

Dynamical Mean Field Theory + Band Structure Method

1 GW+DMFT

We will express the various types of approximations in language of Luttinger-Ward functionals.

The exact Luttinger Ward functional takes the form

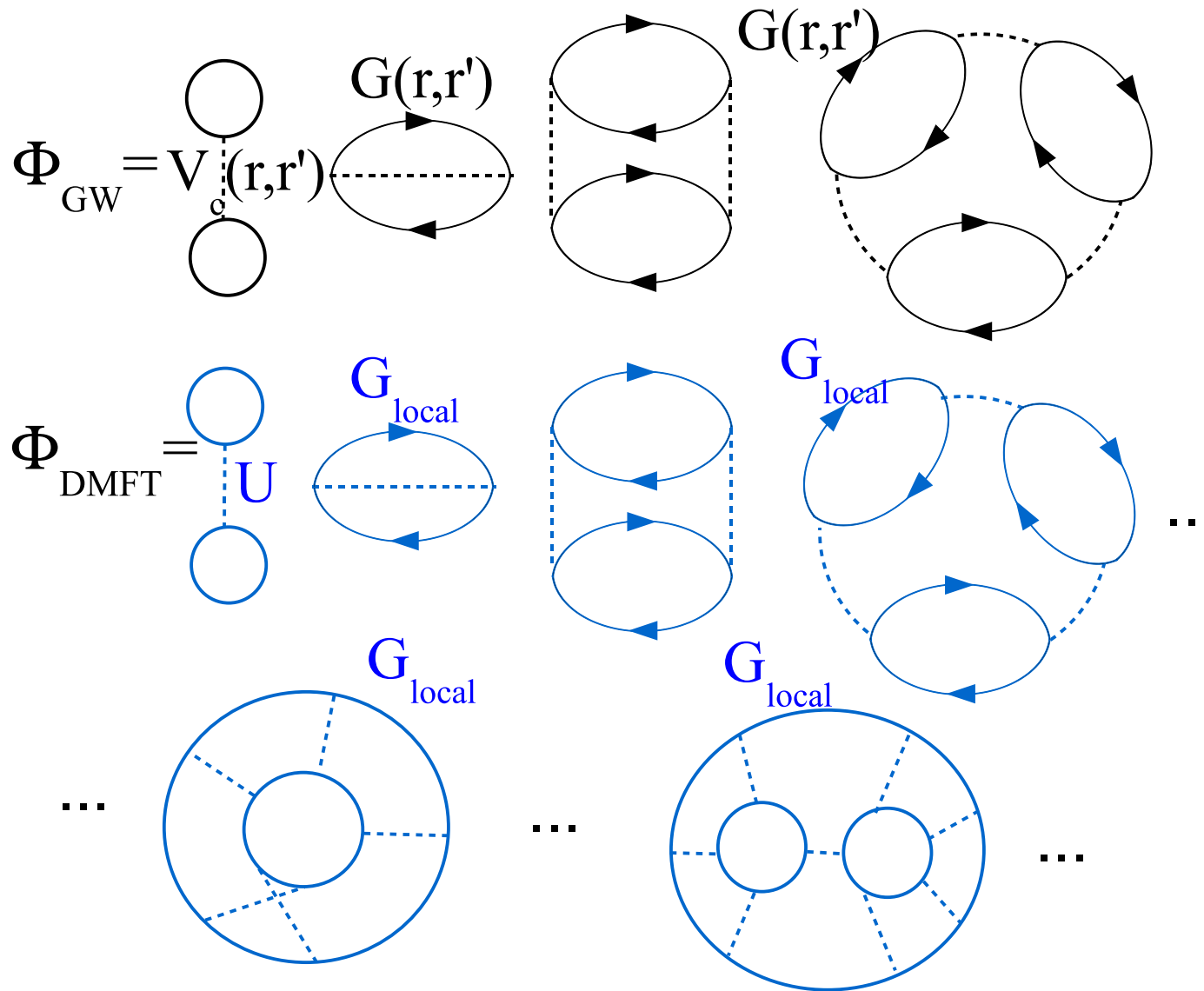
$$\Gamma[G] = \text{Tr} \log G - \text{Tr}(\Sigma G) + \Phi[G] \quad (1)$$

where $\Phi[G]$ is the sum of all possible two particle irreducible skeleton diagrams obtained by the bare Coulomb interaction $V_C(\mathbf{r} - \mathbf{r}') = \frac{1}{|\mathbf{r} - \mathbf{r}'|}$ and the fully dressed propagator $G(\mathbf{r}, \mathbf{r}')$.

We notice the following

- When bands are very wide, the kinetic energy is much bigger than the potential energy. The perturbation theory in Coulomb interaction V_C is converging rapidly and band structure methods, such as LDA or GW are very accurate. Typical examples are noble metals (Cu, Ag, Au).
- In narrow band materials, such as transition metals, transition metal oxides, intermetallic f materials,... the potential energy is large compared to kinetic energy. The band structure methods such as LDA or GW perform much worse. They dramatically break down in Mott insulators.
- In correlated materials, all higher order Feynman graphs are important.
- The higher order graphs are very local (only Hartree-Fock graph is nonlocal in infinite D when interaction is non-local), and could be summed by the DMFT method.

Let's first explain the idea of GW+DMFT, because GW is diagrammatic method, and there is no ambiguity in defining GW+DMFT. The Φ functionals of the two methods, GW and DMFT are



The GW method sums all RPA-like diagrams, but the propagator is the fully interacting Green's function $G^{-1}(\mathbf{r}, \mathbf{r}') = G_0^{-1}(\mathbf{r}, \mathbf{r}') - \Sigma_{GW}(\mathbf{r}, \mathbf{r}')$. Here $G_0^{-1} = \delta(\mathbf{r} - \mathbf{r}')(\omega + \mu + \nabla^2 - V_{ext}(\mathbf{r}))$ and $\Sigma_{GW}(\mathbf{r}, \mathbf{r}')$ is the correction due to the Coulomb interaction. The GW diagrams are plotted in black in the above figure.

The DMFT method sums *all local* digrams, regarding of their topology or order. The number of diagrams is increasing exponentially with order, and we can not plot them even at modest orders. All these diagrams are large in correlated materials. Since the high order diagrams are much more local then the diagrams at low orders, it makes sense to combine the two methods GW and DMFT into GW+DMFT. The Luttinger Ward functional is

$$\Phi_{GW+DