \mathcal{W}^{j*}_{\mathbf{G}'} \\
=& \delta_{ij} - \mathcal{W}^i_0 \mathcal{W}^{j*}_0 - \sum_{i'j'} \tilde{v}^{\frac{1}{2}}_{ii'} P_{i'j'}(0,\omega) \tilde{v}^{\frac{1}{2}}_{j'j}
\end{aligned} \tag{10.37}$$

Note that the second term will cancel the first term in the head.

10.4 Dielectric matrix in the basis of bare Coulomb matrix eigenvectors

In practice it is much more efficient to use the eigenvectors of bare Coulomb matrix constructed from the original mixed basis functions, which is essentially a unitary transform of the original mixed basis. The usefulness of such a transformation can be seen from the expression of the dielectric matrix as represented by $M^i_{nm}(\mathbf{k},\mathbf{q})$

$$\varepsilon_{ij}(\mathbf{q},i\omega) = \delta_{ij} - N_c^{-1} \sum_{\mathbf{k}}^{BZ} \sum_{n}^{\text{occ}} \sum_{m}^{\text{unocc}} F_{nm\mathbf{k}}(\mathbf{q},\omega) \sum_{kl} v^{\frac{1}{2}}_{ik}(\mathbf{q}) M^k_{nm}(\mathbf{k},\mathbf{q}) \left[M^l_{nm}(\mathbf{k},\mathbf{q}) \right]^* v^{\frac{1}{2}}_{lj}(\mathbf{q}) \tag{10.38}$$

As a matter of fact, in both the dielectric function and in the GW self-energy, it is always the $M^i_{nm}(\mathbf{k},\mathbf{q})$ is always appears

In the completeness limit, this new basis set, denoted as $\left|\chi^{\mathbf{q}}_{\mu}\right\rangle$, is equivalent to the plane wave basis functions $|\chi^{\mathbf{q}}_{\mathbf{G}}\rangle$. Since the new basis is constructed from the MB, it should be almost as accurate as the original mixed basis set. In particular, for $\mathbf{q}\neq 0$, the new basis set is equivalent to the original MB, but for $\mathbf{q}=0$, there are a little subtle differences.

Using the plane wave basis we have

$$\begin{aligned}
v_{\mathbf{G}\mathbf{G}'}(\mathbf{q}) =& \frac{4\pi}{|\mathbf{G}+\mathbf{q}|^2} \delta_{\mathbf{G},\mathbf{G}'} \\
v_{\mathbf{G}\mathbf{G}'}(\mathbf{q}\to 0) =& \frac{4\pi}{q^2} \delta_{\mathbf{G}0}\delta_{\mathbf{G}'0} + \tilde{v}_{\mathbf{G}\mathbf{G}'}
\end{aligned} \tag{10.39}$$

In the mixed basis representation

$$\begin{aligned}
v_{ij}(\mathbf{q}\to 0) =& \left\langle \chi^0_i \right| v \left| \chi^0_j \right\rangle \\
=& \sum_{\mathbf{G}\mathbf{G}'} \left\langle \chi^0_i | \chi^0_{\mathbf{G}} \right\rangle \left\langle \chi^0_{\mathbf{G}} \right| v \left| \chi^0_{\mathbf{G}'} \right\rangle \left\langle \chi^0_{\mathbf{G}'} | \chi^0_j \right\rangle \\
=& \sum_{\mathbf{G}\mathbf{G}'} \mathcal{W}^i_{\mathbf{G}} v_{\mathbf{G}\mathbf{G}'}(\mathbf{q}\to 0) \mathcal{W}^{j*}_{\mathbf{G}'} \\
=& \sum_{\mathbf{G}\mathbf{G}'} \mathcal{W}^i_{\mathbf{G}} \left[\frac{4\pi}{q^2} \delta_{\mathbf{G}0}\delta_{\mathbf{G}'0} + \tilde{v}_{\mathbf{G}\mathbf{G}'} \right] \mathcal{W}^{j*}_{\mathbf{G}'} = \frac{4\pi}{q^2} \mathcal{W}^i_0 \mathcal{W}^{j*}_0 + \sum_{\mathbf{G}} \mathcal{W}^i_{\mathbf{G}} \tilde{v}_{\mathbf{G}} \mathcal{W}^{j*}_{\mathbf{G}} \\
=& \frac{v^s_{ij}}{q^2} + \tilde{v}_{ij}
\end{aligned} \tag{10.40}$$

Now we use the eigenvectors of the matrix $\tilde{v}_{ij}$ as the new basis set,

$$\left|\chi^{\mathbf{q}}_{\mu}\right\rangle = \sum_i \left|\chi^{\mathbf{q}}_i\right\rangle U^{\mathbf{q}}_{i\mu} \tag{10.41}$$

where $U^{\mathbf{q}}_{i\mu} = \langle \chi^{\mathbf{q}}_i | \chi^{\mathbf{q}}_{\mu} \rangle$ is the matrix that diagonalize the Coulomb matrix v (or $\tilde{v}$ for $\mathbf{q}=0$). Rigorously the matrix

$\{v^s_{ij}\}$ is not diagonal,

$$\begin{aligned} v^s_{\mu\nu} =& \left\langle \chi^0_\mu \right| v^s \left| \chi^0_\nu \right\rangle \\ =& \sum_{ij} \left\langle \chi^0_\mu | \chi^0_i \right\rangle \left\langle \chi^0_i \right| v^s \left| \chi^0_j \right\rangle \left\langle \chi^0_j | \chi^0_\nu \right\rangle \\ =& \sum_{ij} U^{0*}_{i\mu} v^s_{ij} U^0_{j\nu} \end{aligned} \tag{10.42}$$

So in the new basis we have

$$v_{\mu\nu}(\mathbf{q}\to 0) = \frac{v^s_{\mu\nu}}{q^2} + \tilde{v}_\mu \delta_{\mu\nu} \tag{10.43}$$

Now as an approxmation one assumse $v^s_{\mu\nu} = 4\pi\delta_{\mu 0}\delta_{\nu 0}$. Since

$$\begin{aligned} v^s_{\mu\nu} =& \sum_{ij} U^{0*}_{i\mu} v^s_{ij} U^0_{j\nu} \\ =& 4\pi \sum_{ij} U^{0*}_{i\mu} W^i_0 W^{j*}_0 U^0_{j\nu} \\ =& 4\pi \sum_i U^0_{\mu i} W^i_0 \sum_j W^{j*}_0 U^0_{j\nu} \end{aligned} \tag{10.44}$$

Then the approximation aboves implies

$$\sum_i U_{\mu i} W^i_0 = \left\langle \chi^0_\mu | \chi^0_{\mathbf{G}=0} \right\rangle \equiv \mathcal{W}^\mu_{\mathbf{G}=0} = \delta_{\mu 0} \tag{10.45}$$

With this can easily obtain the dielectric matrix represented using the new basis set. We will still use i, j as the indices for the new basis set from now on.

$$\begin{aligned} \varepsilon^h_{ij}(\omega) =& \delta_{i0}\delta_{j0}\varepsilon_{00}(\mathbf{q}\to 0,\omega)\delta_{j0} \\ =& \delta_{i0}\delta_{j0}\left\{ 1 - \frac{4\pi}{N_c\Omega} \sum_{\mathbf{k}}^{BZ} \left[\sum_n \frac{(-2f'(\epsilon_{n\mathbf{k}}))}{\omega^2} |\mathbf{p}_{nn\mathbf{k}}\cdot\mathbf{q}|^2 + \sum_{n'\neq n} F_{nn'\mathbf{k}}(0,\omega) |\frac{\mathbf{p}_{nn'\mathbf{k}}\cdot\mathbf{q}}{\epsilon_{n\mathbf{k}} - \epsilon_{n'\mathbf{k}}}|^2 \right] \right\} \\ \varepsilon^{w1}_{ij}(\omega) =& \tilde{\delta}_{i0}\delta_{j0} \left(-\sqrt{\frac{4\pi}{\Omega}} \right) N_c^{-1} \sum_{\mathbf{k}}^{BZ} \sum_{n'\neq n} F_{nn'\mathbf{k}}(0,\omega) \frac{\mathbf{p}_{nn'\mathbf{k}}\cdot\hat{\mathbf{q}}}{\epsilon_{n\mathbf{k}} - \epsilon_{n'\mathbf{k}}} \tilde{v}_i^{\frac{1}{2}} M^i_{nn'}(\mathbf{k},0) \\ \varepsilon^{w2}_{ij}(\omega) =& \delta_{i0}\tilde{\delta}_{j0} \left(-\sqrt{\frac{4\pi}{\Omega}} \right) N_c^{-1} \sum_{\mathbf{k}}^{BZ} \sum_{n'\neq n} F_{nn'\mathbf{k}}(0,\omega) \frac{\mathbf{p}^*_{nn'\mathbf{k}}\cdot\hat{\mathbf{q}}}{\epsilon_{n\mathbf{k}} - \epsilon_{n'\mathbf{k}}} \left[\tilde{v}_j^{\frac{1}{2}} M^j_{nn'}(\mathbf{k},0) \right]^* \\ \varepsilon^b_{ij}(\omega) =& \tilde{\delta}_{i0}\tilde{\delta}_{j0} \left\{ \delta_{ij} - N_c^{-1} \sum_{\mathbf{k}}^{BZ} \sum_n^{\text{occ}} \sum_m^{\text{unocc}} F_{nm\mathbf{k}}(\mathbf{q},\omega)(0,\omega) \tilde{v}_i^{\frac{1}{2}} M^i_{nm}(\mathbf{k},\mathbf{q}) \left[\tilde{v}_j^{\frac{1}{2}} M^j_{nm}(\mathbf{k},\mathbf{q}) \right]^* \right\} \end{aligned} \tag{10.46}$$

where we have used $\tilde{\delta}_{ij} \equiv 1 - \delta_{ij}$. For $\mathbf{q} \neq 0$, we have

$$\varepsilon^b_{ij}(\mathbf{q},\omega) = \delta_{ij} - N_c^{-1} \sum_{\mathbf{k}}^{BZ} \sum_n^{\text{occ}} \sum_m^{\text{unocc}} F_{nm\mathbf{k}}(\mathbf{q},\omega)(0,\omega) v_i^{\frac{1}{2}} M^i_{nm}(\mathbf{k},\mathbf{q}) \left[v_j^{\frac{1}{2}} M^j_{nm}(\mathbf{k},\mathbf{q}) \right]^* \tag{10.47}$$

10.5 Inverse dielectric function at Γ point

When using the mixed basis functions, inverting the dielectric matrix is done in the same way as for other $\mathbf{q}$, but when using v-diagonalized basis set, $\varepsilon^{-1}(\mathbf{q}=0,\omega)$ is calculated by the block-wise inversion technique, as described in Ref.[**?**].

For a general matrix with the block form

$$M = \begin{pmatrix} P & Q \\ R & S \end{pmatrix} \tag{10.48}$$

where P, Q, R, S are matrices of $m\times m$, $m\times n$, $n\times m$ and $n\times n$, respectively. then the inverse of M reads

$$M^{-1} = \begin{pmatrix} W & X \\ Y & Z \end{pmatrix} \tag{10.49}$$

with

$$\begin{aligned} W &= (P - QS^{-1}R)^{-1} \\ X &= -WQS^{-1} \\ Y &= -S^{-1}RW \\ Z &= S^{-1} + YW^{-1}X = S^{-1} - S^{-1}RX \end{aligned} \tag{10.50}$$

In the special case of

$$\varepsilon = \begin{pmatrix} H & W_i^\dagger \\ W_i & B_{ij} \end{pmatrix} \tag{10.51}$$

$$\varepsilon^{-1} = \begin{pmatrix} \varepsilon_{00}^{-1} & \varepsilon_{0i}^{-1} \\ \varepsilon_{i0}^{-1} & \varepsilon_{ij}^{-1} \end{pmatrix} \tag{10.52}$$

with

$$\begin{aligned} \varepsilon_{00}^{-1} &= \left[H - \sum_i W_i^\dagger B_{ij}^{-1} W_j \right]^{-1} \\ \varepsilon_{0i}^{-1} &= -\varepsilon_{00}^{-1} \sum_j W_j^\dagger B_{ji}^{-1} \\ \varepsilon_{i0}^{-1} &= -\left(\sum_j B_{ij}^{-1} W_j \right) \varepsilon_{00}^{-1} \\ \varepsilon_{ij}^{-1} &= B_{ij}^{-1} + \varepsilon_{i0}^{-1} \left(\varepsilon_{00}^{-1} \right)^{-1} \varepsilon_{0j}^{-1} \end{aligned} \tag{10.53}$$

Chapter 11

The Dynamically screened potential

11.1 General expressions

From the definition given in Eq. 2.7 we have:

$$W_0(\mathbf{r}_1, \mathbf{r}_2; \omega) = \int \varepsilon^{-1}(\mathbf{r}_1, \mathbf{r}_3; \omega) v(\mathbf{r}_3, \mathbf{r}_2) d\mathbf{r}_3 \tag{11.1}$$

From Eq. A.12 the matrix form can be written:

$$W_{ij}(\mathbf{q}, \omega) = \sum_l \varepsilon^{-1}_{il}(\mathbf{q}, \omega) v_{lj}(\mathbf{q}) \tag{11.2}$$

Using Eq. 10.3 the screened potential is then written then as:

$$\begin{aligned} W_{ij}(\mathbf{q}, \omega) &= \sum_m \epsilon^{-1}_{im}(\mathbf{q}, \omega) v_{mj}(\mathbf{q}) \\ &= \sum_{lmn} v^{\frac{1}{2}}_{il}(\mathbf{q}) \tilde{\epsilon}^{-1}_{lm}(\mathbf{q}, \omega) v^{-\frac{1}{2}}_{mn}(\mathbf{q}) v_{nj}(\mathbf{q}) \\ &= \sum_{lm} v^{\frac{1}{2}}_{il}(\mathbf{q}) \tilde{\epsilon}^{-1}_{lm}(\mathbf{q}, \omega) \sum_n v^{-\frac{1}{2}}_{mn}(\mathbf{q}) v_{nj}(\mathbf{q}) \\ &= \sum_{lm} v^{\frac{1}{2}}_{il}(\mathbf{q}) \tilde{\epsilon}^{-1}_{lm}(\mathbf{q}, \omega) v^{\frac{1}{2}}_{mj}(\mathbf{q}) \end{aligned} \tag{11.3}$$

And we can, as already mentioned in section 2.1, separate it into and exchange and a correlation term, where:

$$\begin{aligned} W^x_{ij}(\mathbf{q}) &= v_{ij}(\mathbf{q}) \\ W^c_{ij}(\mathbf{q}, \omega) &= W_{ij}(\mathbf{q}, \omega) - v_{ij}(\mathbf{q}) \\ &= \sum_{lm} v^{\frac{1}{2}}_{il}(\mathbf{q}) \left[\tilde{\epsilon}^{-1}_{lm}(\mathbf{q}, \omega) - \delta_{lm} \right] v^{\frac{1}{2}}_{mj}(\mathbf{q}) \end{aligned} \tag{11.4}$$

To simplify the notation we introduce $D_{ij}(\mathbf{q}, \omega) \equiv \tilde{\epsilon}^{-1}_{ij}(\mathbf{q}, \omega) - \delta_{ij}$ so that we have

$$W^c_{ij}(\mathbf{q}, \omega) = \sum_{lm} v^{\frac{1}{2}}_{il}(\mathbf{q}) D_{lm}(\mathbf{q}, \omega) v^{\frac{1}{2}}_{mj}(\mathbf{q}) \tag{11.5}$$

11.2 Singularity at the Γ point ($\mathbf{q} = 0$)

As we have seen in Appendix 10.1 the symmetrized dielectric function has no divergencies, but we are still left with the singularity of v and hence of W at the Γ point. As in Appendix 7.4, Eqs. 7.48 to 7.51, for the bare Coulomb matrix we can write:

$$v^{\frac{1}{2}}_{ij}(\mathbf{q} \to 0) = \frac{v^{s\frac{1}{2}}_{ij}}{|\mathbf{q}|} + \tilde{v}^{\frac{1}{2}}_{ij} \tag{11.6}$$

Using eq. 11.3 we can write, for the screened potential:

$$\begin{aligned} W^c_{ij}(\mathbf{q}\to 0,\omega) =& \sum_{lm} v^{\frac{1}{2}}_{il}(\mathbf{q}\to 0) D_{lm}(0,\omega) v^{\frac{1}{2}}_{mj}(\mathbf{q}\to 0) \\ =& \frac{1}{|\mathbf{q}|^2}\sum_{lm} v^{s\frac{1}{2}}_{il} D_{lm}(0,\omega) v^{s\frac{1}{2}}_{mj} \\ &+\frac{1}{|\mathbf{q}|}\left\{\sum_{lm} v^{s\frac{1}{2}}_{il} D_{lm}(0,\omega)\tilde{v}^{\frac{1}{2}}_{mj} + \tilde{v}^{\frac{1}{2}}_{il} D_{lm}(0,\omega) v^{s\frac{1}{2}}_{mj}\right\} \\ &+\sum_{lm}\tilde{v}^{\frac{1}{2}}_{il} D_{lm}(0,\omega)\tilde{v}^{\frac{1}{2}}_{mj} \end{aligned} \tag{11.7}$$

Defining:

$$\begin{aligned} W^{cs2}_{ij}(\omega) =& \sum_{lm} v^{s\frac{1}{2}}_{il} D_{lm}(0,\omega) v^{s\frac{1}{2}}_{mj} \\ W^{cs1}_{ij}(\omega) =& \sum_{lm} v^{s\frac{1}{2}}_{il} D_{lm}(0,\omega)\tilde{v}^{\frac{1}{2}}_{mj} + \tilde{v}^{\frac{1}{2}}_{il} D_{lm}(0,\omega) v^{s\frac{1}{2}}_{mj} \\ \tilde{W}^c_{ij}(\omega) =& \sum_{lm}\tilde{v}^{\frac{1}{2}}_{il} D_{lm}(0,\omega)\tilde{v}^{\frac{1}{2}}_{mj} \end{aligned} \tag{11.8}$$

we can write

$$\boxed{W^c_{ij}(\mathbf{q}\to 0,\omega) = \frac{1}{|\mathbf{q}|^2} W^{cs2}_{ij}(\omega) + \frac{1}{|\mathbf{q}|} W^{cs1}_{ij}(\omega) + \tilde{W}^c_{ij}(\omega)} \tag{11.9}$$

11.3 Formulalism using v-diagonalized basis set

When using v-diagonalized basis set, the expressions for the screened Coulomb interaction, in particular those of the singular terms can be drammatically simplified. In the new basis set, we have

$$\begin{aligned} v^{s\frac{1}{2}}_{ij} &= \sqrt{2\pi}\delta_{i,0}\delta_{j,0} \\ \tilde{v}_{ij} &= \sqrt{\tilde{v}_i}\delta_{i,j} \end{aligned} \tag{11.10}$$

from which we can obtain

$$\begin{aligned} W^{cs2}_{ij} &= 4\pi D_{00}\delta_{i,0}\delta_{j,0} \\ W^{cs1}_{ij} &= \sqrt{4\pi}\left[\delta_{i,0} D_{0,j}\sqrt{\tilde{v}_j}(1-\delta_{j,0}) + (1-\delta_{i,0}) D_{i,0}\sqrt{\tilde{v}_i}\delta_{j,0}\right] \\ \tilde{W}_{ij} &= \sqrt{\tilde{v}_i} D_{ij}\sqrt{\tilde{v}_j} \end{aligned} \tag{11.11}$$

Chapter 12

Evaluation of the sef-energy Σ

12.1 Exchange self-energy

The exchange self-energy in periodic systems reads

$$\Sigma^x(\mathbf{r},\mathbf{r}') = -\sum_{n'\mathbf{k}'}^{\text{occ}} \psi_{n'\mathbf{k}'}(\mathbf{r}) v(\mathbf{r}',\mathbf{r}) \psi^*_{n'\mathbf{k}'}(\mathbf{r}') \tag{12.1}$$

Now expanding the bare Coulomb potential by the orthogonal basis set $\{\chi_i^{\mathbf{q}}\}$, we have:

$$\begin{aligned}\Sigma^x(\mathbf{r},\mathbf{r}') &= -\sum_{n'\mathbf{k}'}^{\text{occ}} \psi_{n'\mathbf{k}'}(\mathbf{r}) \sum_{\mathbf{q}}^{BZ}\sum_{ij} \chi_i^{\mathbf{q}}(\mathbf{r}) v_{ij}(\mathbf{q}) (\chi_j^{\mathbf{q}}(\mathbf{r}'))^* \psi^*_{n'\mathbf{k}'}(\mathbf{r}') \\ &= -\sum_{\mathbf{q}}^{BZ}\sum_{ij} v_{ij}(\mathbf{q}) \sum_{n'\mathbf{k}'}^{\text{occ}} \psi_{n'\mathbf{k}'}(\mathbf{r}) \chi_i^{\mathbf{q}}(\mathbf{r}) (\chi_j^{\mathbf{q}}(\mathbf{r}'))^* \psi^*_{n'\mathbf{k}'}(\mathbf{r}')\end{aligned} \tag{12.2}$$

Matrix elements of the exchange self-energy with respect to the single-particle wave functions now reads

$$\begin{aligned}\Sigma^x_{mn}(\mathbf{k}) &= \iint_V \psi^*_{m\mathbf{k}}(\mathbf{r}) \Sigma^x(\mathbf{r},\mathbf{r}') \psi_{n\mathbf{k}}(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \\ &= -\iint_V \psi^*_{m\mathbf{k}}(\mathbf{r}) \sum_{\mathbf{q}}^{BZ}\sum_{ij} v_{ij}(\mathbf{q}) \sum_{n'\mathbf{k}'}^{\text{occ}} \psi_{n'\mathbf{k}'}(\mathbf{r}) \chi_i^{\mathbf{q}}(\mathbf{r}) (\chi_j^{\mathbf{q}}(\mathbf{r}'))^* \psi^*_{n'\mathbf{k}'}(\mathbf{r}') \psi_{n\mathbf{k}}(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \\ &= -\sum_{\mathbf{q}}^{BZ}\sum_{ij} v_{ij}(\mathbf{q}) \sum_{n'\mathbf{k}'}^{\text{occ}} \left(\int_V \chi_i^{\mathbf{q}}(\mathbf{r}) \psi^*_{m\mathbf{k}}(\mathbf{r}) \psi_{n'\mathbf{k}'}(\mathbf{r}) d\mathbf{r}\right) \left(\int_V \chi_j^{\mathbf{q}*}(\mathbf{r}') \psi_{n\mathbf{k}}(\mathbf{r}') \psi^*_{n'\mathbf{k}'}(\mathbf{r}') d\mathbf{r}'\right) \\ &= -N_c^{-1} \sum_{\mathbf{q}}^{BZ}\sum_{ij} v_{ij}(\mathbf{q}) \sum_{n'}^{\text{occ}} \left[M^i_{mn'}(\mathbf{k},\mathbf{q})\right]^* M^j_{nn'}(\mathbf{k},\mathbf{q}) \\ &\equiv N_c^{-1} \sum_{\mathbf{q}}^{BZ} \Upsilon^x_{mn}(\mathbf{k},\mathbf{q})\end{aligned} \tag{12.3}$$

where we have used Eq. (9.25).

12.2 Correlation term

For the correlation term in frequency space one has to calculate the convolution:

$$\Sigma^c(\mathbf{r},\mathbf{r}',\omega) = \frac{i}{2\pi}\int_{-\infty}^{\infty} G_0(\mathbf{r},\mathbf{r}',\omega+\omega') W_0^c(\mathbf{r},\mathbf{r}',\omega') d\omega' \tag{12.4}$$

We follow the same steps as for the exchange term. The screened Coulomb potential can be expranded by the basis functions as

$$W_0^c(\mathbf{r},\mathbf{r}',\omega) = \sum_{\mathbf{q}}^{BZ}\sum_{ij} \chi_i^{\mathbf{q}}(\mathbf{r}) W^c_{ij}(\mathbf{q},\omega) (\chi_j^{\mathbf{q}}(\mathbf{r}'))^* \tag{12.5}$$

Inserting 12.5 and the definition of G_0 into 12.4 we have:

$$\begin{aligned}\Sigma^c(\mathbf{r},\mathbf{r}',\omega) =& \frac{i}{2\pi}\int_{-\infty}^{\infty} d\omega' \sum_{n'\mathbf{k}'} \frac{\psi_{n'\mathbf{k}'}(\mathbf{r})\psi^*_{n'\mathbf{k}'}(\mathbf{r}')}{\omega+\omega'-\tilde{\epsilon}_{n\mathbf{k}}} \sum_{\mathbf{q}}^{BZ}\sum_{ij} \chi_i^{\mathbf{q}}(\mathbf{r}) W^c_{ij}(\mathbf{q},\omega')(\chi_j^{\mathbf{q}}(\mathbf{r}'))^* \\ =& \sum_{\mathbf{q}}\sum_{ij}\sum_{\mathbf{k}'}\sum_{n'} \chi_i^{\mathbf{q}}(\mathbf{r})\psi_{n'\mathbf{k}'}(\mathbf{r})\chi_j^{\mathbf{q}*}(\mathbf{r}')\psi^*_{n'\mathbf{k}'}(\mathbf{r}')\frac{i}{2\pi}\int_{-\infty}^{\infty} d\omega' \frac{W^c_{ij}(\mathbf{q},\omega')}{\omega+\omega'-\tilde{\epsilon}_{n\mathbf{k}}}\end{aligned} \tag{12.6}$$

Matrix elements of correlation self-energy can therefore be calculated as

$$\begin{aligned}\Sigma^c_{mn}(\mathbf{k},\omega) =& \iint_V \psi^*_{m\mathbf{k}}(\mathbf{r})\Sigma^c(\mathbf{r},\mathbf{r}',\omega)\psi_{n\mathbf{k}}(\mathbf{r}')d\mathbf{r}d\mathbf{r}' \\ =& N_c^{-1}\sum_{\mathbf{q}}\sum_{ij}\sum_{n'} \left[M^i_{mn'}(\mathbf{k},\mathbf{q})\right]^* \frac{i}{2\pi}\int_{-\infty}^{\infty} d\omega' \frac{W^c_{ij}(\mathbf{q},\omega')}{\omega+\omega'-\tilde{\epsilon}_{n'\mathbf{k}-\mathbf{q}}} M^j_{nn'}(\mathbf{k},\mathbf{q}) \\ =& N_c^{-1}\sum_{\mathbf{q}}\sum_{n'}\frac{i}{2\pi}\int_{-\infty}^{\infty} d\omega' \frac{X_{mn;n'}(\mathbf{k},\mathbf{q},\omega')}{\omega+\omega'-\tilde{\epsilon}_{n'\mathbf{k}-\mathbf{q}}}\end{aligned} \tag{12.7}$$

where we have introduced

$$X_{mn;n'}(\mathbf{k},\mathbf{q},\omega) = \sum_{ij}\left[M^i_{mn'}(\mathbf{k},\mathbf{q})\right]^* W^c_{ij}(\mathbf{q},\omega) M^j_{nn'}(\mathbf{k},\mathbf{q}) \tag{12.8}$$

The frequency integrals in Eq. 12.7 are extremely difficult to perform, due to the poles of W_c as well as those of the Greens function. A smart solution to this problem has been given by Godby, Schlüter and Sham [24], and used in [8]. By performing the analytic continuation of the integrand into the ω' complex plane, and taking a closed contour for the integration, it can be shown that the integrals in Eq. 12.7 are equivalent to an integral of the same function over the imaginary ω' axis plus the sum of the residues of the integrand at the poles of the Greens Function between ω and the Fermi energy. The former requires the evaluation of W^c for imaginary frequencies, while the latter requires the evaluation of W^c at a certain number of real frequencies (or its interpolation).

We have chosen a different approach. We continue analytically the self-energy by taking the same expression of Eq. 12.4 in the imaginary axis, that is:

$$\Sigma^c(\mathbf{r},\mathbf{r}',i\omega) = \frac{i}{2\pi}\int_{-i\infty}^{i\infty} G_0(\mathbf{r},\mathbf{r}',i\omega+i\omega')W^c_0(\mathbf{r},\mathbf{r}',i\omega')di\omega' \tag{12.9}$$

Note this expression of the selfenergy along the imaginary frequency is NOT obtained directly from Eq. 12.10 by analytical continuation. Instead it is obtained by starting from the self-energy in the *imaginary time*. Using now Eq. 8.5 instead of 8.1 and following the same steps as before we obtain:

$$\Sigma^c_{mn}(\mathbf{k},iu) = N_c^{-1}\sum_{\mathbf{q}}^{BZ}\sum_{n'}\frac{-1}{2\pi}\int_{-\infty}^{\infty} du' \frac{X_{mn;n'}(\mathbf{k},\mathbf{q},iu')}{iu+iu'-\epsilon_{n'\mathbf{k}+\mathbf{q}}} \tag{12.10}$$

Using the fact that:

$$W^c_{ij}(\mathbf{q},iu) = W^c_{ij}(\mathbf{q},-iu) \tag{12.11}$$

we can further simplify 12.10 by:

$$\begin{aligned}\Sigma^c_{mn}(\mathbf{k},iu) =& N_c^{-1}\sum_{\mathbf{q}}\sum_{n'}\left(-\frac{1}{2\pi}\right)\int_0^{\infty} du' X_{mn;n'}(\mathbf{k},\mathbf{q},iu')\left[\frac{1}{iu+iu'-\epsilon_{n'\mathbf{k}-\mathbf{q}}}+\frac{1}{iu-iu'-\epsilon_{n'\mathbf{k}-\mathbf{q}}}\right] \\ =& N_c^{-1}\sum_{\mathbf{q}}\Upsilon^c_{mn}(\mathbf{k},\mathbf{q},iu)\end{aligned} \tag{12.12}$$

where

$$\Upsilon^c_{mn}(\mathbf{k},\mathbf{q},iu) \equiv \sum_{n'}\left(-\frac{1}{2\pi}\right)\int_0^{\infty} du' X_{mn;n'}(\mathbf{k},\mathbf{q},iu')\frac{2(iu-\epsilon_{n'\mathbf{k}-\mathbf{q}})}{(iu-\epsilon_{n'\mathbf{k}-\mathbf{q}})^2+u'^2} \tag{12.13}$$

12.3 Brillouin-Zone integration of the singular terms

Both exchange and correlation terms of the self-energy involve the Brillouin-Zone integration of a function that diverges at the Γ point. Let's write it (we don't write explicitly the ω-dependence, it is implicit in the correlation term):

$$\Sigma^{x/c}_{mn}(\mathbf{k}) = N_c^{-1}\sum_{\mathbf{q}}^{BZ}\Upsilon^{x/c}_{mn}(\mathbf{k},\mathbf{q}) \tag{12.14}$$

with

$$\begin{aligned}\Upsilon^{x}_{mn}(\mathbf{k},\mathbf{q}) &= -\sum_{ij}\sum_{n'}^{\text{occ}}\left[M^{i}_{mn'}(\mathbf{k},\mathbf{q})\right]^{*} v_{ij}(\mathbf{q}) M^{j}_{nn'}(\mathbf{k},\mathbf{q}) \\ \Upsilon^{c}_{mn}(\mathbf{k},\mathbf{q},iu) &= \sum_{n'}\left(-\frac{1}{2\pi}\right)\int_{0}^{\infty} du' X_{mn;n'}(\mathbf{k},\mathbf{q},iu')\frac{2(iu-\epsilon_{n'\mathbf{k}-\mathbf{q}})}{(iu-\epsilon_{n'\mathbf{k}-\mathbf{q}})^{2}+iu'^{2}}\end{aligned} \tag{12.15}$$

In the $\mathbf{q}\to 0$ limit we can separate the singular terms as:

$$\Upsilon^{x/c}_{mn}(\mathbf{k},\mathbf{q}\to 0) = \frac{\Upsilon^{x/c-s2}_{mn}(\mathbf{k})}{q^{2}} + \frac{\Upsilon^{x/c-s1}_{mn}(\mathbf{k})}{q} + \tilde{\Upsilon}^{x/c}_{mn}(\mathbf{k}) \tag{12.16}$$

The singularity can be integrated out by using the technique as formulated in Sec. A.2.

12.4 Exchange and correlation selfenergy using v-diagonalized basis set

Using the new basis set we have

$$\begin{aligned} v^{s}_{ij} &= 4\pi\delta_{i,0}\delta_{j,0} \\ \tilde{v}_{ij}(\mathbf{q}) &= \tilde{v}_{i}\delta_{i,j} \\ W^{cs2}_{ij}(\omega) &= 4\pi D_{00}(0,\omega)\delta_{i,0}\delta_{j,0} \\ W^{cs1}_{ij}(\omega) &= \sqrt{4\pi}\left[\delta_{i,0}D_{0,j}(\mathbf{q}=0,\omega)\tilde{v}^{\frac{1}{2}}_{j}(1-\delta_{j,0}) + (1-\delta_{i,0})D_{i,0}(\mathbf{q}=0,\omega)\tilde{v}^{\frac{1}{2}}_{i}\delta_{j,0}\right] \\ \tilde{W}_{ij}(\mathbf{q},\omega) &= \tilde{v}^{\frac{1}{2}}_{i} D_{ij}(\mathbf{q},\omega)\tilde{v}^{\frac{1}{2}}_{j}\end{aligned} \tag{12.17}$$

The corresponding expressions for the exchange and correlation selfenergies can be greatly simplified.

12.4.0.1 Exchange

$$\begin{aligned}\Upsilon^{xs2}_{mn}(\mathbf{k}) &= -\sum_{ij}\sum_{n'}^{\text{occ}}\left[M^{i}_{mn'}(\mathbf{k},\mathbf{q})\right]^{*} v^{s}_{ij}(\mathbf{q}) M^{j}_{nn'}(\mathbf{k},\mathbf{q}) \\ &= -(4\pi)\sum_{n'}^{\text{occ}}\left[M^{0}_{mn'}(\mathbf{k},0)\right]^{*} M^{0}_{nn'}(\mathbf{k},0) \\ \tilde{\Upsilon}^{x}_{mn}(\mathbf{k},\mathbf{q}) &= \sum_{n'}^{\text{occ}}\tilde{v}_{i}\left[M^{i}_{mn'}(\mathbf{k},\mathbf{q})\right]^{*} M^{i}_{nn'}(\mathbf{k},\mathbf{q})\end{aligned} \tag{12.18}$$

Now considering that

$$\begin{aligned} M^{0}_{nm}(\mathbf{k},0) &= \int_{\Omega}\left[\chi_{0}^{\mathbf{q}=0}(\mathbf{r})\right]^{*}\psi_{n\mathbf{k}}(\mathbf{r})\psi^{*}_{m\mathbf{k}}(\mathbf{r}) \\ &= \frac{1}{\Omega^{1/2}}\int_{\Omega}\psi_{n\mathbf{k}}(\mathbf{r})\psi^{*}_{m\mathbf{k}}(\mathbf{r}) \\ &= \frac{1}{\Omega^{1/2}}\delta_{nm}\end{aligned} \tag{12.19}$$

we can further simplify $\Upsilon^{xs2}_{n\mathbf{k}}$

$$\Upsilon^{xs2}_{mn}(\mathbf{k}) = -\frac{4\pi}{\Omega}f_{n\mathbf{k}}\delta_{mn} \tag{12.20}$$

12.4.0.2 Correlation

From

$$\Upsilon^{c}_{mn}(\mathbf{k},\mathbf{q}) = \sum_{n'}\left(-\frac{1}{2\pi}\right)\int_{0}^{\infty} du' X_{mn;n'}(\mathbf{k},\mathbf{q},u')\frac{2(i\omega-\epsilon_{n'\mathbf{k}-\mathbf{q}})}{(i\omega-\epsilon_{n'\mathbf{k}-\mathbf{q}})^{2}+\omega'^{2}} \tag{12.21}$$

$$X_{mn;n'}(\mathbf{k},\mathbf{q},\omega) = \sum_{ij}\left[M^{i}_{mn'}(\mathbf{k},\mathbf{q})\right]^{*} W^{c}_{ij}(\mathbf{q},\omega) M^{j}_{nn'}(\mathbf{k},\mathbf{q}) \tag{12.22}$$

we obtain the singular terms

$$\begin{aligned}
X^{s2}_{mn;n'}(\mathbf{k},\omega) =& \sum_{ij} \left[M^i_{mn'}(\mathbf{k},0)\right]^* W^{cs2}_{ij}(\omega) M^j_{nn'}(\mathbf{k},0) \\
=& 4\pi D_{00}(0,\omega) \left[M^0_{mn'}(\mathbf{k},0)\right]^* M^0_{nn'}(\mathbf{k},0) \\
=& \frac{4\pi}{\Omega}\delta_{nn'}\delta_{mn} D_{00}(0,\omega) \\
X^{s1}_{mn;n'}(\mathbf{k},\omega) =& \sum_{ij} \left[M^i_{mn'}(\mathbf{k},0)\right]^* W^{cs1}_{ij}(\omega) M^j_{nn'}(\mathbf{k},0) \\
=& \sum_{ij} \left[M^i_{mn'}(\mathbf{k},0)\right]^* \sqrt{4\pi}\left[\delta_{i,0} D_{0,j}(0,\omega)\tilde{v}^{\frac{1}{2}}_j (1-\delta_{j,0}) + (1-\delta_{i,0}) D_{i,0}(0,\omega)\tilde{v}^{\frac{1}{2}}_i \delta_{j,0}\right] M^j_{nn'}(\mathbf{k},0) \\
=& \sqrt{4\pi}\sum_{i\neq 0}\left\{\left[M^0_{mn'}(\mathbf{k},0)\right]^* D_{0,i}(0,\omega)\tilde{v}^{\frac{1}{2}}_i M^i_{nn'}(\mathbf{k},0) + \left[M^i_{mn'}(\mathbf{k},0)\right]^* D_{i,0}(0,\omega)\tilde{v}^{\frac{1}{2}}_i M^0_{nn'}(\mathbf{k},0)\right\} \\
=& \sqrt{\frac{4\pi}{\Omega}}\sum_{i\neq 0}\left\{\delta_{mn'} D_{0,i}(0,\omega)\tilde{v}^{\frac{1}{2}}_i M^i_{nm}(\mathbf{k},0) + \delta_{nn'} D_{i,0}(0,\omega)\tilde{v}^{\frac{1}{2}}_i \left[M^i_{mn}(\mathbf{k},0)\right]^*\right\} \\
\tilde{X}_{mn;n'}(\mathbf{k},\mathbf{q},\omega) =& \sum_{ij}\left[M^i_{mn'}(\mathbf{k},\mathbf{q})\right]^* \tilde{v}^{\frac{1}{2}}_i(\mathbf{q}) D_{ij}(\mathbf{q},\omega)\tilde{v}^{\frac{1}{2}}_j(\mathbf{q}) M^j_{nn'}(\mathbf{k},\mathbf{q})
\end{aligned} \tag{12.23}$$

12.5 Combining $\tilde{v}^{\frac{1}{2}}$ and M^i_{nm}

An noteworthy feature in the formulation above is that for both the dielectric matrix and selfenergy, M^i_{nm} always appears together with $\tilde{v}^{\frac{1}{2}}$. We can therefore define a new quantity

$$\tilde{M}^i_{nm}(\mathbf{k},\mathbf{q}) \equiv v^{\frac{1}{2}}_i M^i_{nm}(\mathbf{k},\mathbf{q}) \tag{12.24}$$

Using this quantity we have the following working formula for the dielectric matrix, exchange and correlation self-energy.

12.5.0.1 Dielectric matrix

$$\begin{aligned}
\varepsilon^H_{ij}(\omega) =& \delta_{i0}\delta_{j0} - 4\pi\delta_{i0}P^H(\omega)\delta_{j0} = \left[1 - 4\pi P^H(\omega)\right]\delta_{i0}\delta_{j0} \\
\varepsilon^{W1}_{ij}(\omega) =& \left(-\sqrt{\frac{4\pi}{\Omega}}\right) N_c^{-1}\sum_{\mathbf{k}}^{BZ}\sum_{n'\neq n} F_{nn'\mathbf{k}}(0,\omega)\frac{\mathbf{p}_{nn'\mathbf{k}}\cdot\hat{\mathbf{q}}}{\epsilon_{n\mathbf{k}} - \epsilon_{n'\mathbf{k}}}\tilde{M}^i_{nn'}(\mathbf{k},0)\delta_{j0} \\
\varepsilon^{W2}_{ij}(\omega) =& \left(-\sqrt{\frac{4\pi}{\Omega}}\right) N_c^{-1}\sum_{\mathbf{k}}^{BZ}\sum_{n'\neq n} F_{nn'\mathbf{k}}(0,\omega)\frac{\mathbf{p}^*_{nn'\mathbf{k}}\cdot\hat{\mathbf{q}}}{\epsilon_{n\mathbf{k}} - \epsilon_{n'\mathbf{k}}}\left[\tilde{M}^j_{nn'}(\mathbf{k},0)\right]^*\delta_{i0} \\
\varepsilon_{ij}(\mathbf{q},\omega) =& \delta_{ij} - N_c^{-1}\sum_{\mathbf{k}}^{BZ}\sum_{n}^{\text{occ}}\sum_{m}^{\text{unocc}} \tilde{M}^i_{nm}(\mathbf{k},\mathbf{q})\left[\tilde{M}^j_{nm}(\mathbf{k},\mathbf{q})\right]^* F_{nm\mathbf{k}}(\mathbf{q},\omega)
\end{aligned} \tag{12.25}$$

12.5.0.2 Exchange self-energy

$$\begin{aligned}
\Upsilon^{xs2}_{mn}(\mathbf{k}) =& -\frac{4\pi}{\Omega} f_{n\mathbf{k}}\delta_{mn} \\
\tilde{\Upsilon}^x_{mn}(\mathbf{k},\mathbf{q}) =& \sum_{n'}^{\text{occ}}\sum_i \left[\tilde{M}^i_{mn'}(\mathbf{k},\mathbf{q})\right]^* \tilde{M}^i_{nn'}(\mathbf{k},\mathbf{q})
\end{aligned} \tag{12.26}$$

12.5.0.3 Correlation selfenergy

$$\begin{aligned}
X^{s2}_{mn;n'}(\mathbf{k},\omega) =& \frac{4\pi}{\Omega}\delta_{nn'}\delta_{mn} D_{00}(0,\omega) \\
X^{s1}_{mn;n'}(\mathbf{k},\omega) =& \sqrt{\frac{4\pi}{\Omega}}\sum_{i\neq 0}\left\{\delta_{mn'} D_{0,i}(0,\omega)\tilde{M}^i_{nm}(\mathbf{k},0) + \delta_{nn'} D_{i,0}(0,\omega)\left[\tilde{M}^i_{mn}(\mathbf{k},0)\right]^*\right\} \\
\tilde{X}_{mn;n'}(\mathbf{k},\mathbf{q},\omega) =& \sum_{ij}\left[\tilde{M}^i_{mn'}(\mathbf{k},\mathbf{q})\right]^* D_{ij}(\mathbf{q},\omega)\tilde{M}^j_{nn'}(\mathbf{k},\mathbf{q})
\end{aligned} \tag{12.27}$$

12.6 Static COHSEX approximation

The self-energy in the static COHSEX approximation reads

$$\begin{aligned}\Sigma^{\mathrm{xc}}(\mathbf{x},\mathbf{x}') &= \frac{1}{2}\delta(\mathbf{x}-\mathbf{x}')\left[W(\mathbf{x},\mathbf{x}';0)-v(\mathbf{x},\mathbf{x}')\right] - \sum_{n\mathbf{k}} f_{n\mathbf{k}}\psi_{n\mathbf{k}}(\mathbf{x})\psi^*_{n\mathbf{k}}(\mathbf{x}')W(\mathbf{x},\mathbf{x}';0) \\ &= \Sigma^{\mathrm{x}}(\mathbf{x},\mathbf{x}') + \Sigma^{\mathrm{c-CHSX}}(\mathbf{x},\mathbf{x}')\end{aligned} \tag{12.28}$$

with

$$\Sigma\mathrm{c}-\mathrm{CHSX}(\mathbf{x},\mathbf{x}') = \frac{1}{2}\delta(\mathbf{x}-\mathbf{x}')W_c(\mathbf{x},\mathbf{x}';0) - \sum_{n\mathbf{k}} f_{n\mathbf{k}}\psi_{n\mathbf{k}}(\mathbf{x})\psi^*_{n\mathbf{k}}(\mathbf{x}')W_c(\mathbf{x},\mathbf{x}';0) \tag{12.29}$$

Using the cloure relation

$$\delta(\mathbf{x}-\mathbf{x}') = \sum_{n\mathbf{k}} \psi_{n\mathbf{k}}(\mathbf{x})\psi^*_{n\mathbf{k}}(\mathbf{x}') \tag{12.30}$$

we have

$$\Sigma\mathrm{c}-\mathrm{CHSX}(\mathbf{x},\mathbf{x}') = \sum_{n\mathbf{k}}\left[\frac{1}{2}-f_{n\mathbf{k}}\right]\psi_{n\mathbf{k}}(\mathbf{x})\psi^*_{n\mathbf{k}}(\mathbf{x}')W_c(\mathbf{x},\mathbf{x}';0) \tag{12.31}$$

Now using the expansion of W_c by the mixed basis

$$W_c(\mathbf{x},\mathbf{x}';0) = \sum_{\mathbf{q}}\sum_{i,j}\left[W_c(\mathbf{q},0)\right]_{ij}\chi_{\mathbf{q}i}(\mathbf{x})\left[\chi_{\mathbf{q}j}(\mathbf{x}')\right]^* \tag{12.32}$$

One obtains

$$\Sigma^{\mathrm{c-CHSX}}(\mathbf{x},\mathbf{x}') = \sum_{\mathbf{q}}\sum_{i,j}\sum_{n\mathbf{k}}\left[\frac{1}{2}-f_{n\mathbf{k}}\right]\left[W_c(\mathbf{q},0)\right]_{ij}\chi_{\mathbf{q}i}(\mathbf{x})\left[\chi_{\mathbf{q}j}(\mathbf{x}')\right]^*\psi_{n\mathbf{k}}(\mathbf{x})\psi^*_{n\mathbf{k}}(\mathbf{x}') \tag{12.33}$$

The matrix elements of $\Sigma^{\mathrm{c-CHSX}}$ therefore read

$$\begin{aligned}\left[\Sigma^{\mathrm{c-CHSX}}\right]_{mn}(\mathbf{k}) &\equiv \int d\mathbf{x}\int d\mathbf{x}'\psi^*_{m\mathbf{k}}(vecx)\Sigma^{\mathrm{c-CHSX}}(\mathbf{x},\mathbf{x}')\psi_{n\mathbf{k}}(vecx) \\ &= \sum_{\mathbf{q}}\sum_{i,j}\sum_{n'\mathbf{k}'}\left[\frac{1}{2}-f_{n\mathbf{k}}\right]\left[W_c(\mathbf{q},0)\right]_{ij} \\ &\times \int d\mathbf{x}\psi^*_{m\mathbf{k}}(\mathbf{x})\chi_{\mathbf{q}i}(\mathbf{x})\psi_{n'\mathbf{k}'}(\mathbf{x})\int d\mathbf{x}'\psi_{n\mathbf{k}}(\mathbf{x})\chi^*_{\mathbf{q}j}(\mathbf{x})\psi^*_{n'\mathbf{k}'}(\mathbf{x}') \\ &\equiv N_c^{-1}\sum_{\mathbf{q}}\sum_{i,j}\sum_{n'\mathbf{k}'}\left[\frac{1}{2}-f_{n\mathbf{k}}\right]\left[W_c(\mathbf{q},0)\right]_{ij}\left[M^i_{mn'}(\mathbf{k},\mathbf{q})\right]^* M^j_{nn'}(\mathbf{k},\mathbf{q})\delta_{\mathbf{k}',\mathbf{k}-\mathbf{q}} \\ &= N_c^{-1}\sum_{\mathbf{q}}\sum_{i,j}\sum_{n'}\left[\frac{1}{2}-f_{n\mathbf{k}}\right]\left[W_c(\mathbf{q},0)\right]_{ij}\left[M^i_{mn'}(\mathbf{k},\mathbf{q})\right]^* M^j_{nn'}(\mathbf{k},\mathbf{q})\end{aligned} \tag{12.34}$$

Using the previous defined quantity

$$X_{mn;n'}(\mathbf{k},\mathbf{q};\omega) = \sum_{i,j}\left[W_c(\mathbf{q},0)\right]_{ij}\left[M^i_{mn'}(\mathbf{k},\mathbf{q})\right]^* M^j_{nn'}(\mathbf{k},\mathbf{q}) \tag{12.35}$$

We have

$$\left[\Sigma^{\mathrm{c-CHSX}}\right]_{mn}(\mathbf{k}) = N_c^{-1}\sum_{\mathbf{q}}\sum_{i,j}\sum_{n'}\left[\frac{1}{2}-f_{n\mathbf{k}}\right]X_{mn;n'}(\mathbf{k},\mathbf{q};0) \tag{12.36}$$

Chapter 13

G_0W_0 and GW_0 Approximation

In this chapter we describe how quasi-particle energies are obtained one we have obtained matrix elements of exchange and correlatoin selfenergies.

13.1 G_0W_0 approximation

The quasi-particle equation even under the GW approximation is still very complicated. In practice, the so- called G_0W_0 approach is usually used, in which the quasiparticle energy $\mathcal{E}_{n\mathbf{k}}$ is calculated from the first order perturbation theory based on Kohn-Sham (usually LDA) eigenenergies $\epsilon_{n\mathbf{k}}$ and eigenfunctions $\psi_{n\mathbf{k}}(\mathbf{r})$

$$\begin{aligned}\mathcal{E}_{n\mathbf{k}} =&\epsilon_{n\mathbf{k}} + \Re \langle\psi_{n\mathbf{k}}| \Sigma(\mathcal{E}_{n\mathbf{k}}) - V_{\rm xc} |\psi_{n\mathbf{k}}\rangle \\ \equiv&\epsilon_{n\mathbf{k}} + \delta\Sigma_{n\mathbf{k}}(\mathcal{E}_{n\mathbf{k}})\end{aligned} \tag{13.1}$$

Expanding $\Sigma(\mathcal{E}_{n\mathbf{k}})$ around $\epsilon_{n\mathbf{k}}$ by the Taylor's expansion we have

$$\begin{aligned}\mathcal{E}_{n\mathbf{k}} =&\epsilon_{n\mathbf{k}} + Z_{n\mathbf{k}} \langle\psi_{n\mathbf{k}}| \Sigma(\epsilon_{n\mathbf{k}}) - V_{\rm xc} |\psi_{n\mathbf{k}}\rangle \\ \equiv&\epsilon_{n\mathbf{k}} + Z_{n\mathbf{k}}\delta\Sigma_{n\mathbf{k}}(\epsilon_{n\mathbf{k}})\end{aligned} \tag{13.2}$$

where $V_{\rm xc}(\mathbf{r})$ is the DFT exchange correlation potential. $Z_{n\mathbf{k}}$ is the QP renormalization factor,

$$Z_{n\mathbf{k}} = \left[1 - \left(\frac{\partial}{\partial\omega} \langle\psi_{n\mathbf{k}}| \Sigma(\omega) |\psi_{n\mathbf{k}}\rangle\right)_{\omega=\epsilon_{n\mathbf{k}}}\right]^{-1} \tag{13.3}$$

and accounts for the fact that Σ is evaluated at the DFT energy rather that the QP energy. The self- energy is calculated from G_0 and W_0 that are all evaluated from KS eigen-energies and wavefunctions.

13.2 Analytic continuation of correlation selfenergy

In the current implementation of our code, the selfenergy is first calculated along the imaginary frequency and then analytically continued to the real frequency. The accuracy of final results relies sensitively on the accuracy of such an analytical continuation procedure. Here we investigate two AC approaches.

13.2.1 Multipole fitting method

In this method, the selfenergy calculated along the imaginary frequency is fitted to the following multipole function (the dependence on the band indexes $n\mathbf{k}$ is dropped to simplify the notation)

$$\Sigma(i\omega) = \sum_i^{N_p} \frac{a_i}{i\omega - b_i} \tag{13.4}$$

where the parameters $\{a_i\}$ and $\{b_i\}$ are determined by the nonlinear least squareroot (NLS) fitting procedure. This method will be denoted as MPF.

13.2.2 Pade approximant method

A function $f(z)$, whose values at N discrete points $\{z_n|n = 1..N\}$ are given $f(z_n) = f_n$, can be fitted to a N-point Pade approximant

$$P_N(z) = \frac{A_N(z)}{B_N(z)} \tag{13.5}$$

$A_N(z)$ and $B_N(z)$ are complex polynominal of $N/2$ and $N/2-1$-th order for even N. For odd N, both $A_N(z)$ and $B_N(z)$ are the $(N-1)/2$-order polynomials. In this work we always use even N. Therefore the number of poles that are represented by the N-point Pade approximant is equal to $N/2$. The $A_N(z)$ and $B_N(z)$, based on the Thiele's reciprocal difference method, [62, 36] can be calculated recursively according to

$$A_n(z) = A_{n-1}(z) + (z - z_{n-1})a_n A_{n-2}(z) \tag{13.6}$$
$$B_n(z) = B_{n-1}(z) + (z - z_{n-1})a_n B_{n-2}(z) \tag{13.7}$$

with $A_0 = 0$, $A_1 = a1$ and $B_0 = B_1 = 1$. The coefficients $\{a_n\}$ are also calculated recursively by

$$a_n = g_n(z_n) \tag{13.8}$$
$$g_1(z_n) = f_n \tag{13.9}$$
$$g_p(z) = \frac{g_{p-1}(z_{p-1}) - g_{p-1}(z)}{(z - z_{p-1})g_{p-1}(z)} \quad p \geq 2 \tag{13.10}$$

Pade approximant has the feature that it is the "best" approximation of a function by a rational function of given order. To be more specific, $P_N(z)$ corresponding to $f(z)$ at $z = 0$ agrees up to the N-th order derivative

$$\begin{aligned} f(0) &= P_N(0) \\ f'(0) &= P'_N(0) \\ &\cdots \\ f^{(N)}(0) &= P_N^{(N)}(0) \end{aligned} \tag{13.11}$$

As shown in the previous section, to calculate the quasi-particle energies, one needs only the selfenergy $\Sigma_{n\mathbf{k}}(z)$ evaluated around the corresponding KS eigenenergy $\epsilon_{n\mathbf{k}}$. Therefore the requirement for the AC function is that it has minimal error around $z = \epsilon_{n\mathbf{k}}$. One would think that $\Sigma(z)$ should be related to the PA function by

$$\Sigma_{n\mathbf{k}}(z) = P_N(z - \epsilon_{n\mathbf{k}}) \tag{13.12}$$

and the PA function $P_N(z)$ is fitted on the set of points $\{z_p = -\epsilon_{n\mathbf{k}} + i\omega_p, f_p = \Sigma_{n\mathbf{k}}(i\omega_p)\}$ This additional transformation is actually not necessary due to the fact that both the PA function (Eq. (13.5)) and the multipole function (Eq. (13.4) have the feature that

$$P_N(z + z_0; \{z_p\}) = P_N(z; \{z_p - z_0\}) \tag{13.13}$$

so that

$$\Sigma_{n\mathbf{k}}(z) = P_N(z - \epsilon_{n\mathbf{k}}; \{-\epsilon_{n\mathbf{k}} + i\omega_p\}) = P_N(z; \{i\omega_p\}) \tag{13.14}$$

The PA function depends on the set of input complex points used for the fitting. In our case, the selfenergy is calculated on N_ω imaginary frequency points. When using PA approach one can use $N = 4..N_\omega$ points to obtain the AC function on the real frequency, corresponding to $N_p = 2..N_\omega/2$. In the following section, we will test the effects of using different N_p.

The validity of the analytical continuation method relies on the fact that the selfenergy is analytic for $\omega < \mu$ in the upper half-plane and for $\omega > \mu$ in the lower-half plane. The AC function does not necessarily satisfy this requirement rigorously, but it should be fine as long as the abnormal singularity occurs far away from the relevant energy region.

13.3 Fermi energy shift

This part is mainly adapted from Patrick's thesis. [46] A significant consequence of approximating the full Green's function G by the LDA Green's function G_0 is that the particle number is not necessarily conserved. This is related to the fact that the GW quasi-particle corrections to the Fermi level is in general not zero,

$$\mu_{GW} = \mu_{\mathrm{KS}} + \epsilon_s \tag{13.15}$$

where the chemical potential in both GW and KS are taken as the middle of the band gap in the case of insulating materials at zero temperature. As first suggested by Hedin [27], a simple way of recovering the conservation of particle number and therefore simulating self-consistency is to introduce the shift ϵ_s into G_0

$$\tilde{G}_0(\omega) = G_0(\omega - \epsilon_s), \tag{13.16}$$

as a better approximation to G. The resultant self-energy reads

$$\begin{aligned} \Sigma(\omega) =& \frac{i}{2\pi} \int d\omega' W_0(\omega') \tilde{G}_0(\omega' + \omega) \\ =& \frac{i}{2\pi} \int d\omega' W_0(\omega') G_0(\omega' + \omega - \epsilon_s). \end{aligned} \tag{13.17}$$

Since in practice the self-energy is calculated based on the unshifted Green's function

$$\Sigma^{\text{calc}}(\omega) = \frac{i}{2\pi} \int d\omega' W_0(\omega') G_0(\omega' + \omega), \tag{13.18}$$

we have

$$\Sigma(\omega) = \Sigma^{\text{calc}}(\omega - \epsilon_s). \tag{13.19}$$

The corresponding quasi-particle equation becomes

$$H(E_{n\mathbf{k}} - \epsilon_s)\Psi_{n\mathbf{k}} = E_{n\mathbf{k}}\Psi_{n\mathbf{k}}. \tag{13.20}$$

from which, we obtain, using the first-order perturbation theory

$$E_{n\mathbf{k}} = \epsilon_{n\mathbf{k}} + \delta\Sigma_{n\mathbf{k}}(E_{n\mathbf{k}} - \epsilon_s). \tag{13.21}$$

By expanding the correlation selfenergy around the KS eigenenergy $\epsilon_{n\mathbf{k}}$,we have

$$\begin{aligned} E_{n\mathbf{k}} =& \epsilon_{n\mathbf{k}} + Z_{n\mathbf{k}} \left[\delta\Sigma_{n\mathbf{k}}(\epsilon_{n\mathbf{k}}) - \epsilon_s\right] + \epsilon_s \\ =& \epsilon_{n\mathbf{k}} + Z_{n\mathbf{k}}\delta\Sigma_{n\mathbf{k}}(\epsilon_{n\mathbf{k}}) + (1 - Z_{n\mathbf{k}})\epsilon_s \end{aligned} \tag{13.22}$$

Comparing this equation to Eq.(13.1), we see that the contribution of this Fermi energy shift to the band gap is proportal to the difference in $Z_{n\mathbf{k}}$ for the valence band maximum (VBM) and conduction band minimum (CBM)

$$\delta E^{\text{es}}_{\text{gap}} = (Z_{\text{VBM}} - Z_{\text{CBM}})\epsilon_s. \tag{13.23}$$

For normal sp semiconductors like Si and GaAs in which the valence band and conduction band are of similar spcharacters, Z_{VBM} and Z_{CBM} are very close so that the contribution of $\delta E^{\text{es}}_{\text{gap}}$ is negligible. But for materials in which the VBM and CBM have very different characters, as in the case of CeO_2 and ThO_2, the difference between Z_{VBM} and Z_{CBM} can be significant, so that the contribution of the Fermil energy shift is non-negligible.

In practice, the Fermi energy shift can be included either self-consistently or perturbatively. In the self-consistent approach based on Eq.13.1 we have

$$\begin{aligned} \mathcal{E}^{(i)}_{n\mathbf{k}} &= \mathcal{E}^{(i-1)}_{n\mathbf{k}} + \delta\Sigma_{n\mathbf{k}}(\mathcal{E}^{(i-1)}_{n\mathbf{k}} - \epsilon^{(i-1)}_s) \\ \epsilon^{(i-1)}_s &= \mu^{(i-1)}_{GW} - \mu_{\text{KS}}. \end{aligned} \tag{13.24}$$

In the perturbative approach based on Eq.13.2, by assuming that GW quasi-particle corrections do not reorder the energy spectrum, the Fermi energy shift for finite systems can be calculated directly by

$$\epsilon_s = \frac{Z_{\text{HO}}\delta\Sigma_{\text{HO}} + Z_{\text{LU}}\delta\Sigma_{\text{LU}}}{Z_{\text{HO}} + Z_{\text{LU}}} \tag{13.25}$$

where HO and LU represent highest occupied and lowest unoccupied orbitals. The perturbative approach for solid is a little complicated due to the k-dependence of the selfenergy. The location of VBM and CBM of GW bands are not known a priori, so that ϵ_s can not be calculated directly as in finite systems. One can, however, calculate ϵ_s also in an iterative manner

$$\begin{aligned} \mathcal{E}^{(i)}_{n\mathbf{k}} &= \epsilon_{n\mathbf{k}} + Z_{n\mathbf{k}}\delta\Sigma_{n\mathbf{k}}(\epsilon_{n\mathbf{k}}) - \epsilon^{(i-1)}_s \\ \epsilon^{(i)}_s &= \mu^{(i)}_{GW} - \mu_{\text{KS}}. \end{aligned} \tag{13.26}$$

with $\epsilon^{(0)}_s = 0$. The most significant difference between these two iterative approach the argument that enters the selfenergy as a function. In Eq. 13.24 the selfenergy is evaluated in each iteration at different energy points while in Eq. 13.26 the selfenergy is evaluated only once, at the corresponding KS eigenenergy. A priori it is not clear whether these two iterative approaches are stable at. In the first approach the selfenergy is evaluated not only at the KS eigenenergy $\epsilon_{n\mathbf{k}}$, but also in the energy region around $\epsilon_{n\mathbf{k}}$, therefore the accuracy requirement for the selfenergy as a function of real energy is more stringent.

In the remaining part of this paper, we will compare the following four variants FES scheme:

i. **FES-0**: perturbative treatment without FES (Eq. (13.2));

$$\mathcal{E}_{n\mathbf{k}} = \epsilon_{n\mathbf{k}} + Z_{n\mathbf{k}}\delta\Sigma_{n\mathbf{k}}(\epsilon_{n\mathbf{k}}) \tag{13.27}$$

ii. **FES-1**: perturbative treatment with FES (Eq. (13.26)) ;

$$\begin{aligned} \mathcal{E}^{(i)}_{n\mathbf{k}} &= \epsilon_{n\mathbf{k}} + Z_{n\mathbf{k}}\delta\Sigma_{n\mathbf{k}}(\epsilon_{n\mathbf{k}}) - \epsilon^{(i-1)}_s \\ \epsilon^{(i)}_s &= \mu^{(i)}_{GW} - \mu_{\rm KS}. \end{aligned} \tag{13.28}$$

iii. **FES-2**: iterative treatment with FES (Eq. (13.24));

$$\begin{aligned} \mathcal{E}^{(i)}_{n\mathbf{k}} &= \mathcal{E}^{(i-1)}_{n\mathbf{k}} + \delta\Sigma_{n\mathbf{k}}(\mathcal{E}^{(i-1)}_{n\mathbf{k}} - \epsilon^{(i-1)}_s) \\ \epsilon^{(i-1)}_s &= \mu^{(i-1)}_{GW} - \mu_{\rm KS}. \end{aligned} \tag{13.29}$$

iv. **FES-3**: iterative treatment without FES.

$$\mathcal{E}^{(i)}_{n\mathbf{k}} = \mathcal{E}^{(i-1)}_{n\mathbf{k}} + \delta\Sigma_{n\mathbf{k}}(\mathcal{E}^{(i-1)}_{n\mathbf{k}}) \tag{13.30}$$

13.4 GW_0 approach

The basic idea of the so-called GW_0 approach is to update G using quasi-particle energies with fixed screened Coulomb interaction W_0, in the meanwhile quasi-particle wave-functions are still approximated by KS eigenvectors. In practice, QP energies can calculated self-consistently by two different ways. In the first scheme, QP energies are calculated self-consistently in terms of the following iterative relation,

$$\mathcal{E}^{(i)}_{n\mathbf{k}} = \epsilon_{n\mathbf{k}} + \delta\Sigma^{(i-1)}_{n\mathbf{k}}(\mathcal{E}^{(i-1)}_{n\mathbf{k}}; \{\mathcal{E}^{(i-1)}_{n\mathbf{k}} - \epsilon^{(i-1)}_s\}). \tag{13.31}$$

The second argument for $\Sigma_{n\mathbf{k}}$ in the equation above indicates that QP energies of the last iteration, shifted by its Fermi energy with respect to the original KS Fermi energy, are used in the calculation of the correlation self-energies, which are dropped from now on to simplify the notation. Because the Fermi energy shift is already taken into account in the correlation self-energies, it is therefore not necessary to be included in the first argument of $\Sigma_{n\mathbf{k}}$. One can derive an alternative self-consistent scheme based on

$$\mathcal{E}^{(i)}_{n\mathbf{k}} = \epsilon_{n\mathbf{k}} + \delta\Sigma^{(i-1)}_{n\mathbf{k}}(\mathcal{E}^{(i)}_{n\mathbf{k}}). \tag{13.32}$$

By expanding $\Sigma^{(i-1)}_{n\mathbf{k}}$ linearly around $\mathcal{E}^{(i-1)}_{n\mathbf{k}}$, one can obtain the following iterative relation

$$\mathcal{E}^{(i)}_{n\mathbf{k}} = \mathcal{E}^{(i-1)}_{n\mathbf{k}} + Z^{(i-1)}_{n\mathbf{k}}(\delta\Sigma^{(i-1)}_{n\mathbf{k}} + \epsilon_{n\mathbf{k}} - \mathcal{E}^{(i-1)}_{n\mathbf{k}}). \tag{13.33}$$

We note that the GW_0 calculation costs almost nothing once a G_0W_0 calculation has been done: As clear from Eq. 12.7, the quantity that are most time-consuming to calculate, $X_{mn;n'}$, need to be calculated only once, which is already done in G_0W_0.

Chapter 14

G_0W_0 based on LDA+U

14.1 LDA+U method

For systems with d/f-shells, the severe self-interaction error of LDA or GGA often results in an inadequate description. A simple and effective approach to correct for this is to introduce a local, Hubbard-like correction (LDA+U), characterized by the on-site Coulomb (U) and the exchange interaction (J). [5, 6, 4] In its most general form, the LDA+U total energy is written as

$$E_{\mathrm{LDA}+U} = E_{\mathrm{LDA}}[\rho^{\sigma}(\mathbf{r})] + E_{\mathrm{ee}}[\hat{n}^{\sigma}] - \overline{E}_{\mathrm{ee}}[n^{\sigma}], \tag{14.1}$$

where $\sigma = \uparrow, \downarrow$ is the spin index (from now on we will write out the spin degree of freedom explicitly, assuming a collinear spin-polarization). $\hat{n}^{\sigma}$ is the local density matrix defined as

$$n^{\sigma}_{m,m'} = \sum_{n\mathbf{k}} f^{\sigma}_{n\mathbf{k}} \langle m|\psi^{\sigma}_{n\mathbf{k}}\rangle \langle \psi^{\sigma}_{n\mathbf{k}}|m'\rangle , \tag{14.2}$$

where $f^{\sigma}_{n\mathbf{k}}$ denotes the occupation number of the state $\psi^{\sigma}_{n\mathbf{k}}$, and $\{|m\rangle \equiv |In_plm\rangle\}$ denote a set of atomic-like local orbitals on the I-th atom with the principle, angular and magnetic quantum numbers n_p, l and m, respectively. $n^{\sigma} \equiv \mathrm{Tr}\hat{n}^{\sigma}$ is the local occupation number. E_{ee} contains the electron-electron interaction of the localized electrons and the double counting term $\overline{E}_{\mathrm{ee}}$ removes the part that was already included in the LDA Hamiltonian. The LDA+U approach is obtained by treating E_{ee} in a Hartree-Fock like fashion [37]

$$\begin{aligned} E_{\mathrm{ee}}[\hat{n}^{\sigma}] =& \frac{1}{2} \sum_{\{m=-l,l\},\sigma} \Big\{ (\langle m_1 m_2| V_{\mathrm{ee}} |m_3 m_4\rangle - \langle m_1 m_2| V_{\mathrm{ee}} |m_4 m_3\rangle) n^{\sigma}_{m_3 m_1} n^{\sigma}_{m_4 m_2} \\ &+ \langle m_1 m_2| V_{\mathrm{ee}} |m_3 m_4\rangle n^{\sigma}_{m_3 m_1} n^{-\sigma}_{m_4 m_2} \Big\}, \end{aligned} \tag{14.3}$$

with an effective screened Coulomb interaction V_{ee}. Using the angular expansion of V_{ee}

$$V_{\mathrm{ee}}(\mathbf{r}, \mathbf{r}') = \sum_{L} \sum_{M=-L}^{L} v_L(r, r') \frac{4\pi}{2L+1} Y_{LM}(\hat{\mathbf{r}}) Y^{*}_{LM}(\hat{\mathbf{r}}'), \tag{14.4}$$

the Coulomb matrix element $\langle m_1 m_2| V_{ee} |m_3 m_4\rangle$ can be expanded as follows,

$$\langle m_1 m_2| V_{ee} |m_3, m_4\rangle = \sum_{L} F_L C_L(m_1, m_2, m_3, m_4). \tag{14.5}$$

F_L are radial Coulomb integrals (Slater's integrals)

$$F_L \equiv \int dr \int dr' r^2 r'^2 |R_{n_p l}(r)|^2 v_L(r, r') |R_{n_p l}(r')|^2, \tag{14.6}$$

and $C_L(m_1, m_2, m_3, m_4)$ are angular integrals, which, using Wigner's 3-j symbols, [**?**] read

$$\begin{aligned} C_L(m_1, m_2, m_3, m_4) =& \sum_{M=-L}^{L} (2l+1)^2 (-1)^{m_1+m_2+M} \\ &\times \begin{pmatrix} l & L & l \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{pmatrix} l & L & l \\ -m_1 & -M & m_3 \end{pmatrix} \begin{pmatrix} l & L & l \\ -m_2 & M & m_4 \end{pmatrix}. \end{aligned} \tag{14.7}$$

For d-electrons, only F_0, F_2, and F_4 are non-vanishing, and they are related to U and J by $U = F_0$ and $J = (F_2 + F_4)/14$. By fixing the ratio F_4/F_2, which is nearly constant (~ 0.625) in free atoms, [**?**] one can use U and J as only parameters to determine $E_{\rm ee}$. [37, 4]

The double counting correction term $\overline{E}_{\rm ee}[n^\sigma]$, on the other hand, is more arbitrary and is one of the largest problems in the LDA+U approach.[5, 6, 19, 37, 21, 43, 64] Most frequently $\overline{E}_{\rm ee}$ is taken as the following function of the local occupation numbers n^σ

$$\overline{E}_{\rm ee}[n^\sigma] = \frac{1}{2}Un(n-1) - \frac{1}{2}J\sum_\sigma n^\sigma(n^\sigma - 1), \tag{14.8}$$

which can be obtained from Eq. (14.3) by neglecting orbital polarization effects, often called fully localization limit (FLL). [59, 19]

The single-particle Hamiltonian corresponding to $E_{\rm LDA+U}[\rho(\mathbf{r})]$ reads

$$H_0^{{\rm LDA}+U,\sigma} = -\frac{1}{2}\nabla^2 + V_{\rm ext} + V_{\rm H} + V_{\rm xc}^\sigma + \delta\hat{V}_U{}^\sigma, \tag{14.9}$$

where $\delta\hat{V}_U{}^\sigma \equiv \sum_{mm'} |m\rangle\, \delta V_{mm'}^\sigma\, \langle m'|$ is a site- and orbital-dependent non-local potential arising from the LDA+U correction term,

$$\begin{aligned}
\delta V_{mm'}^\sigma &\equiv \frac{\delta\left\{E_{\rm ee}[\hat{n}^\sigma] - \overline{E}_{\rm ee}[n^\sigma]\right\}}{\delta n_{mm'}^\sigma} \\
&= \sum_{m_1 m_2} \langle mm_1|\, V_{\rm ee}\, |m'm_2\rangle\, n_{m_2,m_1} \\
&- \langle mm_1|\, V_{\rm ee}\, |m_2m'\rangle\, n_{m_2,m_1}^\sigma \\
&- \delta_{mm'}\left[\left(n - \frac{1}{2}\right)U - \left(n^\sigma - \frac{1}{2}\right)J\right].
\end{aligned} \tag{14.10}$$

Neglecting the anisotropy of the local Coulomb interaction, i.e. dropping all $L > 0$ terms in Eq. (14.4) and further using the identity $C_{L=0}(m_1, m_2, m_3, m_4) = \delta_{m_1,m_3}\delta_{m_2,m_4}$,[**?**] we obtain

$$\langle m_1, m_2|\, V_{ee}\, |m_3, m_4\rangle \simeq F_0\delta_{m_1m_3}\delta_{m_2m_4}. \tag{14.11}$$

Within this approximation we have

$$\delta V_{mm'}^\sigma = \left[\frac{1}{2}\delta_{mm'} - n_{mm'}^\sigma\right]U. \tag{14.12}$$

If we define the local projection so that the on-site density matrix is diagonal, $\delta\hat{V}_U$ takes the simple form

$$\delta\hat{V}_U{}^\sigma = \sum_m U\left(\frac{1}{2} - n_m^\sigma\right)|m\rangle\,\langle m|\,. \tag{14.13}$$

The main physical effect of $\delta\hat{V}_U$ is therefore to push occupied localized states down and unoccupied ones up in energy, which effectively opens a gap that might have been absent in the LDA description.

14.2 LDA+*U* as an approximation to *GW*

For *highly localized* d/f-states LDA+U can be viewed as an approximate GW scheme, as first pointed out by Anisimov *et al.* [4] The original derivation is fairly involved and based on several specific assumptions that turn out to be not necessary. We present here a new derivation that is simpler and more general, starting from the static Coulomb-hole and screened exchange (COHSEX) approximation [27, 10] to the GW self-energy. The COHSEX approximation is obtained by omitting the dynamic features of the screened Coulomb interaction

$$\begin{aligned}
\Sigma^\sigma(\mathbf{r}, \mathbf{r}') \simeq &\frac{1}{2}\delta(\mathbf{r} - \mathbf{r}')\left[W(\mathbf{r}, \mathbf{r}'; 0) - v(\mathbf{r} - \mathbf{r}')\right] \\
&- \sum_{n\mathbf{k}} f_{n\mathbf{k}}^\sigma \psi_{n\mathbf{k}}^\sigma(\mathbf{r})\psi_{n\mathbf{k}}^{\sigma*}(\mathbf{r}')W(\mathbf{r}, \mathbf{r}'; 0).
\end{aligned} \tag{14.14}$$

Using the closure relation of the KS states

$$\delta(\mathbf{r}, \mathbf{r}') = \sum_{n\mathbf{k}} \psi_{n\mathbf{k}}^\sigma(\mathbf{r})\psi_{n\mathbf{k}}^{\sigma*}(\mathbf{r}'), \tag{14.15}$$

we obtain

$$\begin{aligned}\Sigma^\sigma(\mathbf{r},\mathbf{r}') = &\sum_{n\mathbf{k}}\left(\frac{1}{2}-f^\sigma_{n\mathbf{k}}\right)\psi^\sigma_{n\mathbf{k}}(\mathbf{r})\psi^{\sigma*}_{n\mathbf{k}}(\mathbf{r}')W(\mathbf{r},\mathbf{r}';0)\\ &-\frac{1}{2}\sum_{n\mathbf{k}}\psi^\sigma_{n\mathbf{k}}(\mathbf{r})\psi^{\sigma*}_{n\mathbf{k}}(\mathbf{r}')v(\mathbf{r},\mathbf{r}').\end{aligned} \tag{14.16}$$

The matrix elements of $\Sigma^\sigma(\mathbf{r},\mathbf{r}')$ projected onto the local subspace $\{|m\rangle\}$ can therefore be written as

$$\begin{aligned}\Sigma^\sigma_{mm'} = &\sum_{n\mathbf{k}}\left(\frac{1}{2}-f^\sigma_{n\mathbf{k}}\right)\langle\phi_m\psi^\sigma_{n\mathbf{k}}|\,W(0)\,|\psi^\sigma_{n\mathbf{k}}\phi_{m'}\rangle\\ &-\frac{1}{2}\sum_{n\mathbf{k}}\langle\phi_m\psi^\sigma_{n\mathbf{k}}|\,v\,|\psi^\sigma_{n\mathbf{k}}\phi_{m'}\rangle\,.\end{aligned} \tag{14.17}$$

We now decompose the Kohn-Sham wavefunctions according to

$$|\psi^\sigma_{n\mathbf{k}}\rangle = \sum_m C^\sigma_{m;n\mathbf{k}}\,|\phi_m\rangle + \left|\tilde{\psi}^\sigma_{n\mathbf{k}}\right\rangle, \tag{14.18}$$

with $C^\sigma_{m;n\mathbf{k}}\equiv\langle\phi_m|\psi^\sigma_{n\mathbf{k}}\rangle$. $\left|\tilde{\psi}^\sigma_{n\mathbf{k}}\right\rangle$ can be regarded as a "pure" itinerant state in which the contribution of localized states has been projected out. Inserting Eq. (14.18) into Eq. (14.17) and further assuming that *any matrix element that involves the overlap of* $\phi_m(\mathbf{r})$ *and* $\tilde{\psi}_{n\mathbf{k}}(\mathbf{r})$ *can be neglected*, we obtain

$$\begin{aligned}\Sigma^\sigma_{mm'} = &\sum_{m_1m_2}\sum_{n\mathbf{k}}\left\{\left(\frac{1}{2}-f^\sigma_{n\mathbf{k}}\right)C^{\sigma*}_{m_1;n\mathbf{k}}C^\sigma_{m_2;n\mathbf{k}}\right.\\ &\times\langle mm_1|\,W(0)\,|m_2m'\rangle\\ &\left.-\frac{1}{2}C^{\sigma*}_{m_1;n\mathbf{k}}C^\sigma_{m_2;n\mathbf{k}}\,\langle mm_1|\,v\,|m_2m'\rangle\right\}\\ = &\sum_{m_1m_2}\left(\frac{1}{2}\delta_{m_1m_2}-n^\sigma_{m_2m_1}\right)\langle mm_1|\,W(0)\,|m_2m'\rangle\\ &-\frac{1}{2}\sum_{m_1}\langle mm_1|\,v\,|m_1m'\rangle\,,\end{aligned} \tag{14.19}$$

where we have used the relations

$$\begin{aligned}\sum_{n\mathbf{k}}f^\sigma_{n\mathbf{k}}C^{\sigma*}_{m_1;n\mathbf{k}}C^\sigma_{m_2;n\mathbf{k}} &\equiv n^\sigma_{m_2m_1}\\ \sum_{n\mathbf{k}}C^{\sigma*}_{m_1;n\mathbf{k}}C^\sigma_{m_2;n\mathbf{k}} &\equiv \delta_{m_1m_2}.\end{aligned} \tag{14.20}$$

In the spirit of the LDA+U approach, we consider only corrections to localized states

$$\delta V^\sigma_{mm'} = \langle m|\,V^{\rm loc}_{\rm H}+\Sigma^\sigma-V^{{\rm loc},\sigma}_{\rm LDA}\,|m'\rangle\,, \tag{14.21}$$

where $V^{\rm loc}_{\rm H}$ is the Hartree potential of the localized electron density

$$n^{\rm loc}(\mathbf{r})\equiv\sum_{m_1m_2}n_{m_1m_2}\phi_{m_1}(\mathbf{r})\phi^*_{m_2}(\mathbf{r}), \tag{14.22}$$

$$\begin{aligned}\left[V^{\rm loc}_{\rm H}\right]_{mm'} &\equiv \langle m|\,V^{\rm loc}_{\rm H}\,|m'\rangle\\ &= \sum_{m_1m_2}n_{m_2m_1}\,\langle mm_1|\,v\,|m'm_2\rangle\,.\end{aligned} \tag{14.23}$$

$V^{{\rm loc},\sigma}_{\rm LDA}(\mathbf{r})\equiv\delta\overline{E}^{\rm loc}_{\rm ee}/\delta\rho^\sigma(\mathbf{r})$ is the interaction potential among the localized states in the LDA. Using a similar argument as for the FLL approximation to the double counting correction, i.e. Eq. (14.8), we obtain

$$\begin{aligned}\overline{E}^{\rm loc}_{\rm ee} &= \frac{1}{2}F^{(0)}_0n(n-1)-\frac{1}{2}J^{(0)}\sum_\sigma n^\sigma(n^\sigma-1)\\ V^{{\rm loc},\sigma}_{\rm LDA}(\mathbf{r}) &= \left(n-\frac{1}{2}\right)F^{(0)}_0-\left(n^\sigma-\frac{1}{2}\right)J^{(0)},\end{aligned} \tag{14.24}$$

where $F_0^{(0)}$ and $J^{(0)}$ are the first Slater integral and the on-site exchange term from the bare Coulomb interaction $v(\mathbf{r},\mathbf{r}')$, respectively.

We therefore have

$$\begin{aligned}\delta V^{\sigma}_{mm'} = &\sum_{m_1 m_2}\Bigg\{ n_{m_2 m_1}\langle mm_1|\, v\,|m'm_2\rangle \\ &+\left(\frac{1}{2}\delta_{m_1 m_2} - n^{\sigma}_{m_2 m_1}\right)\langle mm_1|\, W(0)\,|m_2 m'\rangle\Bigg\} \\ &-\frac{1}{2}\sum_{m_1}\langle mm_1|\, v\,|m_1 m'\rangle \\ &-\delta_{mm'}\left[\left(n-\frac{1}{2}\right)F_0^{(0)} - \left(n^{\sigma}-\frac{1}{2}\right)J^{(0)}\right].\end{aligned} \tag{14.25}$$

By neglecting the anisotropy in both the bare and screened Coulomb interaction, i.e. using the approximation in Eq. (14.11), we obtain exactly the same expression as in LDA+U (Eq. (14.12))

$$\delta V^{\sigma}_{mm'} = \left[\frac{1}{2}\delta_{mm'} - n^{\sigma}_{mm'}\right]U, \tag{14.26}$$

where U is identified as the first Slater integral F_0 arising from the static screened Coulomb interaction $W(\mathbf{r},\mathbf{r}';0)$. [4]

To summarize, LDA+U follows from the GW approach under the assumption that:

i. The frequency dependence of the screened Coulomb interaction is neglected;

ii. Quasiparticle corrections are only applied to localized states, whereas itinerant states are still treated at the LDA level;

iii. All Coulomb matrix elements that involve the overlap of a localized state and an itinerant state are neglected (which is equivalent to omitting the many-body exchange interaction between localized and itinerant electrons).

None of these assumptions are of course fully satisfied in realistic systems. The dynamic character of the screened Coulomb interaction is actually stronger for localized electrons than for itinerant ones, as demonstrated by the fact that the renormalization factor (Eq. (**??**)) typically takes a value of $\sim 0.5-0.6$ for localized states , in contrast to the typical value of $\sim 0.8-0.9$ for itinerant states. [49] The LDA description of the itinerant states suffers from the band gap problem and the coupling between localized and itinerant states is critical for the physical and chemical properties of d/f-electron systems.

14.3 KS equation in LDA+U

In the LDA+U formalism, the corresponding "Kohn-Sham" equation (The spin index is dropped for brevity) becomes

$$\left[-\frac{1}{2}\nabla^2 + V^{\mathrm{LDA}}(\mathbf{r})\right]\psi_{n\mathbf{k}}(\mathbf{r}) + \sum_{m,m'} v_{m,m'}\frac{1}{f_{n\mathbf{k}}}\frac{\delta n_{m,m'}}{\delta\psi^*_{n\mathbf{k}}(\mathbf{r})} = \epsilon_{n\mathbf{k}}\psi_{n\mathbf{k}}(\mathbf{r}) \tag{14.27}$$

The KS eigen functions $\psi_{n\mathbf{k}}(\mathbf{r})$ within the atom a-MT sphere can be written generally as

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{lm}\left[\mathcal{A}^a_{nlm}(\vec{k})u_{al}(r^a,E_l) + \mathcal{B}^a_{nlm}(\vec{k})\dot{u}_{al}(r^a,E_l) + \mathcal{C}^a_{nlm}(\vec{k})u_{al}(r^a,E_{l_2})\right]Y_{lm}(\hat{r}^a) \tag{14.28}$$

To simplify the notation, we introduce another index, ν, and use $u_{al\nu}$ to refer to u_{al}, $\dot{u}_{al}$ or $u_{al}(r^a,E_{l_2})$. Now $\psi_{n\mathbf{k}}(\mathbf{r})$ can be written as

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{lm\nu}\mathcal{A}^a_{n\mathbf{k},lm\nu}u_{al\nu}(r^a)Y_{lm}(\hat{r}^a) \tag{14.29}$$

The electron density in the a-MT sphere reads

$$\begin{aligned}\rho(\mathbf{r}) &= \sum_{n\mathbf{k}} f_{n\mathbf{k}}|\psi_{n\mathbf{k}}(\mathbf{r})|^2 \\ &= \sum_{n\mathbf{k}} f_{n\mathbf{k}}\sum_{lm\nu}\sum_{l'm'\nu'}\left[\mathcal{A}^a_{n\mathbf{k},lm\nu}\right]^*\mathcal{A}^a_{n\mathbf{k},l'm'\nu'}u_{al\nu}(r^a)u_{al\nu'}(r^a)Y^*_{lm}(\hat{r}^a)Y_{l'm'}(\hat{r}^a) \\ &= \sum_{lm}\sum_{l'm'}\left[\sum_{\nu,\nu'}\sum_{n\mathbf{k}} f_{n\mathbf{k}}\left[\mathcal{A}^a_{n\mathbf{k},lm\nu}\right]^*\mathcal{A}^a_{n\mathbf{k},l'm'\nu'}u_{al\nu}(r^a)u_{al'\nu'}(r^a)\right]Y^*_{lm}(\hat{r}^a)Y_{l'm'}(\hat{r}^a)\end{aligned} \tag{14.30}$$

which gives the density matrix projected to the a-MT sphere

$$n^a_{lm,l'm'} = \sum_{n\mathbf{k}} f^\sigma_{n\mathbf{k}} \sum_{\nu,\nu'} \mathcal{A}^a_{n\mathbf{k},lm\nu} \left[\mathcal{A}^a_{n\mathbf{k},l'm'\nu'}\right]^* \int_0^\infty dr r^2 u_{al\nu}(r) u_{al'\nu'}(r) \tag{14.31}$$

In the case of LDA+U, one only needs the l-diagonal densty matrix, $n^{al}_{m,m'} \equiv n^a_{lm,lm'}$. We denote the radial integral in the equation above as

$$I^{al}_{\nu,\nu'} \equiv \int_0^\infty dr r^2 u_{al\nu}(r) u_{al\nu'}(r) \tag{14.32}$$

To carry out the functional derivative in Eq. (14.27), one needs to express $n^{al}_{m,m'}$ explicitly as a functional of $\psi_{n\mathbf{k}}(\mathbf{r})$. To do that, we first project $\psi_{n\mathbf{k}}(\mathbf{r})$ into the local atomic orbital $u_{al\nu}(r^a)Y_{lm}(\hat{r}^a)$

$$\langle u_{al\nu} Y_{lm} | \psi_{n\mathbf{k}} \rangle = \sum_{\nu'} \mathcal{A}^a_{n\mathbf{k},lm\nu'} I^{al}_{\nu,\nu'} \tag{14.33}$$

Inverting this equation, we have

$$\mathcal{A}^a_{n\mathbf{k},lm\nu} = \sum_{\nu'} \left[I^{al}\right]^{-1}_{\nu,\nu'} \langle u_{al\nu'} Y_{lm} | \psi_{n\mathbf{k}} \rangle \tag{14.34}$$

With this relation between $\mathcal{A}^a_{n\mathbf{k},lm\nu}$ and $\psi_{n\mathbf{k}}$ we have

$$\begin{aligned} n^{al}_{m,m'} &= \sum_{n\mathbf{k}} f_{n\mathbf{k}} \sum_{\nu,\nu'} \mathcal{A}^a_{n\mathbf{k},lm\nu} I^{al}_{\nu,\nu'} \left[\mathcal{A}^a_{n\mathbf{k},lm'\nu'}\right]^* \\ &= \sum_{n\mathbf{k}} f_{n\mathbf{k}} \sum_{\nu,\nu'} \sum_{\nu_1,\nu_2} \left[I^{al}\right]^{-1}_{\nu,\nu_1} \langle u_{al\nu_1} Y_{lm} | \psi_{n\mathbf{k}} \rangle \\ &\times I^{al}_{\nu,\nu'} \left[I^{al}\right]^{-1}_{\nu',\nu_2} \langle u_{al\nu_2} Y_{lm'} | \psi_{n\mathbf{k}} \rangle^* \\ &= \sum_{n\mathbf{k}} f_{n\mathbf{k}} \sum_{\nu_1,\nu_2} \langle \psi_{n\mathbf{k}} | u_{al\nu_1} Y_{lm'} \rangle \left[I^{al}\right]^{-1}_{\nu_1,\nu_2} \langle u_{al\nu_2} Y_{lm} | \psi_{n\mathbf{k}} \rangle \end{aligned} \tag{14.35}$$

Now the functional derivative of the density matrix with respect to the KS eigen-vector can be done straightforwardly,

$$\frac{1}{f^\sigma_{n\mathbf{k}}} \frac{\delta n^\sigma_{m,m'}}{\delta \psi^{\sigma *}_{n\mathbf{k}}} = \sum_{\nu_1,\nu_2} |u_{al\nu_1} Y_{lm'}\rangle \left[I^{al}\right]^{-1}_{\nu_1,\nu_2} \langle u_{al\nu_2} Y_{lm} | \psi_{n\mathbf{k}} \rangle \tag{14.36}$$

The KS equation in LDA+U can be written explicitly as

$$\left[-\frac{1}{2}\nabla^2 + V^{\mathrm{LDA}}(\mathbf{r}) + \delta\hat{V}^{\mathrm{LDA+U}}\right] \psi_{n\mathbf{k}}(\mathbf{r}) = \epsilon_{n\mathbf{k}} \psi_{n\mathbf{k}}(\mathbf{r}) \tag{14.37}$$

where

$$\delta\hat{V}^{\mathrm{LDA+U}} = \sum_{m,m'} v_{m,m'} \sum_{\nu_1,\nu_2} |u_{al\nu_1} Y_{lm'}\rangle \left[I^{al}\right]^{-1}_{\nu_1,\nu_2} \langle u_{al\nu_2} Y_{lm}| \tag{14.38}$$

14.4 Derive LDA+U from GW

The LDA+U method can be "derived" from the GW theory for *highly localized* d/f-states within several assumptions, which is first pointed out by Anisimov *et al.* [4] As their formulation is quite complicated, here we present a simplified derivation starting from the static Coulomb-hole and screened exchange (CHSX) approximation [27, 10] to the GW selfenergy.

$$\Sigma(\mathbf{r},\mathbf{r}';\omega) = \frac{i}{2\pi} \int G_0(\mathbf{r},\mathbf{r}';\omega+\omega') W_0(\mathbf{r}',\mathbf{r};\omega') d\omega' \tag{14.39}$$

The static CHSX approximation is obtained by neglecting the dynamic features of the screened Coulomb interaction, and reads

$$\begin{aligned} \Sigma^{\mathrm{CH}}(\mathbf{r},\mathbf{r}') &= \frac{1}{2}\delta(\mathbf{r}-\mathbf{r}') \left[W_0(\mathbf{r},\mathbf{r}';0) - v(\mathbf{r}-\mathbf{r}')\right] \\ \Sigma^{\mathrm{SX}}(\mathbf{r},\mathbf{r}') &= -\sum_{n\mathbf{k}}^{\mathrm{occ}} \psi_{n\mathbf{k}}(\mathbf{r}) \psi_{n\mathbf{k}}(\mathbf{r}')^* W_0(\mathbf{r},\mathbf{r}';0) \end{aligned} \tag{14.40}$$

Using

$$\delta(\mathbf{r},\mathbf{r}') = \sum_{n\mathbf{k}} \psi_{n\mathbf{k}}(\mathbf{r})\psi_{n\mathbf{k}}(\mathbf{r}')^* \tag{14.41}$$

the CHSX selfenergy can be rewritten as

$$\begin{aligned}\Sigma^{\mathrm{CHSX}}(\mathbf{r},\mathbf{r}') = &\sum_{n\mathbf{k}} \left(\frac{1}{2} - f_{n\mathbf{k}}\right) \psi_{n\mathbf{k}}(\mathbf{r})\psi_{n\mathbf{k}}(\mathbf{r}')^* W(\mathbf{r},\mathbf{r}';0) \\ &- \frac{1}{2}\sum_{n\mathbf{k}} \psi_{n\mathbf{k}}(\mathbf{r})\psi_{n\mathbf{k}}(\mathbf{r}')^* v(\mathbf{r}-\mathbf{r}')\end{aligned} \tag{14.42}$$

For d- or f-electron systems, we further assume that highly localized d or f-states, denoted as ϕ_m, are essentially separated from other itinerant states and the whole Hilbert space can be decomposed into two subsystems that are approximately orthogonal to each other.

$$\delta(\mathbf{r},\mathbf{r}') = \sum_{m} \phi_m(\mathbf{r})\phi_m(\mathbf{r}')^* + \sum_{n\mathbf{k}} \tilde{\psi}_{n\mathbf{k}}(\mathbf{r})\tilde{\psi}_{n\mathbf{k}}(\mathbf{r}')^* \tag{14.43}$$

The LDA+U approach considers only the quasi-particle correction $\delta\Sigma$ for highly localized d or f states, which is equivalent to to approximate $\delta\Sigma$ by

$$\delta\Sigma \simeq \sum_{m,m'} |m\rangle\, \delta\Sigma_{mm'}\, \langle m'| \tag{14.44}$$

where $\delta\Sigma \equiv \Sigma^{\mathrm{xc}} - V_{\mathrm{xc}}$ considers only the contributions from localized states. Under the CHSX approximation, we have

$$\begin{aligned}\delta\Sigma_{mm'} = &\sum_{m_1 m_2} \left(\frac{1}{2} - n_{m_1 m_2}\right) \langle m m_2|\, W(0)\, |m_1 m'\rangle \\ &- \sum_{m_1 m_2} \langle m m_2|\, v\, |m_1 m'\rangle - \langle m|\, V_{\mathrm{xc}}\, |m'\rangle\end{aligned} \tag{14.45}$$

If we neglect anisotropy of the Coulomb interaction, and further assume the LDA e-e interaction energy can be approximated by a Hartree-Fock like expression, which is the same assumption underlying the standard LDA+U formalism, [4] the last two terms in Eq. (14.46 will cancel each other, and we have

$$\delta\Sigma_{mm'} = \delta_{mm'} \left(\frac{1}{2} - n_m\right) U \tag{14.46}$$

where U is identified as the Slater integral F^0 from the static screened Coulomb interaction $W(\mathbf{r},\mathbf{r}';0)$. [4]

To summarize, in order to obtain the LDA+U from the GW, the following assumptions have been made:

i. static approximation: the frequency dependence of the screened Coulomb interaction is neglected;

ii. quasi-particle corrections are assumed to be important only for highly-localized d- or f- states, and the LDA description is adequate for itinerant states;

iii. the target localized states are well-separated from itinerant states, i.e. the whole system can be literally decomposed into two subsystems that are coupled only by classical electro-static interactions.

It is obvious that none of these assumptions is rigorously valid. The dynamic character of the screened Coulomb interaction is actually stronger for localized electrons than for itinerant electrons. As the $\delta\hat{V}_U$ correction has only direct effects on states with strong d or f characters, the description of itinerant states is still at the LDA level. In contrast to the last assumption, the coupling between localized and itinerant states is critical for the physical and chemical properties of d/f-electron systems. In practice, the $\delta\hat{V}_U$ correction is applied to KS single-particle states via some local projection, and the LDA+U calculations are always done self-consistently. As a result, the $\delta\hat{V}_U$ correction can have indirect influences on itinerant states as well.

14.5 LDA+U correction in G_0W_0

Formally, the only difference between LDA-based and LDA+U-based G_0W_0 is the contribution from Eq. (14.38)

$$\begin{aligned}\delta V_{n\mathbf{k}}^{\mathrm{LDA+U}} &\equiv \langle\psi_{n\mathbf{k}}|\, \delta\hat{V}^{\mathrm{LDA+U}}\, |\psi_{n\mathbf{k}}\rangle \\ &= \sum_{m,m'} v_{m,m'} \sum_{\nu_1,\nu_2} \langle\psi_{n\mathbf{k}}|u_{al\nu_1}Y_{lm'}\rangle \left[I^{al}\right]^{-1}_{\nu_1,\nu_2} \langle u_{al\nu_2}Y_{lm}|\psi_{n\mathbf{k}}\rangle\end{aligned} \tag{14.47}$$

Using the relation between $\mathcal{A}^a_{n\mathbf{k},lm\nu}$ and $\langle u_{al\nu_2} Y_{lm}|\psi_{n\mathbf{k}}\rangle$ we have

$$\begin{aligned}\delta V^{\mathrm{LDA+U}}_{n\mathbf{k}} &= \sum_{m,m'} v_{m,m'} \sum_{\nu_1,\nu_2}\sum_{\nu,\nu'} \left[I^{al}\right]_{\nu_1,\nu'} \left[\mathcal{A}^a_{n\mathbf{k},lm'\nu'}\right]^* \left[I^{al}\right]^{-1}_{\nu_1,\nu_2} \left[I^{al}\right]_{\nu_2,\nu} \mathcal{A}^a_{n\mathbf{k},lm\nu} \\ &= \sum_{m,m'} v_{m,m'} \sum_{\nu,\nu'} \mathcal{A}^a_{n\mathbf{k},lm\nu} \left[I^{al}\right]_{\nu,\nu'} \left[\mathcal{A}^a_{n\mathbf{k},lm'\nu'}\right]^* \end{aligned} \tag{14.48}$$

$$\mathcal{E}_{n\mathbf{k}} = \epsilon_{n\mathbf{k}} + \Re\left[\langle\psi_{n\mathbf{k}}|\,\Sigma(\mathcal{E}_{n\mathbf{k}}) - V_{\mathrm{xc}} - \delta V^U\,|\psi_{n\mathbf{k}}\rangle\right]$$

To see the relation between LDA and LDA+U based G_0W_0 more explicitly, we notice that the KS eigen-energies obtained from LDA+U, denoted as $\epsilon^{\mathrm{LDA+U}}_{n\mathbf{k}}$, contain a contribution from $\delta V^{\mathrm{LDA+U}}$ so that

$$\begin{aligned}\epsilon^{\mathrm{LDA+U}}_{n\mathbf{k}} =& \langle\psi_{n\mathbf{k}}| -\frac{1}{2}\nabla^2 + V^{\mathrm{LDA}} + \delta\hat{V}^{\mathrm{LDA+U}}\,|\psi_{n\mathbf{k}}\rangle \\ =& \tilde{\epsilon}^{\mathrm{LDA}}_{n\mathbf{k}} + \delta V^{\mathrm{LDA+U}}_{n\mathbf{k}}\end{aligned} \tag{14.49}$$

where $\tilde{\epsilon}^{\mathrm{LDA}}_{n\mathbf{k}}$ are the LDA KS eigen-energies calculated using LDA+U wave functions. The final quasi-particle energies can be written as

$$\begin{aligned}\epsilon^{\mathrm{QP-LDA+U}}_{n\mathbf{k}} =& \epsilon^{\mathrm{LDA+U}}_{n\mathbf{k}} + Z_{n\mathbf{k}}\left(\epsilon^{\mathrm{LDA+U}}_{n\mathbf{k}}\right)\left[\Sigma_{n\mathbf{k}}\left(\epsilon^{\mathrm{LDA+U}}_{n\mathbf{k}}\right) - V^{\mathrm{XC}}_{n\mathbf{k}} - \delta V^{\mathrm{LDA+U}}_{n\mathbf{k}}\right] \\ =& \tilde{\epsilon}^{\mathrm{LDA}}_{n\mathbf{k}} + Z_{n\mathbf{k}}\left(\epsilon^{\mathrm{LDA+U}}_{n\mathbf{k}}\right)\left[\Sigma_{n\mathbf{k}}\left(\epsilon^{\mathrm{LDA+U}}_{n\mathbf{k}}\right) - V^{\mathrm{XC}}_{n\mathbf{k}}\right] + \left(1 - Z_{n\mathbf{k}}\right)\delta V^{\mathrm{LDA+U}}_{n\mathbf{k}}\end{aligned} \tag{14.50}$$

For the test purpose, we consider the following three variants of LDA+U based G_0W_0 quasi-particle energies:

$$\begin{aligned}\epsilon^{\mathrm{QP-LDA+U-1}}_{n\mathbf{k}} =& \epsilon^{\mathrm{LDA+U}}_{n\mathbf{k}} + Z_{n\mathbf{k}}\left(\epsilon^{\mathrm{LDA+U}}_{n\mathbf{k}}\right)\left[\Sigma_{n\mathbf{k}}\left(\epsilon^{\mathrm{LDA+U}}_{n\mathbf{k}}\right) - V^{\mathrm{XC}}_{n\mathbf{k}}\right], \\ \epsilon^{\mathrm{QP-LDA+U-2}}_{n\mathbf{k}} =& \tilde{\epsilon}^{\mathrm{LDA}}_{n\mathbf{k}} + Z_{n\mathbf{k}}\left(\epsilon^{\mathrm{LDA+U}}_{n\mathbf{k}}\right)\left[\Sigma_{n\mathbf{k}}\left(\epsilon^{\mathrm{LDA+U}}_{n\mathbf{k}}\right) - V^{\mathrm{XC}}_{n\mathbf{k}}\right], \\ \epsilon^{\mathrm{QP-LDA+U-3}}_{n\mathbf{k}} =& \tilde{\epsilon}^{\mathrm{LDA}}_{n\mathbf{k}} + Z_{n\mathbf{k}}\left(\tilde{\epsilon}^{\mathrm{LDA}}_{n\mathbf{k}}\right)\left[\Sigma_{n\mathbf{k}}\left(\tilde{\epsilon}^{\mathrm{LDA}}_{n\mathbf{k}}\right) - V^{\mathrm{XC}}_{n\mathbf{k}}\right].\end{aligned} \tag{14.51}$$

14.6 How to calculate U?

14.6.1 Constrained DFT method

14.6.2 RPA without or with constaint

$$\begin{aligned}G(\omega) =& G_d(\omega) + G_r(\omega) \\ P(\omega) =& P_d(\omega) + P_r(\omega) \\ W(\omega) =& (1 - vP(\omega))^{-1} v \\ =& (1 - W_r(\omega)P_d(\omega))^{-1} W_r(\omega) \\ W_r(\omega) =& (1 - vP_r(\omega))^{-1} v\end{aligned}$$

$$U \equiv < \phi_d\phi_d|W_r(0)|\phi_d\phi_d > \tag{14.52}$$

Chapter 15

SOC-GW

This part we formulate the implementation of the G_0W_0 method with spin-orbit coupling. We start from the general expressions

$$P(\mathbf{x}_1,\mathbf{x}_2;\omega)=\sum_{n,m}f_n(1-f_m)\left\{\frac{\Phi_{nm}(\mathbf{x}_1)\Phi^*_{nm}(\mathbf{x}_2)}{-\omega-\omega_{nm}+i\eta}+\frac{\Phi_{nm}(\mathbf{x}_1)^*\Phi_{nm}(\mathbf{x}_2)}{\omega-\omega_{nm}+i\eta}\right\} \tag{15.1}$$

where

$$\begin{aligned}\Phi_{nm}(\mathbf{x})&\equiv\psi_n(\mathbf{x})\psi_m(\mathbf{x})^*\\ \omega_{nm}&\equiv\epsilon_m-\epsilon_n\end{aligned} \tag{15.2}$$

$$\Sigma(\mathbf{x}_1,\mathbf{x}_2;\omega)=\frac{i}{2\pi}\int d\omega' G_0(\mathbf{x}_1,\mathbf{x}_2;\omega+\omega')W(\mathbf{x}_2,\mathbf{x}_1;\omega') \tag{15.3}$$

$$\begin{aligned}G_0(\mathbf{x}_1,\mathbf{x}_2;\omega)&=\sum_n\frac{\phi_n(\mathbf{x}_1)\phi^*_n(\mathbf{x}_2)}{\omega-\tilde{\epsilon}_n}\\ &\equiv\sum_n C_n(\omega)\phi_n(\mathbf{x}_1)\phi^*_n(\mathbf{x}_2)\end{aligned} \tag{15.4}$$

Now consider the expansion of P, W, and $\Phi_{nm}(\mathbf{x})$ by the basis set $\chi_i(\mathbf{r})\eta_\sigma(s)$. Here we use s to denote the spin coordinate, and σ as the spin quantum number.

$$\begin{aligned}\Phi_{nm}(\mathbf{x})&=\sum_{i\sigma}M^{i\sigma}_{nm}\chi_i(\mathbf{r})\eta_\sigma(s)\\ P(\mathbf{x}_1,\mathbf{x}_2;\omega)&=\sum_{\sigma,\sigma'}\sum_{i,j}P^{\sigma\sigma'}_{ij}(\omega)\chi_i(\mathbf{r}_1)\eta_\sigma(s_1)\chi^*_j(\mathbf{r}_2)\eta^*_{\sigma'}(s_2)\\ W(\mathbf{x}_1,\mathbf{x}_2;\omega)&=\sum_{\sigma,\sigma'}\sum_{i,j}W^{\sigma\sigma'}_{ij}(\omega)\chi_i(\mathbf{r}_1)\eta_\sigma(s_1)\chi^*_j(\mathbf{r}_2)\eta^*_{\sigma'}(s_2)\end{aligned} \tag{15.5}$$

With these expansion it is straightforward to obtain

$$\begin{aligned}P^{\sigma\sigma'}_{ij}&\equiv\int d\mathbf{r}_1ds_1d\mathbf{r}_2ds_2\chi^*_i(\mathbf{r}_1)\eta^*_\sigma(s_1)P(\mathbf{x}_1,\mathbf{x}_2;\omega)\chi_j(\mathbf{r}_2)\eta_\sigma(s_2)\\ &=\sum_{n,m}f_n(1-f_m)\left\{\frac{M^{i\sigma}_{mn}\left[M^{j\sigma'}_{mn}\right]^*}{\omega-\omega_{nm}+i\eta}-\frac{M^{i\sigma}_{nm}\left[M^{j\sigma'}_{nm}\right]^*}{\omega+\omega_{nm}-i\eta}\right\}\end{aligned} \tag{15.6}$$

Now consider the self-energy

$$
\begin{aligned}
\Sigma_{nm}(\omega) &= \int d\mathbf{x}_1\mathbf{x}_2\phi_n^*(\mathbf{x}_1)\Sigma(\mathbf{x}_1,\mathbf{x}_2;\omega)\phi_m(\mathbf{x}_2) \\
&= \int d\mathbf{x}_1\mathbf{x}_2\phi_n^*(\mathbf{x}_1)\phi_m(\mathbf{x}_2)\frac{i}{2\pi}\int d\omega' \sum_{n'} C_{n'}(\omega+\omega')\phi_{n'}(\mathbf{x}_1)\phi_{n'}^*(\mathbf{x}_2) \\
&\quad \times \sum_{ij}\sum_{\sigma,\sigma'} W_{ij}^{\sigma\sigma'}(\omega)\chi_i(\mathbf{r}_2)\eta_\sigma(s_2)\chi_j^*(\mathbf{r}_1)\eta_{\sigma'}^*(s_1) \\
&= \sum_{n'}\sum_{ij}\sum_{\sigma,\sigma'}\frac{i}{2\pi}\int d\omega' C_{n'}(\omega+\omega')W_{ij}^{\sigma\sigma'}(\omega')\int d\mathbf{x}_1\phi_n^*(\mathbf{x}_1)\phi_{n'}(\mathbf{x}_1)\chi_j^*(\mathbf{r}_1)\eta_{\sigma'}^*(s_1) \\
&\quad \times \int d\mathbf{x}_2\phi_m(\mathbf{x}_2)\phi_{n'}^*(\mathbf{x}_2)\chi_i(\mathbf{r}_2)\eta_\sigma(s_2) \\
&= \sum_{n'}\sum_{ij}\sum_{\sigma,\sigma'}\frac{i}{2\pi}\int d\omega' C_{n'}(\omega+\omega')W_{ij}^{\sigma\sigma'}(\omega')\left[M_{n'm}^{i\sigma}\right]^* M_{n'n}^{j\sigma'}
\end{aligned}
\tag{15.7}
$$

Chapter 16

Selfconsistent GW

16.1 Full self-consistent GW

The G_0W_0 method has the major drawback that it depends on the reference single-particle Hamiltonian H_0 from which G_0 and W_0 are calculated. In addition, the lack of self-consistency also results in the violation of the conservation of particle number and energy when the system under study is subject to external perturbations. [10] These problems can be avoided by using the GW method in a self-consistent way, as illustrated in Fig. **??**. As proved by Baym and Kadanoff, [14, 13] a conserving Green's function has to meet the requirements that it has to be a self-consistent solution of the Dyson's equation with the corresponding self-energy being derivable from the Luttinger-Ward (LW) energy functional $\Sigma[G] = \delta\Phi/\delta G$. However, full self-consistent GW (SCGW) calculations are mathematically complicated and computationally very demanding, due to the fact that the self-energy operator is non-local, non-Hermitian and energy dependent. As a result, the solutions of the QP equation are not orthonormal, and they can not be obtained by standard linear algebra techniques. On the other hand, the full SCGW does not necessarily provide more accurate QP properties. The full self-consistency for G can surely improve the ground state total energy due to the variational nature of the LW functional, but quasiparticle properties are not variational. From a conceptual point of view, a self-consistent solution of the Hedin's equations with the GW approximation to the self-energy would successively introduce higher order electron-electron interaction terms of certain types without a balanced treatment of other higher order terms contained in the vertex function.

Whether the full self-consistency improves or deteriorates quasi-particle properties has been under fierce debate in recent years. The first full SCGW calculation was undertaken for a quasi-one-dimensional model semiconductor [20]. Although the relevance of such a highly simplified model system to real materials seems to be rather weak, the main features revealed in this study are very illuminating. The band gaps obtained from the full SCGW were found to be very close to the Hartree-Fock gaps, probably due to much weaker screening in 1D systems than that in 3D bulk systems. Compared to the quantum Monte Carlo results, the full SCGW gaps are significantly overestimated, indicating that the vertex corrections are important in this model system.

The partial and full SCGW (GW_0 and GW, respectively) are also applied to homogeneous electron gas. [63, 51, 30] It was found that by introducing self-consistency, the band width of the HEG is increased with respect to the non-self-consistent value, and therefore deviates more severely from that of the experimental value for the alkali metals. The self-consistency also increases the weight of the quasi-particle peak; concomitantly the plasmon satellite is broadened and shifted towards to the Fermi energy, and almost disappears in the full SCGW. Qualitatively similar features were also observed in full SCGW studies of real nearly-free-electron-(NFE)-like metals K [50] and Al [35].

The SCGW has also been applied to simple semiconductors like Si and Ge by several groups. [50, 34, 65, 35] Different groups obtained dramatically different band gaps for such simple systems like Si, an indication of the complexity of the issue. In Ref. [50], a fundamental gap of 1.91 eV is obtained by full SCGW, in contrast to the experimental value of 1.17 eV (G_0W_0@LDA gives 1.34 eV in the same work). A possible cause of this dramatic overestimation is the use of the pseudo-potential. [34, 61, 25] Ku and Eguiluz reinvestigated the full SCGW band gap of Si using an all-electron LAPW approach, and obtained a gap of 1.03 eV, apparently in good agreement with the experimental value.[34] However, in this study, only 14 bands (10 unoccupied) were used. As discussed in Refs. [61, 25], the convergence of the GW band gap with respect to the number of unoccupied bands used is actually quite slow, and the results obtained from 10 bands are probably not converged. In another full SCGW study, also using the LAPW approach, Kutepov *et al.* [35] obtain a gap of 1.55 eV for Si. We should also mention the work by Zein et al., [65] who developed a local self-energy approach using the linearized muffin-tin orbital (LMTO) method within atomic sphere approximation (ASA) to perform full SCGW calculations, and obtained a gap of 1.10 eV. The accuracy of this approach is, however, doubtful, as indicated by the fact this approach gives a G_0W_0@LDA gap of only 1.33 eV for AlAs, significantly different from other all-electron G_0W_0 studies. The fact

that different groups obtain severely disparate full SCGW results for such simple systems like Si is very disturbing, indicating clearly that further systematic and benchmark studies are needed.

16.2 Approximate self-consistent GW

To avoid the computational complication of the full SCGW, recently there have been intensive efforts to developing approximate self-consistent GW. To put these apparently different schemes in a unified framework, we start with the QP equation, written in the Dirac's notation,

$$\hat{H}(\mathcal{E}_n)\,|\Psi_n\rangle \equiv \left[\hat{H}_0 + \hat{\Sigma}(\mathcal{E}_n)\right]|\Psi_n\rangle = \mathcal{E}_n\,|\Psi_n\rangle \tag{16.1}$$

Now let's expand Ψ_n by a set of orthonormal single-particle wave functions $|\phi_\nu\rangle$, which are eigenfunctions of some single-particle effective Hamiltonian $\hat{H}_s$

$$\begin{aligned} \hat{H}_s\,|\psi_\nu\rangle &= \epsilon_\nu\,|\psi_\nu\rangle \\ |\Psi_n\rangle &= \sum_\nu C_{\nu n}\,|\psi_\nu\rangle \end{aligned} \tag{16.2}$$

we then obtain the matrix form of Eq. (16.1)

$$\begin{aligned} &\sum_\nu \left[H_{\mu\nu}(\mathcal{E}_n) - \mathcal{E}_n\delta_{\mu\nu}\right] C_{\nu n} = 0 \\ &H_{\mu\nu}(\mathcal{E}_n) = \langle\psi_\mu|\,\hat{H}_0\,|\psi_\nu\rangle + \Sigma_{\mu\nu}(\mathcal{E}_n) \end{aligned} \tag{16.3}$$

with $\Sigma_{\mu\nu}(\mathcal{E}_n) \equiv \langle\psi_\mu|\,\hat{\Sigma}(\mathcal{E}_n)\,|\psi_\nu\rangle$. The self-energy operator is in general non-Hermtitian, and therefore mathematically difficult to treat. As a first approximation, one can regularize the self-energy by replacing $\Sigma_{\mu\nu}(\mathcal{E}_n)$ by its Hermitized form,

$$\overline{\Sigma}_{\mu\nu}(\mathcal{E}_n) \equiv \frac{1}{2}\left[\Sigma_{\mu\nu}(\mathcal{E}_n) + \Sigma^*_{\nu\mu}(\mathcal{E}_n)\right] \tag{16.4}$$

and in the meanwhile we neglect the imaginary part of the quasi-particle energies, i.e. assuming $\mathcal{E}_n$ to be all real. Due to the energy dependence of self-energy, Eq. (16.4) still can not be solved by standard linear algebra techniques. More importantly the QP wave functions at different energies are not orthogonal as a result of the energy dependence, which makes the construction of a self-consistent loop difficult. Different approximations are introduced to tackle this difficulty.

16.2.1 Faleev-van Schilfgaarde-Kotani scheme

In the so-called quasi-particle self-consistent GW (QSGW) scheme proposed by Faleev, van Schilfgaarde and Kotani (FvSK)[22, 33], Eq. (16.3) is converted to an iterative equation by defining an effective Hamiltonian at i-th iteration as

$$\overline{H}^{(i)}_{\mu\nu} \equiv \langle\psi_\mu|\,\hat{H}_0\,|\psi_\nu\rangle + \frac{1}{2}\left[\overline{\Sigma}_{\mu\nu}(\epsilon_\mu) + \overline{\Sigma}_{\mu\nu}(\epsilon_\nu)\right] \tag{16.5}$$

16.2.2 Shishkin-Marsman-Kresse scheme

Shishkin, Marsman and Kresse (SMK) developed a slightly more sophisticated way to treat the energy dependence of the self-energy [52]. The self-energy $\hat{\Sigma}(\mathcal{E}_n)$ is first expanded around a reference energy $\tilde{\mathcal{E}}_n$

$$\left[\hat{H}_0 + \hat{\Sigma}(\tilde{\mathcal{E}}_n) + \hat{\Sigma}'(\tilde{\mathcal{E}}_n)\left(\mathcal{E}_n - \tilde{\mathcal{E}}_n\right)\right]|\Psi_n\rangle = \mathcal{E}_n\,|\Psi_n\rangle \tag{16.6}$$

where the prime denotes the derivative with respect to the energy. After some simple algebraic transformations one obtains

$$\begin{aligned} &\left[\hat{H}_0 + \hat{\Sigma}(\tilde{\mathcal{E}}_n) - \tilde{\mathcal{E}}_n\hat{\Sigma}'(\tilde{\mathcal{E}}_n)\right]|\Psi_n\rangle \\ &= \mathcal{E}_n\left[1 - \hat{\Sigma}'(\tilde{\mathcal{E}}_n)\right]|\Psi_n\rangle \end{aligned} \tag{16.7}$$

Using the expansion defined in Eq. (16.2), we then obtain the matrix form of Eq. (16.7)

$$\sum_\nu H_{\mu\nu}(\tilde{\mathcal{E}}_n)C_{\nu n} = \mathcal{E}_n S_{\mu\nu}(\tilde{\mathcal{E}}_n)C_{\nu n} \tag{16.8}$$

where

$$\begin{aligned} H_{\mu\nu}(\tilde{\mathcal{E}}_n) &\equiv \langle\psi_\mu|\,\hat{H}_0 + \Sigma(\tilde{\mathcal{E}}_n) - \tilde{\mathcal{E}}_n\hat{\Sigma}'(\tilde{\mathcal{E}}_n)\,|\psi_\nu\rangle \\ S_{\mu\nu}(\tilde{\mathcal{E}}_n) &\equiv \delta_{\mu\nu} - \Sigma'_{\mu\nu}(\tilde{\mathcal{E}}_n) \end{aligned} \tag{16.9}$$

A self-consistent loop can be constructed by choosing the reference energy $\tilde{\mathcal{E}}_n = \mathcal{E}_n^{(i-1)}$ for i-th iteration, and further using the Hermitized form of $H_{\mu\nu}$ and $S_{\mu\nu}$ similarly as in the FvSK scheme (Eq. (16.5)). We note that the FvSK scheme can be recovered by dropping terms related to $\hat{\Sigma}'$ in Eq. (16.9). Since the contribution of the latter vanishes when reaching convergence (re. Eq. (16.6)), we can see that the two schemes are actually equivalent.

16.2.3 self-consistent COHSEX

An even simpler way to overcome the energy-dependence difficulty is to use Hedin's static Coulomb hole and screened exchange (COHSEX) approximation [27, 10]. To see the underlying physical assumption, the real part of the self-energy can be written down as

$$\begin{aligned} \mathrm{Re}\Sigma^{\mathrm{xc}}(\mathbf{x},\mathbf{x}';\omega) &= \sum_n^{\mathrm{occ}} \psi_n(\mathbf{x})\psi_n^*(\mathbf{x}')\mathrm{Re}W(\mathbf{x}',\mathbf{x};\omega-\epsilon_n) \\ &- \sum_n \psi_n(\mathbf{x})\psi_n^*(\mathbf{x}')\frac{1}{\pi}\mathcal{P}\int_0^\infty d\omega' \frac{\mathrm{Im}W_c(\mathbf{x}',\mathbf{x};\omega')}{\omega-\epsilon_n-\omega'} \end{aligned} \tag{16.10}$$

where $W_c \equiv W - v$ and $\mathcal{P}$ represents taking the Cauchy principle value. A static approximation to the self-energy is obtained by setting $\omega - \epsilon_n = 0$ in Eq. (16.10)

$$\begin{aligned} \Sigma^{\mathrm{xc-COHSEX}}(\mathbf{x},\mathbf{x}') &= \Sigma^{\mathrm{COH}}(\mathbf{x},\mathbf{x}') + \Sigma^{\mathrm{SEX}}(\mathbf{x},\mathbf{x}') \\ \Sigma^{\mathrm{COH}}(\mathbf{x},\mathbf{x}') &= \frac{1}{2}\delta(\mathbf{x}-\mathbf{x}')\left[W(\mathbf{x},\mathbf{x}';0) - v(\mathbf{r}-\mathbf{r}')\right] \\ \Sigma^{\mathrm{SEX}}(\mathbf{x},\mathbf{x}') &= -\sum_n^{\mathrm{occ}} \psi_n(\mathbf{x})\psi_n^*(\mathbf{x}')W(\mathbf{x},\mathbf{x}';0) \end{aligned} \tag{16.11}$$

The COHSEX self-energy is energy-independent and Hermitian, and therefore can be calculated in a self-consistent manner quite straightforwardly. The COHSEX itself tends to overestimate the band gaps of semiconductors, but one can use COHSEX orbital energies and wave-functions as the input for full G_0W_0. This COHSEX based G_0W_0 approach has been used by R. Reining and coworkers for Cu_2O [17] and VO_2 [23] with remarkable success.

An approach closely related to the COHSEX approximation is the model GW approach first proposed by Gygi and Baldereschi [26], in which the self-energy correction with respect to the LDA exchange-correlation potential is approximated by

$$\delta\Sigma^{\mathrm{xc}}(\mathbf{r},\mathbf{r}') = -\rho(\mathbf{r},\mathbf{r}')\delta W(\mathbf{r}-\mathbf{r}') \tag{16.12}$$

where $\rho(\mathbf{r},\mathbf{r}')$ is the density matrix function, and $\delta W(\mathbf{r}-\mathbf{r}')$ is a model function for the screened Coulomb interaction correction, whose Fourier transform takes the form

$$\delta W(q) = \frac{4\pi}{\Omega q^2}\left[\varepsilon_{\mathrm{SC}}^{-1}(\mathbf{q},\omega=0) - \varepsilon_{\mathrm{M}}^{-1}(\mathbf{q},\omega=0)\right] \tag{16.13}$$

$\varepsilon_{\mathrm{SC}}^{-1}$ and $\varepsilon_{\mathrm{M}}^{-1}$ are the inverse dielectric functions for a semiconductor and a metal, respectively, both approximated by some model functions. This model GW approach was used by Massida and coworkers to investigate electronic band structure properties of transition metal oxides [38, 39, 18].

16.2.4 Sakuma-Miyake-Aryasetiawan scheme

Sakuma, Miyake and Aryasetiawan (SMA) proposed another approximate self-consistent scheme with some interesting new features. [49] For a given set of single-particle orbitals, the quasi-particle energies and wave functions are calculated by solving Eq. (16.3) with the regularized self-energy Eq. (16.4) without introducing additional approximation to the energy-dependence. The price of this more rigorous treatment is that quasi-particle wave functions obtained in this manner are not orthogonal and therefore unsuitable as the input for the next iteration of GW calculations. SMA proposed to define the following effective quasi-particle Hamiltonian,

$$H_{\mathrm{QP}} = \sum_n |\Psi_n\rangle\,\mathcal{E}_n\,\langle\Psi_n| \tag{16.14}$$

Using the corresponding eigen-energies and wavefuctions, one obtains a close loop to perform approximate SCGW calculations.

16.3 Implementation of QSGW

16.3.1 General issues

It is useful to define three different Hamiltonians:

i. H_s is the Hermitian single-particle whose eigenfunctions, denoted as $\phi_{\mu\mathbf{k}}$ are used to expand the quasi-particle wave functions, denoted as $\Psi_{n\mathbf{k}}$;

ii. $H^{\rm qp}$ is the full QP Hamiltonian which is non-Hermitian, energy-dependent.

iii. $H^{\rm eff}$ is the effective quasi-particle Hamiltonian that is used in the self-consistency;

The essense of the quasi-particle self-consistent GW (QSGW) method is to construct $H^{\rm eff}$ based on $H^{\rm qp}$.

There are two possible approaches to implement the QSGW methods. In the first approach, one can use fixed H_s, i.e. using fixed $\phi_{\mu\mathbf{k}}$ as basis functions to expand QP wave functions $\Psi_{n\mathbf{k}}$. In the second approach, one can use the effective $H^{\rm qp}$ at $i-1$-th iteration as H_s at i-th interation. We will denote the former as the fixed-basis (FB) approach, and the second one adapted-basis (AB) approach.

The quasi-particle equation reads

$$H^{\rm eff}\left|\Psi_{n\mathbf{k}}\right\rangle \equiv \left[H_s+\Delta\Sigma^{\rm xc}\right]\left|\Psi_{n\mathbf{k}}\right\rangle = \mathcal{E}_{n\mathbf{k}}\left|\Psi_{n\mathbf{k}}\right\rangle. \tag{16.15}$$

$\Delta\Sigma^{\rm xc}$ is the self-energy correction,

$$\Delta\Sigma^{\rm xc} = \Sigma^{\rm xc} - V^{\rm xc0} + V^{\rm H} - V^{\rm H0} \equiv \Sigma^{\rm xc} - V^{\rm xc0} + \delta V^{\rm H} \tag{16.16}$$

where $V^{\rm xc0}$ and $V^{\rm H0}$ are xc and Hartree potential corresponding to H_s, respectively. Now expanding $\Psi_{n\mathbf{k}}$ by eigenfunctions of H_s

$$\begin{aligned} H_s\left|\phi_{\mu\mathbf{k}}\right\rangle &= \epsilon_{\mu\mathbf{k}}\left|\phi_{\mu\mathbf{k}}\right\rangle \\ \left|\Psi_{n\mathbf{k}}\right\rangle &= \sum_{\mu} C_{\mu n}(\mathbf{k})\left|\phi_{\mu\mathbf{k}}\right\rangle \end{aligned} \tag{16.17}$$

we obtain a standard eigen-equation

$$\begin{aligned} &\mathbf{H}^{\rm eff}\mathbf{C} = \mathcal{E}\mathbf{C} \\ &H^{\rm eff}_{\mu\nu} = \epsilon_\nu\delta_{\mu\nu} + \Delta\Sigma_{\mu\nu} \\ &\Delta\Sigma_{\mu\nu} = \Sigma^{\rm x}_{\mu\nu} + \Sigma^{\rm c}_{\mu\nu} - V^{\rm xc}_{\mu\nu} + \delta V^{\rm H}_{\mu\nu} \end{aligned} \tag{16.18}$$

16.3.2 Matrix elements in the FB approach

In the FB approach, the reference Hamiltonian H_s is fixed, i.e. using fixed $\phi_{\mu\mathbf{k}}$ as the basis to expand QP wave functions $\Psi_{n\mathbf{k}}$.

16.3.2.1 Bare-exchange $\Sigma^{\rm x}_{\mu\nu}$

$$\begin{aligned} \Sigma^{{\rm x}\sigma}_{\mu\nu}(\mathbf{k}) &= -\sum_{\mathbf{k}'}\sum_{n} f^{\sigma}_{n\mathbf{k}'}\sum_{\mathbf{q}}\sum_{i,j} v_{ij}(\mathbf{q}) \\ &\times \int d\mathbf{r}\phi^{\sigma*}_{\mu\mathbf{k}}(\mathbf{r})\chi^{\mathbf{q}}_i(\mathbf{r})\Psi^{\sigma}_{n\mathbf{k}'}\int d\mathbf{r}'\phi^{\sigma}_{\nu\mathbf{k}}(\mathbf{r}')\chi^{\mathbf{q}*}_j(\mathbf{r}')\Psi^{\sigma*}_{n\mathbf{k}'}(\mathbf{r}') \\ &= N_c^{-1}\sum_{\mathbf{q}}\sum_{i,j}\sum_{n} f^{\sigma}_{n\mathbf{k}-\mathbf{q}} v_{ij}(\mathbf{q})\left[M^{i\sigma}_{\mu n}(\mathbf{k},\mathbf{q})\right]^* M^{j\sigma}_{\nu n}(\mathbf{k},\mathbf{q}) \end{aligned} \tag{16.19}$$

where $M^{i}_{\mu n}(\mathbf{k},\mathbf{q})$ is calculated by

$$\begin{aligned} M^{i\sigma}_{\mu n}(\mathbf{k},\mathbf{q}) &= N_c^{1/2}\int d\mathbf{r}\chi^{\mathbf{q}*}_j(\mathbf{r})\phi^{\sigma}_{\mu\mathbf{k}}(\mathbf{r})\Psi^{\sigma*}_{n\mathbf{k}-\mathbf{q}}(\mathbf{r}) \\ &= \sum_{\mu'} C^{\sigma*}_{\mu' n}(\mathbf{k}-\mathbf{q}) N_c^{1/2}\int d\mathbf{r}\chi^{\mathbf{q}*}_j(\mathbf{r})\phi^{\sigma}_{\mu\mathbf{k}}(\mathbf{r})\phi^{\sigma*}_{\mu'\mathbf{k}}(\mathbf{r}) \\ &= \sum_{\mu'} C^{\sigma*}_{\mu' n}(\mathbf{k}-\mathbf{q}) M^{i\sigma}_{\mu\mu'}(\mathbf{k},\mathbf{q}) \end{aligned} \tag{16.20}$$

so that we can have

$$\begin{aligned}\Sigma^{\mathrm{x}\sigma}_{\mu\nu}(\mathbf{k}) &= -N_c^{-1}\sum_{\mathbf{q}}\sum_{i,j}\sum_{n} f^{\sigma}_{n\mathbf{k}-\mathbf{q}} v_{ij}(\mathbf{q}) \sum_{\mu'\nu'} C^{\sigma}_{\mu' n}(\mathbf{k}-\mathbf{q}) C^{\sigma *}_{\nu' n}(\mathbf{k}-\mathbf{q}) \\ &\times \left[M^{i\sigma}_{\mu\mu'}(\mathbf{k},\mathbf{q})\right]^* M^{j\sigma}_{\nu\nu'}(\mathbf{k},\mathbf{q}) \\ &= -N_c^{-1}\sum_{\mathbf{q}}\sum_{i,j} v_{ij}(\mathbf{q}) \sum_{\mu'\nu'} \left[M^{i\sigma}_{\mu\mu'}(\mathbf{k},\mathbf{q})\right]^* M^{j\sigma}_{\nu\nu'}(\mathbf{k},\mathbf{q}) \rho^{\sigma}_{\mu'\nu'}(\mathbf{k}-\mathbf{q})\end{aligned} \tag{16.21}$$

where we have introduced the density matrix

$$\rho^{\sigma}_{\mu'\nu'}(\mathbf{k}) \equiv \sum_n f^{\sigma}_{n\mathbf{k}} C^{\sigma}_{\mu' n}(\mathbf{k}) C^{\sigma *}_{\nu' n}(\mathbf{k}) \tag{16.22}$$

Further using v-diagonalized basis

$$\Sigma^{\mathrm{x}\sigma}_{\mu\nu}(\mathbf{k}) = -N_c^{-1}\sum_{\mathbf{q}}\sum_{i}\sum_{\mu'\nu'} \left[\tilde{M}^{i\sigma}_{\mu\mu'}(\mathbf{k},\mathbf{q})\right]^* \tilde{M}^{i\sigma}_{\nu\nu'}(\mathbf{k},\mathbf{q}) \rho^{\sigma}_{\mu'\nu'}(\mathbf{k}-\mathbf{q}) \tag{16.23}$$

16.3.2.2 COHSEX correlation self-energy

The correlation self-energy in the static COHSEX approximation reads

$$\Sigma^{\mathrm{c}}(\mathbf{x},\mathbf{x}') = \sum_{n\mathbf{k}} \left[\frac{1}{2} - f_{n\mathbf{k}}\right] \Psi_{n\mathbf{k}}(\mathbf{x}) \Psi^*_{n\mathbf{k}}(\mathbf{x}') W_c(\mathbf{x},\mathbf{x}';0) \tag{16.24}$$

so we have

$$\Sigma^{\mathrm{c}\sigma}_{\mu\nu}(\mathbf{k}) = N_c^{-1}\sum_{\mathbf{q}}\sum_{i,j} \left[\frac{1}{2} - f^{\sigma}_{n\mathbf{k}-\mathbf{q}}\right] W^c_{ij}(\mathbf{q},0) \left[M^{i\sigma}_{\mu n}(\mathbf{k},\mathbf{q})\right]^* M^{j\sigma}_{\nu n}(\mathbf{k},\mathbf{q}) \tag{16.25}$$

16.3.2.3 GW correlation selfenergy in the FvSK scheme

For the correlation term in frequency space one has to calculate the convolution:

$$\Sigma^c(\mathbf{r},\mathbf{r}',\omega) = \frac{i}{2\pi}\int_{-\infty}^{\infty} G_0(\mathbf{r},\mathbf{r}',\omega+\omega') W^c_0(\mathbf{r},\mathbf{r}',\omega') d\omega' \tag{16.26}$$

We follow the same steps as for the exchange term. The screened Coulomb potential can be expranded by the basis functions as

$$W^c_0(\mathbf{r},\mathbf{r}',\omega) = \sum_{\mathbf{q}}^{BZ}\sum_{ij} \chi^{\mathbf{q}}_i(\mathbf{r}) W^c_{ij}(\mathbf{q},\omega) (\chi^{\mathbf{q}}_j(\mathbf{r}'))^* \tag{16.27}$$

Inserting 16.27 and the definition of G_0 into 16.26 we have:

$$\begin{aligned}\Sigma^c(\mathbf{r},\mathbf{r}',\omega) =& \frac{i}{2\pi}\int_{-\infty}^{\infty} d\omega' \sum_{n'\mathbf{k}'} \frac{\psi_{n'\mathbf{k}'}(\mathbf{r}) \psi^*_{n'\mathbf{k}'}(\mathbf{r}')}{\omega+\omega'-\tilde{\epsilon}_{n\mathbf{k}}} \sum_{\mathbf{q}}^{BZ}\sum_{ij} \chi^{\mathbf{q}}_i(\mathbf{r}) W^c_{ij}(\mathbf{q},\omega') (\chi^{\mathbf{q}}_j(\mathbf{r}'))^* \\ =& \sum_{\mathbf{q}}\sum_{ij}\sum_{\mathbf{k}'}\sum_{n'} \chi^{\mathbf{q}}_i(\mathbf{r}) \psi_{n'\mathbf{k}'}(\mathbf{r}) \chi^{\mathbf{q}*}_j(\mathbf{r}') \psi^*_{n'\mathbf{k}'}(\mathbf{r}') \frac{i}{2\pi}\int_{-\infty}^{\infty} d\omega' \frac{W^c_{ij}(\mathbf{q},\omega')}{\omega+\omega'-\tilde{\epsilon}_{n\mathbf{k}}}\end{aligned} \tag{16.28}$$

Matrix elements of correlation self-energy can therefore be calculated as

$$\begin{aligned}\Sigma^c_{\mu\nu}(\mathbf{k},\omega) =& \iint_V \phi^*_{\mu\mathbf{k}}(\mathbf{r}) \Sigma^c(\mathbf{r},\mathbf{r}',\omega) \phi_{\nu\mathbf{k}}(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \\ =& N_c^{-1}\sum_{\mathbf{q}}\sum_{ij}\sum_{n'} \left[M^i_{\mu n'}(\mathbf{k},\mathbf{q})\right]^* \frac{i}{2\pi}\int_{-\infty}^{\infty} d\omega' \frac{W^c_{ij}(\mathbf{q},\omega')}{\omega+\omega'-\tilde{\epsilon}_{n'\mathbf{k}-\mathbf{q}}} M^j_{\nu n'}(\mathbf{k},\mathbf{q}) \\ =& N_c^{-1}\sum_{\mathbf{q}}\sum_{n'} \frac{i}{2\pi}\int_{-\infty}^{\infty} d\omega' \frac{X_{\mu\nu;n'}(\mathbf{k},\mathbf{q},\omega')}{\omega+\omega'-\tilde{\epsilon}_{n'\mathbf{k}-\mathbf{q}}}\end{aligned} \tag{16.29}$$

where we have introduced

$$X_{\mu\nu;n'}(\mathbf{k},\mathbf{q},\omega) = \sum_{ij} \left[M^i_{\mu n'}(\mathbf{k},\mathbf{q})\right]^* W^c_{ij}(\mathbf{q},\omega) M^j_{\nu n'}(\mathbf{k},\mathbf{q}) \tag{16.30}$$

In practice, we use the imaginary frequency technique,

$$\Sigma^c_{\mu\nu}(\mathbf{k}, iu) = N_c^{-1} \sum_{\mathbf{q}}^{BZ} \sum_{n'} \int_0^\infty \frac{du'}{2\pi} X_{\mu\nu;n'}(\mathbf{k}, \mathbf{q}, iu') \frac{2(\epsilon_{n'\mathbf{k}-\mathbf{q}} - iu)}{(\epsilon_{n'\mathbf{k}-\mathbf{q}} - iu)^2 + u'^2} \tag{16.31}$$

Using the fact that

$$\begin{aligned} [X_{\mu\nu;n'}(\mathbf{k}, \mathbf{q}, iu')]^* &= \sum_{ij} M^i_{\mu n'}(\mathbf{k}, \mathbf{q}) W^{c*}_{ij}(\mathbf{q}, iu) \left[M^j_{\nu n'}(\mathbf{k}, \mathbf{q}) \right]^* \\ &= \sum_{ij} \left[M^j_{\nu n'}(\mathbf{k}, \mathbf{q}) \right]^* W^c_{ji}(\mathbf{q}, iu) M^i_{\mu n'}(\mathbf{k}, \mathbf{q}) \\ &= X_{\nu\mu;n'}(\mathbf{k}, \mathbf{q}, iu') \end{aligned} \tag{16.32}$$

we therefore have

$$\begin{aligned} &\Sigma^c_{\mu\nu}(\mathbf{k}, -iu) \\ &= N_c^{-1} \sum_{\mathbf{q}}^{BZ} \sum_{n'} \int_0^\infty \frac{du'}{2\pi} X_{\mu\nu;n'}(\mathbf{k}, \mathbf{q}, iu') \frac{2(\epsilon_{n'\mathbf{k}-\mathbf{q}} + iu)}{(\epsilon_{n'\mathbf{k}-\mathbf{q}} + iu)^2 + u'^2} \\ &= \left\{ N_c^{-1} \sum_{\mathbf{q}}^{BZ} \sum_{n'} \int_0^\infty \frac{du'}{2\pi} [X_{\mu\nu;n'}(\mathbf{k}, \mathbf{q}, iu')]^* \frac{2(\epsilon_{n'\mathbf{k}-\mathbf{q}} - iu)}{(\epsilon_{n'\mathbf{k}-\mathbf{q}} - iu)^2 + u'^2} \right\}^* \\ &= \left\{ N_c^{-1} \sum_{\mathbf{q}}^{BZ} \sum_{n'} \int_0^\infty \frac{du'}{2\pi} X_{\nu\mu;n'}(\mathbf{k}, \mathbf{q}, iu') \frac{2(\epsilon_{n'\mathbf{k}-\mathbf{q}} - iu)}{(\epsilon_{n'\mathbf{k}-\mathbf{q}} - iu)^2 + u'^2} \right\}^* \\ &= \left\{ \Sigma^c_{\mu\nu}(\mathbf{k}, iu) \right\}^* \end{aligned} \tag{16.33}$$

From the identity above, we can see that only $\Sigma^c_{\mu\nu}$ along the positive imaginary frequncy axis needs to be calculated.

16.3.2.4 Hartree potential δV^{H}

$$\begin{aligned} V^{\mathrm{H}\sigma}_{\mu\nu}(\mathbf{k}) &= \int d\mathbf{r} \phi^{\sigma*}_{\mu\mathbf{k}}(\mathbf{r}) V^{\mathrm{H}}(\mathbf{r}) \phi^{\sigma}_{\nu\mathbf{k}}(\mathbf{r}) \\ &= \sum_{\sigma'} \sum_{n'\mathbf{k}'} f^{\sigma}_{n'\mathbf{k}'} \int d\mathbf{r} d\mathbf{r}' \phi^{\sigma*}_{\mu\mathbf{k}}(\mathbf{r}) \phi^{\sigma}_{\nu\mathbf{k}}(\mathbf{r}) v(\mathbf{r}, \mathbf{r}') \Psi^{\sigma'*}_{n'\mathbf{k}'}(\mathbf{r}') \Psi^{\sigma'}_{n'\mathbf{k}'}(\mathbf{r}') \end{aligned} \tag{16.34}$$

Now using

$$v(\mathbf{r}, \mathbf{r}') = \sum_{i,j} \sum_{\mathbf{q}} v_{ij}(\mathbf{q}) \chi^{\mathbf{q}}_i(\mathbf{r}) \chi^{\mathbf{q}*}_j(\mathbf{r}') \tag{16.35}$$

we have

$$\begin{aligned} V^{\mathrm{H}\sigma}_{\mu\nu}(\mathbf{k}) &= \sum_{\sigma'} \sum_{n'\mathbf{k}'} f^{\sigma}_{n'\mathbf{k}'} \sum_{i,j} \sum_{\mathbf{q}} v_{ij}(\mathbf{q}) \\ &\quad \times \int d\mathbf{r} \chi^{\mathbf{q}}_i(\mathbf{r}) \phi^{\sigma*}_{\mu\mathbf{k}}(\mathbf{r}) \phi^{\sigma}_{\nu\mathbf{k}}(\mathbf{r}) \int d\mathbf{r}' \chi^{\mathbf{q}*}_j(\mathbf{r}') \Psi^{\sigma'*}_{n'\mathbf{k}'}(\mathbf{r}') \Psi^{\sigma'}_{n'\mathbf{k}'}(\mathbf{r}') \\ &= N_c^{-1} \sum_{i,j} v_{ij}(\mathbf{q} = 0) \left[M^{i\sigma}_{\mu\nu}(\mathbf{k}, 0) \right]^* \sum_{\sigma'} \sum_{n'\mathbf{k}'} f^{\sigma'}_{n'\mathbf{k}'} M^{j\sigma'}_{n'n'}(\mathbf{k}', 0) \end{aligned} \tag{16.36}$$

As we know, $v_{ij}(\mathbf{q})$ is singular in the limit of $\mathbf{q} \to 0$, but since what we really need is the change of V^{H}, the singularity will can cancel, and therefore we can just look at the regularized part of $v_{ij}(\mathbf{q} \to 0)$. Using the v-diagonalized basis, we have

$$V^{\mathrm{H}\sigma}_{\mu\nu}(\mathbf{k}) = N_c^{-1} \sum_{i} \left[\tilde{M}^{i\sigma}_{\mu\nu}(\mathbf{k}, 0) \right]^* \sum_{\sigma'} \sum_{n'\mathbf{k}'} f^{\sigma'}_{n'\mathbf{k}'} \tilde{M}^{i\sigma'}_{n'n'}(\mathbf{k}', 0) \tag{16.37}$$

$M^{j\sigma'}_{n'n'}$ can be calculated by

$$M^{i\sigma}_{mn}(\mathbf{k}, \mathbf{q}) = \sum_{\mu\nu} C^{\sigma}_{\mu m}(\mathbf{k}) C^{\sigma*}_{\nu n}(\mathbf{k} - \mathbf{q}) M^{i\sigma}_{\mu\nu}(\mathbf{k}, \mathbf{q}). \tag{16.38}$$

Using the density matrix as defined previously, we have

$$\begin{aligned} V^{\mathrm{H}\sigma}_{\mu\nu}(\mathbf{k}) &= N_c^{-1} \sum_i \left[\tilde{M}^{i\sigma}_{\mu\nu}(\mathbf{k},0)\right]^* \sum_{\sigma'} \sum_{n'\mathbf{k}'} f^{\sigma'}_{n'\mathbf{k}'} \sum_{\mu'\nu'} C^{\sigma'}_{\mu' n'}(\mathbf{k}') C^{\sigma *}_{\nu' n'}(\mathbf{k}') \tilde{M}^{i\sigma'}_{\mu'\nu'}(\mathbf{k}',0) \\ &= N_c^{-1} \sum_i \left[\tilde{M}^{i\sigma}_{\mu\nu}(\mathbf{k},0)\right]^* \sum_{\sigma'} \sum_{\mathbf{k}'} \sum_{\mu'\nu'} \rho^{\sigma'}_{\mu'\nu'}(\mathbf{k}') \tilde{M}^{i\sigma'}_{\mu'\nu'}(\mathbf{k}',0) \end{aligned} \tag{16.39}$$

Chapter 17

ACFD total energy

17.1 Exact exchange energy

The exact exchange energy in KS-DFT is just the Hatree-Fock exchange energy calculated using the KS orbitals

$$\begin{aligned} E_x =& -\frac{1}{2}N_c^{-1}\sum_{\sigma}\sum_{n\mathbf{k}}^{\text{occ}}\sum_{n'\mathbf{k}'}^{\text{occ}}\int_V d\mathbf{r}_1\int_V \mathbf{r}_2 v(\mathbf{r}_1,\mathbf{r}_2)\psi^{\sigma *}_{n\mathbf{k}}(\mathbf{r}_1)\psi^{\sigma *}_{n'\mathbf{k}'}(\mathbf{r}_2)\psi_{n'\mathbf{k}'}(\mathbf{r}_1)\psi_{n\mathbf{k}}(\mathbf{r}_2) \\ =& -\frac{1}{2}N_c^{-1}\sum_{\sigma}\sum_{n\mathbf{k}}^{\text{occ}}\sum_{n'\mathbf{k}'}^{\text{occ}}\int d\mathbf{r}_1\int \mathbf{r}_2 v(\mathbf{r}_1,\mathbf{r}_2)\left[\psi^{\sigma}_{n\mathbf{k}}(\mathbf{r}_1)\psi^{\sigma *}_{n'\mathbf{k}'}(\mathbf{r}_1)\right]^*\left[\psi_{n\mathbf{k}}(\mathbf{r}_2)\psi^{*}_{n'\mathbf{k}'}(\mathbf{r}_2)\right] \end{aligned} \tag{17.1}$$

Note that the factor N_c^{-1} comes from the fact that one usually calculate the exchange energy per unit cell. Expanding the bare Coulomb interaction $v(\mathbf{r}_1,\mathbf{r}_2)$ by the basis functions $\chi_i^{\mathbf{q}}(\mathbf{r})$

$$\begin{aligned} E_x =& -\frac{1}{2}N_c^{-1}\sum_{\sigma}\sum_{n\mathbf{k}}^{\text{occ}}\sum_{i,j}\sum_{\mathbf{q}} v_{ij}(\mathbf{q})\sum_{n'\mathbf{k}'}^{\text{occ}}\int_V d\mathbf{r}_1\int_V \mathbf{r}_2\left[\chi_i^{\mathbf{q}*}(\mathbf{r})\psi^{\sigma}_{n\mathbf{k}}(\mathbf{r}_1)\psi^{\sigma *}_{n'\mathbf{k}'}(\mathbf{r}_1)\right]^*\left[\chi_i^{\mathbf{q}*}(\mathbf{r}')\psi^{\sigma}_{n\mathbf{k}}(\mathbf{r}_2)\psi^{\sigma *}_{n'\mathbf{k}'}(\mathbf{r}_2)\right] \\ =& -\frac{1}{2}N_c^{-2}\sum_{\mathbf{k},\mathbf{q}}^{\text{BZ}}\sum_{n,n'} f_{n\mathbf{k}}f_{n'\mathbf{k}-\mathbf{q}}\sum_{i,j}\left[M^i_{nn'}(\mathbf{k},\mathbf{q})\right]^* v_{ij}(\mathbf{q})M^j_{nn'}(\mathbf{k},\mathbf{q}) \end{aligned} \tag{17.2}$$

Using the defintion of the exchange self-energy, we have

$$E_x = -\frac{1}{2}N_c^{-1}\sum_{\mathbf{k}}^{\text{BZ}}\sum_{n} f_{n\mathbf{k}}\Sigma^{\text{x}}_{n\mathbf{k}} \tag{17.3}$$

So apparently, one can obtain the exchange energy as a by-product of the GW calculation. However, in the case of GW calculation, only $\Sigma^{\text{x}}_{n\mathbf{k}}$ for valence and a few low-lying conduction bands are calculated, but to calculate E_x, one needs also those for core orbitals.

Without constructing exchange self-energy, E_x can be calcuated as

$$E_x = N_c^{-1}\sum_{\mathbf{q}}^{\text{BZ}} e_x(\mathbf{q}) \tag{17.4}$$

with $e_x(\mathbf{q})$ defined as

$$e_x(\mathbf{q}) := -\frac{1}{2}N_c^{-1}\sum_{\mathbf{k}}^{\text{BZ}}\sum_{n,n'} f_{n\mathbf{k}}f_{n'\mathbf{k}-\mathbf{q}}\sum_{i,j}\left[M^i_{nn'}(\mathbf{k},\mathbf{q})\right]^* v_{ij}(\mathbf{q})M^j_{nn'}(\mathbf{k},\mathbf{q}) \tag{17.5}$$

At the Γ point ($\mathbf{q}\to 0$), the bare Coulomb interaction is singular,

$$v_{ij}(\mathbf{q}) \to \frac{v^s_{ij}}{q^2} + \tilde{v}_{ij}(\mathbf{q}). \tag{17.6}$$

the corresponding $e_x(\mathbf{q})$ becomes

$$e_x(\mathbf{q}) \to \frac{e^s_x}{q^2} + \tilde{e}_x(\mathbf{q}). \tag{17.7}$$

where

$$
\begin{aligned}
e_x^s &\equiv -\frac{1}{2}N_c^{-1}\sum_{\sigma}\sum_{\mathbf{k}}^{\mathrm{BZ}}\sum_{n,n'} f_{n\mathbf{k}}^{\sigma} f_{n'\mathbf{k}}^{\sigma}\sum_{i,j}\left[M_{nn'}^{i\sigma}(\mathbf{k},0)\right]^* v_{ij}^s M_{nn'}^{j\sigma}(\mathbf{k},0) \\
\tilde{e}_x(\mathbf{q}) &\equiv -\frac{1}{2}N_c^{-1}\sum_{\sigma}\sum_{\mathbf{k}}^{\mathrm{BZ}}\sum_{n,n'} f_{n\mathbf{k}}^{\sigma} f_{n'\mathbf{k}-\mathbf{q}}^{\sigma}\sum_{i,j}\left[M_{nn'}^{i\sigma}(\mathbf{k},\mathbf{q})\right]^* \tilde{v}_{ij}(\mathbf{q}) M_{nn'}^{j\sigma}(\mathbf{k},\mathbf{q})
\end{aligned}
\tag{17.8}
$$

The integration around the singular point is calculated analytically as in the case of the self-energy.

When using the v-diagonalized basis,

$$
\begin{aligned}
v_{ij}^s &= 4\pi\delta_{i,0}\delta_{j,0} \\
\tilde{v}_{ij}(\mathbf{q}) &= \tilde{v}_i(\mathbf{q})\delta_{ij}
\end{aligned}
\tag{17.9}
$$

then we have

$$
\begin{aligned}
e_x^s &= -\frac{1}{2}N_c^{-1}(4\pi)\sum_{\sigma}\sum_{\mathbf{k}}^{\mathrm{BZ}}\sum_{n,n'} f_{n\mathbf{k}}^{\sigma} f_{n'\mathbf{k}}^{\sigma}\left[M_{nn'}^{0\sigma}(\mathbf{k},0)\right]^* M_{nn'}^{0\sigma}(\mathbf{k},0) \\
&= -2\pi N_c^{-1}\sum_{\sigma}\sum_{\mathbf{k}}^{\mathrm{BZ}}\sum_{nn'} f_{n\mathbf{k}}^{\sigma} f_{n'\mathbf{k}}^{\sigma}\Omega^{-1}\delta_{n,n'} \\
&= -\frac{2\pi}{\Omega}N_e N_c^{-1}\sum_{\mathbf{k}}^{\mathrm{BZ}} 1 \\
&= -\frac{2\pi}{\Omega}N_e
\end{aligned}
\tag{17.10}
$$

and

$$
\begin{aligned}
\tilde{e}_x(\mathbf{q}) &\equiv -\frac{1}{2}N_c^{-1}\sum_{\sigma}\sum_{\mathbf{k}}^{\mathrm{BZ}}\sum_{n,n'} f_{n\mathbf{k}}^{\sigma} f_{n'\mathbf{k}-\mathbf{q}}^{\sigma}\sum_{i}\left[M_{nn'}^{i\sigma}(\mathbf{k},\mathbf{q})\right]^* \tilde{v}_i(\mathbf{q}) M_{nn'}^{i\sigma}(\mathbf{k},\mathbf{q}) \\
&= -\frac{1}{2}N_c^{-1}\sum_{\sigma}\sum_{\mathbf{k}}^{\mathrm{BZ}}\sum_{n,n'} f_{n\mathbf{k}}^{\sigma} f_{n'\mathbf{k}-\mathbf{q}}^{\sigma}\sum_{i}\left[\tilde{M}_{nn'}^{i\sigma}(\mathbf{k},\mathbf{q})\right]^* \tilde{M}_{nn'}^{i\sigma}(\mathbf{k},\mathbf{q}) \\
&= -\frac{1}{2}\sum_{\sigma}\frac{\Omega}{(2\pi)^3}\int_{BZ} d\mathbf{k}\sum_{n,n'} f_{n\mathbf{k}}^{\sigma} f_{n'\mathbf{k}-\mathbf{q}}^{\sigma}\sum_{i}\left[\tilde{M}_{nn'}^{i\sigma}(\mathbf{k},\mathbf{q})\right]^* \tilde{M}_{nn'}^{i\sigma}(\mathbf{k},\mathbf{q})
\end{aligned}
\tag{17.11}
$$

17.2 RPA correlation energy

The RPA correlation energy for periodic systems reads

$$
\begin{aligned}
E_{\mathrm{c}}^{\mathrm{RPA}} =& N_c^{-1}\sum_{\mathbf{q}}\frac{1}{2\pi}\int_0^{\infty} du \mathrm{Tr}\left\{\mathrm{Ln}\left[1-\mathbf{v}(\mathbf{q})\mathbf{P}(\mathbf{q},iu)\right]+\mathbf{v}(\mathbf{q})\mathbf{P}(\mathbf{q},iu)\right\} \\
:=& N_c^{-1}\sum_{\mathbf{q}}\frac{1}{2\pi}\int_0^{\infty} du E_{\mathrm{c}}^{\mathrm{RPA}}(\mathbf{q},iu)
\end{aligned}
\tag{17.12}
$$

Using the relation between the diectric function and the polarization function $\mathbf{P}(\mathbf{q},iu)$

$$
\varepsilon(\mathbf{q},iu) = 1-\mathbf{v}(\mathbf{q})\mathbf{P}(\mathbf{q},iu) \tag{17.13}
$$

we have

$$
E_{\mathrm{c}}^{\mathrm{RPA}}(\mathbf{q},iu) = \mathrm{Tr}\left\{\mathrm{Ln}\left[\varepsilon(\mathbf{q},iu)\right]+(1-\varepsilon(\mathbf{q},iu))\right\} \tag{17.14}
$$

In the GW code, the symmetrized dielectric matrix is used

$$
\begin{aligned}
\tilde{\varepsilon}(\mathbf{q},iu) :=& \mathbf{v}^{-\frac{1}{2}}(\mathbf{q})\varepsilon(\mathbf{q},iu)\mathbf{v}^{\frac{1}{2}}(\mathbf{q}) \\
=& 1-\mathbf{v}^{\frac{1}{2}}(\mathbf{q})\mathbf{P}(\mathbf{q},iu)\mathbf{v}^{\frac{1}{2}}(\mathbf{q})
\end{aligned}
\tag{17.15}
$$

Using $\mathrm{Tr}\left\{\mathbf{AB}\right\} = \mathrm{Tr}\left\{\mathbf{BA}\right\}$, we have

$$
E_{\mathrm{c}}^{\mathrm{RPA}}(\mathbf{q},iu) = \mathrm{Tr}\left\{\mathrm{Ln}\left[\tilde{\varepsilon}(\mathbf{q},iu)\right]+(1-\tilde{\varepsilon}(\mathbf{q},iu))\right\} \tag{17.16}
$$

Apparently the implementation of ACFD correlation energy in our GW code is quite straightforward. Special cares may be needed for:

i. Integration over $\mathbf{q}$: It is not clear whether standard BZ integration method already implemented in the code is enough to obtain optimal efficiency;

ii. Integration over frequency;

iii. Convergence with respect to unoccupied bands.

17.3 ACFD correlation energy with ALDA f^{xc}

Chapter 18

Constrained RPA

We are interested in computing the matrix elements of the operator W in a Wannier basis $\{|\phi_{\mathbf{R},L}\phi_{\mathbf{R}',L'}>\}$ that we need to construct. This is a step before computing the matrix element s of the constrained RPA (cRPA) $W_{\mathbf{r}}$. We first will consider the case of disentangled correlated bands at the Fermi level. The band structure of $SrVO_3$ is then a toy-model.

18.1 U-matrix elements

What we are intertested is matrix elements of the cRPA screened Coulomb interation W_r with respect to a set of local orbitals, denoted as $|\phi_{\mathbf{R}L}\rangle$, where $\mathbf{R}$ denotes the lattive vectors, and L is a collective index for a, l and m, denoting the atom, angular and magnetic quantum numbers, respectively. A Bloch function can be constructed from $|\phi_{\mathbf{R}L}\rangle$ by

$$|\phi_{\mathbf{k}L}\rangle = \frac{1}{N_c^{1/2}} \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} |\phi_{\mathbf{R}L}\rangle \tag{18.1}$$

Inversely we have

$$|\phi_{\mathbf{R}L}\rangle = \frac{1}{N_c^{1/2}} \sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{R}} |\phi_{\mathbf{k}L}\rangle \tag{18.2}$$

Here we follow J. M. Ziman's convention for the normalization and phase [66]. We will also use the abbreviation $\lambda \to (\mathbf{R}L)$ to simplify the notation in the followings.

We now have

$$\begin{aligned}
&U_{\lambda_1\lambda_2\lambda_3\lambda_4} \\
&\equiv \langle \phi_{\mathbf{R}_1L_1}\phi_{\mathbf{R}_2L_2}| \, W_r \, |\phi_{\mathbf{R}_3L_3}\phi_{\mathbf{R}_4L_4}\rangle \\
&= N_c^{-2} \sum_{\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4} e^{i(\mathbf{k}_1\cdot\mathbf{R}_1+\mathbf{k}_2\cdot\mathbf{R}_2-\mathbf{k}_3\cdot\mathbf{R}_3-\mathbf{k}_4\cdot\mathbf{R}_4)} \\
&\times \langle \phi_{\mathbf{k}_1L_1}\phi_{\mathbf{k}_2L_2}| \, W_r \, |\phi_{\mathbf{k}_3L_3}\phi_{\mathbf{k}_4L_4}\rangle \\
&= N_c^{-2} \sum_{\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4} e^{i(\mathbf{k}_1\cdot\mathbf{R}_1+\mathbf{k}_2\cdot\mathbf{R}_2-\mathbf{k}_3\cdot\mathbf{R}_3-\mathbf{k}_4\cdot\mathbf{R}_4)} \\
&\times \sum_{n_1,n_2,n_3,n_4} \langle \phi_{\mathbf{k}_1L_1}|\psi_{\mathbf{k}_1n_1}\rangle \langle \phi_{\mathbf{k}_2L_2}|\psi_{\mathbf{k}_2n_2}\rangle \\
&\times \langle \psi_{\mathbf{k}_1n_1}\psi_{\mathbf{k}_2n_2}| \, W_r \, |\psi_{\mathbf{k}_3n_3}\psi_{\mathbf{k}_4n_4}\rangle \langle \psi_{\mathbf{k}_3n_3}|\phi_{\mathbf{k}_3L_3}\rangle \langle \psi_{\mathbf{k}_4n_2}|\phi_{\mathbf{k}_4L_4}\rangle
\end{aligned} \tag{18.3}$$

where we have introduced the Kohn-Sham vector basis $|\psi_{\mathbf{k}n}\rangle$. In the followings we will denote the projection of a Kohn-Sham vector to the localized orbitals as

$$P_{Ln}(\mathbf{k}) \equiv \langle \phi_{\mathbf{k}L}|\psi_{\mathbf{k}n}\rangle \tag{18.4}$$

Now the matrix elementes of W_r in the Kohn-Sham basis can be expanded using the product basis

$$\begin{aligned}
&\langle \psi_{\mathbf{k}_1n_1}\psi_{\mathbf{k}_2n_2}| \, W_r \, |\psi_{\mathbf{k}_3n_3}\psi_{\mathbf{k}_4n_4}\rangle \\
&= \int d\mathbf{r}_1 \int d\mathbf{r}_2 \psi^*_{\mathbf{k}_1n_1}(\mathbf{r}_1)\psi^*_{\mathbf{k}_2n_2}(\mathbf{r}_2) \sum_{\mathbf{q}} \sum_{i,j} \chi_i^{\mathbf{q}}(\mathbf{r}_1) W_{ij}(\mathbf{q}) \left[\chi_j^{\mathbf{q}}(\mathbf{r}_2)\right]^* \psi_{\mathbf{k}_3n_3}(\mathbf{r}_1)\psi_{\mathbf{k}_4n_4}(\mathbf{r}_2) \\
&= \sum_{\mathbf{q}} \sum_{i,j} W_{ij}(\mathbf{q}) \int d\mathbf{r}_1 \psi^*_{\mathbf{k}_1n_1}(\mathbf{r}_1)\chi_i^{\mathbf{q}}(\mathbf{r}_1)\psi_{\mathbf{k}_3n_3}(\mathbf{r}_1) \int d\mathbf{r}_2 \psi^*_{\mathbf{k}_2n_2}(\mathbf{r}_2) \left[\chi_j^{\mathbf{q}}(\mathbf{r}_2)\right]^* \psi_{\mathbf{k}_4n_4}(\mathbf{r}_2) \\
&= N_c^{-1} \sum_{\mathbf{q}} \sum_{i,j} W_{ij}(\mathbf{q}) \left[M^i_{n_1n_3}(\mathbf{k}_1,\mathbf{q})\right]^* M^j_{n_4n_2}(\mathbf{k}_4,\mathbf{q}) \delta_{\mathbf{k}_3,\mathbf{k}_1-\mathbf{q}} \delta_{\mathbf{k}_2,\mathbf{k}_4-\mathbf{q}}.
\end{aligned} \tag{18.5}$$

from which we have

$$\begin{aligned}
U_{\lambda_1\lambda_2\lambda_3\lambda_4} &= N_c^{-2}\sum_{\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4} e^{i(\mathbf{k}_1\cdot\mathbf{R}_1+\mathbf{k}_2\cdot\mathbf{R}_2-\mathbf{k}_3\cdot\mathbf{R}_3-\mathbf{k}_4\cdot\mathbf{R}_4)}\sum_{n_1,n_2,n_3,n_4} P_{L_1n_1}(\mathbf{k}_1)P_{L_2n_2}(\mathbf{k}_2)\\
&\times N_c^{-1}\sum_{\mathbf{q}}\sum_{i,j} W_{ij}(\mathbf{q})\left[M^i_{n_1n_3}(\mathbf{k}_1,\mathbf{q})\right]^* M^j_{n_4n_2}(\mathbf{k}_4,\mathbf{q})\delta_{\mathbf{k}_3,\mathbf{k}_1-\mathbf{q}}\delta_{\mathbf{k}_2,\mathbf{k}_4-\mathbf{q}}\left[P_{L_3n_3}(\mathbf{k}_3)\right]^*\left[P_{L_4n_4}(\mathbf{k}_4)\right]^*\\
&= N_c^{-3}\sum_{\mathbf{q}}\sum_{\mathbf{k}_1,\mathbf{k}_4} e^{i\mathbf{k}_1\cdot(\mathbf{R}_1-\mathbf{R}_3)}e^{-i\mathbf{k}_4\cdot(\mathbf{R}_4-\mathbf{R}_2)}e^{i\mathbf{q}\cdot(\mathbf{R}_3-\mathbf{R}_2)}\sum_{n_1,n_2,n_3,n_4} P_{L_1n_1}(\mathbf{k}_1)P_{L_2n_2}(\mathbf{k}_4-\mathbf{q})\\
&\times W_{ij}(\mathbf{q})\left[M^i_{n_1n_3}(\mathbf{k}_1,\mathbf{q})\right]^* M^j_{n_4n_2}(\mathbf{k}_4,\mathbf{q})\left[P_{L_3n_3}(\mathbf{k}_1-\mathbf{q})\right]^*\left[P_{L_4n_4}(\mathbf{k}_4)\right]^*
\end{aligned} \tag{18.6}$$

Recombining different terms and changing the dummy index $\mathbf{k}_4 \to \mathbf{k}_2$, we obtain

$$\begin{aligned}
U_{\lambda_1\lambda_2\lambda_3\lambda_4} &= N_c^{-1}\sum_{\mathbf{q}} e^{i\mathbf{q}\cdot(\mathbf{R}_3-\mathbf{R}_2)}\sum_{i,j} W_{ij}(\mathbf{q})\\
&\times N_c^{-1}\sum_{\mathbf{k}_1} e^{i\mathbf{k}_1\cdot(\mathbf{R}_1-\mathbf{R}_3)}\sum_{n_1,n_3} P_{L_1n_1}(\mathbf{k}_1)\left[P_{L_3n_3}(\mathbf{k}_1-\mathbf{q})\right]^*\left[M^i_{n_1n_3}(\mathbf{k}_1,\mathbf{q})\right]^*\\
&\times N_c^{-1}\sum_{\mathbf{k}_2} e^{-i\mathbf{k}_2\cdot(\mathbf{R}_4-\mathbf{R}_2)}\sum_{n_2,n_4}\left[P_{L_4n_4}(\mathbf{k}_2)\right]^* P_{L_2n_2}(\mathbf{k}_2-\mathbf{q})M^j_{n_4n_2}(\mathbf{k}_2,\mathbf{q})\\
&= N_c^{-1}\sum_{\mathbf{q}} e^{i\mathbf{q}\cdot(\mathbf{R}_3-\mathbf{R}_2)}\sum_{i,j}\left[M^i_{\lambda_1\lambda_3}(\mathbf{q})\right]^* W_{ij}(\mathbf{q})M^j_{\lambda_4\lambda_2}(\mathbf{q}).
\end{aligned} \tag{18.7}$$

We have introduced the intermediate quantity

$$M^i_{\lambda\lambda'}(\mathbf{q}) = N_c^{-1}\sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot(\mathbf{R}-\mathbf{R}')}\sum_{n,n'}\left[P_{Ln}(\mathbf{k})\right]^* P_{L'n'}(\mathbf{k}-\mathbf{q})M^i_{nn'}(\mathbf{k},\mathbf{q}) \tag{18.8}$$

Using the v-diag basis we have

$$W_{ij}(\mathbf{q}) = v_i^{\frac{1}{2}}\tilde{\varepsilon}^{-1}_{ij}v_j^{\frac{1}{2}} \tag{18.9}$$

and therefore

$$U_{\lambda_1\lambda_2\lambda_3\lambda_4} = N_c^{-1}\sum_{\mathbf{q}} e^{i\mathbf{q}\cdot(\mathbf{R}_3-\mathbf{R}_2)}\sum_{i,j}\left[\tilde{M}^i_{\lambda_1\lambda_3}(\mathbf{q})\right]^*\tilde{\varepsilon}^{-1}_{ij}(\mathbf{q})\tilde{M}^j_{\lambda_4\lambda_2}(\mathbf{q}). \tag{18.10}$$

The calculation of $U_{\lambda_1\lambda_2\lambda_3\lambda_4}$ involves the summation over $\mathbf{q}$. Just like for the self-energy, the Γ point ($\mathbf{q}=0$) needs the special treatment as explained in Appendix A.2

$$U_{\lambda_1\lambda_2\lambda_3\lambda_4} = \sum_{\mathbf{q}} w_{\mathbf{q}}\tilde{\mathcal{U}}_{\lambda_1\lambda_2\lambda_3\lambda_4}(\mathbf{q}) + C_{\mathrm{s}2}\mathcal{U}^{\mathrm{s}2}_{\lambda_1\lambda_2\lambda_3\lambda_4} + C_{\mathrm{s}1}\mathcal{U}^{\mathrm{s}1}_{\lambda_1\lambda_2\lambda_3\lambda_4} \tag{18.11}$$

Using the v-diag basis, the screened Coulomb matrix has the following limiting bebavior as $\mathbf{q}\to 0$,

$$W_{ij}(\mathbf{q}\to 0) = \frac{W^{\mathrm{s}2}_{ij}}{q^2} + \frac{W^{\mathrm{s}1}_{ij}}{q} + \tilde{W}_{ij}(\mathbf{q}) \tag{18.12}$$

where

$$\begin{aligned}
W^{\mathrm{s}2}_{ij} &= 4\pi\tilde{\varepsilon}^{-1}_{00}\delta_{i0}\delta_{j0}\\
W^{\mathrm{s}1}_{ij} &= \sqrt{4\pi}\left[\delta_{i0}\tilde{\varepsilon}^{-1}_{0j}\tilde{v}_j^{\frac{1}{2}}(1-\delta_{j0}) + (1-\delta_{i0})\tilde{\varepsilon}^{-1}_{i0}\tilde{v}_i^{\frac{1}{2}}\delta_{j0}\right]
\end{aligned} \tag{18.13}$$

We first consider $\mathcal{U}^{\mathrm{s}2}$,

$$\begin{aligned}
\mathcal{U}^{\mathrm{s}2}_{\lambda_1\lambda_2\lambda_3\lambda_4} &= \sum_{i,j}\left[M^i_{\lambda_1\lambda_3}(0)\right]^* W^{\mathrm{s}2}_{ij}M^j_{\lambda_4\lambda_2}(0)\\
&= 4\pi\tilde{\varepsilon}^{-1}_{00}\left[M^0_{\lambda_1\lambda_3}(0)\right]M^0_{\lambda_4\lambda_2}(0)
\end{aligned} \tag{18.14}$$

Now using

$$\begin{aligned}
M^0_{\lambda\lambda'}(0) &= N_c^{-1}\sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot(\mathbf{R}-\mathbf{R}')}\sum_{n,n'}\left[P_{Ln}(\mathbf{k})\right]^* P_{L'n'}(\mathbf{k})M^0_{nn'}(\mathbf{k},0)\\
&= N_c^{-1}\sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot(\mathbf{R}-\mathbf{R}')}\sum_{n,n'}\left[P_{Ln}(\mathbf{k})\right]^* P_{L'n'}(\mathbf{k})\Omega^{-1/2}\delta_{nn'}\\
&= \Omega^{-1/2}N_c^{-1}\sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot(\mathbf{R}-\mathbf{R}')}\sum_{n}\left[P_{Ln}(\mathbf{k})\right]^* P_{L'n}(\mathbf{k})\\
&= \Omega^{-1/2}\delta_{\lambda\lambda'}
\end{aligned} \tag{18.15}$$

we have

$$\mathcal{U}^{\mathrm{s2}}_{\lambda_1\lambda_2\lambda_3\lambda_4} = \frac{4\pi}{\Omega}\tilde{\varepsilon}^{-1}_{00}\delta_{\lambda_1\lambda_3}\delta_{\lambda_4\lambda_2} \tag{18.16}$$

Similarly for $\mathcal{U}^{\mathrm{s1}}$, we have

$$\begin{aligned}
\mathcal{U}^{\mathrm{s1}}_{\lambda_1\lambda_2\lambda_3\lambda_4} &= \sum_{i,j}\left[M^i_{\lambda_1\lambda_3}(0)\right]^* W^{\mathrm{s1}}_{ij} M^j_{\lambda_4\lambda_2}(0) \\
&= \sqrt{4\pi}\sum_{j\neq 0}\left[M^0_{\lambda_1\lambda_3}(0)\right]^* \tilde{\varepsilon}^{-1}_{0j}\tilde{v}^{\frac{1}{2}}_j M^j_{\lambda_4\lambda_2}(0) + \sqrt{4\pi}\sum_{i\neq 0}\left[M^i_{\lambda_1\lambda_3}(0)\right]^* \tilde{\varepsilon}^{-1}_{i0}\tilde{v}^{\frac{1}{2}}_i M^0_{\lambda_4\lambda_2}(0) \\
&= \sqrt{\frac{4\pi}{\Omega}}\sum_{i\neq 0}\left\{\tilde{\varepsilon}^{-1}_{0i}\tilde{M}^i_{\lambda_4\lambda_2}(0)\delta_{\lambda_1\lambda_3} + \tilde{\varepsilon}^{-1}_{i0}\left[\tilde{M}^i_{\lambda_1\lambda_3}(0)\right]^*\delta_{\lambda_4\lambda_2}\right\}
\end{aligned} \tag{18.17}$$

As obvious from the formulation above, the key ingredients for the calculation of U matrix is $\tilde{M}^i_{\lambda\lambda'}(\mathbf{q})$

18.2 Projection-based disentanglement approach

We start with the polarization functoin in th basis $\{\chi_i^{\mathbf{q}}(\mathbf{r})\}$.

18.2.1 The $\mathbf{q} \to 0$ limit

In the projection-based disentanglement approach, the limit of $\mathbf{q} \to 0$ has to be treated carefully. We will show that the head (H) and wing parts (W) of $\varepsilon_{\rm r}^{-1}$ are actually divergent in the $\mathbf{q} \to 0$ limit as

$$\begin{aligned} H(\mathbf{q} \to 0, \omega) &= H_0(\hat{\mathbf{q}}) + \frac{H_1(\hat{\mathbf{q}})}{q} + \frac{H_2(\hat{\mathbf{q}})}{q^2} \\ W_i(\mathbf{q} \to 0, \omega) &= W_{0;i}(\hat{\mathbf{q}}) + \frac{W_{1;i}(\hat{\mathbf{q}})}{q} \end{aligned} \tag{18.18}$$

Using the block-wise inversition technique

$$\varepsilon = \begin{pmatrix} H & W_i^\dagger \\ W_i & B_{ij} \end{pmatrix} \tag{18.19}$$

$$\varepsilon^{-1} = \begin{pmatrix} \varepsilon_{00}^{-1} & \varepsilon_{0i}^{-1} \\ \varepsilon_{i0}^{-1} & \varepsilon_{ij}^{-1} \end{pmatrix} \tag{18.20}$$

with

$$\begin{aligned} \varepsilon_{00}^{-1} &= \left[H - \sum_i W_i^\dagger B_{ij}^{-1} W_j \right]^{-1} \\ \varepsilon_{0i}^{-1} &= -\varepsilon_{00}^{-1} \sum_j W_j^\dagger B_{ji}^{-1} \\ \varepsilon_{i0}^{-1} &= -\left(\sum_j B_{ij}^{-1} W_j \right) \varepsilon_{00}^{-1} \\ \varepsilon_{ij}^{-1} &= B_{ij}^{-1} + \varepsilon_{i0}^{-1} \left(\varepsilon_{00}^{-1} \right)^{-1} \varepsilon_{0j}^{-1} \end{aligned} \tag{18.21}$$

$$\begin{aligned} \varepsilon_{00}^{-1} &= \left[H_0 + \frac{H_1}{q} + \frac{H_2}{q^2} - \sum_{i,j} (W_{0;i}^\dagger + \frac{W_{1;i}^\dagger}{q}) B_{ij}^{-1} (W_{0;j} + \frac{W_{1;j}}{q}) \right]^{-1} \\ &= \left\{ \left[H_0 - \sum_{i,j} W_{0;i}^\dagger B_{ij}^{-1} W_{0;j} \right] + \frac{H_1 - \sum_{i,j} W_{0;i}^\dagger B_{ij}^{-1} W_{1;j} - \sum_{i,j} W_{1;i}^\dagger B_{ij}^{-1} W_{0;j}}{q} + \frac{H_2 - \sum_{i,j} W_{1;i}^\dagger B_{ij}^{-1} W_{1;j}}{q^2} \right\}^{-1} \\ &\equiv \left[\tilde{H}_0 + \frac{\tilde{H}_1}{q} + \frac{\tilde{H}_2}{q^2} \right]^{-1} \longrightarrow 0 \end{aligned} \tag{18.22}$$

In the limit of $q \to 0$, $\varepsilon_{00}^{-1} = 0$. Similarly one can show that ε_{0i}^{-1} and ε_{i0}^{-1} also vanish.

$$\begin{aligned} \varepsilon_{i0}^{-1} &= -\sum_j B_{ij}^{-1} W_j \varepsilon_{00}^{-1} \\ &= -\sum_j B_{ij}^{-1} \frac{W_{0;j} + \frac{W_{1;j}}{q}}{\tilde{H}_0 + \frac{\tilde{H}_1}{q} + \frac{\tilde{H}_2}{q^2}} \longrightarrow 0 \end{aligned} \tag{18.23}$$

Similarly

$$\begin{aligned} \varepsilon_{0i}^{-1} &= -\sum_j W_j^\dagger B_{ji}^{-1} \varepsilon_{00}^{-1} \\ &= -\sum_j \frac{W_{0;j}^\dagger + \frac{W^\dagger{}_{1;j}}{q}}{\tilde{H}_0 + \frac{\tilde{H}_1}{q} + \frac{\tilde{H}_2}{q^2}} B_{ji}^{-1} \longrightarrow 0 \end{aligned} \tag{18.24}$$

Now let's look the second term of ε_{ij}^{-1}.

$$
\begin{aligned}
&\varepsilon_{i0}^{-1}\left(\varepsilon_{00}^{-1}\right)^{-1}\varepsilon_{0j}^{-1} \\
&= \left(\sum_{i'} B_{ii'}^{-1} W_{i'}\right) \varepsilon_{00}^{-1}\left(\varepsilon_{00}^{-1}\right)^{-1}\varepsilon_{00}^{-1}\sum_{j'} W_{j'}^{\dagger} B_{j'j}^{-1} \\
&= \frac{\sum_{i'} B_{ii'}^{-1}(W_{0;i'} + \frac{W_{1;i'}}{q})\sum_{j'}(W_{0;j'}^{\dagger} + \frac{W_{1;j'}^{\dagger}}{q})B_{j'i}^{-1}}{\tilde{H}_0 + \frac{\tilde{H}_1}{q} + \frac{\tilde{H}_2}{q^2}} \\
&\longrightarrow \frac{(\sum_{i'} B_{ii'}^{-1} W_{1;i'})(\sum_{j'} W_{1;j'}^{\dagger} B_{j'i}^{-1})}{\tilde{H}_2} = \frac{(\sum_{i'} B_{ii'}^{-1} W_{1;i'})(\sum_{j'} W_{1;j'}^{\dagger} B_{j'i}^{-1})}{H_2 - \sum_{i,j} W_{1;i}^{\dagger} B_{ij}^{-1} W_{1;j}}
\end{aligned}
\tag{18.25}
$$

18.3 Construction of the Wannier functions

At this stage, only small notes about how to build the Wannier functions $\phi^{\alpha}_{R,L}(r)$, using the energy window $\mathcal{W}$ and orthogonalization, atom index explicitely used as α.

Step 1 : construction of

$$|\chi^{\alpha}_{kL}>=\sum_{\nu\in\mathcal{W}}|\psi_{k\nu}><\psi_{k\nu}|\chi^{\text{atomic}}_{kL}>$$

Step 2 : orthogonalization of the basis $\{|\chi^{\alpha}_{kL}>\}$ and construction of the Wannier-like basis

$$|\phi^{\alpha}_{kL}>=\sum_{L',\alpha'}S^{\alpha\alpha'}_{LL'}|\chi^{\alpha'}_{kL'}>$$

.

18.3.1 k-summation: Symmetrization

In the case of the one-particle Green function, when computing the summation over k, (in order to build the local Green functions, involved in the DMFT method), we use the symmetries of the solid in order to reduce the size of the integration window. Instead of summing over the full Brillouin zone, we restrict the sum over the irreducible Brillouin zone (IBZ) and then apply the symmetries. We note O_S as the symmetry operations of the lattice, in the real space, that we find in case.struct and $D(R_S)$ are the representations in the orbital space (l=2) of the matrices O_S.

As an example : the matrix elements of G^{local} in the orbital space write (where $\omega(k)$ is the weight)

$$G^{local}_{LL'}=\sum_S\sum_{L_1L_2}D(R_S)_{LL_1}(\sum_{k\in IBZ}{}' G(k)_{L_1L_2}\omega(k))D^{-1}(R_S)_{L_2L'}$$

18.3.1.1 In the case of two-particle functions

Let us try to extend this method to the case of the two-particles operator W, where we have to consider two summations over the Brillouin zone (summation over q is different and will be treated in a different way) and we would like to benefit from the symmetries of the solid. We use the formula aiming that, for transformations $\mathbf{R}_1,\mathbf{R}_2$, $f(\mathbf{R}_1\mathbf{k}_1,\mathbf{R}_2\mathbf{k}_2)=\mathbf{R}_1\mathbf{R}_2f(\mathbf{k}_1,\mathbf{k}_2)R_1^{-1}R_2^{-1}$.

In the equation **??**, we interpret the coefficients $<\phi_{\mathbf{k}_1L_1}|\psi_{\mathbf{k}_1n_1}><\psi_{\mathbf{k}_1+q,n_3}|\phi_{\mathbf{k}_1+q,L_3}>$ as the (L_1,L_3) matrix element of the operator $Z_{n_1n_3}(\mathbf{k}_1,q)$ in the basis $\{|\phi_{k,L}>\}$, therefore

$$<\phi_{\mathbf{k}_1L_1}|\psi_{\mathbf{k}_1n_1}><\psi_{\mathbf{k}_1+q,n_3}|\phi_{\mathbf{k}_1+q,L_3}>=[Z_{n_1n_3}(\mathbf{k}_1,q)]_{L_1L_3} \tag{18.26}$$

Rewriting the equation **??** :

$$\begin{aligned}W^{L_1L_2L_3L_4}_{\mathbf{R}_1\mathbf{R}_2\mathbf{R}_3\mathbf{R}_4}=\sum_q e^{iq(\mathbf{R}_4-\mathbf{R}_3)}\sum_{n_1,n_2,n_3,n_4}\sum_{\mathbf{k}_1,\mathbf{k}_2}e^{-i(\mathbf{k}_1(\mathbf{R}_1-\mathbf{R}_3)+\mathbf{k}_2(\mathbf{R}_2-\mathbf{R}_4))}[Z_{n_1n_3}(\mathbf{k}_1,q)]_{L_1L_3}\\ \times[Z_{n_2n_4}(\mathbf{k}_2,-q)]_{L_2L_4}<\psi_{\mathbf{k}_1,n_1}\psi_{\mathbf{k}_2,n_2}|W|\psi_{\mathbf{k}_1+q,n_3}\psi_{\mathbf{k}_2-q,n_4}>\end{aligned} \tag{18.27}$$

Using the representations of the symmetries :

$$\begin{aligned}W^{L_1L_2L_3L_4}_{\mathbf{R}_1\mathbf{R}_2\mathbf{R}_3\mathbf{R}_4}=\sum_q e^{iq(\mathbf{R}_4-\mathbf{R}_3)}\sum_{n_1,n_2,n_3,n_4}\sum_{S_1,S_2}\Big[D(R_{S_1})\sum_{\mathbf{k}_1\in IBZ}{}'\omega(\mathbf{k}_1)Z_{n_1n_3}(\mathbf{k}_1,q)e^{-i(\mathbf{k}_1(\mathbf{R}_1-\mathbf{R}_3))}\\ \Big(D(R_{S_2})\Big(\sum_{\mathbf{k}_2\in IBZ}{}'\omega(\mathbf{k}_2)Z_{n_2n_4}(\mathbf{k}_2,-q)e^{-i(\mathbf{k}_2(\mathbf{R}_2-\mathbf{R}_4))}W^{n_1n_2n_3n_4}_{\mathbf{k}_1\mathbf{k}_2q}\Big)D^{-1}(R_{S_2})\Big)D^{-1}(R_{S_1})\Big]_{L_1L_3,L_2L_4}\end{aligned} \tag{18.28}$$

To clarify the notations:

$$\begin{aligned}\Big[D(R_{S_1})Z_{n_1n_3}(\mathbf{k}_1,q)\Big(D(R_{S_2})Z_{n_2n_4}(\mathbf{k}_2,-q)D^{-1}(R_{S_2})\Big)D^{-1}(R_{S_1})\Big]_{L_1L_3,L_2L_4}=\\ \sum_{L_1'L_3'}\sum_{L_2'L_4'}D(R_{S_1})_{L_1L_1'}[Z_{n_1n_3}]_{L_1'L_3'}(\mathbf{k}_1,q)D^{-1}(R_{S_1})_{L_3'L_3}D(R_{S_2})_{L_2L_2'}[Z_{n_2n_4}]_{L_2'L_4'}(\mathbf{k}_2,-q)D^{-1}(R_{S_2})_{L_4'L_4}\end{aligned} \tag{18.29}$$

At a given $\mathbf{k}_1\in$ IBZ, for one couple R_{S_1},R_{S_2} symmetry, we first sum over $\mathbf{k}_2\in$ IBZ. Then we perform the sum over $\mathbf{k}_1\in$ IBZ and go to another couple of symmetry.

18.4 Implementation

18.4.1 Data structure

The following variables and arrays are used for the cRPA implementation.

i. *nlorb*: the number of correlated orbitials counting only (a, l), e.g. for FeO in the cubic structure, $nlorb = 1$, but for FeSe, which has two equivalent atoms, $nlorb = 2$.

ii. *nlmorb*: the total number of correlated states (countering a, l and m).

iii. *info_orb(1:4,nlorb)*: the information about each set of (a,l) orbitals, (1,:) = the index of the atom that (a,l) belong to; (2,:) = l; (3,:) = number of different "m"-state for each (a,l); (4,:) = the type of (a,l)-orbitals.

Chapter 19

GW+DMFT

19.1 Theory

19.2 Implementation

The basic precedures are as follows:

1) Initial guess for the the Weiss field $\mathcal{G}$ and the auxiliary Hubbard $\mathcal{U}$ matrix, represented as $\mathcal{G}_{LL'}(\omega)$ and $\mathcal{U}_{\alpha\beta}(\omega)$, respectively. Here we use $\{\phi_{\mathbf{R}L}\}$ to represent the local orbitals that define the correlated subspace, which are in practice Wannier functions, and $\{\chi_{\mathbf{R}\alpha}(\mathbf{r})\}$ are the local product basis functions. When $\mathbf{R}$ is dropped, $\mathbf{R}=0$ is assumed.

2) Using the DMFT solvers one obtains $\Sigma^{\rm imp}_{LL'}(\omega)$ and $P^{\rm imp}_{\alpha\beta}(\omega)$.

3) Combining the GW and DMFT self-energy and polarization functions.

$$\begin{aligned}\Sigma &= \Sigma^{GW} - \Sigma^{GW-d} + \Sigma^{\rm imp}\\ P &= P^{GW} - P^{GW-d} + P^{\rm imp}\end{aligned} \tag{19.1}$$

More explicitly, Σ is represented in the LDA wave functions

$$\Sigma_{nn'}(\mathbf{k},\omega) = \Sigma^{GW}_{nn'}(\mathbf{k},\omega) - \Sigma^{GW-d}_{nn'}(\mathbf{k},\omega) + \Sigma^{\rm imp}_{nn'}(\mathbf{k},\omega) \tag{19.2}$$

Here it is important to note that the $\mathbf{k}$-dependence in the matrix elements of Σ^{GW-d} and $\Sigma^{\rm imp}$ come from that of the basis (here LDA orbitals).

$$\begin{aligned}\Sigma^{\rm imp}_{nn'}(\mathbf{k},\omega) &= \langle n\mathbf{k}|\,\Sigma^{\rm imp}\,|n'\mathbf{k}\rangle\\ &= \sum_{L,L'}\langle n\mathbf{k}|L\mathbf{k}\rangle\,\langle L\mathbf{k}|\,\Sigma^{\rm imp}\,|L'\mathbf{k}\rangle\,\langle L'\mathbf{k}|n\mathbf{k}\rangle\\ &= \sum_{L,L'}\langle n\mathbf{k}|L\mathbf{k}\rangle\,\Sigma^{\rm imp}_{LL'}\,\langle L'\mathbf{k}|n\mathbf{k}\rangle\end{aligned} \tag{19.3}$$

The last equation comes from

$$\Sigma^{\rm imp} = \sum_{\mathbf{R}}|\mathbf{R}L\rangle\,\langle\mathbf{R}L|\,\Sigma^{\rm imp}\,|\mathbf{R}L'\rangle\,\langle\mathbf{R}L'| = \sum_{\mathbf{R}}|\mathbf{R}L\rangle\,\Sigma^{\rm imp}_{LL'}\,\langle\mathbf{R}L'| \tag{19.4}$$

and

$$\begin{aligned}&\langle L\mathbf{k}|\,\Sigma^{\rm imp}\,|L'\mathbf{k}\rangle = \langle L\mathbf{k}|\sum_{\mathbf{R}}|\mathbf{R}L\rangle\,\Sigma^{\rm imp}_{LL'}\,\langle\mathbf{R}L'|\,|L'\mathbf{k}\rangle\\ &= \sum_{\mathbf{R}}\Sigma^{\rm imp}_{LL'}\frac{e^{-i\mathbf{k}\cdot\mathbf{R}}}{N^{1/2}}\frac{e^{i\mathbf{k}\cdot\mathbf{R}}}{N^{1/2}}\\ &= \Sigma^{\rm imp}_{LL'}\end{aligned} \tag{19.5}$$

Using the previously defined projection matrix $P_{Ln}(\mathbf{k})$ we can obtain

$$\Sigma^{\rm imp}_{nn'}(\mathbf{k},\omega) = \sum_{L,L'}\left[P_{Ln}(\mathbf{k})\right]^*\Sigma^{\rm imp}_{LL'}P_{L'n}(\mathbf{k}) \tag{19.6}$$

How to define Σ^{GW-d}? There are two possibilities.

$$\Sigma^{GW-d} = \sum_{\mathbf{R}} \sum_{L,L' \in d} |\mathbf{R}L\rangle \, \Sigma^{GW}_{LL'}(\omega) \, \langle \mathbf{R}L'| \tag{19.7}$$

where

$$\begin{aligned} \Sigma^{GW}_{LL'}(\omega) &= \sum_{\mathbf{k}} \Sigma^{GW}_{LL'}(\mathbf{k},\omega) = \sum_{\mathbf{k}} \langle \phi_{\mathbf{k}L} | \, \Sigma^{GW} \, | \phi_{\mathbf{k}L'} \rangle \\ &= \sum_{\mathbf{k}} \sum_{n,n'} \langle \phi_{\mathbf{k}L} | \psi_{\mathbf{k}n} \rangle \, \Sigma^{GW}_{nn'}(\mathbf{k},\omega) \, \langle \psi_{\mathbf{k}n'} | \phi_{\mathbf{k}L'} \rangle \end{aligned} \tag{19.8}$$

In the KS representation, we have

$$\Sigma^{GW-d}_{nn'}(\mathbf{k},\omega) = \langle \psi_{\mathbf{k}n} | \, \Sigma^{GW-d}(\omega) \, | \psi_{\mathbf{k}n'} \rangle = \sum_{LL'} \langle \psi_{\mathbf{k}n} | \phi_{\mathbf{k}L} \rangle \, \Sigma^{GW-d}_{LL'}(\omega) \, \langle \phi_{\mathbf{k}L'} | \psi_{\mathbf{k}n'} \rangle \tag{19.9}$$

Chapter 20

The Brillouin-Zone Integration

Brillouin-zone integration is an important ingredient of any reciprocal space method and has been a subject of interest since the earliest implementation of electronic structure codes. Fundamental quantities like the total energy or the density of states require an integration over the Brillouin-zone of a certain operator, *e. g.* the eigenvalues weighted by the Fermi distribution function for the former, the energy derivative of the Fermi distribution for the latter.

In the 1970's, a large number of studies were carried out for solving these problems, among which the special point [**?**, **?**, **?**, **?**] and the linear tetrahedron method [**?**, **?**, **?**] are the most used ones nowadays. These two methods perform identically well for insulators and semiconductors. For metals, the Brillouin-zone integration becomes more cumbersome due to the presence of the Fermi surface, which defines the integration region in the Brillouin-zone. The linear tetrahedron method becomes advantageous in these systems thanks to its better description of the Fermi surface (Fig. 20.1) and, therefore, of the integration region[**?**].

In the linear tetrahedron method, first proposed by Jepsen and Andersen in Ref. [**?**] and Lehmann *et al.* in Ref. [**?**], the Brillouin-zone is divided into a set of tetrahedra. The energy eigenvalues ($\epsilon_{n,\mathbf{k}}$) and the integrand are calculated on the vertices of these tetrahedra and, through the procedure known as isoparametrization, linearly interpolated inside each of them. The values of the integrand can be factorized out of the integral. The remaining integrals, independent of the values at the vertices, can be integrated analytically and added to obtain integration weights dependent only on the $\mathbf{k}$-point and the band index. In metallic systems the Fermi surface is approximated, through the isoparametrization, by a plane that limits the integration region inside the tetrahedra it intersects. The occupied region of the Brillouin-zone can thus be described much better than in any of the special points methods (Fig. 20.1).

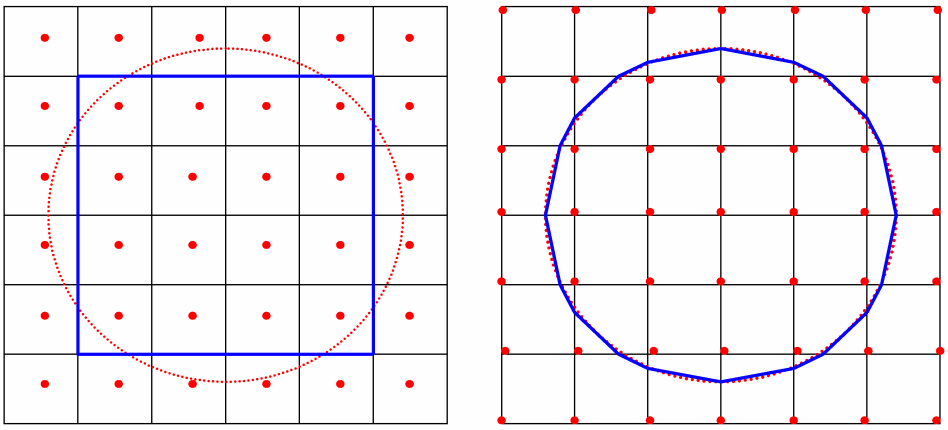

Figure 20.1: Two dimensional sketches of the description of the Fermi surface in the special points (left panel) and the linear tetrahedron method (right panel). In dotted red line the exact Fermi surface, in full blue line the approximated one. The $\mathbf{k}$-points grid is represented by red dots. Tetrahedron method gives better description of the Fermi surface.

The calculation of quantities like the polarizability (Eq. 2.17) or magnetic susceptibility, presents particular characteristics that require a different treatment. The integral depends on a second vector $\mathbf{q}$, it is weighted by two Fermi functions, so that the states at $\mathbf{k}$ are occupied while those at $\mathbf{k}-\mathbf{q}$ are unoccupied, and finally, the eigenvalues appear in the denominator of the integrand. The grid of $\mathbf{k}$-points for this integration is chosen as usual in the tetrahedron method. On the other hand, the calculation of the self-energy (Eq. 2.20 and 2.21), requires a

grid of $\mathbf{q}$-points also be suitable for integration. To avoid the repeated generation of eigenvalues and eigenvectors at several different grids, the set of $\mathbf{q}$-points should be such that $\{\mathbf{k}\} = \{\mathbf{k} - \mathbf{q}\}$. For this equality to hold, the set of $\mathbf{q}$-points must include the Γ point. In our implementation, we take the same mesh for $\mathbf{k}$ and $\mathbf{q}$.

Due to the presence of the eigenvalues in the denominator of the integrand, a simultaneous isoparametrization of both, the integrand and the eigenvalues, becomes inappropriate. In 1975, Rath and Freeman proposed a solution to this problem for the calculation of the static magnetic susceptibilities in metals [**?**]. They approximated the numerator of the integrand by its mean value in each tetrahedron, while the denominator was included in the analytic integration to obtain the weights. In this work, we go two steps further. We apply the isoparametrization not only to the eigenvalues but also to the numerator of the integrand, improving the accuracy, and also extended the method to include the frequency dependence. The integration inside each tetrahedron can still be performed analytically.

Since the integration runs simultaneously on two tetrahedra (at $\mathbf{k}$ and $\mathbf{k}-\mathbf{q}$), there will be situations, in metallic systems, where both tetrahedra are intersected by the Fermi surface. In this case the integration region inside the tetrahedron is delimited by the two Fermi "planes" under the condition $\epsilon_{n\mathbf{k}} < \epsilon_F < \epsilon_{m\mathbf{k}-\mathbf{q}}$, as shown in Fig. 20.2. The complexity of the integration region is such that the integration can not be performed analytically on the whole tetrahedron as in the standard tetrahedron method. However, as pointed out in Ref. [**?**], the integration region can always be subdivided into, at most six, tetrahedra. The integration can be performed analytically inside each of these tetrahedra and then projected onto the vertices of the original tetrahedron to obtain the weights for each $\mathbf{k}$-point. We have analyzed and classified the different configurations of the distinct integration regions determined by two Fermi

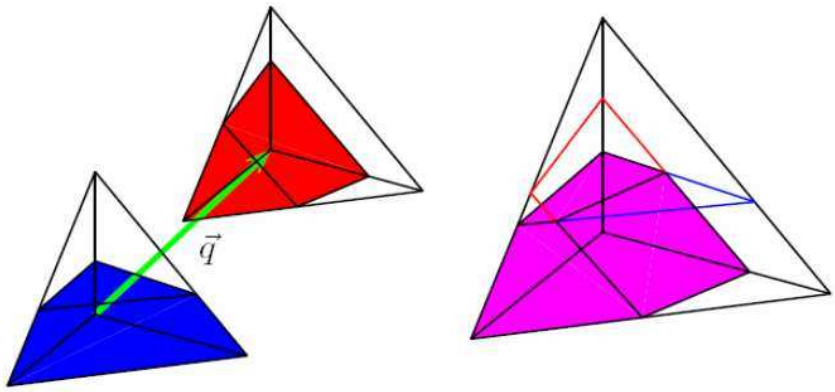

Figure 20.2: The integration region in the tetrahedron method for $\mathbf{q}$-dependent Brillouin-zone integration. The two tetrahedra on the left side are connected by the vector $\mathbf{q}$ (green arrow). The blue zone corresponds to the occupied region for the state $(n, \mathbf{k})$, the red one to the unoccupied region for the state $(n', \mathbf{k} - \mathbf{q})$. The resulting integration region, determined by superimposing the two tetrahedra on the left and taking the intersection of the blue and red zones, is the lilac region in the tetrahedron on the right hand side.

20.1 The Linear Tetrahedron Method

The task of this Brillouin-zone integration is to calculate the average expectation value of an operator satisfying the form:

$$\langle X \rangle = \frac{1}{V_G} \sum_n \int_{V_G} X_n(\mathbf{k}) f(\epsilon_n(\mathbf{k})) d\mathbf{k}, \tag{20.1}$$

where

$$X_n(\mathbf{k}) = \langle \varphi_n(\mathbf{k}) | X | \varphi_n(\mathbf{k}) \rangle. \tag{20.2}$$

This $X_n(\mathbf{k})$ is the expectation value of this operator on the state $(n, \mathbf{k})$. $V_G \equiv (2\pi)^3/\Omega$ is the volume of the reciprocal unit cell, with Ω being the volume of the primitive unit cell in the real space. $f(\epsilon)$ is the Fermi function. An exact evaluation of Eq. 20.1 requires calculating the expectation value of this operator over all its occupied states, including infinite number of $\mathbf{k}$ points in the Brillouin-zone. In practice, this average expectation value is determined from a set of sample points in the Brillouin-zone, each has a certain weight addressing the integration of Eq. 20.1 over the region around it.

In the tetrahedron method, this is obtained by dividing the Brillouin-zone into a set of tetrahedra using a grid (as shown in Fig. 20.3 for the two-dimensional case). The values of $X_n(\mathbf{k})$ are calculated on the discrete set of vectors $\mathbf{k}_i$ at the vertices of all these tetrahedra, namely the grid points. A function $\bar{X}_n(\mathbf{k})$ obtained by linearly

interpolating the function $X_n(\mathbf{k})$ within the tetrahedra using its expectation values on the vertices can be written as a superposition of functions $w_i(\mathbf{k})$, such that

$$\bar{X}_n(\mathbf{k}) = \sum_i X_n(\mathbf{k}_i) w_i(\mathbf{k}), \tag{20.3}$$

where $w_i(\mathbf{k}_j) = \delta_{ij}$ and it is linear within the corresponding tetrahedron and zoro outside of it. Now replacing $X_n(\mathbf{k})$ in Eq. 20.1 by it's linear approximation, one has:

$$\begin{aligned}
\langle X \rangle &\cong \frac{1}{V_G} \sum_n \int_{V_G} \bar{X}_n(\mathbf{k}) f(\epsilon_n(\mathbf{k})) d\mathbf{k} \\
&= \frac{1}{V_G} \sum_n \int_{V_G} \sum_i X_n(\mathbf{k}_i) w_i(\mathbf{k}) f(\epsilon_n(\mathbf{k})) d\mathbf{k} \\
&= \sum_n \sum_i X_n(\mathbf{k}_i) \frac{1}{V_G} \int_{V_G} w_i(\mathbf{k}) f(\epsilon_n(\mathbf{k})) d\mathbf{k}.
\end{aligned}$$

Defining:

$$w_{n,i} = \frac{1}{V_G} \int_{V_G} w_i(\mathbf{k}) f(\epsilon_n(\mathbf{k})) d\mathbf{k}, \tag{20.4}$$

one can write the average expectation value of X in Eq. 20.1 as a weighted sum over the discrete set of $\mathbf{k}$ points:

$$\langle X \rangle = \sum_{i,n} X_n(\mathbf{k}_i) w_{n,i}. \tag{20.5}$$

Since $w_i(\mathbf{k})$ is zero for all $\{\mathbf{k}_j\}$ except $\mathbf{k}_i$, we can rewrite the weights as:

$$\begin{aligned}
w_{n,i} &= \frac{1}{V_G} \sum_{T_i} \iiint_{V_T} w_i(\mathbf{k}) f(\epsilon_n(\mathbf{k})) d^3k \\
&= \sum_{T_i} w_{n,i}^{1T},
\end{aligned} \tag{20.6}$$

where T_i means that the sum runs only over those tetrahedra containing $\mathbf{k}_i$ as one of its vertices. And one has defined $w_{n,i}^{1T} = \frac{1}{V_G} \iiint_{V_T} w_i(\mathbf{k}) f(\epsilon_n(\mathbf{k})) d\mathbf{k}$.

With this, it is clear that the integration in Eq. 20.1 can be approximated by a sum of the form in Eq. 20.5 where $w_{n,i}$ can be calculated by summing its contribution from each tetrahedron containing this $\mathbf{k}_i$ as a vertex. The next job is to define the function $w_i(\mathbf{k})$ in order to calculate these $w_{n,i}$, for this, one needs the isoparametric transformation to be introduced in the next chapter.

20.1.1 The Isoparametric Transfromation

In Eq. 20.3, the function behaviour is approximated inside each tetrahedron by a linear interpolation between the function values at the vertices. Let $\mathcal{F}$ be such a function, and x, y and z be the coordinates, then:

$$\mathcal{F} = A \cdot x + B \cdot y + C \cdot z + D, \tag{20.7}$$

where the constants A, B, C and D are to be determined. Substituting $x = x_i$, $y = y_i$ and $z = z_i$ where $i = 0, 1, 2, 3$ label the vertices, the values of $\mathcal{F}_i$ at the vertices (which are known) can be written as:

$$\mathcal{F}_i = A \cdot x_i + B \cdot y_i + C \cdot z_i + D. \tag{20.8}$$

Clearly, Eq. 20.8 for $i = 0$ can be used to eliminate the constant D. Then we have

$$\mathcal{F} - \mathcal{F}_0 = A \cdot (x - x_0) + B \cdot (y - y_0) + C \cdot (z - z_0). \tag{20.9}$$

The constants A, B and C are determined by solving the system of equations:

$$\begin{aligned}
\mathcal{F}_1 - \mathcal{F}_0 =& A \cdot (x_1 - x_0) + B \cdot (y_1 - y_0) + C \cdot (z_1 - z_0) \\
\mathcal{F}_2 - \mathcal{F}_0 =& A \cdot (x_2 - x_0) + B \cdot (y_2 - y_0) + C \cdot (z_2 - z_0) \\
\mathcal{F}_3 - \mathcal{F}_0 =& A \cdot (x_3 - x_0) + B \cdot (y_3 - y_0) + C \cdot (z_3 - z_0),
\end{aligned} \tag{20.10}$$

with solution:

$$\begin{pmatrix} A \\ B \\ C \end{pmatrix} = \begin{pmatrix} x_1 - x_0 & y_1 - y_0 & z_1 - z_0 \\ x_2 - x_0 & y_2 - y_0 & z_2 - z_0 \\ x_3 - x_0 & y_3 - y_0 & z_3 - z_0 \end{pmatrix}^{-1} \begin{pmatrix} \mathcal{F}_1 - \mathcal{F}_0 \\ \mathcal{F}_2 - \mathcal{F}_0 \\ \mathcal{F}_3 - \mathcal{F}_0 \end{pmatrix}. \tag{20.11}$$

If one defines a coordinate (ξ, η, ζ) inside this tetrahedron, with each vertex 0, 1, 2, 3 having coordinates (0,0,0), (1,0,0), (0,1,0), (0,0,1) respectively, the function $\mathcal{F}$ can be linearly interpolated as:

$$\mathcal{F} - \mathcal{F}_0 = \xi(\mathcal{F}_1 - \mathcal{F}_0) + \eta(\mathcal{F}_2 - \mathcal{F}_0) + \zeta(\mathcal{F}_3 - \mathcal{F}_0). \tag{20.12}$$

Putting Eq. 20.10 into the above equation, we have:

$$\begin{aligned} \mathcal{F} - \mathcal{F}_0 &= \begin{pmatrix} \xi & \eta & \zeta \end{pmatrix} \begin{pmatrix} \mathcal{F}_1 - \mathcal{F}_0 \\ \mathcal{F}_2 - \mathcal{F}_0 \\ \mathcal{F}_3 - \mathcal{F}_0 \end{pmatrix} \\ &= \begin{pmatrix} \xi & \eta & \zeta \end{pmatrix} \begin{pmatrix} x_1 - x_0 & y_1 - y_0 & z_1 - z_0 \\ x_2 - x_0 & y_2 - y_0 & z_2 - z_0 \\ x_3 - x_0 & y_3 - y_0 & z_3 - z_0 \end{pmatrix} \begin{pmatrix} A \\ B \\ C \end{pmatrix}. \end{aligned} \tag{20.13}$$

On the other hand, Eq. 20.9 can be written as:

$$\mathcal{F} - \mathcal{F}_0 = \begin{pmatrix} x - x_0 & y - y_0 & z - z_0 \end{pmatrix} \begin{pmatrix} A \\ B \\ C \end{pmatrix}. \tag{20.14}$$

Comparing Eq. 20.14 with Eq. 20.13, we have:

$$\begin{aligned} x - x_0 &= \xi(x_1 - x_0) + \eta(x_2 - x_0) + \zeta(x_3 - x_0) \\ y - y_0 &= \xi(y_1 - y_0) + \eta(y_2 - y_0) + \zeta(y_3 - y_0) \\ z - z_0 &= \xi(z_1 - z_0) + \eta(z_2 - z_0) + \zeta(z_3 - z_0) \end{aligned}. \tag{20.15}$$

Combining Eq. 20.15 with Eq. 20.12, we see that the *same* expression holds for the function $\mathcal{F}$ as well as for the coordinates x, y, and z. This coordinate transition from outside the tetrahedron to inside the tetrahedron is called as an isoparametric transformation. The functions $w_i(\mathbf{k})$ used in Eq. 20.3 can be simply written as:

$$\begin{aligned} w_0(\xi, \eta, \zeta) &= 1 - \xi - \eta - \zeta \\ w_1(\xi, \eta, \zeta) &= \xi \\ w_2(\xi, \eta, \zeta) &= \eta \\ w_3(\xi, \eta, \zeta) &= \zeta, \end{aligned} \tag{20.16}$$

in terms of this internal coordinates. The energy eigenvalue of the state $(n, \mathbf{k})$ with the coordinate (ξ, η, ζ) inside this tetrahedron is linearly interpolated as:

$$\epsilon_n(\xi, \eta, \zeta) = (\epsilon_{n,1} - \epsilon_{n,0})\xi + (\epsilon_{n,2} - \epsilon_{n,0})\eta + (\epsilon_{n,2} - \epsilon_{n,0})\zeta + \epsilon_{n,0}, \tag{20.17}$$

where $\epsilon_{n,i}$ is the energy eigenvalue on the vertex i.

20.1.2 Integrals in One Tetrahedron

The integral of any function $\mathcal{F}$ inside one tetrahedron, after applying the isoparametric transformation, is given by:

$$\begin{aligned} \iiint_{V_T} \mathcal{F}(x, y, z) f(\epsilon_n(x, y, z)) dx dy dz = \int_0^1 \int_0^{1-\zeta} \int_0^{1-\zeta-\eta} \big[\xi(\mathcal{F}_1 - \mathcal{F}_0) + \eta(\mathcal{F}_2 - \mathcal{F}_0) + \\ \zeta(\mathcal{F}_3 - \mathcal{F}_0) + \mathcal{F}_0\big] \left|\frac{\partial(xyz)}{\partial(\xi\eta\zeta)}\right| f(\epsilon_n(\xi, \eta, \zeta)) d\xi d\eta d\zeta, \end{aligned} \tag{20.18}$$

where V_T is the volume of the tetrahedron and $|\frac{\partial(xyz)}{\partial(\xi\eta\zeta)}|$ is the Jacobian determinant given by:

$$\left|\frac{\partial(xyz)}{\partial(\xi\eta\zeta)}\right| = \begin{vmatrix} \frac{\partial x}{\partial \xi} & \frac{\partial x}{\partial \eta} & \frac{\partial x}{\partial \zeta} \\ \frac{\partial y}{\partial \xi} & \frac{\partial y}{\partial \eta} & \frac{\partial y}{\partial \zeta} \\ \frac{\partial z}{\partial \xi} & \frac{\partial z}{\partial \eta} & \frac{\partial z}{\partial \zeta} \end{vmatrix} = \begin{vmatrix} x_1 - x_0 & y_1 - y_0 & z_1 - z_0 \\ x_2 - x_0 & y_2 - y_0 & z_2 - z_0 \\ x_3 - x_0 & y_3 - y_0 & z_3 - z_0 \end{vmatrix}. \tag{20.19}$$

This is just the volume of a parallelepiped whose sides are given by those of the tetrahedron, clearly:

$$\left|\frac{\partial(xyz)}{\partial(\xi\eta\zeta)}\right| = 6V_T. \tag{20.20}$$

Then Eq. 20.18 is just:

$$\begin{aligned}&\iiint_{V_T}\mathcal{F}(x,y,z)dxdydz\\=&6V_T\int_0^1\int_0^{1-\zeta}\int_0^{1-\zeta-\eta}\left[\xi(\mathcal{F}_1-\mathcal{F}_0)+\eta(\mathcal{F}_2-\mathcal{F}_0)+\zeta(\mathcal{F}_3-\mathcal{F}_0)+\mathcal{F}_0\right]\\&f(\epsilon_n(\xi,\eta,\zeta))d\xi d\eta d\zeta.\end{aligned}\tag{20.21}$$

20.1.3 The Integration Weights

Let's take one of the tetrahedra, its four vertices are denoted as 0, 1, 2, and 3. Using the $w_i(\mathbf{k})$ and $\epsilon_n(\mathbf{k})$ defined in Eq. 20.16 and Eq. 20.17, one can calculate the integration weights on these vertices. If the four energies are below the Fermi energy, the occupation is identically one and we have:

$$\begin{aligned}w_{n,i}^{1T}=&\frac{6V_T}{V_G}\int_0^1\int_0^{1-\zeta}\int_0^{1-\zeta-\eta}\zeta d\xi d\eta d\zeta=\frac{6V_T}{V_G}\int_0^1\int_0^{1-\zeta}\zeta(1-\zeta-\eta)d\eta d\zeta\\=&\frac{6V_T}{V_G}\int_0^1\frac{1}{2}\zeta(1-\zeta)^2d\zeta=\frac{3V_T}{V_G}(\frac{1}{2}-\frac{2}{3}+\frac{1}{4})=\frac{V_T}{4V_G}.\end{aligned}\tag{20.22}$$

Let's now take the case where only $\epsilon_{n,0}<\epsilon_F$ and, for the sake of simplicity $\epsilon_{n,3}>\epsilon_{n,2}>\epsilon_{n,1}>\epsilon_{n,0}$, then the integration limits are changed, and one gets:

$$\begin{aligned}w_{n,3}^{1T}=&\frac{6V_T}{V_G}\int_0^{\frac{\epsilon_F-\epsilon_{n,0}}{\epsilon_{n,3}-\epsilon_{n,0}}}\int_0^{\frac{\epsilon_F-\epsilon_{n,0}-\zeta(\epsilon_{n,3}-\epsilon_{n,0})}{\epsilon_{n,2}-\epsilon_{n,0}}}\int_0^{\frac{\epsilon_F-\epsilon_{n,0}-\zeta(\epsilon_{n,3}-\epsilon_{n,0})-\eta(\epsilon_{n,2}-\epsilon_{n,0})}{\epsilon_{n,1}-\epsilon_{n,0}}}\zeta d\xi d\eta d\zeta\\=&\frac{V_T}{4V_G}\frac{(\epsilon_F-\epsilon_{n,0})^4}{(\epsilon_{n,1}-\epsilon_{n,0})(\epsilon_{n,2}-\epsilon_{n,0})(\epsilon_{n,3}-\epsilon_{n,0})^2}.\end{aligned}\tag{20.23}$$

A similar calculation for the rest of the vertices leads to:

$$\begin{aligned}w_{n,2}^{1T}=&\frac{V_T}{4V_G}\frac{(\epsilon_F-\epsilon_{n,0})^4}{(\epsilon_{n,1}-\epsilon_{n,0})(\epsilon_{n,2}-\epsilon_{n,0})^2(\epsilon_{n,3}-\epsilon_{n,0})}\\w_{n,1}^{1T}=&\frac{V_T}{4V_G}\frac{(\epsilon_F-\epsilon_{n,0})^4}{(\epsilon_{n,1}-\epsilon_{n,0})^2(\epsilon_{n,2}-\epsilon_{n,0})(\epsilon_{n,3}-\epsilon_{n,0})}\\w_{n,0}^{1T}=&\frac{V_T}{V_G}\frac{(\epsilon_F-\epsilon_{n,0})^3}{(\epsilon_{n,1}-\epsilon_{n,0})(\epsilon_{n,2}-\epsilon_{n,0})(\epsilon_{n,3}-\epsilon_{n,0})}-w_{n,1}^{1T}-w_{n,2}^{1T}-w_{n,3}^{1T}.\end{aligned}\tag{20.24}$$

The last line in Eq. 20.24 can be calculated using $w_0(\mathbf{k})=1-\xi-\eta-\zeta=w_t-w_1(\mathbf{k})-w_2(\mathbf{k})-w_3(\mathbf{k})$, where w_t means the total weight over this tetrahedron. Expressions for the remaining cases can be found in Ref. [**?**]. Since these vertices are also sample points in the grid mesh, the integration weight on each grid points can be calculated from Eq. 20.6.

20.2 Tetrahedron Method for q-dependent Brillouin-zone Integration

If one wants to calculate the mean value of a **q**-dependent operator, the situation becomes more complicated. In this section, we discuss the case when the expectation value of this operator satisfies:

$$\langle X(\mathbf{q})\rangle=\frac{1}{V_G}\sum_{n,n'}\int_{V_G}X_{nn'}(\mathbf{k},\mathbf{q})f[\epsilon_n(\mathbf{k})]\left(1-f[\epsilon_{n'}(\mathbf{k}-\mathbf{q})]\right)d^3k,\tag{20.25}$$

where

$$X_{n,n'}(\mathbf{k},\mathbf{q})=\langle\varphi_n(\mathbf{k})|X(\mathbf{q})|\varphi_{n'}(\mathbf{k}-\mathbf{q})\rangle.\tag{20.26}$$

To evaluate this operator, one needs to know $X_{nn'}(\mathbf{k},\mathbf{q})$ on each $\mathbf{k}$ point in the Brillouin-zone in principle. In practice, again, this is obtained by calculating the expectation value of this operator on a set of sample points

weighted by a certain factor. In addition to $\epsilon_n(\mathbf{k}_i)$ and $\varphi_n(\mathbf{k}_i)$ on the set of sample points $\{\mathbf{k}_i\}$, one also needs to know $\epsilon_{n'}(\mathbf{k}_i - \mathbf{q})$ and $\varphi_{n'}(\mathbf{k}_i - \mathbf{q})$ on another set of sample points $\{\mathbf{k}_i - \mathbf{q}\}$.

In our implementation, we make an even division of the Brillouin-zone along each axis. Then, we take the $\mathbf{q}$ vector from this mesh. With this treatment, the meshes of $\mathbf{k}_i$ and $\mathbf{k}_i - \mathbf{q}$ overlap totally with each other. We just need to know the eigen wave functions and the energy eigenvalues in one mesh. A two-dimensional sketch for the $\mathbf{k}$-mesh is shown in Fig. 20.3.

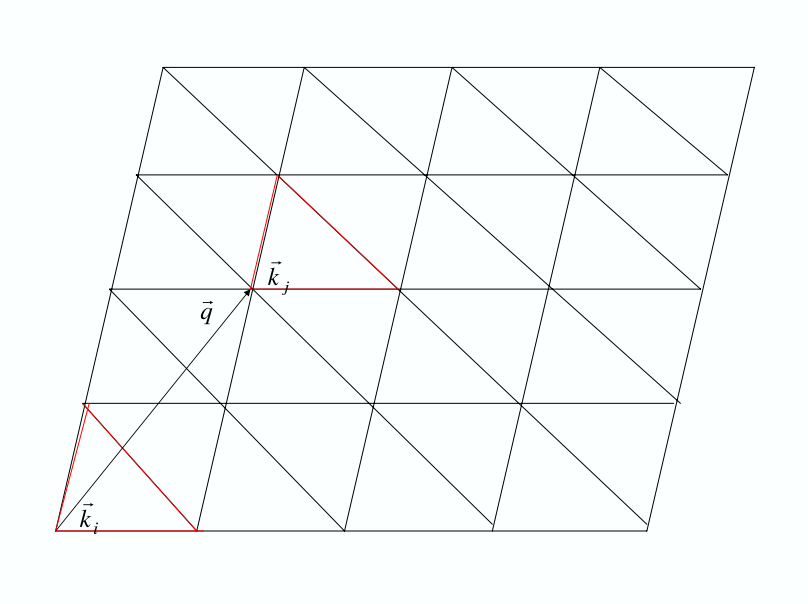

Figure 20.3: The two-dimensional sketch of the BZ in the tetrahedron method, in this case, the space is divided into a list of triangles. One triangle is related to another by a vector $\mathbf{q}$.

Using this grid, the Brillouin-zone is divided into a set of tetrahedra. The expectation values of the function $X_{n,n'}(\mathbf{k}, \mathbf{q})$ are calculated on the vertices of these tetrahedra, namely, the grid points, giving $X_{n,n'}(\mathbf{k}_i, \mathbf{q})$.

Following the same procedure as the above section, we interpolate the function $X_{n,n'}(\mathbf{k}, \mathbf{q})$ linearly within each tetrahedron using:

$$\bar{X}_{n,n'}(\mathbf{k}, \mathbf{q}) = \sum_i X_{n,n'}(\mathbf{k}_i, \mathbf{q}) w_i(\mathbf{k}, \mathbf{q}), \tag{20.27}$$

where $w_i(\mathbf{k}_j, \mathbf{q}) = \delta_{i,j}$ and it is a linear function. Since the integration is over the vector $\mathbf{k}$ and this $w_i(\mathbf{k}_j, \mathbf{q})$ is only a function of the coordinates of $\mathbf{k}$ for a fixed $\mathbf{q}$, it is easy to see that we can get rid of the $\mathbf{q}$ dependence. Eq. 20.27 becomes:

$$\bar{X}_{n,n'}(\mathbf{k}, \mathbf{q}) = \sum_i X_{n,n'}(\mathbf{k}_i, \mathbf{q}) w_i(\mathbf{k}). \tag{20.28}$$

For the expectation value, we get:

$$\langle X(\mathbf{q}) \rangle = \sum_{i,n,n'} X_{n,n'}(\mathbf{k}_i, \mathbf{q}) w_{n,n',i}(\mathbf{q}), \tag{20.29}$$

with

$$w_{n,n',i}(\mathbf{q}) = \frac{1}{V_G} \int_{V_G} w_i(\mathbf{k}) f[\epsilon_n(\mathbf{k})] \left(1 - f[\epsilon_{n'}(\mathbf{k} - \mathbf{q})]\right) d^3k. \tag{20.30}$$

To calculate the weights, following the steps as in the previous section, we obtain:

$$w_{n,n',i}(\mathbf{q}) = \sum_{T_i} w^{1T}_{n,n',i}(\mathbf{q}), \tag{20.31}$$

where

$$w^{1T}_{n,n',i}(\mathbf{q}) = \frac{1}{V_G} \iiint_{V_T} w_i(\mathbf{k}) f[\epsilon_n(\mathbf{k})] \left(1 - f[\epsilon_{n'}(\mathbf{k} - \mathbf{q})]\right) d^3k. \tag{20.32}$$

T_i runs over all the tetrahedra in which the sample point $\mathbf{k}_i$ serves as a vertex.

20.2.1 Isoparametric Transformation

Now, we perform the isoparametic transformation to calculate the integration of Eq. 20.32 in one tetrahedron. If we denote the vertices of this tetrahedron as 0, 1, 2, 3 respectively, we have:

$$\begin{aligned} w_0(\mathbf{k}) =& w_0(\xi,\eta,\zeta) = 1-\xi-\eta-\zeta \\ w_1(\mathbf{k}) =& w_1(\xi,\eta,\zeta) = \xi \\ w_2(\mathbf{k}) =& w_2(\xi,\eta,\zeta) = \eta \\ w_3(\mathbf{k}) =& w_3(\xi,\eta,\zeta) = \zeta \\ \epsilon_n(\mathbf{k}) =& \epsilon_n(\xi,\eta,\zeta) = \xi(\epsilon_{n,1}-\epsilon_{n,0}) + \eta(\epsilon_{n,2}-\epsilon_{n,0}) + \zeta(\epsilon_{n,3}-\epsilon_{n,0}) + \epsilon_{n,0} \\ \epsilon_{n'}(\mathbf{k}-\mathbf{q}) =& \epsilon_{n'}(\xi,\eta,\zeta) = \xi(\epsilon_{n',1}-\epsilon_{n',0}) + \eta(\epsilon_{n',2}-\epsilon_{n',0}) + \zeta(\epsilon_{n',3}-\epsilon_{n',0}) + \epsilon_{n',0}, \end{aligned} \tag{20.33}$$

where we have used the shorthand notation $\epsilon_{n,i}$ and $\epsilon_{n',i}$ to represent the energy eigenvalues of the state $(n,\mathbf{k})$ and $(n',\mathbf{k}-\mathbf{q})$ on the vertices of this tetrahedron.

Then, the general formula for the contribution of one tetrahedron to the weight is:

$$\begin{aligned} & w^{1T}_{n,n',i}(\mathbf{q}) = \\ & \frac{6V_T}{V_G}\int_0^1\int_0^{1-\zeta}\int_0^{1-\zeta-\eta} w_i(\xi,\eta,\zeta)\Theta[\epsilon_F - \xi(\epsilon_{n,1}-\epsilon_{n,0}) - \eta(\epsilon_{n,2}-\epsilon_{n,0}) - \zeta(\epsilon_{n,3}-\epsilon_{n,0}) - \epsilon_{n,0}] \\ & \times \Theta[\xi(\epsilon_{n',1}-\epsilon_{n',0}) + \eta(\epsilon_{n',2}-\epsilon_{n',0}) + \zeta(\epsilon_{n',3}-\epsilon_{n',0}) + \epsilon_{n',0} - \epsilon_F] d\xi d\eta d\zeta, \end{aligned} \tag{20.34}$$

where Θ is the step function to address the Fermi function in Eq. 20.32.

20.2.2 The Integration Region

From Eq. 20.34, we see that the Θ functions determine the integration region within this tetrahedron. For insulators and semiconductors, this region is either the full tetrahedron or zero. For metals, the situation becomes more complicated. If not all the $\epsilon_{n,i}$s are smaller or bigger than ϵ_F, the Fermi surface represented by the first Θ function in Eq. 20.34 will intersect with this tetrahedron, leading to only part of it satisfying the condition the first Θ function equals one. If not all the $\epsilon_{n',i}$ are smaller or bigger than ϵ_F, the Fermi surface represented by the second Θ function in Eq. 20.34 will intersect with this tetrahedron, leading to only part of it satisfying the condition the second Θ function equals one. If neither of these cases happen, the integration region is either the full tetrahedron or zero. Otherwise, the integration region is determined by the intersection of these Fermi surfaces with this tetrahedron (Fig. 20.2 shows one example when both of them intersect with this tetrahedron).

There are in total 9 different configurations for this region. They are shown in Fig. 20.4 except the simplest case of a tetrahedron. All of them can be subdivided into samller tetrahedron. Then, we perform one further isoparametric transformation inside each of these small tetrahedron. The wieght on each of its vertices is:

$$\begin{aligned} w_0 &= \frac{6V_{\mathrm{T}}}{V_{\mathrm{G}}}\frac{V_{\mathrm{ST}}}{V_{\mathrm{T}}}\int_0^1\int_0^{1-z}\int_0^{1-y-z}(1-x-y-z)dxdydz = \frac{V_{\mathrm{ST}}}{4V_{\mathrm{G}}} \\ w_1 &= w_2 = w_3 = w_0, \end{aligned} \tag{20.35}$$

where V_{ST} is the volume of the small tetrahedron, and $w_i(i=0,3)$ represents the weight on each vertex. We further distribute these weights linearly into the vertices of the big tetrahedron. Assuming the coordinates of one vertex of this small tetrahedron is (ξ_1,η_1,ζ_1) in the big tetrahedron before the second parametric transformation, the integration weight on this point will be distributed with the ration $1-\xi_1-\eta_1-\zeta_1$, ξ_1, η_1, and ζ_1 to the vertices 0, 1, 2, 3 of the big tetrahedron.

20.2.3 Polarizability

As already mentioned in Sec. **??**, for the polarizability we can not assume both the energies and the integrand to be simultaneously linear in the coordinates of the tetrahedron. In this case, we have to include the energy-dependent factor of Eq. 2.17 into the analytical integration. In Sec. **??**, we have discussed the frequency integrations in the GW calculations, where we pointed out that we calculate all the frequency dependent properties on the imaginary frequency axis. The polarizability is such a property. In this section, we will discuss the integration weight of the polarizability on both the real and imaginary frequency axis. The latter is the one used in the GW calculation. The former can be used to calculate the macroscopic dielectric constant.

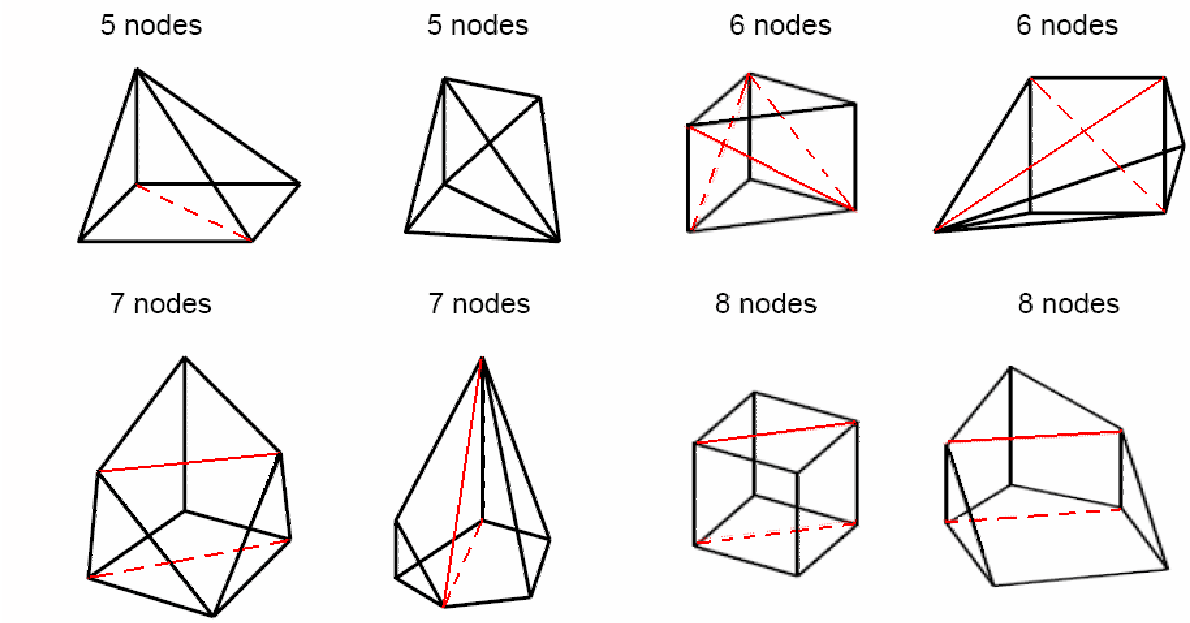

Figure 20.4: The configurations for the region to be integrated. How these regions are decomposed into the principle units of the small tetrahedra is shown by the red lines in the graph.

20.2.3.1 Polarisability on the Real Frequency Axis

On the real frequency axis, the polarization matrix is:

$$P_{i,j}(\mathbf{q},\omega)=\frac{N_c}{\hbar}\sum_{\mathbf{k}}^{BZ}\sum_{n}^{\text{occ}}\sum_{n'}^{\text{unocc}}M^i_{n,n'}(\mathbf{k},\mathbf{q})[M^i_{n,n'}(\mathbf{k},\mathbf{q})]^* \{\frac{1}{\omega-\epsilon_{n',\mathbf{k}-\mathbf{q}}+\epsilon_{n,\mathbf{k}}+i\eta}-\frac{1}{\omega-\epsilon_{n,\mathbf{k}}+\epsilon_{n',\mathbf{k}-\mathbf{q}}-i\eta}\}. \quad (20.36)$$

We define the weight as:

$$w_{n,n',i}(\mathbf{q},\omega)=\sum_{T_i}w^{1T}_{n,n',i}(\mathbf{q},\omega), \quad (20.37)$$

where

$$w^{1T}_{n,n',i}(\mathbf{q},\omega)=\frac{1}{V_{\text{G}}}\int\int\int_{V_T}w_i(\mathbf{k})f[\epsilon_n(\mathbf{k})](1-f[\epsilon_{n'}(\mathbf{k}-\mathbf{q})])\times \{\frac{1}{\omega-\epsilon_{n'}(\mathbf{k}-\mathbf{q})+\epsilon_n(\mathbf{k})+i\eta}-\frac{1}{\omega-\epsilon_n(\mathbf{k})+\epsilon_{n'}(-\mathbf{q})-i\eta}\}d^3\mathbf{k}. \quad (20.38)$$

Following the procedures in Sec. 20.2.2, the weight on each vertex of the small tetrahedron is calculated by:

$$\begin{aligned}
w_0&=\frac{6V_{\text{ST}}}{V_{\text{G}}}\int_0^1\int_0^{1-z}\int_0^{1-y-z}\frac{2(1-x-y-z)}{\omega^2-(x\Delta_{1,0}+y\Delta_{2,0}+z\Delta_{3,0}+\Delta_0)^2}dxdydz\\
w_1&=\frac{6V_{\text{ST}}}{V_{\text{G}}}\int_0^1\int_0^{1-z}\int_0^{1-y-z}\frac{2x}{\omega^2-(x\Delta_{1,0}+y\Delta_{2,0}+z\Delta_{3,0}+\Delta_0)^2}dxdydz\\
w_2&=\frac{6V_{\text{ST}}}{V_{\text{G}}}\int_0^1\int_0^{1-z}\int_0^{1-y-z}\frac{2y}{\omega^2-(x\Delta_{1,0}+y\Delta_{2,0}+z\Delta_{3,0}+\Delta_0)^2}dxdydz\\
w_3&=\frac{6V_{\text{ST}}}{V_{\text{G}}}\int_0^1\int_0^{1-z}\int_0^{1-y-z}\frac{2z}{\omega^2-(x\Delta_{1,0}+y\Delta_{2,0}+z\Delta_{3,0}+\Delta_0)^2}dxdydz.
\end{aligned} \quad (20.39)$$

Here, $\Delta_i=\epsilon_{n',i}-\epsilon_{n,i}$ and $\Delta_{i,j}=\Delta_i-\Delta_j$.

The first equation in Eqs. 20.39 is more complicated to be solved analytically compared with the other three due to the presence of three variables in the numerator. So, we solve the other three respectively and then calculate the total integration weight over this tetrahedron with:

$$w_{\mathrm{t}} = \frac{6V_{\mathrm{ST}}}{V_{\mathrm{G}}} \int_0^1 \int_0^{1-z} \int_0^{1-y-z} \frac{2}{\omega^2 - (x\Delta_{1,0} + y\Delta_{2,0} + z\Delta_{3,0} + \Delta_0)^2} dxdydz. \tag{20.40}$$

The correponding w_0 is then calculated from $w_0 = w_{\mathrm{t}} - w_1 - w_2 - w_3$.

Even with this treatment, these analytical integration is very complicated to be solved. We use Mathematica to treat it. There exists a general solution. To restict the size of this appendix, we just list that of w_{t} here which is the simplest case due to the absence of variables in the numerator in Eq. 20.39:

$$\begin{aligned}
f(\omega) &= (\omega - \Delta_3)^3 \Delta_{1,0}^2 \Delta_{2,0} \Delta_{2,1}^2 \ln[|\omega - \Delta_3|] - (\omega - \Delta_2)^3 \Delta_{1,0}^2 \Delta_{3,0} \Delta_{3,1}^2 \ln[|\omega - \Delta_2|] \\
f(\omega) &= f(\omega) + [\Delta_{1,0}\Delta_{2,1}(\omega - \Delta_3) - (\omega - \Delta_0)\Delta_{2,1}\Delta_{3,1} + (\omega - \Delta_2)\Delta_{1,0}\Delta_{3,1}] \times \\
&\quad \Delta_{2,0}\Delta_{3,0}\Delta_{3,2}(\omega - \Delta_1)^2 \ln[|\omega - \Delta_1|] \\
f(\omega) &= f(\omega) + (\omega - \Delta_0)^3 \Delta_{2,1}^2 \Delta_{3,2} \Delta_{3,1}^2 \ln[|\omega - \Delta_0|] - (\omega - \Delta_1)^2 \Delta_{1,0}\Delta_{2,0} \times \\
&\quad \Delta_{2,1}\Delta_{3,0}\Delta_{3,1}\Delta_{3,2} \\
f(\omega) &= \frac{f(\omega)}{6\Delta_{1,0}^2 \Delta_{2,0} \Delta_{2,1}^2 \Delta_{3,0} \Delta_{3,1}^2 \Delta_{3,2}} \\
w_{\mathrm{t}} &= \frac{6V_{\mathrm{ST}}}{V_{\mathrm{G}}}[f(\omega) + f(-\omega)]
\end{aligned} \tag{20.41}$$

(this equations is written following the programming rules cause it is too long). In this equation, it is required that $\omega \neq \Delta_i$ and $\Delta_{i,j} \neq 0$. $\Delta_{i,j} \neq 0$ is required because of this analytical solution. $\omega \neq \Delta_i$ is required because the denominators in Eq. 20.39 and Eq. 20.40 can not be zero. When these conditions are not fulfilled, we use Mathematica to get the analytical solution of that specific case respectively.

20.2.3.2 Polarisability on the Imaginary Frequency Axis

The polarization matrix of our calculation on the imaginary frequency axis is:

$$P_{i,j}(\mathbf{q}, \omega) = \frac{N_c}{\hbar} \sum_{\mathbf{k}}^{BZ} \sum_{n}^{\mathrm{occ}} \sum_{n'}^{\mathrm{unocc}} M_{n,n'}^i(\mathbf{k}, \mathbf{q}) [M_{n,n'}^i(\mathbf{k}, \mathbf{q})]^* \frac{-2(\epsilon_{n',\mathbf{k}-\mathbf{q}} - \epsilon_{n,\mathbf{k}})}{\omega^2 + (\epsilon_{n',\mathbf{k}-\mathbf{q}} - \epsilon_{n,\mathbf{k}})^2}. \tag{20.42}$$

In this case, the procedure is essentially the same as above, except for the fact that the weight on the vertices of each small tetrahedron is calculated with:

$$\begin{aligned}
w_0 &= \frac{6V_{\mathrm{ST}}}{V_G} \int_0^1 \int_0^{1-z} \int_0^{1-y-z} \frac{2(1-x-y-z)}{\omega^2 + (x\Delta_{1,0} + y\Delta_{2,0} + z\Delta_{3,0} + \Delta_0)^2} dxdydz \\
w_1 &= \frac{6V_{\mathrm{ST}}}{V_G} \int_0^1 \int_0^{1-z} \int_0^{1-y-z} \frac{2x}{\omega^2 + (x\Delta_{1,0} + y\Delta_{2,0} + z\Delta_{3,0} + \Delta_0)^2} dxdydz \\
w_2 &= \frac{6V_{\mathrm{ST}}}{V_G} \int_0^1 \int_0^{1-z} \int_0^{1-y-z} \frac{2y}{\omega^2 + (x\Delta_{1,0} + y\Delta_{2,0} + z\Delta_{3,0} + \Delta_0)^2} dxdydz \\
w_3 &= \frac{6V_{\mathrm{ST}}}{V_G} \int_0^1 \int_0^{1-z} \int_0^{1-y-z} \frac{2z}{\omega^2 + (x\Delta_{1,0} + y\Delta_{2,0} + z\Delta_{3,0} + \Delta_0)^2} dxdydz.
\end{aligned} \tag{20.43}$$

Again, we introduce w_{t} as:

$$w_{\mathrm{t}} = \frac{6V_{ST}}{V_G} \int_0^1 \int_0^{1-z} \int_0^{1-y-z} \frac{2}{\omega^2 + (x\Delta_{1,0} + y\Delta_{2,0} + z\Delta_{3,0} + \Delta_0)^2} dxdydz, \tag{20.44}$$

to avoid solving the first equation of Eqs. 20.43 directly. Its general solution is:

$$
\begin{aligned}
f(\omega) &= 2(\omega-\Delta_0^2)\Delta_{0,1}\Delta_{0,2}\Delta_{0,3}\Delta_{1,2}\Delta_{1,3}\Delta_{2,3}\\
f(\omega) &= f(\omega)+2\omega[3\Delta_0^4-\omega^2(\Delta_1\Delta_2+\Delta_2\Delta_3+\Delta_3\Delta_1)\\
&\quad -3\Delta_0^2(\omega^2+\Delta_2\Delta_3+\Delta_1\Delta_2+\Delta_1\Delta_3)\\
&\quad +2\Delta_0(\omega^2\Delta_2+\omega^2\Delta_3+\Delta_1\omega^2+3\Delta_1\Delta_2\Delta_3)]\Delta_{1,2}\Delta_{1,3}\Delta_{2,3}\mathrm{ArcTan}[\Delta_0/\omega]\\
f(\omega) &= f(\omega)+2\omega(\omega^2-3\Delta_1^2)\Delta_{0,2}^2\Delta_{0,3}^2\Delta_{2,3}\mathrm{ArcTan}[\Delta_1/\omega]\\
f(\omega) &= f(\omega)-2\omega(\omega^2-3\Delta_2^2)\Delta_{0,1}^2\Delta_{0,3}^2\Delta_{1,3}\mathrm{ArcTan}[\Delta_2/\omega]\\
f(\omega) &= f(\omega)+2\omega(\omega^2-3\Delta_3^2)\Delta_{0,1}^2\Delta_{0,2}^2\Delta_{1,2}\mathrm{ArcTan}[\Delta_3/\omega]\\
f(\omega) &= f(\omega)+[\Delta_0^4(\Delta_1+\Delta_2+\Delta_3)-3\omega^2\Delta_1\Delta_2\Delta_3\\
&\quad -2\Delta_0^3(3\omega^2+\Delta_2\Delta_3+\Delta_1\Delta_2+\Delta_1\Delta_3)\\
&\quad +3\Delta_0^2(\omega^2\Delta_1+\omega^2\Delta_2+\omega^2\Delta_3+\Delta_1\Delta_2\Delta_3)]\Delta_{1,2}\Delta_{1,3}\Delta_{2,3}\ln[\omega^2+\Delta_0^2]\\
f(\omega) &= f(\omega)+\Delta_1(3\omega^2-\Delta_1^2)\Delta_{0,2}^2\Delta_{0,3}^2\Delta_{2,3}\ln[\omega^2+\Delta_1^2]\\
f(\omega) &= f(\omega)+\Delta_2(\Delta_2^2-3\omega^2)\Delta_{0,1}^2\Delta_{0,3}^2\Delta_{1,3}\ln[\omega^2+\Delta_2^2]\\
f(\omega) &= f(\omega)-\Delta_3(\Delta_3^2-3\omega^2)\Delta_{0,1}^2\Delta_{0,2}^2\Delta_{1,2}\ln[\omega^2+\Delta_3^2]\\
w_{\mathrm{t}} &= \frac{6V_{\mathrm{ST}}}{V_{\mathrm{G}}}\frac{f(\omega)}{6\Delta_{0,1}^2\Delta_{0,2}^2\Delta_{0,3}^2\Delta_{1,2}\Delta_{1,3}\Delta_{2,3}}.
\end{aligned}
\tag{20.45}
$$

Again, in this equation, it is required that $\Delta_{i,j}\neq 0$. When this condition is not fulfilled, same as the above section, we use Mathematica to get the analytical solution of that case again specifically.

Chapter 21

Speeding up GW calculations

This chapter discusses various numerical techniques that can be used to speed up GW calculations.

21.1 Using static COHSEX to include static remainder in selfenergy

Following [**?**], we can use the static COHSEX approximation to the self-energy to reduce the number of unoccupied orbitals. The full GWA correlation selfenergy reads

$$\Sigma^c(\mathbf{r}_1,\mathbf{r}_2;\omega) = \frac{i}{2\pi}\int d\omega' G(\mathbf{r}_1,\mathbf{r}_2;\omega+\omega')W^c(\mathbf{r}_2,\mathbf{r}_1;\omega') \tag{21.1}$$

The corresponding static COHSEX approximation reads

$$\Sigma^{\mathrm{c-sCOHSEX}}(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{2}\delta(\mathbf{r}_1,\mathbf{r}_2)W^c(\mathbf{r}_2,\mathbf{r}_1;0) - \sum_{n\mathbf{k}}^{\mathrm{occ}} W^c(\mathbf{r}_2,\mathbf{r}_1;0)\psi_{n\mathbf{k}}(\mathbf{r}_1)\psi^*_{n\mathbf{k}}(\mathbf{r}_2). \tag{21.2}$$

One notices that the static COHSEX approximation contains a δ-function, implying a sum over complete KS eigenfunctions. It has been well-known that the convergence of the correlation selfenergy $\Sigma^c(\mathbf{r}_1,\mathbf{r}_2;\omega)$ is quite slow, which poses a critical computational challenge. It is possible to speed up the convergence with respect to the number of unoccupied states by including the following static correction

$$\Delta\Sigma^c(\mathbf{r}_1,\mathbf{r}_2) = \Sigma^{\mathrm{c-sCOHSEX}}(\mathbf{r}_1,\mathbf{r}_2) - \tilde{\Sigma}^{\mathrm{c-sCOHSEX}}(\mathbf{r}_1,\mathbf{r}_2) \tag{21.3}$$

where the second term is the static COHSEX correlation energy calculated with a finite number of unoccupied states,

$$\begin{aligned}\tilde{\Sigma}^{\mathrm{c-sCOHSEX}}(\mathbf{r}_1,\mathbf{r}_2) =& \frac{1}{2}\sum_{n\mathbf{k}}\psi_{n\mathbf{k}}(\mathbf{r}_1)\psi^*_{n\mathbf{k}}(\mathbf{r}_2)W^c(\mathbf{r}_2,\mathbf{r}_1;0) - \sum_{n\mathbf{k}}^{\mathrm{occ}} W^c(\mathbf{r}_2,\mathbf{r}_1;0)\psi_{n\mathbf{k}}(\mathbf{r}_1)\psi^*_{n\mathbf{k}}(\mathbf{r}_2) \\ =& \frac{1}{2}\sum_{n\mathbf{k}}^{\mathrm{unocc}}\psi_{n\mathbf{k}}(\mathbf{r}_1)\psi^*_{n\mathbf{k}}(\mathbf{r}_2)W^c(\mathbf{r}_2,\mathbf{r}_1;0) - \frac{1}{2}\sum_{n\mathbf{k}}^{\mathrm{occ}} W^c(\mathbf{r}_2,\mathbf{r}_1;0)\psi_{n\mathbf{k}}(\mathbf{r}_1)\psi^*_{n\mathbf{k}}(\mathbf{r}_2)\end{aligned} \tag{21.4}$$

Now combining Eqs.(25.2) and (25.4), we have

$$\Delta\Sigma^c(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{2}\delta(\mathbf{r}_1,\mathbf{r}_2)W^c(\mathbf{r}_2,\mathbf{r}_1,0) - \frac{1}{2}\sum_{n\mathbf{k}} W^c(\mathbf{r}_2,\mathbf{r}_1,0)\psi_{n\mathbf{k}}(\mathbf{r}_1)\psi^*_{n\mathbf{k}}(\mathbf{r}_2). \tag{21.5}$$

Obviouly, when the sum over unoccupied states are complete, $\Delta\Sigma^c(\mathbf{r}_1,\mathbf{r}_2)$ vanishes.

In practice, one needs the diagonal matrix elements of $\Delta\Sigma^c$ with respect to KS eigenfunctions

$$\Delta\Sigma^c_{n\mathbf{k}} = \frac{1}{2}W^{c0}_{n\mathbf{k}} - \frac{1}{2}\sum_{m\mathbf{q}}\sum_{i,j}\left[M^i_{nm}(\mathbf{k},\mathbf{q})\right]^* W^c_{ij}(\mathbf{q},0)M^j_{nm}(\mathbf{k},\mathbf{q}) \tag{21.6}$$

where

$$W^{c0}_{n\mathbf{k}} := \int d\mathbf{r}\psi^*_{n\mathbf{k}}(\mathbf{r})W^c(\mathbf{r},\mathbf{r},0)\psi_{n\mathbf{k}}(\mathbf{r}). \tag{21.7}$$

While the second term is straightforward to calculate in the current GW code, the first term requires some special treatment. Expanding $W^c(\mathbf{r},\mathbf{r},0)$ and $\psi_{n\mathbf{k}}(\mathbf{r})\psi^*_{n\mathbf{k}}(\mathbf{r})$ by the mixed basis functions, we have

$$W^{c0}_{n\mathbf{k}} = \sum_{\mathbf{q}}\sum_{i,j}\sum_{p} W^c_{ij}(\mathbf{q},0)M^p_{nn}(\mathbf{k},0)\int d\mathbf{r}\chi^{\mathbf{q}}_i(\mathbf{r})\left[\chi^{\mathbf{q}}_j(\mathbf{r})\right]^*\chi^0_p(\mathbf{r}) \tag{21.8}$$

Denoting the integral in the equation above as $\Gamma_{ij;p}$ and defining

$$T_p(\mathbf{q}) := \sum_{ij} W^c_{ij}(\mathbf{q},0)\Gamma_{ij;p} \tag{21.9}$$

we have

$$W^{c0}_{n\mathbf{k}} = \sum_{\mathbf{q}}\sum_{p} M^p_{nn}(\mathbf{k},0)T_p(\mathbf{q}) \tag{21.10}$$

21.2 Core pproximations

One can speed up the GW calculations by neglecting core states in all or some parts of GW calculations. Roughly three levels of core approximations can be defined, as controled by `core:iopcore`

i. All-electron calculation: core states are included in all calculations;

ii. Core states are included for the exchange self-energy, but neglected for the correlation part;

iii. Core states are neglected in all calculations.

21.3 Reducing the size of mixed basis set

21.4 Using symmetries

21.4.1 The LAPW basis functions

Let $\{\mathbf{T}\}$ be the set of symmetry operations of the reciprocal lattice in the three dimensional space. Then, two reciprocal vectors are symmetry related if there exists a matrix operation $\mathbf{T}_i$ such that $\mathbf{k} = \mathbf{T}_i\mathbf{k}$.

Since $\mathbf{T}_i$ is a symmetry of the lattice, for each $\mathbf{G}$ vector of the reciprocal lattice there is a vector $\mathbf{G}'$ such that $\mathbf{G} = \mathbf{T}_i\mathbf{G}$. And thus we can also write: $\mathbf{k} + \mathbf{G} = \mathbf{T}_i(\mathbf{k} + \mathbf{G})$. It is easy to show then, that the LAPW basis transforms as:

$$\phi^{\mathbf{k}}_{\mathbf{G}}(\mathbf{T}^{-1}\mathbf{r}) = \phi^{\mathbf{Tk}}_{\mathbf{TG}}(\mathbf{r}) \tag{21.11}$$

Chapter 22

On the calculation of lattice sums

The difficulty met with in the evaluation of lattice sums always has been the question of their convergence. It presents itself under two aspects, first the convergence of the series as such and second the rapidity of the convergence. The latter question, being mainly of practical importance, is the subject of this appendix. For an analysis of the former question, I suggest the reader to look at [16][68] and references therein.

22.1 Ewald's method

When calculating the Coulomb terms in any solid state problem, a major dificulty that usually appears is the lattice summation of the type $\sum_{\vec{R}} \frac{1}{|\vec{R}-\vec{r}|}$. There is a very elegant procedure, known as *Ewald's method*, by which the problem may be solved. We derive this method following [67]

First consider the function

$$F(\vec{r},\rho) = \frac{2}{\sqrt{\pi}} \sum_{\vec{R}} e^{-|\vec{R}-\vec{r}|^2\rho^2} \tag{22.1}$$

This functions is periodic in $\vec{r}$, with the periodicity of the lattice. Therefore it can be expanded in a Fourier series

$$F(\vec{r},\rho) = \sum_{\vec{G}} F_{\vec{G}} e^{i\vec{G}\cdot\vec{r}}, \tag{22.2}$$

where

$$F_{\vec{G}} = \frac{2}{V\sqrt{\pi}} \int_V \sum_{\vec{R}} e^{-|\vec{R}-\vec{r}|^2\rho^2} e^{-i\vec{G}\cdot\vec{r}} d^3r \tag{22.3}$$

introducing a factor $\exp\left(i\vec{G}\cdot\vec{R}\right) = 1$ in each term of the series, we have:

$$\begin{aligned} F_{\vec{G}} &= \frac{2}{V\sqrt{\pi}} \sum_{\vec{R}} \int_V e^{-|\vec{R}-\vec{r}|^2\rho^2} e^{-i\vec{G}\cdot(\vec{r}-\vec{R})} d^3r \\ &= \frac{2N_c}{V\sqrt{\pi}} \int_V e^{-r^2\rho^2 - i\vec{G}\cdot\vec{r}} d^3r \end{aligned} \tag{22.4}$$

since each term in the sum is now the same, except for being measured from a different origin $\vec{R}$ in the crystal.

The integral in equation 22.4 can easily be evaluated to give

$$F_{\vec{G}} = \frac{2\pi}{\Omega} \rho^{-3} e^{-\frac{G^2}{4\rho^2}}. \tag{22.5}$$

Substituting 22.5 into 22.2 and 22.1 we obtain:

$$\frac{2}{\sqrt{\pi}} \sum_{\vec{R}} e^{-|\vec{R}-\vec{r}|^2\rho^2} = \frac{2\pi}{\Omega} \rho^{-3} \sum_{\vec{G}} e^{-\frac{G^2}{4\rho^2}} e^{i\vec{G}\cdot\vec{r}}. \tag{22.6}$$

Now consider the identity

$$\frac{2}{\sqrt{\pi}} \int_0^\infty e^{-z^2\rho^2} d\rho = \frac{1}{|z|} \tag{22.7}$$

Applying this to the left hand side of equation 22.6, we have

$$\sum_{\vec{R}} \frac{1}{\left|\vec{R}-\vec{r}\right|} = \frac{2}{\sqrt{\pi}} \sum_{\vec{R}} \int_0^\infty e^{-\left|\vec{R}-\vec{r}\right|^2 \rho^2} d\rho. \tag{22.8}$$

We split the integration over the dummy variable ρ into two parts at some arbitrary point α, and substitute for the integrand from 22.6 in the first part

$$\begin{aligned} \sum_{\vec{R}} \frac{1}{\left|\vec{R}-\vec{r}\right|} &= \frac{2\pi}{\Omega} \int_0^\alpha \rho^{-3} \sum_{\vec{G}} e^{-\frac{G^2}{4\rho^2}} e^{i\vec{G}\cdot\vec{r}} d\rho + \frac{2}{\sqrt{\pi}} \sum_{\vec{R}} \int_\alpha^\infty e^{-\left|\vec{R}-\vec{r}\right|^2 \rho^2} d\rho. \\ &= \frac{\pi}{\Omega} \frac{1}{\alpha^2} \sum_{\vec{G}} \frac{e^{-\frac{G^2}{4\alpha^2}}}{\frac{G^2}{4\alpha^2}} e^{i\vec{G}\cdot\vec{r}} + \sum_{\vec{R}} \frac{\operatorname{erfc}\left(\alpha\left|\vec{R}-\vec{r}\right|\right)}{\left|\vec{R}-\vec{r}\right|}, \end{aligned} \tag{22.9}$$

where erfc is the complementari error function, equal to $(1-\text{erf})$.

22.2 Treatment of more general lattice sums

Following ref. [42] for a lattice sum of the form 7.12:

$$\Sigma_{\lambda,\mu}^{a,a'}(\vec{q}) = \sum_{\vec{R}} \frac{e^{i\vec{q}\cdot\left(\vec{R}+\vec{r}_{aa'}\right)}}{|\vec{R}+\vec{r}_{aa'}|^{(\lambda+1)}} Y_{\lambda\mu}\left(\hat{R}_{aa'}\right) \tag{22.10}$$

a convenient form for the auxiliary function $\mathfrak{F}(\vec{r})$ is

$$\mathfrak{F}(\vec{r}) = \frac{\Gamma\left(\lambda+\frac{1}{2}, \left[\frac{r}{\eta}\right]^2\right)}{\Gamma(\lambda+\frac{1}{2})} \tag{22.11}$$

Where $\Gamma(a,x)$ is the *Incomplete Gamma Function* and $\Gamma(\lambda+\frac{1}{2})$ is the well known *Gamma Function* (See A.9):

Let's now write Σ as the integral:

$$\Sigma_{\lambda,\mu}^{a,a'}(\vec{q}) = \int \frac{w(\vec{r},\vec{q})\, Y_{\lambda\mu}(\hat{r})}{r^{(\lambda+1)}} d^3r \tag{22.12}$$

with $w_{\lambda\mu}(\vec{r},\vec{q}) \equiv \sum_{\vec{R}} e^{i\vec{q}\cdot(\vec{r})}\delta\left(\vec{r}-\vec{R}_{aa'}\right)$. Equation 22.12 can be rewriten as:

$$\begin{aligned} \Sigma_{\lambda,\mu}^{a,a'}(\vec{q}) &= \int \frac{w(\vec{r},\vec{q})\, Y_{\lambda\mu}(\hat{r})\mathfrak{F}(\vec{r})}{r^{(\lambda+1)}} d^3r + \int \frac{w(\vec{r},\vec{q})\, Y_{\lambda\mu}(\hat{r})[1-\mathfrak{F}(\vec{r})]}{r^{(\lambda+1)}} d^3r \\ &= \frac{1}{\Gamma(\lambda+\frac{1}{2})} \left\{ \int \frac{w(\vec{r},\vec{q})\, Y_{\lambda\mu}(\hat{r})\Gamma(\lambda+\frac{1}{2}, \left[\frac{r}{\eta}\right]^2)}{r^{(\lambda+1)}} d^3r + \right. \\ &\quad \left. \int \frac{w(\vec{r},\vec{q})\, Y_{\lambda\mu}(\hat{r})\gamma(\lambda+\frac{1}{2}, \left[\frac{r}{\eta}\right]^2)}{r^{(\lambda+1)}} d^3r \right\} \end{aligned} \tag{22.13}$$

where $\gamma(\lambda,x) \equiv \Gamma(\lambda) - \Gamma(\lambda,x) = \int_0^x e^{-t} t^{a-1} dt$. The first integral in equation 22.13 can be directly converted to a -now rapidly converging- sum:

$$\int \frac{w(\vec{r},\vec{q})\, Y_{\lambda\mu}(\hat{r})\Gamma(\lambda+\frac{1}{2}, \left[\frac{r}{\eta}\right]^2)}{r^{(\lambda+1)}} d^3r = \sum_{\vec{R}} \frac{e^{i\vec{q}\cdot(\vec{R}_{aa'})}\Gamma(\lambda+\frac{1}{2}, \left[\frac{R_{aa'}}{\eta}\right]^2) Y_{\lambda\mu}\left(\hat{R}_{aa'}\right)}{R_{aa'}^{(\lambda+1)}} \tag{22.14}$$

For the second integral, we make use of *Parseval's formula*[58], which states that, if $F(\vec{k})$ and $G(\vec{k})$ are the three-dimensional Fourier transforms of $f(\vec{r})$ and $g(\vec{r})$ respectively, then:

$$\begin{aligned} \int F(\vec{k}) G^*(\vec{k}) d^3k &= \int F(\vec{k}) \left[\frac{1}{(2\pi)^{\frac{3}{2}}} \int g^*(\vec{r}) e^{-i\vec{k}\cdot\vec{r}} d^3r \right] d^3k \\ &= \int g^*(\vec{r}) \left[\frac{1}{(2\pi)^{\frac{3}{2}}} \int F(\vec{k}) e^{-i\vec{k}\cdot\vec{r}} d^3k \right] d^3r \\ &= \int f(\vec{r}) g^*(\vec{r}) d^3r \end{aligned} \tag{22.15}$$

If we take $f(\vec{r}) = w(\vec{r}, \vec{q})$ then:

$$\begin{aligned} G(\vec{k}) =& \frac{1}{(2\pi)^{\frac{3}{2}}} \int w(\vec{r}, \vec{q}) e^{i\vec{k}\cdot\vec{r}} d^3r \\ =& \frac{1}{(2\pi)^{\frac{3}{2}}} \int \sum_{\vec{R}} \delta\left(\vec{r} - \vec{R}_{aa'}\right) e^{i\left(\vec{q}-\vec{k}\right)\cdot\vec{r}} d^3r \\ =& \frac{1}{(2\pi)^{\frac{3}{2}}} \sum_{\vec{R}} e^{i\left(\vec{q}+\vec{k}\right)\cdot\vec{R}_{aa'}} = \frac{e^{i\left(\vec{q}+\vec{k}\right)\cdot\vec{r}_{aa'}}}{(2\pi)^{\frac{3}{2}}} \sum_{\vec{R}} e^{i\left(\vec{q}+\vec{k}\right)\cdot\vec{R}} \end{aligned} \tag{22.16}$$

Now, following [42], we use the *Poisson's sum formula*

$$\sum_{n=-\infty}^{\infty} f(x-n) = \sum_{\nu=-\infty}^{\infty} e^{i2\pi\nu x} \int_{-\infty}^{\infty} f(\xi) e^{i2\pi\nu\xi} d\xi \tag{22.17}$$

Inserting for $f(x)$ the function $\delta(x)$ we find:

$$\sum_{n=-\infty}^{\infty} \delta(x-n) = \sum_{\nu=-\infty}^{\infty} e^{i2\pi\nu x} \tag{22.18}$$

Using $\vec{R} = \sum_j n_j \vec{a}_j$ $(j = 1, 2, 3)$ we can write:

$$\sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} = \sum_{n_j} e^{i\sum_j n_j \vec{k}\cdot\vec{a}_j} \tag{22.19}$$

which, using 22.18, leads to:

$$\sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} = \sum_{n_j} \left\{ \prod_j \delta\left(\frac{\vec{k}\cdot\vec{a}_j}{2\pi} - n_j\right) \right\} = (2\pi)^3 \sum_{n_j} \left\{ \prod_j \delta\left(\vec{k}\cdot\vec{a}_j - 2\pi n_j\right) \right\} \tag{22.20}$$

taking into account that if $\vec{G} = \sum_j n_j \vec{b}_j$ then $\vec{G}\cdot\vec{a}_j = 2\pi n_j$, we can write

$$\sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} = (2\pi)^3 \sum_{n_j} \left\{ \prod_j \delta\left[\left(\vec{k} - \vec{G}\right)\cdot\vec{a}_j\right] \right\} \tag{22.21}$$

Let the basisvectors $\vec{a}_j$ have the cartesian components a_{jm}, and let's call $\bar{A}$ the matrix transformation that they define. Then the numbers $\vec{k}\cdot\vec{a}_j$ are the components of the vector $\bar{A}\vec{k}$ resulting from applying to $\vec{k}$ the transformation $\bar{A}$. Using $\delta(\vec{r}) = \delta(x)\delta(y)\delta(z)$ we can write

$$\sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} = (2\pi)^3 \sum_{n_j} \left\{ \delta\left[\bar{A}\left(\vec{k} - \vec{G}\right)\right] \right\} \tag{22.22}$$

If we now use $\delta(\bar{A}\vec{x}) = \frac{1}{|\det \bar{A}|}$ and $|\det \bar{A}| = |\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)| = \Omega$ (the unit cell volume) we arrive at:

$$\sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} = \frac{(2\pi)^3}{\Omega} \sum_{\vec{G}} \delta\left(\vec{k} - \vec{G}\right) \tag{22.23}$$

Applying 22.23 to 22.16 we find:

$$F(\vec{k}) = \frac{e^{i\left(\vec{q}+\vec{k}\right)\cdot\vec{r}_{aa'}}}{(2\pi)^{\frac{3}{2}}} \sum_{\vec{R}} e^{i\left(\vec{q}+\vec{k}\right)\cdot\vec{R}} = \frac{(2\pi)^{\frac{3}{2}}}{\Omega} \sum_{\vec{G}} e^{i\left(\vec{q}+\vec{k}\right)\cdot\vec{r}_{aa'}} \delta(\vec{q} + \vec{k} - \vec{G}) \tag{22.24}$$

We are thus left with $g^*(\vec{r}) = \frac{Y_{\lambda\mu}(\hat{r})\gamma(\lambda+\frac{1}{2}, \left[\frac{r}{\eta}\right]^2)}{r^{(\lambda+1)}}$ for which we obtain:

$$G^*(\vec{k}) = \frac{(-i)^\lambda}{2^{\lambda-\frac{1}{2}}} k^{\lambda-2} \Gamma(1, \left[\frac{\eta k}{2}\right]^2) Y_{\lambda\mu}(\hat{k}) \tag{22.25}$$

Proof of equation 22.25:

Following the proof of eq. A.13 in [42], we will proove the reverse statement, viz. that the inverse Fourier transform of $F(\vec{k})$ is equal to $f(\vec{r})$.

According to [58], p. 366 ff., it can be shown that[1] :

$$\frac{1}{(2\pi)^{\frac{3}{2}}}\int h(k)Y_{\lambda\mu}(\hat{k})e^{i\vec{k}\cdot\vec{r}}d^3k = i^{\lambda}Y_{\lambda\mu}(\hat{r})r^{-\frac{1}{2}}\int_0^{\infty} k^{\frac{3}{2}}h(k)J_{\lambda+\frac{1}{2}}(kr)dk \tag{22.26}$$

Applying 22.26 to the righthand side of equation 22.25 we have:

$$\begin{aligned}\mathfrak{g}(\vec{r}) =&\frac{(-i)^{\lambda}}{(2\pi)^{\frac{3}{2}}2^{\lambda-\frac{1}{2}}}\int k^{\lambda-2}\Gamma(1,\left[\tfrac{\eta k}{2}\right]^2)Y_{\lambda\mu}(\hat{k})e^{-i\vec{k}\cdot\vec{r}}d^3k\\ =&\frac{(-i)^{\lambda}}{2^{\lambda-\frac{1}{2}}}i^{\lambda}Y_{\lambda\mu}(\hat{r})r^{-\frac{1}{2}}\int_0^{\infty} k^{\lambda-\frac{1}{2}}\Gamma(1,\left[\tfrac{\eta k}{2}\right]^2)J_{\lambda+\frac{1}{2}}(kr)dk\\ =&\frac{Y_{\lambda\mu}(\hat{r})}{2^{\lambda-\frac{1}{2}}r^{\frac{1}{2}}}\int_0^{\infty} k^{\lambda-\frac{1}{2}}\Gamma(1,\left[\tfrac{\eta k}{2}\right]^2)J_{\lambda+\frac{1}{2}}(kr)dk\end{aligned} \tag{22.27}$$

Replacing $\Gamma(1,\left[\frac{\eta k}{2}\right]^2) = e^{-\left(\frac{\eta k}{2}\right)^2}$ we get

$$\mathfrak{g}(\vec{r}) = \frac{Y_{\lambda\mu}(\hat{r})}{2^{\lambda-\frac{1}{2}}r^{\frac{1}{2}}}\int_0^{\infty} k^{\lambda-\frac{1}{2}}J_{\lambda+\frac{1}{2}}(kr)e^{-\left(\frac{\eta k}{2}\right)^2}dk \tag{22.28}$$

Changing the integration variable from k to $t = kr$

$$\mathfrak{f}(\vec{r}) = \frac{Y_{\lambda\mu}(\hat{r})}{2^{\lambda-\frac{1}{2}}r^{\lambda+1}}\int_0^{\infty} t^{\lambda-\frac{1}{2}}J_{\lambda+\frac{1}{2}}(t)e^{-\left(\frac{\eta t}{2r}\right)^2}dt \tag{22.29}$$

Now we can use the identity[2]:

$$\int_0^{\infty} t^{\lambda-\frac{1}{2}}J_{\lambda+\frac{1}{2}}(t)e^{-\left(\frac{\eta t}{2r}\right)^2}dt = 2^{\lambda-\frac{1}{2}}\gamma\left(\lambda+\tfrac{1}{2}[\tfrac{r}{\eta}]^2\right) \tag{22.30}$$

to obtain

$$\mathfrak{g}(\vec{r}) = \frac{Y_{\lambda\mu}(\hat{r})}{r^{\lambda+1}}\gamma\left(\lambda+\tfrac{1}{2}[\tfrac{r}{\eta}]^2\right) = g^*(\vec{r}) \tag{22.31}$$

Finally, replacing equations 22.24 and 22.25 into 22.15 we get:

$$\begin{aligned}\int\frac{w\left(\vec{r},\vec{q}\right)Y_{\lambda\mu}(\hat{r})\gamma\left(\lambda+\frac{1}{2},\left[\frac{r}{\eta}\right]^2\right)}{r^{(\lambda+1)}}d^3r =&\frac{(2\pi)^{\frac{3}{2}}(-i)^{\lambda}}{\Omega 2^{\lambda-\frac{1}{2}}}\times\\ &\int\sum_{\vec{G}}e^{i\left(\vec{q}+\vec{k}\right)\cdot\vec{r}_{aa'}}\delta(\vec{q}+\vec{k}-\vec{G})k^{\lambda-2}\Gamma(1,\left[\tfrac{\eta k}{2}\right]^2)Y_{\lambda\mu}(\hat{k})d^3k\end{aligned} \tag{22.32}$$

It can be easily verified that:

$$\begin{aligned}&\int e^{i\left(\vec{q}+\vec{k}\right)\cdot\vec{r}_{aa'}}\delta(\vec{q}+\vec{k}-\vec{G})k^{\lambda-2}\Gamma(1,\left[\tfrac{\eta k}{2}\right]^2)Y_{\lambda\mu}(\hat{k})d^3k =\\ &\qquad= \begin{cases} e^{i\vec{G}\cdot\vec{r}_{aa'}}|\vec{G}-\vec{q}|^{\lambda-2}\Gamma(1,\left[\frac{\eta|\vec{G}-\vec{q}|}{2}\right]^2)Y_{\lambda\mu}(\widehat{(\vec{G}-\vec{q})}) & \vec{G}-\vec{q}\neq 0\\ 0 & \vec{G}-\vec{q}=0\ \&\ \lambda>2\end{cases}\end{aligned} \tag{22.33}$$

Since $\vec{q}\in$ 1BZ the condition $\vec{G}-\vec{q}=0$ means $\vec{G}=\vec{q}=0$. Finally, including equation 22.33 into 22.32 we end up with:

[1] There is an error in the eq. that defines χ_{nlm}

[2] Calculated with Mathematica®

$$\Sigma^{a,a'}_{\lambda,\mu}(\vec{q}) = \frac{1}{\Gamma(\lambda+\frac{1}{2})}\left\{\sum_{\vec{R}} \frac{e^{i\vec{q}\cdot(\vec{R}_{aa'})}\Gamma(\lambda+\frac{1}{2},\left[\frac{R_{aa'}}{\eta}\right]^2)Y_{\lambda\mu}\left(\hat{R}_{aa'}\right)}{R^{(\lambda+1)}_{aa'}} + \frac{(2\pi)^{\frac{3}{2}}(-i)^{\lambda}}{\Omega 2^{\lambda-\frac{1}{2}}}\sum_{\vec{G}} e^{i\vec{G}\cdot\vec{r}_{aa'}}|\vec{G}-\vec{q}|^{\lambda-2}\Gamma(1,\left[\frac{\eta|\vec{G}-\vec{q}|}{2}\right]^2)Y_{\lambda\mu}(\widehat{G-q})\right\} \tag{22.34}$$

Valid for $\vec{q} \neq 0$. If $\vec{q} = 0$ a primed sum has to be performed (not including the $\vec{G} = 0$), but the sum only exists for $\lambda > 2$. For $\lambda = 2$ the sum is conditionally convergent.

22.2.1 Selection of η

The parameter η should be chosen to optimize the convergence of both the real and reciprocal lattice sums. In [42], it's value is arbitrarily set to $\eta = \frac{1}{\sqrt{\pi}}$, while in [32] a more detailed analysis is done, which we follow.

If the value of η is too small, the reciprocal lattice sum does not converge quickly since $\frac{1}{2}G\eta$ remains small even for large values of G. With the same reasoning, if η is too large, $\frac{R}{\eta}$ will remain small for large R's. In both cases, the terms of the sum decay as e^{-x^2}(or erfc(x)) with $x = \frac{1}{2}G\eta$ in reciprocal space and $x = \frac{R}{\eta}$ in real space, a simple way of optimizing the value of η is choosing it such that:

$$\frac{R_{aa'}}{\eta_{opt}} = \frac{1}{2}|\vec{G}-\vec{q}|\eta_{opt} \tag{22.35}$$

leading to:

$$\eta^2_{opt} = \frac{R_{aa'}}{2|\vec{G}-\vec{q}|} \simeq \frac{R}{2G} \tag{22.36}$$

The simplest choice is to use the minimum values for R and G to have the same order of magnitude. That is:

$$\eta_{opt} = \sqrt{\frac{R_{min}}{2G_{min}}} \tag{22.37}$$

22.2.2 Determination of the *cutoffs*

The calculations shown up to now have lead us to a set of two fast converging sums, in real and reciprocal space, and the determination of an optimal value of the dummy constant η. Still we have to deal with infinite sums, which have to be stopped at some *cutoff radius* R_c (G_c in reciprocal space) with the condition that the error due to this partial sum is smaller than certain -in principe arbitrary- tolerance.

For the sum in real space, the error can be expressed as:

$$\mathfrak{E}_{R,\lambda} = \frac{1}{\Gamma(\lambda+\frac{1}{2})}\sum_{\vec{R}} \frac{e^{i\vec{q}\cdot(\vec{R}_{aa'})}\Gamma(\lambda+\frac{1}{2},\left[\frac{R_{aa'}}{\eta}\right]^2)Y_{\lambda\mu}\left(\hat{R}_{aa'}\right)}{R^{(\lambda+1)}_{aa'}}\Theta(R_{aa'}-R_c) \tag{22.38}$$

Where $\Theta(x)$ is the Heaviside step function. Our interest is to limit the absolute value of the error. Since the factor $e^{i\vec{q}\cdot\vec{R}_{aa'}}$ only adds a phase to each term, the sum will always be bigger than taken it equal to one. A similar reasoning can be applied to the Spherical Harmonic $Y_{\lambda\mu}\left(\hat{R}_{aa'}\right)$, although in some particular angles it can be bigger that one, its mean value will always be smaller[3]. Thus, we can confidently write:

$$\mathfrak{E}_{R,\lambda} < \frac{1}{\Gamma(\lambda+\frac{1}{2})}\sum_{\vec{R}} \frac{\Gamma(\lambda+\frac{1}{2},\left[\frac{R_{aa'}}{\eta}\right]^2)}{R^{(\lambda+1)}_{aa'}}\Theta(R_{aa'}-R_c) \tag{22.39}$$

and then replace the sum by and integral

[3] In the extreme case of $R_c \to \infty$ the number of points in the sphere surface would also go to infinity, and the sum would became an integral, which would be identically zero (except for $\lambda = 0$ due to the orthogonality of the $Y_{\lambda\mu}$'s)

$$\begin{aligned}\mathfrak{E}_{R,\lambda} <& \frac{4\pi}{\Gamma(\lambda+\frac{1}{2})}\int_{R_c}^{\infty}\frac{\Gamma(\lambda+\frac{1}{2},\left[\frac{r}{\eta}\right]^2)}{r^{(\lambda+1)}}\,r^2dr = \\ =& \frac{4\pi}{\Gamma(\lambda+\frac{1}{2})}\int_{R_c}^{\infty}\frac{1}{r^{(\lambda-1)}}\int_{\left(\frac{r}{\eta}\right)^2}^{\infty}t^{\lambda-\frac{1}{2}}e^{-t}dt\;dr \\ =& \frac{4\pi}{\Gamma(\lambda+\frac{1}{2})}\int_{\left(\frac{R_c}{\eta}\right)^2}^{\infty}t^{\lambda-\frac{1}{2}}e^{-t}\int_{R_c}^{\eta\sqrt{t}}\frac{1}{r^{(\lambda-1)}}dr\;dt\end{aligned} \tag{22.40}$$

If $\lambda \neq 2$ it gives:

$$\begin{aligned}\mathfrak{E}_{R,\lambda} <& \frac{4\pi}{(2-\lambda)\Gamma(\lambda+\frac{1}{2})}\int_{\left(\frac{R_c}{\eta}\right)^2}^{\infty}t^{\lambda-\frac{1}{2}}e^{-t}\left[\frac{1}{\eta^{\lambda-2}t^{\frac{\lambda}{2}-1}}-\frac{1}{R_c^{\lambda-2}}\right]dt \\ =& \frac{4\pi}{(2-\lambda)\Gamma(\lambda+\frac{1}{2})}\int_{\left(\frac{R_c}{\eta}\right)^2}^{\infty}t^{\frac{\lambda}{2}+\frac{1}{2}}e^{-t}\frac{1}{\eta^{\lambda-2}}-t^{\lambda-\frac{1}{2}}e^{-t}\frac{1}{R_c^{\lambda-2}}dt \\ =& \frac{4\pi}{(\lambda-2)\Gamma(\lambda+\frac{1}{2})}\left(\frac{\Gamma[\frac{\lambda}{2}+\frac{3}{2},\left(\frac{R_c}{\eta}\right)^2]}{\eta^{\lambda-2}}-\frac{\Gamma[\lambda+\frac{1}{2},\left(\frac{R_c}{\eta}\right)^2]}{R_c^{\lambda-2}}\right)\end{aligned} \tag{22.41}$$

In the case of $\lambda = 2$ the integral in equation 22.40 is:

$$\mathfrak{E}_{R,2} < \frac{4\pi}{\Gamma(\frac{5}{2})}\int_{\left(\frac{R_c}{\eta}\right)^2}^{\infty}t^{\frac{3}{2}}e^{-t}\ln\left(\frac{\eta\sqrt{t}}{R_c}\right)\,dt \tag{22.42}$$

This integral gives a too complicated result (including Hypergeometric functions), thus we simplify it further by taking into account that, $\ln(x) < x-1$ if $x > 1$. Then equation 22.42 can be written:

$$\mathfrak{E}_{R,2} < \frac{4\pi}{\Gamma(\frac{5}{2})}\int_{\left(\frac{R_c}{\eta}\right)^2}^{\infty}\left(\frac{\eta}{R_c}t^2e^{-t}-t^{\frac{3}{2}}e^{-t}\right)\,dt = \frac{4\pi}{\Gamma(\frac{5}{2})}\left\{\frac{\eta}{R_c}\Gamma\left[3,\left(\frac{R_c}{\eta}\right)^2\right]-\Gamma\left[\frac{5}{2},\left(\frac{R_c}{\eta}\right)^2\right]\right\} \tag{22.43}$$

Thus, given a maximum tolerance $\mathfrak{E}^{\text{tol}}_{R,\lambda}$ we can calculate the cutoff radius solving:

$$\mathfrak{E}^{\text{tol}}_{R,\lambda} = \begin{cases}\frac{4\pi}{(\lambda-2)\Gamma(\lambda+\frac{1}{2})}\left(\frac{\Gamma[\frac{\lambda}{2}+\frac{3}{2},\left(\frac{R_c}{\eta}\right)^2]}{\eta^{\lambda-2}}-\frac{\Gamma[\lambda+\frac{1}{2},\left(\frac{R_c}{\eta}\right)^2]}{R_c^{\lambda-2}}\right) & \lambda\neq 2 \\ \frac{4\pi}{\Gamma(\frac{5}{2})}\left[\frac{\eta}{R_c}\Gamma[3,\left(\frac{R_c}{\eta}\right)^2]-\Gamma[\frac{5}{2},\left(\frac{R_c}{\eta}\right)^2]\right] & \lambda=2\end{cases} \tag{22.44}$$

The shape of the function is shown in figure **??** for $\eta = \sqrt{\pi}^{-1}$ and $\lambda = 0,\ldots,8$.
In a similar way, we can estimate the error for the sum in reciprocal space:

$$\begin{aligned}\mathfrak{E}_{G,\lambda} =& \frac{(2\pi)^{\frac{3}{2}}(-i)^{\lambda}}{\Omega 2^{\lambda-\frac{1}{2}}\Gamma(\lambda+\frac{1}{2})}\sum_{\vec{G}}e^{i\vec{G}\cdot(\vec{r}_{aa'})}\left|\vec{G}-\vec{q}\right|^{\lambda-2}e^{-\left(\frac{\eta|\vec{G}-\vec{q}|}{2}\right)^2}Y_{\lambda\mu}\left(\widehat{\vec{G}-\vec{q}}\right)\;\Theta(\left|\vec{G}-\vec{q}\right|-G_c) < \\ <& \left|\frac{(2\pi)^{\frac{3}{2}}(-i)^{\lambda}4\pi}{\Omega 2^{\lambda-\frac{1}{2}}\Gamma(\lambda+\frac{1}{2})}\int_{G_c}^{\infty}g^{\lambda}e^{-\left(\frac{\eta g}{2}\right)^2}dg\right|\end{aligned} \tag{22.45}$$

By changing the integration variable to $x = \left(\frac{\eta g}{2}\right)^2$ we obtain:

$$\begin{aligned}\mathfrak{E}_{G,\lambda} <& \frac{(2\pi)^{\frac{3}{2}}4\pi}{\Omega 2^{\lambda-\frac{1}{2}}\Gamma(\lambda+\frac{1}{2})}\frac{2^{\lambda}}{\eta^{\lambda+1}}\int\limits_{(\frac{\eta G_c}{2})^2}^{\infty} x^{\frac{\lambda-1}{2}}e^{-x}dx \\ =& \frac{8(\pi)^{\frac{5}{2}}}{\Omega\Gamma(\lambda+\frac{1}{2})\eta^{\lambda+1}}\Gamma\left[\frac{\lambda+1}{2},\left(\frac{\eta G_c}{2}\right)^2\right]\end{aligned} \tag{22.46}$$

Thus, given a maximum tolerance $\mathfrak{E}^{\text{tol}}_{G,\lambda}$ we can calculate the cutoff radius solving:

$$\mathfrak{E}^{\text{tol}}_{G,\lambda} = \frac{8(\pi)^{\frac{5}{2}}}{\Omega\Gamma(\lambda+\frac{1}{2})\eta^{\lambda+1}}\Gamma\left[\frac{\lambda+1}{2},\left(\frac{\eta G_c}{2}\right)^2\right] \tag{22.47}$$

The shape of the function is shown in figure **??** for $\eta = \sqrt{\pi}^{-1}$ and $\lambda = 0,\ldots,10$.

Chapter 23

The diagonal elements of the exchange-correlation potential

In the Wien2k [15] code the exchange-correlation potential is expanded as:

$$V^{xc}(\mathbf{r}) = \begin{cases} \sum_{LM} V^{xc}_{aLM}(r)\Lambda_{LM}(\hat{\mathbf{r}}) & \mathbf{r} \in S_a \\ \sum_{s} V^{xc}_{s}\Phi_s(\mathbf{r}) & \mathbf{r} \in I \end{cases} \tag{23.1}$$

where $\Lambda_{LM}(\hat{\mathbf{r}})$ are the real spherical harmonics defined in Eq. A.41, and $\Phi_s(\mathbf{r})$ are the stars defined in A.48. According to eq. 2.14 we have to calculate:

$$\langle \psi_{\mathbf{k}n}|V^{xc}|\psi_{\mathbf{k}n}\rangle = \int_V \psi^*_{\mathbf{k}n}(\mathbf{r})V^{xc}(\mathbf{r})\psi_{\mathbf{k}n}(\mathbf{r})d^3r \tag{23.2}$$

As usual, we separate the integration into a MT-Sphere and an Interstitial part.

23.1 MT-Sphere integration

In this case we use the Spherical harmonics expansion of the wavefunctions given in Eq. 6.29, then we have:

$$\begin{aligned} \int_{S_a} \psi^*_{\mathbf{k}n}(\mathbf{r})V^{xc}(\mathbf{r})\psi_{\mathbf{k}n}(\mathbf{r})d^3r = \sum_{LM\pm,l_1m_1,l_2m_2} & \left(\int Y^*_{l_1m_1}(\hat{\mathbf{r}})\Lambda_{LM\pm}(\hat{\mathbf{r}})Y_{l_2m_2}(\hat{\mathbf{r}})d\hat{\mathbf{r}}\right) \\ & \Big[\mathcal{A}^{a*}_{nl_1m_1}(\vec{k})\mathcal{A}^{a}_{nl_2m_2}(\vec{k})\langle l_1|V^{xc}_{aLM\pm}|l_2\rangle_a + \\ & \mathcal{B}^{a*}_{nl_1m_1}(\vec{k})\mathcal{A}^{a}_{nl_2m_2}(\vec{k})\langle \dot{l}_1|V^{xc}_{aLM\pm}|l_2\rangle_a + \\ & \mathcal{A}^{a*}_{nl_1m_1}(\vec{k})\mathcal{B}^{a}_{nl_2m_2}(\vec{k})\langle l_1|V^{xc}_{aLM\pm}|\dot{l}_2\rangle_a + \\ & \mathcal{B}^{a*}_{nl_1m_1}(\vec{k})\mathcal{A}^{a}_{nl_2m_2}(\vec{k})\langle \dot{l}_1|V^{xc}_{aLM\pm}|\dot{l}_2\rangle_a + ...\Big] \end{aligned} \tag{23.3}$$

where

$$\langle \tilde{l}_1|V^{xc}_{aLM\pm}|\tilde{l}_2\rangle_a \equiv \int_0^{R^a_{MT}} \tilde{u}_{l_1a}(r)V^{xc}_{aLM\pm}(r)\tilde{u}_{l_2a}(r)r^2dr \tag{23.4}$$

For the angular integral, using A.43 and **??** we have:

$$\begin{aligned} \int Y^*_{l_1m_1}(\hat{\mathbf{r}})\Lambda_{LM+}(\hat{\mathbf{r}})Y_{l_2m_2}(\hat{\mathbf{r}})d\hat{\mathbf{r}} =& \frac{(-1)^M}{\sqrt{2}}\int Y^*_{l_1m_1}(\hat{\mathbf{r}})Y_{LM}(\hat{\mathbf{r}})Y_{l_2m_2}(\hat{\mathbf{r}})d\hat{\mathbf{r}} \\ &+ \frac{(-1)^M}{\sqrt{2}}\int Y^*_{l_1m_1}(\hat{\mathbf{r}})Y^*_{LM}(\hat{\mathbf{r}})Y_{l_2m_2}(\hat{\mathbf{r}})d\hat{\mathbf{r}} \\ =& \frac{(-1)^M}{\sqrt{2}}\left[\mathcal{G}^{l_1m_1}_{Ll_2,Mm_2} + \left(\mathcal{G}^{l_2m_2}_{Ll_1,Mm_1}\right)^*\right] \end{aligned} \tag{23.5}$$

and

$$\begin{aligned}\int Y^*_{l_1m_1}(\hat{\mathbf{r}})\Lambda_{LM-}(\hat{\mathbf{r}})Y_{l_2m_2}(\hat{\mathbf{r}})d\hat{\mathbf{r}} =& \frac{i(-1)^{M+1}}{\sqrt{2}}\int Y^*_{l_1m_1}(\hat{\mathbf{r}})Y_{LM}(\hat{\mathbf{r}})Y_{l_2m_2}(\hat{\mathbf{r}})d\hat{\mathbf{r}} \\ &+ \frac{i(-1)^{M}}{\sqrt{2}}\int Y^*_{l_1m_1}(\hat{\mathbf{r}})Y^*_{LM}(\hat{\mathbf{r}})Y_{l_2m_2}(\hat{\mathbf{r}})d\hat{\mathbf{r}} \\ =& \frac{i(-1)^{M}}{\sqrt{2}}\left[-\mathcal{G}^{l_1m_1}_{Ll_2,Mm_2} + \left(\mathcal{G}^{l_2m_2}_{Ll_1,Mm_1}\right)^*\right]\end{aligned} \tag{23.6}$$

Thus, sumarizing:

$$\begin{aligned}\int_{MTS} \psi^*_{\mathbf{k}n}(\mathbf{r})V^{xc}(\mathbf{r})\psi_{\mathbf{k}n}(\mathbf{r})d^3r = \sum_{LM,l_1m_1,l_2m_2} & \frac{(-1)^M}{\sqrt{2}}\left[\mathcal{G}^{l_1m_1}_{Ll_2,Mm_2}(1-i) + \left(\mathcal{G}^{l_2m_2}_{Ll_1,Mm_1}\right)^*(1+i)\right] \\ & \Big[\mathcal{A}^{a*}_{nl_1m_1}(\vec{k})\mathcal{A}^{a}_{nl_2m_2}(\vec{k})\langle l_1|V^{xc}_{aLM\pm}|l_2\rangle_a + \\ & \mathcal{B}^{a*}_{nl_1m_1}(\vec{k})\mathcal{A}^{a}_{nl_2m_2}(\vec{k})\langle \dot{l}_1|V^{xc}_{aLM\pm}|l_2\rangle_a + \\ & \mathcal{A}^{a*}_{nl_1m_1}(\vec{k})\mathcal{B}^{a}_{nl_2m_2}(\vec{k})\langle l_1|V^{xc}_{aLM\pm}|\dot{l}_2\rangle_a + \\ & \mathcal{B}^{a*}_{nl_1m_1}(\vec{k})\mathcal{A}^{a}_{nl_2m_2}(\vec{k})\langle \dot{l}_1|V^{xc}_{aLM\pm}|\dot{l}_2\rangle_a + ...\Big]\end{aligned} \tag{23.7}$$

23.2 Interstitial integration

Using eq. A.48 we can expand the exchange correlation potential in the interstitial region as:

$$V^{xc}(\mathbf{r}) = \sum_{\vec{G}} V^{xc}_{\vec{G}} e^{i\vec{G}\cdot\mathbf{r}} \tag{23.8}$$

where $V^{xc}_{\vec{G}_{m_s}} = \frac{\varphi_m}{m_s}V^{xc}_s$. Using the expansion 8.6 we have:

$$\int_I \psi^*_{\mathbf{k}n}(\mathbf{r})V^{xc}(\mathbf{r})\psi_{\mathbf{k}n}(\mathbf{r})d^3r = \sum_{\vec{G}_1\vec{G}_2\vec{G}_3} Z^{*n}_{\vec{k}+\vec{G}_1}V^{xc}_{\vec{G}_2}Z^{n}_{\vec{k}+\vec{G}_3}\frac{1}{V}\int_I e^{i(\vec{G}_2+\vec{G}_3-\vec{G}_1)\cdot\mathbf{r}}d^3\mathbf{r} \tag{23.9}$$

Which, using eq. 6.16 can be written as:

$$\boxed{\int_I \psi^*_{\mathbf{k}n}(\mathbf{r})V^{xc}(\mathbf{r})\psi_{\mathbf{k}n}(\mathbf{r})d^3r = \sum_{\vec{G}_1\vec{G}_2\vec{G}_3} Z^{*n}_{\vec{k}+\vec{G}_1}V^{xc}_{\vec{G}_2}Z^{n}_{\vec{k}+\vec{G}_3}\mathcal{I}_{\vec{G}_2+\vec{G}_3-\vec{G}_1}} \tag{23.10}$$

23.3 Final result

Finally, summing up eqs. 23.7 and 23.10 we obtain:

$$\begin{aligned}\langle\psi_{\mathbf{k}n}|V^{xc}|\psi_{\mathbf{k}n}\rangle = & \sum_{\vec{G}_1\vec{G}_2\vec{G}_3} Z^{*n}_{\vec{k}+\vec{G}_1}V^{xc}_{\vec{G}_2}Z^{n}_{\vec{k}+\vec{G}_3}\mathcal{I}_{\vec{G}_2+\vec{G}_3-\vec{G}_1} + \\ & \sum_{LM,l_1m_1,l_2m_2} \frac{(-1)^M}{\sqrt{2}}\left[\mathcal{G}^{l_1m_1}_{Ll_2,Mm_2}(1-i) + \left(\mathcal{G}^{l_2m_2}_{Ll_1,Mm_1}\right)^*(1+i)\right] \\ & \Big[\mathcal{A}^{a*}_{nl_1m_1}(\vec{k})\mathcal{A}^{a}_{nl_2m_2}(\vec{k})\langle l_1|V^{xc}_{aLM\pm}|l_2\rangle_a + \\ & \mathcal{B}^{a*}_{nl_1m_1}(\vec{k})\mathcal{A}^{a}_{nl_2m_2}(\vec{k})\langle \dot{l}_1|V^{xc}_{aLM\pm}|l_2\rangle_a + \\ & \mathcal{A}^{a*}_{nl_1m_1}(\vec{k})\mathcal{B}^{a}_{nl_2m_2}(\vec{k})\langle l_1|V^{xc}_{aLM\pm}|\dot{l}_2\rangle_a + \\ & \mathcal{B}^{a*}_{nl_1m_1}(\vec{k})\mathcal{A}^{a}_{nl_2m_2}(\vec{k})\langle \dot{l}_1|V^{xc}_{aLM\pm}|\dot{l}_2\rangle_a + ...\Big]\end{aligned} \tag{23.11}$$

Chapter 24

Momentum matrix elements

We want to calculate the momentum matrix elements between different LAPW eigenfunctions.

24.1 Contribution from the MT-sphere

The use of spherical harmonics is the LAPW basis set suggest to calculate the expressions $\langle n_1\mathbf{k}|\partial x \pm i\partial y|n_2\mathbf{k}\rangle$ and derive the x and y components as linear combinations. Inside the MT-Sphere of atom a a KS wave function can be expanded as

$$\begin{aligned}\psi_{n\mathbf{k}}(\mathbf{r}) =& \sum_{lm}\left[\mathcal{A}^{n\mathbf{k}}_{lm}u_l(r) + \mathcal{B}^{n\mathbf{k}}_{lm}\dot{u}_l(r) + \sum_{\nu}\mathcal{C}^{n\mathbf{k}}_{\nu lm}u_{\nu l}(r)\right]Y_{lm}(\theta,\phi)\\ =& \sum_{lm}\mathcal{W}^{n\mathbf{k}}_{lm}(r)Y_{lm}(\theta,\phi)\end{aligned} \tag{24.1}$$

To simplify the notation, we have dropped the dependence on the atomic index a.

24.1.1 $x-$ and $y-$ components

Using the expression for the operators given by A.53

$$\partial x \pm i\partial y = \sin\theta e^{\pm i\phi}\frac{\partial}{\partial r} + \frac{e^{\pm i\phi}}{r}\left(\cos\theta\frac{\partial}{\partial\theta} \pm \frac{i}{\sin\theta}\frac{\partial}{\partial\phi}\right) \tag{24.2}$$

we have

$$\begin{aligned}\hat{p}^{\pm}\psi_{n\mathbf{k}}(\mathbf{r}) \equiv& \left(\partial x \pm i\partial y\right)\psi_{n\mathbf{k}}(\mathbf{r})\\ =& \sum_{lm}\left[\frac{\partial}{\partial r}\mathcal{W}^{n\mathbf{k}}_{lm}(r)\sin\theta e^{\pm i\phi} + \frac{1}{r}\mathcal{W}^{n\mathbf{k}}_{lm}(r)e^{\pm i\phi}\left(\cos\theta\frac{\partial}{\partial\theta} \pm \frac{i}{\sin\theta}\frac{\partial}{\partial\phi}\right)\right]Y_{lm}(\theta,\phi)\end{aligned} \tag{24.3}$$

Using the relations between spherical harmonics (see A.37)

$$\begin{aligned}e^{\pm i\phi}\sin\theta Y_{lm}(\theta,\phi) =& F^{(2\mp1)}_{lm}Y_{l+1,m\pm1}(\theta,\phi) + F^{(3\mp1)}_{lm}Y_{l-1,m\pm1}(\theta,\phi)\\ e^{\pm i\phi}\left(\cos\theta\frac{\partial}{\partial\theta} \pm \frac{i}{\sin\theta}\frac{\partial}{\partial\theta}\right)Y_{lm}(\theta,\phi) =& -lF^{(2\mp1)}_{lm}Y_{l+1,m\pm1}(\theta,\phi) + (l+1)F^{(3\mp1)}_{lm}Y_{l-1,m\pm1}(\theta,\phi)\end{aligned} \tag{24.4}$$

with

$$\begin{aligned}F^{(1)}_{lm} =& -\sqrt{\frac{(l+m+1)(l+m+2)}{2l+1)(2l+3)}}\\ F^{(2)}_{lm} =& \sqrt{\frac{(l-m)(l-m-1)}{2l-1)(2l+1)}}\\ F^{(3)}_{lm} =& \sqrt{\frac{(l-m+1)(l-m+2)}{2l+1)(2l+3)}}\\ F^{(4)}_{lm} =& -\sqrt{\frac{(l+m)(l+m-1)}{2l-1)(2l+1)}}\end{aligned} \tag{24.5}$$

we get:

$$\begin{aligned}\hat{p}^{\pm}\psi_{n\mathbf{k}}(\mathbf{r}) =& \sum_{lm} \frac{\partial \mathcal{W}_{lm}^{n\mathbf{k}}(r)}{\partial r}\left(F_{lm}^{(2\mp1)}Y_{l+1m\pm1}(\theta,\phi) + F_{lm}^{(3\mp1)}Y_{l-1m\pm1}(\theta,\phi)\right) \\ &+\frac{\mathcal{W}_{lm}^{n\mathbf{k}}(r)}{r}\left(-lF_{lm}^{(2\mp1)}Y_{l+1m\pm1}(\theta,\phi) + (l+1)F_{lm}^{(3\mp1)}Y_{l-1m\pm1}(\theta,\phi)\right)\end{aligned} \tag{24.6}$$

which can be reordered to give:

$$\begin{aligned}\hat{p}^{\pm}\psi_{n\mathbf{k}}(\mathbf{r}) =& \sum_{lm}\left(\frac{\partial}{\partial r}\mathcal{W}_{lm}^{n\mathbf{k}}(r) - \frac{l}{r}\mathcal{W}_{lm}^{n\mathbf{k}}(r)\right)F_{lm}^{(2\mp1)}Y_{l+1m\pm1}(\theta,\phi) \\ &+\left(\frac{\partial}{\partial r}\mathcal{W}_{lm}^{n\mathbf{k}}(r) + \frac{l+1}{r}\mathcal{W}_{lm}^{n\mathbf{k}}(r)\right)F_{lm}^{(3\mp1)}Y_{l-1m\pm1}(\theta,\phi)\end{aligned} \tag{24.7}$$

To simplify the notation, we introduce the intermediate operators

$$\begin{aligned}\delta_l \equiv& \partial/\partial r - l/r \\ \Delta_l \equiv& \partial/\partial r + (l+1)/r\end{aligned} \tag{24.8}$$

so that we have

$$\begin{aligned}\hat{p}^{\pm}\psi_{n\mathbf{k}}(\mathbf{r}) =& \sum_{lm} F_{lm}^{(2\mp1)}\delta_l\mathcal{W}_{lm}^{n\mathbf{k}}(r)Y_{l+1m\pm1}(\theta,\phi) \\ &+ F_{lm}^{(3\mp1)}\Delta_l\mathcal{W}_{lm}^{n\mathbf{k}}(r)Y_{l-1m\pm1}(\theta,\phi)\end{aligned} \tag{24.9}$$

Thus we have that the matrix elements are:

$$\begin{aligned}p^{\pm}_{n_1n_2;\mathbf{k}} &\equiv \langle n_1\mathbf{k}|\partial x \pm i\partial y|n_2\mathbf{k}\rangle \\ &= \sum_{l_1m_1}\sum_{l_2m_2}\langle \mathcal{W}_{l_1m_1}^{n_1\mathbf{k}}Y_{l_1m_1}|F_{l_2m_2}^{(2\mp1)}\delta_{l_2}\mathcal{W}_{l_2m_2}^{n_2\mathbf{k}}Y_{l_2+1m_2\pm1} + F_{l_2m_2}^{(3\mp1)}\Delta_{l_2}\mathcal{W}_{l_2m_2}^{n_2\mathbf{k}}Y_{l_2-1m_2\pm1}\rangle \\ &= \sum_{l_1m_1}\sum_{l_2m_2}F_{l_2m_2}^{(2\mp1)}\langle \mathcal{W}_{l_1m_1}^{n_1\mathbf{k}}|\delta_{l_2}\mathcal{W}_{l_2m_2}^{n_2\mathbf{k}}\rangle\delta_{l_1,l_2+1}\delta_{m_1,m_2\pm1} + F_{l_2m_2}^{(3\mp1)}\langle \mathcal{W}_{l_1m_1}^{n_1\mathbf{k}}|\Delta_{l_2}\mathcal{W}_{l_2m_2}^{n_2\mathbf{k}}\rangle\delta_{l_1,l_2-1}\delta_{m_1,m_2\pm1} \\ &= \sum_{l,m}F_{lm}^{(2\mp1)}\langle \mathcal{W}_{l+1m\pm1}^{n_1\mathbf{k}}|\delta_l\mathcal{W}_{lm}^{n_2\mathbf{k}}\rangle + F_{l+1m\mp1}^{(3\mp1)}\langle \mathcal{W}_{lm}^{n_1\mathbf{k}}|\Delta_{l+1}\mathcal{W}_{l+1m\mp1}^{n_2\mathbf{k}}\rangle\end{aligned} \tag{24.10}$$

24.1.2 $z-$ component

For the $z-$component, we start with

$$\partial z \equiv \cos\theta\frac{\partial}{\partial r} - \frac{1}{r}\sin\theta\frac{\partial}{\partial\theta} \tag{24.11}$$

therefore we have for $\mathbf{r}$ in the muffin-tin spheres S_a

$$\partial z\psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{lm}\left[\frac{\partial\mathcal{W}_{lm}^{n\mathbf{k}}(r)}{\partial r}\cos\theta Y_{lm}(\theta,\phi) - \frac{\mathcal{W}_{lm}^{n\mathbf{k}}(r)}{r}\sin\theta\frac{\partial}{\partial\theta}Y_{lm}(\theta,\phi)\right] \tag{24.12}$$

Using the relations

$$\begin{aligned}\cos\theta Y_{lm}(\theta,\phi) =& F_{lm}^{(5)}Y_{l+1m}(\theta,\phi) + F_{lm}^{(6)}Y_{l-1m}(\theta,\phi) \\ -\sin\theta\frac{\partial}{\partial\theta}Y_{lm}(\theta,\phi) =& -lF_{lm}^{(5)}Y_{l+1m}(\theta,\phi) + (l+1)F_{lm}^{(6)}Y_{l-1m}(\theta,\phi)\end{aligned} \tag{24.13}$$

with

$$\begin{aligned}F_{lm}^{(5)} =& \sqrt{\frac{(l-m+1)(l+m+1)}{2l+1)(2l+3)}} \\ F_{lm}^{(6)} =& \sqrt{\frac{(l-m)(l+m)}{2l-1)(2l+1)}}\end{aligned} \tag{24.14}$$

we have

$$\begin{aligned}\partial z\psi_{n\mathbf{k}}(\mathbf{r}) =& \sum_{lm}\frac{\partial \mathcal{W}^{n\mathbf{k}}_{lm}(r)}{\partial r}\left[F^{(5)}_{lm}Y_{l+1m}(\theta,\phi)+F^{(6)}_{lm}Y_{l-1,m}(\theta,\phi)\right]\\ &+\frac{\mathcal{W}^{n\mathbf{k}}_{lm}(r)}{r}\left[-lF^{(5)}_{lm}Y_{l+1m}(\theta,\phi)+(l+1)F^{(6)}_{lm}Y_{l-1m}(\theta,\phi)\right]\\ =&F^{(5)}_{lm}\delta_l\mathcal{W}^{n\mathbf{k}}_{lm}(r)Y_{l+1m}(\theta,\phi)+F^{(6)}_{lm}\Delta_l\mathcal{W}^{n\mathbf{k}}_{lm}(r)Y_{l-1m}(\theta,\phi)\\ =&\left[F^{(5)}_{l-1m}\delta_{l-1}\mathcal{W}^{n\mathbf{k}}_{l-1m}(r)+F^{(6)}_{l+1m}\Delta_{l+1}\mathcal{W}^{n\mathbf{k}}_{l+1m}(r)\right]Y_{lm}(\theta,\phi)\\ \equiv&\sum_{lm}\mathcal{P}^{n\mathbf{k}}_{lm}(r)Y_{lm}(\theta,\phi)\end{aligned} \tag{24.15}$$

Now the matrix element

$$\begin{aligned}\langle\psi_{n_1\mathbf{k}}|\partial z|\psi_{n_2\mathbf{k}}\rangle =& \sum_{lm}\langle\mathcal{W}^{n_1\mathbf{k}}_{lm}|\mathcal{P}^{n_2\mathbf{k}}_{lm}\rangle\\ =&\sum_{lm}F^{(5)}_{l-1m}\langle\mathcal{W}^{n_1\mathbf{k}}_{lm}|\delta_{l-1}\mathcal{W}^{n_2\mathbf{k}}_{l-1m}\rangle+F^{(6)}_{l+1m}\langle\mathcal{W}^{n_1\mathbf{k}}_{lm}|\Delta_{l+1}\mathcal{W}^{n_2\mathbf{k}}_{l+1m}\rangle\\ =&\sum_{lm}F^{(5)}_{lm}\langle\mathcal{W}^{n_1\mathbf{k}}_{l+1m}|\delta_{l}\mathcal{W}^{n_2\mathbf{k}}_{lm}\rangle+F^{(6)}_{l+1m}\langle\mathcal{W}^{n_1\mathbf{k}}_{lm}|\Delta_{l+1}\mathcal{W}^{n_2\mathbf{k}}_{l+1m}\rangle\end{aligned} \tag{24.16}$$

24.1.3 Radial integrals

To summarize, we need to calculate

$$\boxed{\begin{aligned}p^{\pm}_{n_1n_2;\mathbf{k}} =& \sum_{l,m}F^{(2\mp1)}_{lm}\langle\mathcal{W}^{n_1\mathbf{k}}_{l+1m\pm1}|\delta_l\mathcal{W}^{n_2\mathbf{k}}_{lm}\rangle+F^{(3\mp1)}_{l+1m\mp1}\langle\mathcal{W}^{n_1\mathbf{k}}_{lm}|\Delta_{l+1}\mathcal{W}^{n_2\mathbf{k}}_{l+1m\mp1}\rangle\\ \langle n_1|\partial z|n_2\mathbf{k}\rangle =& \sum_{lm}F^{(5)}_{lm}\langle\mathcal{W}^{n_1\mathbf{k}}_{l+1m}|\delta_l\mathcal{W}^{n_2\mathbf{k}}_{lm}\rangle+F^{(6)}_{l+1m}\langle\mathcal{W}^{n_1\mathbf{k}}_{lm}|\Delta_{l+1}\mathcal{W}^{n_2\mathbf{k}}_{l+1m}\rangle\end{aligned}} \tag{24.17}$$

Now let's give the detailed equations for radial integrals appearing in Eq. 24.17. Using Eq. 24.1, we have

$$\begin{aligned}&\langle\mathcal{W}^{n_1\mathbf{k}}_{l+1m'}|\delta_l\mathcal{W}^{n_2\mathbf{k}}_{lm}\rangle =\\ &\left[\mathcal{A}^{n_1\mathbf{k}}_{l+1m'}\right]^*\left[\mathcal{A}^{n_2\mathbf{k}}_{lm}\langle u_{l+1}|\delta_l u_l\rangle+\mathcal{B}^{n_2\mathbf{k}}_{lm}\langle u_{l+1}|\delta_l\dot{u}_l\rangle+\sum_{\nu}\mathcal{C}^{n_2\mathbf{k}}_{\nu lm}\langle u_{l+1}|\delta_l u_{\nu l}\rangle\right]\\ &+\left[\mathcal{B}^{n_1\mathbf{k}}_{l+1m'}\right]^*\left[\mathcal{A}^{n_2\mathbf{k}}_{lm}\langle\dot{u}_{l+1}|\delta_l u_l\rangle+\mathcal{B}^{n_2\mathbf{k}}_{lm}\langle\dot{u}_{l+1}|\delta_l\dot{u}_l\rangle+\sum_{\nu}\mathcal{C}^{n_2\mathbf{k}}_{\nu lm}\langle\dot{u}_{l+1}|\delta_l u_{\nu l}\rangle\right]\\ &+\sum_{\mu}\left[\mathcal{C}^{n_1\mathbf{k}}_{\mu l+1m'}\right]^*\left[\mathcal{A}^{n_2\mathbf{k}}_{lm}\langle u_{\mu l+1}|\delta_l u_l\rangle+\mathcal{B}^{n_2\mathbf{k}}_{lm}\langle u_{\mu l+1}|\delta_l\dot{u}_l\rangle+\sum_{\nu}\mathcal{C}^{n_2\mathbf{k}}_{\mu lm}\langle u_{\mu l+1}|\delta_l u_{\nu l}\rangle\right]\end{aligned} \tag{24.18}$$

and

$$\begin{aligned}&\langle\mathcal{W}^{n_1\mathbf{k}}_{lm}|\Delta_{l+1}\mathcal{W}^{n_2\mathbf{k}}_{l+1m'}\rangle =\\ &\left[\mathcal{A}^{n_1\mathbf{k}}_{lm}\right]^*\left[\mathcal{A}^{n_2\mathbf{k}}_{l+1m'}\langle u_l|\Delta_{l+1}u_{l+1}\rangle+\mathcal{B}^{n_2\mathbf{k}}_{l+1m'}\langle u_l|\Delta_{l+1}\dot{u}_{l+1}\rangle+\sum_{\nu}\mathcal{C}^{n_2\mathbf{k}}_{\nu lm}\langle u_l|\Delta_{l+1}u_{\nu l+1}\rangle\right]\\ &+\left[\mathcal{B}^{n_1\mathbf{k}}_{lm}\right]^*\left[\mathcal{A}^{n_2\mathbf{k}}_{l+1m'}\langle\dot{u}_l|\Delta_{l+1}u_{l+1}\rangle+\mathcal{B}^{n_2\mathbf{k}}_{l+1m'}\langle\dot{u}_l|\Delta_{l+1}\dot{u}_{l+1}\rangle+\sum_{\nu}\mathcal{C}^{n_2\mathbf{k}}_{\nu l+1m'}\langle\dot{u}_l|\Delta_{l+1}u_{\nu l+1}\rangle\right]\\ &+\sum_{\mu}\left[\mathcal{C}^{n_1\mathbf{k}}_{\mu lm}\right]^*\left[\mathcal{A}^{n_2\mathbf{k}}_{l+1m'}\langle u_{\mu l}|\Delta_{l+1}u_{l+1}\rangle+\mathcal{B}^{n_2\mathbf{k}}_{l+1m'}\langle u_{\mu l}|\Delta_{l+1}\dot{u}_{l+1}\rangle+\sum_{\nu}\mathcal{C}^{n_2\mathbf{k}}_{\mu l+1m'}\langle u_{\mu l}|\Delta_{l+1}u_{\nu l+1}\rangle\right]\end{aligned} \tag{24.19}$$

Finally, the MT-Sphere contribution to the $x-$, $y-$ and $z-$ components of the momentum operator can be obtained as:

$$\boxed{\begin{aligned}p^x_{n_1n_2;\mathbf{k}} =& -i\langle n_1\mathbf{k}|\partial x|n_2\mathbf{k}\rangle=-\frac{i}{2}\left(p^+_{n_1n_2;\mathbf{k}}+p^-_{n_1n_2;\mathbf{k}}\right)\\ p^y_{n_1n_2;\mathbf{k}} =& -i\langle n_1\mathbf{k}|\partial y|n_2\mathbf{k}\rangle=-\frac{1}{2}\left(p^+_{n_1n_2;\mathbf{k}}-p^-_{n_1n_2;\mathbf{k}}\right)\\ p^z_{n_1n_2,\mathbf{k}} =& -i\langle n_1\mathbf{k}|\partial z|n_2\mathbf{k}\rangle\end{aligned}} \tag{24.20}$$

24.2 Contribution from the Interstitial

In the interstitial region, the momentum matrix elements can be calculated by:

$$\mathbf{p}^{\mathbf{k}}_{n_1,n_2} = -i\langle n_1\mathbf{k}|\nabla|n_2\mathbf{k}\rangle_I \tag{24.21}$$

Expanding the eigenfunctions according to equation 8.6 we have:

$$\begin{aligned}\langle n_1\mathbf{k}|\nabla|n_2\mathbf{k}\rangle_I =& \frac{1}{\Omega}\int_I \psi^*_{n_1\mathbf{k}}(\mathbf{r})\nabla\psi_{n_2\mathbf{k}}(\mathbf{r})d^3r \\ =& \frac{1}{\Omega}\sum_{\mathbf{G},\mathbf{G}'} Z^{n_1\mathbf{k}*}_{\mathbf{G}} Z^{n_2\mathbf{k}}_{\mathbf{G}'}\int_I e^{-i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}\nabla e^{i(\mathbf{k}+\mathbf{G}')\cdot\mathbf{r}}d^3r \\ =& \frac{i}{\Omega}\sum_{\mathbf{G},\mathbf{G}'} Z^{n_1\mathbf{k}*}_{\mathbf{G}} Z^{n_2\mathbf{k}}_{\mathbf{G}'}(\mathbf{k}+\mathbf{G}')\int_I e^{i(\mathbf{G}'-\mathbf{G})\cdot\mathbf{r}}d^3r\end{aligned} \tag{24.22}$$

which using eq. 6.12 can be writen as

$$\langle n_1\mathbf{k}|\nabla|n_2\mathbf{k}\rangle_I = \frac{i}{\Omega}\sum_{\mathbf{G},\mathbf{G}'} Z^{n_1\mathbf{k}*}_{\mathbf{G}} Z^{n_2\mathbf{k}}_{\mathbf{G}'}(\mathbf{k}+\mathbf{G}')\mathcal{I}_{\mathbf{G}'-\mathbf{G}}. \tag{24.23}$$

Applying eq. 24.23 into 24.21 we have

$$\boxed{\mathbf{p}^{\mathbf{k}}_{n_1,n_2} = \frac{1}{\Omega}\sum_{\mathbf{G},\mathbf{G}'} Z^{n_1\mathbf{k}*}_{\mathbf{G}} Z^{n_2\mathbf{k}}_{\mathbf{G}'}(\mathbf{k}+\mathbf{G}')\mathcal{I}_{\mathbf{G}'-\mathbf{G}}} \tag{24.24}$$

24.3 Core states

24.3.1 Matrix elements between two core states

For the core wave functions we can follow the same steps as in section 24.1, taking into account that:

$$\langle\mathbf{r}|n\kappa m\rangle = \psi_{n\kappa m}(\mathbf{r}) = u_{nl}(r)Y_{lm}(\theta,\phi) \tag{24.25}$$

where l is determined by κ through $l = |\kappa| + \frac{1}{2}\mathrm{sgn}(\kappa) - 1)$ and a factor of $\sqrt{\frac{n_\kappa}{2l+1}}$ is absorbed into the radial function $u_{nl}(r)$. The action of the operators on the ket is:

$$\begin{aligned}(\partial x \pm i\partial y)\,\psi_{n\kappa m}(\mathbf{r}) =& \left(\frac{\partial u_{nl}(r)}{\partial r} - \frac{l}{r}u_{nl}(r)\right)F^{(2\mp1)}_{lm}Y_{l+1m\pm1}(\theta,\phi) \\ &+ \left(\frac{\partial u_{nl}(r)}{\partial r} + \frac{l+1}{r}u_{nl}(r)\right)F^{(3\mp1)}_{lm}Y_{l-1m\pm1}(\theta,\phi) \\ \equiv& F^{(2\mp1)}_{lm}\delta_l u_{nl}(r)Y_{l+1m\pm1}(\theta,\phi) + F^{(3\mp1)}_{lm}\Delta_l u_{nl}(r)Y_{l-1m\pm1}(\theta,\phi)\end{aligned} \tag{24.26}$$

and

$$\partial z\psi_{n\kappa m}(\mathbf{r}) = F^{(5)}_{lm}\delta_l u_{nl}(r)Y_{l+1m}(\theta,\phi) + F^{(6)}_{lm}\Delta_l u_{nl}(r)Y_{l-1m}(\theta,\phi) \tag{24.27}$$

Then the matrix elements are

$$\begin{aligned}&\langle n_1\kappa_1 m_1|\partial x \pm i\partial y|n_2\kappa_2 m_2\rangle \\ =&\langle u_{n_1l_1}Y_{l_1m_1}|F^{(2\mp1)}_{l_2m_2}\delta_{l_2}u_{n_2l_2}Y_{l_2+1m_2\pm1} + F^{(3\mp1)}_{l_2m_2}\Delta_{l_2}u_{n_2l_2}Y_{l_2-1m_2\pm1}\rangle \\ =&F^{(2\mp1)}_{l_2m_2}\langle u_{n_1l_1}|\delta_{l_2}u_{n_2l_2}\rangle\delta_{l_1,l_2+1}\delta_{m_1,m_2\pm1} + F^{(3\mp1)}_{l_2m_2}\langle u_{n_1l_1}|\Delta_{l_2}u_{n_2l_2}\rangle\delta_{l_1,l_2-1}\delta_{m_1,m_2\pm1}\end{aligned} \tag{24.28}$$

and

$$\begin{aligned}&\langle n_1\kappa_1 m_1|\partial z|n_2\kappa_2 m_2\rangle \\ =&\langle u_{n_1l_1}Y_{l_1m_1}|F^{(5)}_{l_2m_2}\delta_{l_2}u_{n_2l_2}Y_{l_2+1m_2} + F^{(6)}_{l_2m_2}\Delta_{l_2}u_{n_2l_2}Y_{l_2-1m_2}\rangle \\ =&F^{(5)}_{l_2m_2}\langle u_{n_1l_1}|\delta_{l_2}u_{n_2l_2}\rangle\delta_{l_1,l_2+1}\delta_{m_1,m_2} + F^{(6)}_{l_2m_2}\langle u_{n_1l_1}|\Delta_{l_2}u_{n_2l_2}\rangle\delta_{l_1,l_2-1}\delta_{m_1,m_2}.\end{aligned} \tag{24.29}$$

24.3.2 Matrix elements between a core and a valence state

Using Eq. 24.9, we have

$$\begin{aligned}\langle n_1\kappa_1 m_1|\partial x \pm i\partial y|n_2,\mathbf{k}\rangle =& \sum_{l_2m_2}\langle u_{n_1l_1}Y_{l_1m_1}|F^{(2\mp1)}_{l_2m_2}\delta_{l_2}\mathcal{W}^{n_2\mathbf{k}}_{l_2m_2}Y_{l_2+1m_2\pm1}+F^{(3\mp1)}_{l_2m_2}\Delta_{l_2}\mathcal{W}^{n_2\mathbf{k}}_{l_2m_2}Y_{l_2-1m_2\pm1}\rangle\\ =&\sum_{l_2m_2}F^{(2\mp1)}_{l_2m_2}\langle u_{n_1l_1}|\delta_{l_2}\mathcal{W}^{n_2\mathbf{k}}_{l_2m_2}\rangle\delta_{l_1,l_2+1}\delta_{m_1,m_2\pm1}+F^{(3\mp1)}_{l_2m_2}\langle u_{n_1l_1}|\Delta_{l_2}\mathcal{W}^{n_2\mathbf{k}}_{l_2m_2}\rangle\delta_{l_1,l_2-1}\delta_{m_1,m_2\pm1}\\ =&F^{(2\mp1)}_{l_1-1m_1\mp1}\langle u_{n_1l_1}|\delta_{l_1-1}\mathcal{W}^{n_2\mathbf{k}}_{l_1-1m_1\mp1}\rangle+F^{(3\mp1)}_{l_1+1m_1\mp1}\langle u_{n_1l_1}|\Delta_{l_1+1}\mathcal{W}^{n_2\mathbf{k}}_{l_1+1m_1\mp1}\rangle.\end{aligned} \tag{24.30}$$

Using Eq. 24.15, we have

$$\begin{aligned}\langle n_1\kappa_1 m_1|\partial z|n_2\mathbf{k}\rangle =&\langle u_{n_1l_1}|P^{n_2\mathbf{k}}_{l_1m_1}\rangle\\ =&F^{(5)}_{l_1-1m_1}\langle u_{n_1l_1}|\delta_{l_1-1}\mathcal{W}^{n_2\mathbf{k}}_{l_1-1m_1}\rangle+F^{(6)}_{l_1+1m_1}\langle u_{n_1l_1}|\Delta_{l_1+1}\mathcal{W}^{n_2\mathbf{k}}_{l_1+1m_1}\rangle.\end{aligned} \tag{24.31}$$

The matrix elements used in the equations above are

$$\langle u_{nl}|\delta_{l-1}\mathcal{W}^{n_2\mathbf{k}}_{l-1m'}\rangle=\mathcal{A}^{n_2\mathbf{k}}_{l-1m'}\langle u_{nl}|\delta_{l-1}u_{l-1}\rangle+\mathcal{B}^{n_2\mathbf{k}}_{l-1m'}\langle u_{nl}|\delta_{l-1}\dot{u}_{l-1}\rangle+\sum_\nu\mathcal{C}^{n_2\mathbf{k}}_{\nu l-1m'}\langle u_{nl}|\delta_{l-1}u_{\nu l-1}\rangle \tag{24.32}$$

and

$$\langle u_{nl}|\Delta_{l+1}\mathcal{W}^{n_2\mathbf{k}}_{l+1m'}\rangle=\mathcal{A}^{n_2\mathbf{k}}_{l+1m'}\langle u_{nl}|\Delta_{l+1}u_{l+1}\rangle+\mathcal{B}^{n_2\mathbf{k}}_{l+1m'}\langle u_{nl}|\Delta_{l+1}\dot{u}_{l+1}\rangle+\sum_\nu\mathcal{C}^{n_2\mathbf{k}}_{\nu l+1m'}\langle u_{nl}|\Delta_{l+1}u_{\nu l+1}\rangle \tag{24.33}$$

Chapter 25

Speeding up GW calculations

This chapter discusses various numerical techniques that can be used to speed up GW calculations.

25.1 Using static COHSEX to include static remainder in selfenergy

Following [**?**], we can use the static COHSEX approximation to the self-energy to reduce the number of unoccupied orbitals. The full GWA correlation selfenergy reads

$$\Sigma^c(\mathbf{r}_1,\mathbf{r}_2;\omega) = \frac{i}{2\pi}\int d\omega' G(\mathbf{r}_1,\mathbf{r}_2;\omega+\omega')W^c(\mathbf{r}_2,\mathbf{r}_1;\omega') \tag{25.1}$$

The corresponding static COHSEX approximation reads

$$\Sigma^{\mathrm{c-sCOHSEX}}(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{2}\delta(\mathbf{r}_1,\mathbf{r}_2)W^c(\mathbf{r}_2,\mathbf{r}_1;0) - \sum_{n\mathbf{k}}^{\mathrm{occ}} W^c(\mathbf{r}_2,\mathbf{r}_1;0)\psi_{n\mathbf{k}}(\mathbf{r}_1)\psi^*_{n\mathbf{k}}(\mathbf{r}_2). \tag{25.2}$$

One notices that the static COHSEX approximation contains a δ-function, implying a sum over complete KS eigenfunctions. It has been well-known that the convergence of the correlation selfenergy $\Sigma^c(\mathbf{r}_1,\mathbf{r}_2;\omega)$ is quite slow, which poses a critical computational challenge. It is possible to speed up the convergence with respect to the number of unoccupied states by including the following static correction

$$\Delta\Sigma^c(\mathbf{r}_1,\mathbf{r}_2) = \Sigma^{\mathrm{c-sCOHSEX}}(\mathbf{r}_1,\mathbf{r}_2) - \tilde{\Sigma}^{\mathrm{c-sCOHSEX}}(\mathbf{r}_1,\mathbf{r}_2) \tag{25.3}$$

where the second term is the static COHSEX correlation energy calculated with a finite number of unoccupied states,

$$\begin{aligned}\tilde{\Sigma}^{\mathrm{c-sCOHSEX}}(\mathbf{r}_1,\mathbf{r}_2) =& \frac{1}{2}\sum_{n\mathbf{k}}\psi_{n\mathbf{k}}(\mathbf{r}_1)\psi^*_{n\mathbf{k}}(\mathbf{r}_2)W^c(\mathbf{r}_2,\mathbf{r}_1;0) - \sum_{n\mathbf{k}}^{\mathrm{occ}} W^c(\mathbf{r}_2,\mathbf{r}_1;0)\psi_{n\mathbf{k}}(\mathbf{r}_1)\psi^*_{n\mathbf{k}}(\mathbf{r}_2)\\ =& \frac{1}{2}\sum_{n\mathbf{k}}^{\mathrm{unocc}}\psi_{n\mathbf{k}}(\mathbf{r}_1)\psi^*_{n\mathbf{k}}(\mathbf{r}_2)W^c(\mathbf{r}_2,\mathbf{r}_1;0) - \frac{1}{2}\sum_{n\mathbf{k}}^{\mathrm{occ}} W^c(\mathbf{r}_2,\mathbf{r}_1;0)\psi_{n\mathbf{k}}(\mathbf{r}_1)\psi^*_{n\mathbf{k}}(\mathbf{r}_2)\end{aligned} \tag{25.4}$$

Now combining Eqs.(25.2) and (25.4), we have

$$\Delta\Sigma^c(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{2}\delta(\mathbf{r}_1,\mathbf{r}_2)W^c(\mathbf{r}_2,\mathbf{r}_1,0) - \frac{1}{2}\sum_{n\mathbf{k}} W^c(\mathbf{r}_2,\mathbf{r}_1,0)\psi_{n\mathbf{k}}(\mathbf{r}_1)\psi^*_{n\mathbf{k}}(\mathbf{r}_2). \tag{25.5}$$

Obviouly, when the sum over unoccupied states are complete, $\Delta\Sigma^c(\mathbf{r}_1,\mathbf{r}_2)$ vanishes.

In practice, one needs the diagonal matrix elements of $\Delta\Sigma^c$ with respect to KS eigenfunctions

$$\Delta\Sigma^c_{n\mathbf{k}} = \frac{1}{2}W^{c0}_{n\mathbf{k}} - \frac{1}{2}\sum_{m\mathbf{q}}\sum_{i,j}\left[M^i_{nm}(\mathbf{k},\mathbf{q})\right]^* W^c_{ij}(\mathbf{q},0)M^j_{nm}(\mathbf{k},\mathbf{q}) \tag{25.6}$$

where

$$W^{c0}_{n\mathbf{k}} := \int d\mathbf{r}\psi^*_{n\mathbf{k}}(\mathbf{r})W^c(\mathbf{r},\mathbf{r},0)\psi_{n\mathbf{k}}(\mathbf{r}). \tag{25.7}$$

While the second term is straightforward to calculate in the current GW code, the first term requires some special treatment. Expanding $W^c(\mathbf{r},\mathbf{r},0)$ and $\psi_{n\mathbf{k}}(\mathbf{r})\psi^*_{n\mathbf{k}}(\mathbf{r})$ by the mixed basis functions, we have

$$W^{c0}_{n\mathbf{k}} = \sum_{\mathbf{q}}\sum_{i,j}\sum_{p} W^c_{ij}(\mathbf{q},0)M^p_{nn}(\mathbf{k},0)\int d\mathbf{r}\chi^{\mathbf{q}}_i(\mathbf{r})\left[\chi^{\mathbf{q}}_j(\mathbf{r})\right]^*\chi^0_p(\mathbf{r}) \tag{25.8}$$

Denoting the integral in the equation above as $\Gamma_{ij;p}$ and defining

$$T_p(\mathbf{q}) := \sum_{ij} W^c_{ij}(\mathbf{q},0)\Gamma_{ij;p} \tag{25.9}$$

we have

$$W^{c0}_{n\mathbf{k}} = \sum_{\mathbf{q}}\sum_{p} M^p_{nn}(\mathbf{k},0)T_p(\mathbf{q}) \tag{25.10}$$

25.2 Core pproximations

One can speed up the GW calculations by neglecting core states in all or some parts of GW calculations. Roughly three levels of core approximations can be defined, as controled by `core:iopcore`

i. All-electron calculation: core states are included in all calculations;

ii. Core states are included for the exchange self-energy, but neglected for the correlation part;

iii. Core states are neglected in all calculations.

25.3 Reducing the size of mixed basis set

25.4 Using symmetries

25.4.1 The LAPW basis functions

Let $\{\mathbf{T}\}$ be the set of symmetry operations of the reciprocal lattice in the three dimensional space. Then, two reciprocal vectors are symmetry related if there exists a matrix operation $\mathbf{T}_i$ such that $\mathbf{k} = \mathbf{T}_i\mathbf{k}$.

Since $\mathbf{T}_i$ is a symmetry of the lattice, for each $\mathbf{G}$ vector of the reciprocal lattice there is a vector $\mathbf{G}'$ such that $\mathbf{G} = \mathbf{T}_i\mathbf{G}$. And thus we can also write: $\mathbf{k} + \mathbf{G} = \mathbf{T}_i(\mathbf{k} + \mathbf{G})$. It is easy to show then, that the LAPW basis transforms as:

$$\phi^{\mathbf{k}}_{\mathbf{G}}(\mathbf{T}^{-1}\mathbf{r}) = \phi^{\mathbf{Tk}}_{\mathbf{TG}}(\mathbf{r}) \tag{25.11}$$

Appendix A

Mathematical Tools

A.1 Fourier series expansion of lattice periodic functions

A.1.1 Local functions

A.1.2 non-local function

We need to calculate a nonlocal function $f(\mathbf{r}_1, \mathbf{r}_2)$

$$f(\mathbf{r}_1 + \mathbf{R}, \mathbf{r}_2 + \mathbf{R}) = f(\mathbf{r}_1, \mathbf{r}_2) \tag{A.1}$$

To calculate a function of this type, we use the expansion in a complete set of Bloch functions $\{\chi_i^{\mathbf{q}}(\mathbf{r})\}$, ($\chi_i^{\mathbf{q}}(\mathbf{r} - \mathbf{R}) = e^{-i\mathbf{q}\cdot\mathbf{R}}\chi_i^{\mathbf{q}}(\mathbf{r})$) normalized to unity in the crystal volume (V)

$$\int_V d\mathbf{r}\left[\chi_i^{\mathbf{q}}(\mathbf{r})\right]^* \chi_j^{\mathbf{q}'}(\mathbf{r}) = \delta_{\mathbf{q},\mathbf{q}'}\delta_{ij} \tag{A.2}$$

Using this basis set we have

$$\begin{cases} f(\mathbf{r}_1, \mathbf{r}_2) = & \sum_{\mathbf{q}}^{BZ}\sum_{\mathbf{q}'}^{BZ}\sum_{ij}\chi_i^{\mathbf{q}}(\mathbf{r}_1) f_{ij}(\mathbf{q}, \mathbf{q}')(\chi_j^{\mathbf{q}'}(\mathbf{r}_1))^* \\ f_{ij}(\mathbf{q}, \mathbf{q}') = & \int_V\int_V (\chi_i^{\mathbf{q}}(\mathbf{r}_1))^* f(\mathbf{r}_1, \mathbf{r}_2)\chi_j^{\mathbf{q}'}(\mathbf{r}_2) d^3r_2 d^3r_1 \end{cases} \tag{A.3}$$

The matrix element $f_{ij}(\mathbf{q}, \mathbf{q}')$ can be evaluated as

$$\begin{aligned} f_{ij}(\mathbf{q}, \mathbf{q}') =& \int_V\int_V (\chi_i^{\mathbf{q}}(\mathbf{r}_1))^* f(\mathbf{r}_1, \mathbf{r}_2)\chi_j^{\mathbf{q}'}(\mathbf{r}_2) d^3r_2 d^3r_1 \\ =& \sum_{\mathbf{R},\mathbf{R}'}\int_\Omega\int_\Omega (\chi_i^{\mathbf{q}}(\mathbf{r}_1 - \mathbf{R}))^* f(\mathbf{r}_1 - \mathbf{R}, \mathbf{r}_2 - \mathbf{R} - \mathbf{R}')\chi_j^{\mathbf{q}'}(\mathbf{r}_2 - \mathbf{R} - \mathbf{R}') d^3r_2 d^3r_1 \\ =& \sum_{\mathbf{R}}\int_\Omega\sum_{\mathbf{R}'}\int_\Omega e^{i\mathbf{q}\cdot\mathbf{R}}(\chi_i^{\mathbf{q}}(\mathbf{r}_1))^* f(\mathbf{r}_1, \mathbf{r}_2 - \mathbf{R}')e^{-i\mathbf{q}'\cdot\mathbf{R}}e^{-i\mathbf{q}'\cdot\mathbf{R}'}\chi_j^{\mathbf{q}'}(\mathbf{r}_2) d^3r_2 d^3r_1 \\ =& \sum_{\mathbf{R}} e^{i(\mathbf{q}-\mathbf{q}')\cdot\mathbf{R}}\int_\Omega\sum_{\mathbf{R}'}\int_\Omega (\chi_i^{\mathbf{q}}(\mathbf{r}_1))^* f(\mathbf{r}_1, \mathbf{r}_2 - \mathbf{R}')e^{-i\mathbf{q}'\cdot\mathbf{R}'}\chi_j^{\mathbf{q}'}(\mathbf{r}_2) d^3r_2 d^3r_1 \\ =& N_c\delta_{\mathbf{q},\mathbf{q}'}\int_\Omega\int_\Omega (\chi_i^{\mathbf{q}}(\mathbf{r}_1))^*\sum_{\mathbf{R}'} f(\mathbf{r}_1, \mathbf{r}_2 - \mathbf{R}')e^{-i\mathbf{q}\cdot\mathbf{R}'}\chi_j^{\mathbf{q}}(\mathbf{r}_2) d^3r_2 d^3r_1 \\ \equiv& \delta_{\mathbf{q},\mathbf{q}'} f_{ij}(\mathbf{q}) \end{aligned} \tag{A.4}$$

where we have made use of the closure relation for the Bravais lattice:

$$\sum_{\mathbf{R}} e^{-i(\mathbf{q}-\mathbf{q}')\cdot\mathbf{R}} = N_c\delta_{\mathbf{q},\mathbf{q}'} \tag{A.5}$$

We have redined the matrix elements

$$\begin{aligned} f_{ij}(\mathbf{q}) \equiv& N_c\int_\Omega\int_\Omega (\chi_i^{\mathbf{q}}(\mathbf{r}_1))^*\sum_{\mathbf{R}'} f(\mathbf{r}_1, \mathbf{r}_2 - \mathbf{R}')e^{-i\mathbf{q}\cdot\mathbf{R}'}\chi_j^{\mathbf{q}}(\mathbf{r}_2) d^3r_2 d^3r_1 \\ =& \int_V\int_V (\chi_i^{\mathbf{q}}(\mathbf{r}_1))^* f(\mathbf{r}_1, \mathbf{r}_2)\chi_j^{\mathbf{q}'}(\mathbf{r}_2) d^3r_2 d^3r_1 \end{aligned} \tag{A.6}$$

Thus, the expansion of equation A.3 is writen as

$$f(\mathbf{r}_1,\mathbf{r}_2) = \sum_{\mathbf{q}}^{BZ}\sum_{ij}\chi_i^{\mathbf{q}}(\mathbf{r}_1)f_{ij}(\mathbf{q})(\chi_j^{\mathbf{q}}(\mathbf{r}_2))^* \tag{A.7}$$

Using the Ω-normalized basis functions,

$$\begin{aligned} f_{ij}(\mathbf{q}) &\equiv \int_\Omega\int_\Omega (\tilde{\chi}_i^{\mathbf{q}}(\mathbf{r}_1))^* \sum_{\mathbf{R}'} f(\mathbf{r}_1,\mathbf{r}_2-\mathbf{R}')e^{-i\mathbf{q}\cdot\mathbf{R}'}\tilde{\chi}_j^{\mathbf{q}}(\mathbf{r}_2)d^3r_2d^3r_1 \\ f(\mathbf{r},\mathbf{r}') &= N_c^{-1}\sum_{\mathbf{q}}^{BZ}\sum_{ij}\tilde{\chi}_i^{\mathbf{q}}(\mathbf{r}_1)f_{ij}(\mathbf{q})\left[\tilde{\chi}_j^{\mathbf{q}}(\mathbf{r}_2)\right]^* \end{aligned} \tag{A.8}$$

If we have a product of operators, say:

$$h(\mathbf{r}_1,\mathbf{r}_2) = \int_V f(\mathbf{r}_1,\mathbf{r}_3)g(\mathbf{r}_3,\mathbf{r}_2)d^3r_3 \tag{A.9}$$

Then, according to Eq. A.7 the expansion of h in the set of functions $\{\chi_i^{\mathbf{q}}(\mathbf{r})\}$ is:

$$\begin{aligned} h_{ij}(\mathbf{q}) &= \int_V\int_V \left[\chi_i^{\mathbf{q}}(\mathbf{r}_1)\right]^* h(\mathbf{r}_1,\mathbf{r}_2)\chi_j^{\mathbf{q}}(\mathbf{r}_2)d^3r_2d^3r_1 \\ &= \int_V\int_V \left[\chi_i^{\mathbf{q}}(\mathbf{r}_1)\right]^* \left(\int_V f(\mathbf{r}_1,\mathbf{r}_3)g(\mathbf{r}_3,\mathbf{r}_2)d^3r_3\right)\chi_j^{\mathbf{q}}(\mathbf{r}_2)d^3r_2d^3r_1 \end{aligned} \tag{A.10}$$

We can now use the second line of equation A.7 for f and g and the orthogonality of the basis to get:

$$\begin{aligned} h_{ij}(\mathbf{q}) &= \int_V\int_V \left[\chi_i^{\mathbf{q}}(\mathbf{r}_1)\right]^* \left(\int_V f(\mathbf{r}_1,\mathbf{r}_3)g(\mathbf{r}_3,\mathbf{r}_2)d^3r_3\right)\chi_j^{\mathbf{q}}(\mathbf{r}_2)d^3r_2d^3r_1 \\ &= \int_V\int_V \left[\chi_i^{\mathbf{q}}(\mathbf{r}_1)\right]^* \left(\int_V \sum_{\mathbf{q}_1}^{BZ}\sum_{lm}\chi_l^{\mathbf{q}_1}(\mathbf{r}_1)f_{lm}(\mathbf{q}_1)\left[\chi_m^{\mathbf{q}_1}(\mathbf{r}_3)\right]^*\times \right. \\ &\qquad \left. \sum_{\mathbf{q}_2}^{BZ}\sum_{np}\chi_n^{\mathbf{q}_2}(\mathbf{r}_3)g_{np}(\mathbf{q}_2)\left[\chi_p^{\mathbf{q}_2}(\mathbf{r}_2)\right]^* d^3r_3\right)\chi_j^{\mathbf{q}}(\mathbf{r}_2)d^3r_2d^3r_1 \\ &= \sum_{\mathbf{q}_1}^{BZ}\sum_{\mathbf{q}_2}^{BZ}\sum_{lm}\sum_{np}\left(\int_V \left[\chi_i^{\mathbf{q}}(\mathbf{r}_1)\right]^*\chi_l^{\mathbf{q}_1}(\mathbf{r}_1)d^3r_1\right)f_{lm}(\mathbf{q}_1)\times \\ &\qquad \left(\int_V \left[\chi_m^{\mathbf{q}_1}(\mathbf{r}_3)\right]^*\chi_n^{\mathbf{q}_2}(\mathbf{r}_3)d^3r_3\right)g_{np}(\mathbf{q}_2)\left(\int_V \left[\chi_p^{\mathbf{q}_2}(\mathbf{r}_2)\right]^*\chi_j^{\mathbf{q}}(\mathbf{r}_2)d^3r_2\right) \\ &= \sum_{\mathbf{q}_1}^{BZ}\sum_{\mathbf{q}_2}^{BZ}\sum_{lm}\sum_{np}\delta(\mathbf{q},\mathbf{q}_1)\delta_{il}f_{lm}(\mathbf{q}_1)\delta(\mathbf{q}_1,\mathbf{q}_2)\delta_{mn}g_{np}(\mathbf{q}_2)\delta(\mathbf{q}_2,\mathbf{q})\delta_{pj} \end{aligned} \tag{A.11}$$

And we arrive to the expected expression:

$$\boxed{h_{ij}(\mathbf{q}) = \sum_l f_{il}(\mathbf{q})g_{lj}(\mathbf{q})} \tag{A.12}$$

A.2 Brillouin-zone integrations of singular functions

Consider the Brillouin-Zone integration of a function that diverges at the Gamma point ($\mathbf{q}=0$).

$$\begin{aligned} \Sigma &= N_c^{-1}\sum_{\mathbf{q}}^{BZ}\Upsilon(\mathbf{q}) \\ &= \frac{\Omega}{(2\pi)^3}\int_{\mathrm{BZ}} d\mathbf{q}\Upsilon(\mathbf{q}) \end{aligned} \tag{A.13}$$

In the $\mathbf{q}\to 0$ limit we can separate the singular terms as:

$$\Upsilon(\mathbf{q}\to 0) = \frac{\Upsilon^{s2}}{q^2} + \frac{\Upsilon^{s1}}{q} + \tilde{\Upsilon}(q) \tag{A.14}$$

where $\tilde{\Upsilon}(q)$ is the regularized form of $\Upsilon(\mathbf{q})$.

The singularity at the Γ point appearing in Eq. A.14 is integrable, but a direct numerical integration will converge very slowly. Following [40], we introduces two auxillary functions which shows similar singularity

$$\begin{aligned} F_1(\mathbf{q}) =& \sum_{\mathbf{G}} \frac{e^{-\alpha|\mathbf{q}+\mathbf{G}|}}{|\mathbf{q}+\mathbf{G}|} \\ F_2(\mathbf{q}) =& \sum_{\mathbf{G}} \frac{e^{-\alpha|\mathbf{q}+\mathbf{G}|^2}}{|\mathbf{q}+\mathbf{G}|^2} \end{aligned} \tag{A.15}$$

One can see that

$$\begin{aligned} F_1(\mathbf{q}\to 0) =& \frac{1}{q} + \tilde{F}_1(\mathbf{q}) \\ F_2(\mathbf{q}\to 0) =& \frac{1}{q^2} + \tilde{F}_2(\mathbf{q}) \end{aligned} \tag{A.16}$$

where $\tilde{F}_1(\mathbf{q})$ and $\tilde{F}_2(\mathbf{q})$ are regularized from of $F_1(\mathbf{q})$ and $F_2(\mathbf{q})$, respectively, obtained by neglecting $\mathbf{G}$=0 in the summation in the right hand side. Now the integration (or summation) of $\Upsilon(\mathbf{q})$ over $\mathbf{q}$ can be written as

$$\begin{aligned} \Sigma &= N_c^{-1}\sum_{\mathbf{q}} \Upsilon(\mathbf{q}) \\ &= N_c^{-1}\sum_{\mathbf{q}} \left[\Upsilon(\mathbf{q}) - \Upsilon^{s1}F_1(\mathbf{q}) - \Upsilon^{s2}F_2(\mathbf{q})\right] + N_c^{-1}\Upsilon^{s1}\sum_{\mathbf{q}} F_1(\mathbf{q}) + N_c^{-1}\Upsilon^{s2}\sum_{\mathbf{q}} F_2(\mathbf{q}) \\ &= N_c^{-1}\sum_{\mathbf{q}} \left[\tilde{\Upsilon}(\mathbf{q}) - \Upsilon^{s1}\tilde{F}_1(\mathbf{q}) - \Upsilon^{s2}\tilde{F}_2(\mathbf{q})\right] + \Upsilon^{s2}I_{s2} + \Upsilon^{s1}I_{s1} \\ &= N_c^{-1}\sum_{\mathbf{q}} \tilde{\Upsilon}(\mathbf{q}) + \Upsilon^{s1}\left[I_{s1} - N_c^{-1}\sum_{\mathbf{q}} \tilde{F}_1(\mathbf{q})\right] + \Upsilon^{s2}\left[I_{s2} - N_c^{-1}\sum_{\mathbf{q}} \tilde{F}_2(\mathbf{q})\right] \\ &= C_{s1}\Upsilon^{s1} + C_{s2}\Upsilon^{s2} + N_c^{-1}\sum_{\mathbf{q}} \tilde{\Upsilon}(\mathbf{q}) \end{aligned} \tag{A.17}$$

with

$$\begin{aligned} I^{s1} \equiv& N_c^{-1}\sum_{\mathbf{q}} F_1(\mathbf{q}) \\ =& N_c^{-1}\sum_{\mathbf{q}}\sum_{\mathbf{G}} \frac{e^{-\alpha|\mathbf{q}+\mathbf{G}|}}{|\mathbf{q}+\mathbf{G}|} = \frac{\Omega}{(2\pi)^3}\int d\mathbf{q}\sum_{\mathbf{G}} \frac{e^{-\alpha|\mathbf{q}+\mathbf{G}|}}{|\mathbf{q}+\mathbf{G}|} = \frac{\Omega}{(2\pi)^3}\int d\mathbf{Q}\frac{e^{-\alpha|\mathbf{Q}|}}{|\mathbf{Q}|} \\ =& \frac{\Omega}{(2\pi)^2\alpha} \\ I^{s2} \equiv& N_c^{-1}\sum_{\mathbf{q}} F_2(\mathbf{q}) \\ =& N_c^{-1}\sum_{\mathbf{q}}\sum_{\mathbf{G}} \frac{e^{-\alpha|\mathbf{q}+\mathbf{G}|^2}}{|\mathbf{q}+\mathbf{G}|^2} = \frac{\Omega}{(2\pi)^3}\int d\mathbf{q}\sum_{\mathbf{G}} \frac{e^{-\alpha|\mathbf{q}+\mathbf{G}|^2}}{|\mathbf{q}+\mathbf{G}|^2} = \frac{\Omega}{(2\pi)^3}\int d\mathbf{Q}\frac{e^{-\alpha|\mathbf{Q}|^2}}{|\mathbf{Q}|^2} \\ =& \frac{\Omega}{(2\pi)^2}\sqrt{\frac{\pi}{\alpha}} \end{aligned} \tag{A.18}$$

and

$$\begin{aligned} C_{s1} &= I_{s1} - N_c^{-1}\sum_{\mathbf{q}} \tilde{F}_1(\mathbf{q}) \\ C_{s2} &= I_{s2} - N_c^{-1}\sum_{\mathbf{q}} \tilde{F}_2(\mathbf{q}) \end{aligned} \tag{A.19}$$

α is a parameter chosen so that the width of the Gaussian is comparable to the Brillouin zone diameter. To obtain the parameter α we require $\alpha R_{BZ} = 1$, using $\frac{4\pi}{3}R_{BZ}^3 = \frac{(2\pi)^3}{\Omega}$ we get:

$$\alpha = \left(\frac{\Omega}{6\pi^2}\right)^{\frac{1}{3}} \tag{A.20}$$

Taking the BZ integration weight into account explicitly, we have

$$\begin{aligned}\Sigma &= N_c^{-1}\sum_{\mathbf{q}}\Upsilon(\mathbf{q}) \\ &= C_{s1}\Upsilon^{s1} + C_{s2}\Upsilon^{s2} + \sum_i w_i\tilde{\Upsilon}(\mathbf{q}_i)\end{aligned} \tag{A.21}$$

A.3 The integration in frequency

In this section we show how to perform the integration of the following form **??**:

$$X = \frac{1}{\pi}\int_0^\infty W(i\omega')\frac{\omega_\epsilon}{\omega_\epsilon^2+\omega'^2}d\omega' \tag{A.22}$$

where $\omega_\epsilon := \epsilon_{n\mathbf{k}-\mathbf{q}} - i\omega$.

A.3.1 Remove the peak at $\omega' = \omega$

The integrand in Eq. A.22 is very peaked around $\omega' = \omega$ when $\epsilon_{n\mathbf{k}-\mathbf{q}}$ is small. To handle this problem one can add and subtract the term

$$\frac{1}{\pi}\int_0^\infty W(i\omega)\frac{\omega_\epsilon}{\omega_\epsilon^2+\omega'^2}d\omega' \quad = \frac{1}{2}\mathrm{sgn}(\epsilon_{n'\mathbf{k}-\mathbf{q}})W(i\omega) \tag{A.23}$$

Then we have:

$$X = \frac{1}{\pi}\int_0^\infty \left[W(i\omega') - W(i\omega)\right]\frac{\omega_\epsilon}{\omega_\epsilon^2+\omega'^2}d\omega' - \frac{1}{2}\mathrm{sgn}(\epsilon_{n'\mathbf{k}+\mathbf{q}})W(i\omega) \tag{A.24}$$

The integrand is now smooth and a Gaussian quadrature may be used.

A more general treatment (following Ref. [7] is to add and substract the term

$$\frac{1}{\pi}\int_0^\infty W(i\omega)e^{-\alpha^2\omega'^2}\frac{\omega_\epsilon}{\omega_\epsilon^2+\omega'^2}d\omega' \quad = W(i\omega)\frac{\pi}{2}e^{\alpha^2\omega_\epsilon^2}\mathrm{erfc}\left[\alpha\omega_\epsilon\right] \tag{A.25}$$

so that

$$X = \frac{1}{\pi}\int_0^\infty \left[W(i\omega') - W(i\omega)e^{-\alpha^2\omega'^2}\right]\frac{\omega_\epsilon}{\omega_\epsilon^2+\omega'^2}d\omega' - W(i\omega)\frac{\pi}{2}e^{\alpha^2\omega_\epsilon^2}\mathrm{erfc}\left[\alpha\omega_\epsilon\right] \tag{A.26}$$

Now the previous scheme is just a special case of $\alpha = 0$

A.3.2 Gaussian quadrature

To solve the semi-infinite integral of eq. A.26 which has the form:

$$X = \int_0^\infty f(\omega)d\omega \tag{A.27}$$

we use the Gaussian quadrature.

A.3.2.1 Gauss-Legendre quadrature

To transform Eq. A.27 into the standard Gauss-Legendre form, we make the transform $\omega = \frac{x}{1-x}$, so that we have

$$\begin{aligned}X &= \int_0^1 f(\frac{x}{1-x})\frac{1}{(1-x)^2}dx \\ &= \sum_i w_i^{\mathrm{GL}}\frac{1}{(1-x_i)^2}f(\frac{x_i}{1-x_i}) \\ &= \sum_i w_i f(\omega_i)\end{aligned} \tag{A.28}$$

with $w_i := w_i^{\mathrm{GL}}\frac{1}{(1-x_i)^2}$ and $\omega_i := \frac{x_i}{1-x_i}$.

A.3.2.2 Double Gauss-Legendre quadrature

In this scheme, we split the semi-infinite integral into (following [24])

$$X = X_1 + X_2 \tag{A.29a}$$
$$X_1 = \int_0^{\omega_0} f(\omega)d\omega \tag{A.29b}$$
$$X_2 = \int_{\omega_0}^{\infty} f(\omega)d\omega, \tag{A.29c}$$

for X_1 we make the change of variables $x = 2\omega/\omega_0 - 1$ and thus $d\omega = \frac{\omega_0}{2}dx$. Then we have:

$$X_1 = \int_0^{\omega_0} f(\omega)d\omega = \frac{\omega_0}{2}\int_{-1}^{1} f[(x+1)\omega_0/2]dx \tag{A.30}$$

which can be solved by standard Gauss-Legendre quadrature. For X_2 we make the change of variables $x = 2\omega_0/\omega - 1$ and thus $d\omega = -\frac{2\omega_0}{(x+1)^2}dx$. Then we have:

$$X_2 = \int_{\omega_0}^{\infty} f(\omega)d\omega = 2\omega_0\int_{-1}^{1} f[\frac{2\omega_0}{x+1}](x+1)^{-2}dx \tag{A.31}$$

which can also be solved by standard Gauss-Legendre quadrature.

A.3.2.3 Generalized Gauss-Laguerre quadrature

The generalized Gauss-Laguerre quadrature approximates the semi-infinite integral of a function in the following way:

$$\int_0^{\infty} e^{-x}x^{\kappa}f(x)dx \cong \sum_{i=1}^{n} w_i f(x_i) \tag{A.32}$$

with $\kappa > -1$. The values of the weights $\{w_i\}$ and abscisas $\{x_i\}$ can be determined using the subroutine `gaussq.f`.

A.4 Matrix computation

A.4.1 Block-wise inversion

For a matrix with the following block form

A.5 Spherical Harmonics

- Definition: In the Condon Shortley convention the spherical harmonics are defined as

$$Y_{lm}(\theta,\phi) \equiv (-1)^m\sqrt{\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}}P_l^m(\cos\theta)e^{im\phi} \tag{A.33}$$

  where $P_l^m(x)$ is the corresponding Legendre-polynomial (See [1]).

- Recurrence relations:

$$Y_{00}(\theta,\phi) = \sqrt{\frac{1}{4\pi}} \tag{A.34a}$$

$$Y_{10}(\theta,\phi) = \sqrt{\frac{3}{4\pi}} cos(\theta) \tag{A.34b}$$

$$Y_{11}(\theta,\phi) = -\sqrt{\frac{3}{8\pi}} sin(\theta) e^{i\phi} \tag{A.34c}$$

$$Y_{1-1}(\theta,\phi) = -Y_{11}(\theta,\phi) \tag{A.34d}$$

$$Y_{ll}(\theta,\phi) = -\sqrt{\frac{2l+1}{2l}} sin(\theta) e^{i\phi} Y_{l-1,l-1} \tag{A.34e}$$

$$Y_{lm}(\theta,\phi) = \sqrt{\frac{(2l-1)(2l+1)}{(l-m)(l+m)}} cos(\theta) Y_{l-1m}(\theta,\phi) - \sqrt{\frac{(l-1+m)(l-1-m)(2l+1)}{(2l-3)(l-m)(l+m)}} Y_{l-2,m}(\theta,\phi) \tag{A.34f}$$

Equations A.34 are used in subroutine `ylm.f90`

- Conjugation:

$$Y_{l,-m}(\theta,\phi) = (-1)^m Y^*_{l,m}(\theta,\phi) \tag{A.35}$$

- Inversion:

$$Y_{l,m}(\hat{r}) = (-1)^l Y_{l,m}(-\hat{r}) \tag{A.36}$$

- Other relations:

$$e^{i\phi} \sin\theta Y_{lm}(\theta,\phi) = F^{(1)} Y_{l+1,m+1}(\theta,\phi) + F^{(2)} Y_{l-1,m+1}(\theta,\phi) \tag{A.37a}$$

$$e^{-i\phi} \sin\theta Y_{lm}(\theta,\phi) = F^{(3)} Y_{l+1,m-1}(\theta,\phi) + F^{(4)} Y_{l-1,m-1}(\theta,\phi) \tag{A.37b}$$

$$\cos\theta Y_{lm}(\theta,\phi) = F^{(5)} Y_{l+1,m}(\theta,\phi) + F^{(6)} Y_{l-1,m}(\theta,\phi) \tag{A.37c}$$

$$e^{i\phi}\left(\cos\theta\frac{\partial}{\partial\theta} + \frac{i}{\sin\theta}\frac{\partial}{\partial\theta}\right) Y_{lm}(\theta,\phi) = -lF^{(1)} Y_{l+1,m+1}(\theta,\phi) + (l+1)F^{(2)} Y_{l-1,m+1}(\theta,\phi) \tag{A.37d}$$

$$e^{-i\phi}\left(\cos\theta\frac{\partial}{\partial\theta} - \frac{i}{\sin\theta}\frac{\partial}{\partial\theta}\right) Y_{lm}(\theta,\phi) = -lF^{(3)} Y_{l+1,m-1}(\theta,\phi) + (l+1)F^{(4)} Y_{l-1,m-1}(\theta,\phi) \tag{A.37e}$$

$$-\sin\theta\frac{\partial}{\partial\theta} Y_{lm}(\theta,\phi) = -lF^{(5)} Y_{l+1,m}(\theta,\phi) + (l+1)F^{(6)} Y_{l-1,m}(\theta,\phi) \tag{A.37f}$$

where:

$$F^{(1)}_{l,m} = -\sqrt{\frac{(l+m+1)(l+m+2)}{2l+1)(2l+3)}} \tag{A.38a}$$

$$F^{(2)}_{l,m} = \sqrt{\frac{(l-m)(l-m-1)}{2l-1)(2l+1)}} \tag{A.38b}$$

$$F^{(3)}_{l,m} = \sqrt{\frac{(l-m+1)(l-m+2)}{2l+1)(2l+3)}} \tag{A.38c}$$

$$F^{(4)}_{l,m} = -\sqrt{\frac{(l+m)(l+m-1)}{2l-1)(2l+1)}} \tag{A.38d}$$

$$F^{(5)}_{l,m} = \sqrt{\frac{(l-m+1)(l+m+1)}{2l+1)(2l+3)}} \tag{A.38e}$$

$$F^{(6)}_{l,m} = \sqrt{\frac{(l-m)(l+m)}{2l-1)(2l+1)}} \tag{A.38f}$$

- Gaunt coefficients:

$$\mathcal{G}^{LM}_{ll',mm'} = \int Y^*_{LM}(\hat{r}) Y_{lm}(\hat{r}) Y_{l'm'}(\hat{r}) d\hat{r} \tag{A.39}$$

A.5.1 Expansion of Plane waves by spherical harmonics

Rayleigh expansion

$$\begin{aligned} e^{i\vec{g}\cdot\vec{r}} =& 4\pi \sum_{\lambda=0}^{\infty} \sum_{\mu=-\lambda}^{+\lambda} i^\lambda j_\lambda(gr) Y^*_{\lambda\mu}(T^{-1}\hat{g}) Y_{\lambda\mu}(T^{-1}\hat{r}) \\ =& 4\pi \sum_{\lambda=0}^{\infty} \sum_{\mu=-\lambda}^{+\lambda} i^\lambda j_\lambda(gr) Y_{\lambda\mu}(T^{-1}\hat{g}) Y^*_{\lambda\mu}(T^{-1}\hat{r}) \end{aligned} \tag{A.40}$$

A.6 Lattice Harmonics

A.6.1 Normalized real spherical harmonics

- Definition:

$$\Lambda_{lm\pm}(\theta,\phi) \equiv \sqrt{\frac{2l+1}{2\pi(1+\delta_{m0})}\frac{(l-m)!}{(l+m)!}} P^m_l(\cos\theta) \begin{cases} \cos m\phi \\ \sin m\phi \end{cases} \quad ; \; m = 0, 1, ..., l. \tag{A.41}$$

- Relation to Spherical Harmonics:

$$\begin{aligned} \Lambda_{l0}(\theta,\phi) =& Y_{l0}(\theta,\phi) \\ \Lambda_{lm\pm}(\theta,\phi) =& \begin{cases} \frac{(-1)^m Y_{lm}(\theta,\phi) + Y_{l-m}(\theta,\phi)}{\sqrt{2}} \\ \frac{i[(-1)^{m+1} Y_{lm}(\theta,\phi) + Y_{l-m}(\theta,\phi)]}{\sqrt{2}} \end{cases} \end{aligned} \tag{A.42}$$

Using equation A.35 it can also be written as:

$$\begin{aligned} \Lambda_{l0}(\theta,\phi) =& Y_{l0}(\theta,\phi) \\ \Lambda_{lm\pm}(\theta,\phi) =& (-1)^m \begin{cases} \frac{Y_{lm}(\theta,\phi) + Y^*_{lm}(\theta,\phi)}{\sqrt{2}} \\ i\frac{[-Y_{lm}(\theta,\phi) + Y^*_{lm}(\theta,\phi)]}{\sqrt{2}} \end{cases} \end{aligned} \tag{A.43}$$

or

$$\begin{aligned} \Lambda_{l0}(\theta,\phi) =& Y_{l0}(\theta,\phi) \\ \Lambda_{lm\pm}(\theta,\phi) =& \sqrt{2}(-1)^m \begin{cases} \Re[Y_{lm}(\theta,\phi)] \\ \Im[Y_{lm}(\theta,\phi)]) \end{cases} \end{aligned} \tag{A.44}$$

A.6.2 Normalized cubic harmonics

- Definition (taken from [31]):

$$K_{lj}(\theta,\phi) = \sum_m k^l_{mj} \Lambda_{lm}(\theta,\phi) \tag{A.45}$$

- Cubic conversion factors (Table A.1)

Table A.1: Cubic conversion factors k^l_{mj} up to tenth order [31]

Even		m					
l	j	0	2+	4+	6+	8+	10+
0	1	1					
4	1	$\frac{1}{2}\sqrt{\frac{7}{3}}$		$\frac{1}{2}\sqrt{\frac{5}{3}}$			
6	1	$\frac{1}{2}\sqrt{\frac{1}{2}}$		$-\frac{1}{2}\sqrt{\frac{7}{2}}$			
6	2		$\frac{1}{4}\sqrt{11}$		$\frac{1}{4}\sqrt{5}$		
8	1	$\frac{1}{8}\sqrt{33}$		$\frac{1}{4}\sqrt{\frac{7}{3}}$		$\frac{1}{8}\sqrt{\frac{65}{3}}$	
10	1	$\frac{1}{8}\sqrt{\frac{65}{6}}$		$-\frac{1}{4}\sqrt{\frac{11}{2}}$		$-\frac{1}{8}\sqrt{\frac{187}{6}}$	
10	2		$\frac{1}{8}\sqrt{\frac{247}{6}}$		$\frac{1}{16}\sqrt{\frac{19}{3}}$		$-\frac{1}{16}\sqrt{85}$

Odd					
		2-	4-	6-	8-
3	1	1			
7	1	$\frac{1}{2}\sqrt{\frac{13}{6}}$		$\frac{1}{2}\sqrt{\frac{11}{6}}$	
9	1	$\frac{1}{4}\sqrt{3}$		$-\frac{1}{4}\sqrt{13}$	
9	2		$\frac{1}{2}\sqrt{\frac{17}{6}}$		$-\frac{1}{2}\sqrt{\frac{7}{6}}$

- Relation to spherical harmonics (up to tenth order):

$$K_{01} = Y_{00} \tag{A.46a}$$
$$K_{31} = \frac{i}{2}\left(-Y_{32} + Y_{3-2}\right) \tag{A.46b}$$
$$K_{41} = \frac{1}{2}\sqrt{\frac{7}{3}}Y_{40} + \frac{1}{2}\sqrt{\frac{5}{6}}\left(Y_{44} + Y_{4-4}\right) \tag{A.46c}$$
$$K_{61} = \frac{1}{2}\sqrt{\frac{1}{2}}Y_{60} - \frac{1}{4}\sqrt{7}\left(Y_{64} + Y_{6-4}\right) \tag{A.46d}$$
$$K_{62} = \frac{1}{4}\sqrt{\frac{11}{2}}\left(Y_{62} + Y_{6-2}\right) + \frac{1}{4}\sqrt{\frac{5}{2}}\left(Y_{66} + Y_{6-6}\right) \tag{A.46e}$$
$$K_{71} = \frac{i}{4}\left[\sqrt{\frac{13}{3}}\left(-Y_{72} + Y_{7-2}\right) + \sqrt{\frac{11}{3}}\left(-Y_{76} + Y_{7-6}\right)\right] \tag{A.46f}$$
$$K_{81} = \frac{1}{8}\sqrt{33}Y_{80} + \frac{1}{4}\sqrt{\frac{7}{6}}\left(Y_{84} + Y_{8-4}\right) + \frac{1}{8}\sqrt{\frac{65}{6}}\left(Y_{88} + Y_{8-8}\right) \tag{A.46g}$$
$$K_{91} = \frac{i}{4}\left[\sqrt{\frac{3}{2}}\left(-Y_{92} + Y_{9-2}\right) + \sqrt{\frac{13}{2}}\left(-Y_{96} + Y_{9-6}\right)\right] \tag{A.46h}$$
$$K_{92} = \frac{i}{4}\left[\sqrt{\frac{17}{3}}\left(-Y_{94} + Y_{9-4}\right) + \sqrt{\frac{7}{3}}\left(-Y_{98} + Y_{9-8}\right)\right] \tag{A.46i}$$
$$K_{101} = \frac{1}{8}\sqrt{\frac{65}{6}}Y_{100} - \frac{1}{8}\sqrt{11}\left(Y_{104} + Y_{10-4}\right) - \frac{1}{16}\sqrt{\frac{187}{3}}\left(Y_{108} + Y_{10-8}\right) \tag{A.46j}$$
$$K_{102} = \frac{1}{16}\sqrt{\frac{247}{3}}\left(Y_{102} + Y_{10-2}\right) + \frac{1}{16}\sqrt{\frac{19}{6}}\left(Y_{106} + Y_{10-6}\right) - \frac{1}{16}\sqrt{\frac{85}{2}}\left(Y_{1010} + Y_{10-10}\right) \tag{A.46k}$$

we can also write:

$$K_{lj}(\theta,\phi) = \sum_{m=0}^{l} \kappa_{mj}^{l}\left[(-1)^{l} Y_{lm}(\theta,\phi) + Y_{l-m}(\theta,\phi)\right] \tag{A.47}$$

with (Table A.2):

Table A.2: Cubic conversion factors κ^l_{mj} up to tenth order

		m					
l	j	0	2+	4+	6+	8+	10+
0	1	1					
3	1		$\frac{i}{\sqrt{2}}$				
4	1	$\frac{1}{2}\sqrt{\frac{7}{3}}$		$\frac{1}{2}\sqrt{\frac{5}{6}}$			
6	1	$\frac{1}{2}\sqrt{\frac{1}{2}}$		$-\frac{1}{4}\sqrt{7}$			
6	2		$\frac{1}{4}\sqrt{\frac{11}{2}}$		$\frac{1}{4}\sqrt{\frac{5}{2}}$		
7	1		$\frac{i}{4}\sqrt{\frac{13}{3}}$		$\frac{i}{4}\sqrt{\frac{11}{3}}$		
8	1	$\frac{1}{8}\sqrt{33}$		$\frac{1}{4}\sqrt{\frac{7}{6}}$		$\frac{1}{8}\sqrt{\frac{65}{6}}$	
9	1		$\frac{i}{4}\sqrt{\frac{3}{2}}$		$-\frac{i}{4}\sqrt{\frac{13}{2}}$		
9	2			$\frac{i}{4}\sqrt{\frac{17}{3}}$		$-\frac{i}{4}\sqrt{\frac{7}{3}}$	
10	1	$\frac{1}{8}\sqrt{\frac{65}{6}}$		$-\frac{1}{8}\sqrt{11}$		$-\frac{1}{16}\sqrt{\frac{187}{3}}$	
10	2		$\frac{1}{16}\sqrt{\frac{247}{3}}$		$\frac{1}{16}\sqrt{\frac{19}{6}}$		$-\frac{1}{16}\sqrt{\frac{85}{2}}$

A.6.3 Stars

Taken from [54]

- Definition: The stars, $\Phi_s(\vec{r})$, are defined by:

$$\begin{aligned}\Phi_s(\vec{r}) &\equiv \frac{1}{N_s}\sum_{\mathbb{R}} e^{i\mathbb{R}\vec{G}\cdot(\vec{r}-\vec{t}_{\mathbb{R}})} \\ &\equiv \frac{1}{m_s}\sum_{m}\varphi_m e^{i\mathbb{R}_m\vec{G}\cdot\vec{r}}.\end{aligned} \tag{A.48}$$

  where $\mathbb{R}$ are the rotational components of the space group operations, $\{\mathbb{R}|t\}$, N_s is the number of space group operations and m_s is the number of independent planewaves in the star. φ_m are the phase factors defined in A.50.

- Orthogonality:

$$\frac{1}{\Omega}\int \Phi_s^*(\vec{r})\Phi_{s'}(\vec{r})d^3\vec{r} = \frac{1}{m_s}\delta_{ss'} \tag{A.49}$$

- Phase factors:

$$\varphi_m \equiv \frac{m_s}{N_s}\sum_{\mathbb{R}\in m} e^{-i\mathbb{R}\vec{G}\cdot\vec{t}_{\mathbb{R}}} \tag{A.50}$$

A.7 Fourier Transform

- Definition:

  We use the following convention for the time-frequency Fourier Transform:

$$\begin{aligned}F(\omega) &= \int_{-\infty}^{\infty} F(t)e^{i\omega t}dt \\ F(t) &= \frac{1}{2\pi}\int_{-\infty}^{\infty} F(\omega)e^{-i\omega t}d\omega\end{aligned} \tag{A.51}$$

- Imaginary axes:

  The Fourier transform between imaginary axes work like its counterpart on the real axes, except that additional factors of $\pm i$ have to be included:

$$\begin{aligned}F(i\omega) &= -i\int_{-\infty}^{\infty} F(i\tau)e^{-i\omega\tau}d\tau \\ F(i\tau) &= \frac{i}{2\pi}\int_{-\infty}^{\infty} F(i\omega)e^{i\omega\tau}d\omega\end{aligned} \tag{A.52}$$

A.8 Spherical coordinates

- Derivatives:

$$\begin{aligned}\partial x \pm i\partial y &= \sin\theta e^{\pm i\phi}\frac{\partial}{\partial r} + \frac{e^{\pm i\phi}}{r}\left(\cos\theta\frac{\partial}{\partial\theta} \pm \frac{i}{\sin\theta}\frac{\partial}{\partial\phi}\right) \\ \partial z &= \cos\theta\frac{\partial}{\partial r} - \frac{1}{r}\sin\theta\frac{\partial}{\partial\theta}\end{aligned} \tag{A.53}$$

A.9 Special Functions

A.9.1 Complete Gamma Function

- Definition:(See [1])

$$\Gamma(a) \equiv \int_0^\infty e^{-t} t^{a-1} dt \tag{A.54}$$

- Particular cases:
  - Integer arguments:
$$\Gamma(n) = (n-1)! \tag{A.55}$$
  - Half-integer argument:
$$\Gamma(n+\tfrac{1}{2}) = \tfrac{(2n-1)!!}{2^n}\Gamma(\tfrac{1}{2}) \tag{A.56}$$
    with $\Gamma(\frac{1}{2}) = \sqrt{\pi}$.

A.9.2 Incomplete Gamma Function

- Definition:(See [1])

$$\Gamma(a,x) \equiv \int_x^\infty e^{-t} t^{a-1} dt \tag{A.57}$$

- Recurrence relation:

$$\Gamma(a+1,x) = a\Gamma(a,x) + x^a e^{-x} \tag{A.58}$$

- Particular cases:

$$\Gamma(1,x) = e^{-x} \tag{A.59}$$
$$\Gamma\left(\tfrac{1}{2},x\right) = \sqrt{\pi}\text{Erfc}(\sqrt{x}) \tag{A.60}$$

A.9.3 The step function

Definition:

$$\Theta(\vec{r}) = \begin{cases} 1 & \vec{r} \in \text{interstitial} \\ 0 & \vec{r} \notin \text{interstitial} \end{cases} \tag{A.61}$$

Since the step function $\Theta(\vec{r})$ has the periodicity of the lattice we may expand it in a Fourier series as:

$$\Theta(\vec{r}) = \sum_{\vec{G}} \tilde{\Theta}_{\vec{G}} e^{i\vec{G}\cdot\vec{r}} \tag{A.62}$$

where $\tilde{\Theta}_{\vec{G}}$ can be calculated analytically, giving:

$$\tilde{\Theta}_{\vec{G}} = \begin{cases} 1 - \sum_a \frac{4\pi r_a^3}{3\Omega} & \vec{G} = 0 \\ -\frac{4\pi}{\Omega G}\sum_a j_1(Gr_a) r_a^2 e^{i\vec{G}\cdot\vec{r}_a} & \vec{G} \neq 0 \end{cases} \tag{A.63}$$

Appendix B

Programming conventions

i. Strict ANSI Fortran90 should be used. Features marked as obsolescent in F90/95 should be avoided (i.e. assigned format specifiers, labeled do-loops, statement functions).

ii. Modules should be used in place of common blocks for declaring global variables.

iii. `use` statements should include the `only` option and the corresponding list of global variables used by the subroutine, unless all the variables in the module are used.

iv. Any code should be written in lower-case form, starting from column 6. An extra indentation of 2 columns should be added inside each loop level. The length of each line should be kept to fewer than 75 characters using the & character for line continuation.

v. Every function or subroutine, no matter how small, should be in its own file named `routine.f90`, where `routine` is the function or subroutine name. It is recommended that the routines are named so as to make their purpose apparent from the name alone.

vi. Use of `implicit none` is mandatory.

vii. Each passed argument should have its `intent` option defined, and a short description of its purport should be added as comment in the same line.

viii. All called procedures within the subroutine (intrinsic or external) should be explicitly declared.

ix. Declarations of the form `datatype*N`, as well as `doble precision` or `double complex` should be avoided. The form `datatype(N)` should be used.

x. Each variable should be declared separately, and, when possible, its purpose should be described in a short comment on the same line.

xi. Subroutines should be "plentifully" commented. If you are not sure, whether or not a comment should be added here... **do it**.

xii. The use of `goto` statements should be kept to a minimum. Only if it is impossible to avoid it. They should be used for exiting loops only and always point to a `continue` statement.

xiii. Local allocatable arrays must be deallocated on exit of the routine to prevent memory leakage.

xiv. Every function or subroutine must be documented with the `Protex` source code documentation system. This should include a short LaTeX description of the algorithms and methods involved. Equations which need to be referenced should be labeled with `routine1`, `routine2`, etc. The autorship of each new piece of code or modification should be indicated in the REVISION HISTORY part of the header. See the `Protex` documentation for details.

xv. Each routine should terminate the program when given improper input.

xvi. Report errors prior to termination with a short description using the `outerr` subroutine.

xvii. Avoid redundant or repeated code: check to see if the routine you need already exists, before writing a new one.

xviii. All internal units should be atomic. Input and output units should be atomic by default and clearly stated otherwise (with exception of WIEN2k output files used as input, it does not depend on us).

Bibliography

[1] M. Abramowitz and I. A. Stegun, editors. *Handbook of Mathematical Functions*. Dover Pub. Inc., 180 Varick St. New York, 9th. edition, December 1972.

[2] C. Ambrosch-Draxl and J. O. Sofo. Linear optical properties of solids within the full-potential linearized augmented planewave method. Unpublished, Feb 2004.

[3] O. K. Andersen. Linear methods in band theory. *Phys. Rev. B*, 12(8):3060–3082, October 1975.

[4] V. I. Anisimov, F. Aryasetiawan, and A. I. Lichtenstein. First-principles calculations of the electronic structure and spectra of strongly correlated systems: the lda+u method. *J. Phys.:Condens. Matter*, 9:767, 1997.

[5] V. I. Anisimov and O. Gunnarsson. Density functional calculation of effective coulomb interaction in metals. *Phys. Rev. B*, 43:7570, 1991.

[6] V. I. Anisimov, I. V. Solovyev, M. A. Korotin, M. T. Czyzyk, and G. A. Sawatzky. Density functional theory and nio photoemission spectra. *Phys. Rev. B*, 48:16929, 1993.

[7] F. Aryasetiawan. Self-energy of ferromagnetic nickel in the gw approximation. *Phys. Rev. B*, 46(20):13051–13064, Nov 1992.

[8] F. Aryasetiawan. *Strong Coulomb Correlations in Electronic Structure Calcualtions: Beyond the Local Density Approximation*, volume 1 of *Advances in Condensed Matter Science*, chapter 1: The GW Approximation and Vertex Corrections, pages 1–95. Gordon and Breach Science Publishers, 2000.

[9] F. Aryasetiawan and O. Gunnarsson. The gw method. *Rep. Prog. Phys.*, 61(3):237–312, March 1998.

[10] F. Aryasetiawan and O. Gunnarsson. The gw method. *Rep. Prog. Phys.*, 61:237, 1998.

[11] N. W. Ashcroft and N. D. Mermin. *Solid State Physics*. Saunders College Publishing, 1976.

[12] A. Baldereschi and E. Tosatti. Dielectric band structure of solids. *Solid State Commun.*, 29(3):131–135, January 1979.

[13] G. Baym. *Phys. Rev.*, 127:1391, 1962.

[14] G. Baym and L. P. Kadanoff. *Phys. Rev.*, 124:287, 1961.

[15] P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, and J. Luitz. *WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties*. Karlheinz Schwarz, Techn. Universität Wien, Austria, 2001.

[16] D. Borwein, J. M. Borwein, and K. F. Taylor. Convergence of lattice sums and madelung's constant. *J. Math. Phys.*, 26(11):2999–3009, 1985.

[17] F. Bruneval, N. Vast, and L. Reining. Effects of self-consistency on quasiparticles in solids. *Phys. Rev. B*, 74:045102, 2006.

[18] A. Continenza, M. S., and M. Posternak. Self-energy corrections in vo2 within a model gw scheme. *Phys. Rev. B*, 60:15699, 1999.

[19] M. T. Czyzyk and G. A. Sawatzky. Local-density functional and on-site correlations: the electronic structure of la2cuo4 and lacuo3. *Phys. Rev. B*, 49:14211, 1994.

[20] H. J. de Groot, P. A. Bobbert, and W. van Haeringen. Self-consistent gw for a quasi-one-dimensional semiconductor. *Phys. Rev. B*, 52(15):11000–11007, Oct 1995.

[21] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, and A. P. Sutton. Electron-energy-loss spectra and the structural stability of nickel oxide: An lsda+u study. *Phys. Rev. B*, 57:1505, 1998.

[22] S. V. Faleev, M. van Schilfgaarde, and T. Kotani. All electron self-consistent gw approximation: application to si, mno, and nio. *Phys. Rev. Lett.*, 93:126406, 2004.

[23] M. Gatti, F. Bruneval, V. Olevano, and L. Reining. Understanding correlations in vanadium dioxide from first principles. *Phys. Rev. Lett.*, 99:266402, 2007.

[24] R. W. Godby, M. Schlüter, and L. J. Sham. Self-energy operators and exchange-correlation potentials in semiconductors. *Phys. Rev. B*, 37(17):10159–10175, June 1988.

[25] R. Gomez-Abal, X. Li, M. Scheffler, and C. Ambrosch-Draxl. Influence of core-valence exchange and correlation and of pseudoization on the electron selfenergy. *Phys. Rev. Lett.*, 101:106404, 2008.

[26] F. Gygi and A. Baldereschi. Quasiparticle energies in semiconductors: Self-energy correction to the local-density approximation. *Phys. Rev. Lett.*, 62(18):2160–2163, May 1989.

[27] L. Hedin. *Phys. Rev.*, 139:A796, 1965.

[28] L. Hedin. New method for calculating the one-particle green's functions with application to the electron-gas problem. *Phys. Rev.*, 139(3A):796–823, August 1965.

[29] L. Hedin and S. Lundqvist. Effects of electron-electron and electron-phonon interactions on the one-electron states of solids. In *Solid State Physics: Advances in Research and Applications*, volume 23, pages 1–181. Academic Press, New York and London, Oct 1969.

[30] B. Holm and U. von Barth. Fully self-consistent gw self-energy of the electron gas. *Phys. Rev. B*, 57(4):2108–2117, Jan 1998.

[31] M. Kara and K. Kurki-Suonio. Symmetrized multipole analysis of orientational distributions. *Acta Cryst. A*, 37(2):201–210, March 1981.

[32] N. Karasawa and W. A. G. III. Acceleration of convergence for lattice sums. *J. Phys. Chem.*, 93(21):7320–7327, October 1989.

[33] T. Kotani, M. van Schilfgaarde, and S. V. Faleev. Quasiparticle self-consistent gw method: A basis for the independent-particle approximation. *Phys. Rev. B*, 76:165106, 2007.

[34] W. Ku and A. G. Eguiluz. Band-gap problem in semiconductors revisited: effects of core states and many-body self-consistency. *Phys. Rev. Lett.*, 89:126401, 2002.

[35] A. Kutepov, Y. Savrasov, and G. Kotliar. Ground-state properties of simple elements from gw calculations. *Phys. Rev. B*, 80:041103(R), 2009.

[36] K.-H. Lee and K. J. Chang. *Phys. Rev. B*, 54:R8285, 1996.

[37] A. I. Liechtenstein, V. I. Anisimov, and J. Zaanen. Density-functional theory and strong interactions: orbital ordering in mott-hubbard insulators. *Phys. Rev. B*, 52:R5467, 1995.

[38] S. Massidda, A. Continenza, M. Posternak, and A. Baldereschi. Band-structure picture for mno reexplored: a model gw calculation. *Phys. Rev. Lett.*, 74:2323, 1995.

[39] S. Massidda, A. Continenza, M. Posternak, and A. Baldereschi. Quasiparticle energy bands of transition-metal oxides within a model gw scheme. *Phys. Rev. B*, 55:13494, 1997.

[40] S. Massidda, M. Posternak, and A. Baldereschi. Hartree-fock lapw approach to the electronic properties of periodic systems. *Phys. Rev. B*, 48(8):5058–5068, August 1993.

[41] A. Messiah. *Quantum Mechanics*. Dover Pub. Inc., N.Y., U.S.A., 1999.

[42] B. Nijboer and F. D. Wette. On the calculation of lattice sums. *Physica*, 23(1–5):309–321, 1957.

[43] A. G. Petukhov, I. I. Mazin, L. Chioncel, and A. I. Lichtenstein. Correlated metals and the lda+u method. *Phys. Rev. B*, 67:153106, 2003.

[44] P. Puschnig. *Excitonic Effects in Organic Semi-Conductors*. PhD thesis, Institute of Theoretical Physics, Faculty of Natural Sciences, Karl-Franzens-University, Graz, January 2002.

[45] M. M. Rieger, L. Steinbeck, I. D. White, H. N. Rojas, and R. W. Godby. The gw space-time method for the self-energy of large systems. *Comput. Phys. Commun.*, 117(3):211–228, March 1999.

[46] P. Rinke. *Exchange and correlation in small spherical clusters*. PhD thesis, University of York, 2003.

[47] M. E. Rose. *Elementary Theory of Angular Momentum*. Structure of Matter Series. John Wiley and sons, Inc., New York, 1957.

[48] M. E. Rose. The electrostatic interaction of two arbitrary charge distributions. *J. Math. and Phys.*, 37:215–222, 1958.

[49] R. Sakuma, T. Miyake, and F. Aryasetiawan. First-principles study of correlation effects in vo2. *Phys. Rev. B*, 78:075106, 2008.

[50] W.-D. Schöne and A. G. Eguiluz. Self-consistent calculations of quasiparticle states in metals and semiconductors. *Phys. Rev. Lett.*, 81:1662, 1998.

[51] E. L. Shirley. Self-consistent gw and higher-order calculations of electron states in metals. *Phys. Rev. B*, 54:7758, 1996.

[52] M. Shishkin, M. Marsman, and G. Kresse. Accurate quasiparticle spectra from self-consistent gw calculations with vertex corrections. *Phys. Rev. Lett.*, 99:246403, 2007.

[53] D. J. Singh. Ground-state properties of lanthanum: Treatment fo extended-core states. *Phys. Rev. B*, 43(8):6388–6392, March 1991.

[54] D. J. Singh. *Planewaves, Pseudopotentials and the LAPW Method*. Kluwer Academic Publishers, Norwell, Massachusetts, USA, 1994.

[55] E. Sjöstedt. *Augmented Planewaves, Developments and Applications to Magnetism*. PhD thesis, Department of Physics, Faculty of Science and Technology, Uspala University, March 2002.

[56] E. Sjöstedt, L. Nordström, and D. J. Singh. An alternative way of linearizing the augmented plane-wave method. *Solid State Commun.*, 114(1):15–20, March 2000.

[57] J. C. Slater. Wave functions in a periodic potential. *Phys. Rev.*, 51(10):846–851, May 1937.

[58] I. N. Sneddon. *Fourier Transforms*. International Series in Pure and Applied Mathematics. McGraw-Hill, New York, USA, 1st edition, 1951.

[59] I. V. Solovyev, P. H. Dederichs, and V. I. Anisimov. Corrected atomic limit in the local density approximation and the electronic structure of d impurities in rb. *Phys. Rev. B*, 50:16861, 1994.

[60] L. Steinbeck, A. Rubio, L. Reining, M. Torrent, I. D. White, and R. W. Godby. Enhancements to the gw space-time method. *Comput. Phys. Commun.*, 125(1-3):105–118, March 2000.

[61] M. L. Tiago, S. Ismail-Beigi, and S. G. Louie. Effect of semicore orbitals on the electronic band gaps of si, ge, and gaas within the gw approximation. *Phys. Rev. B*, 69:125212, 2004.

[62] H. J. Vidberg and J. W. Serene. *J. Low Temp. Phys.*, 29:179, 1977.

[63] U. von Barth and B. Holm. Self-consistent gw_0 results for the electron gas: Fixed screened potential w_0 within the random-phase approximation. *Phys. Rev. B*, 54(12):8411–8419, Sep 1996.

[64] E. R. Ylvisaker and W. E. Pickett. Anisotropy and magnetism in the lsda+u method. *Phys. Rev. B*, 79:035103, 2009.

[65] N. E. Zein, S. Y. Savrasov, and G. Kotliar. Local self-energy approach for electronic structure calculations. *prl*, 96:226403, 2006.

[66] J. M. Ziman. *Principles of The Theory of Solids*. Cambridge University Press, Cambridge, UK, 2nd ed. edition, 1972.

[67] J. M. Ziman. *Principles of the Theory of Solids*. Cambridge University Press, Bentley House, 200 Euston Road, London NW1 2DB, 2nd. edition, 1972.

[68] I. J. Zucker. Madelung constants and lattice sums for invariant cubic lattice complexes and certain tetragonal structures. *Journal of Physics A: Mathematical and General*, 8(11):1734–1745, 1975.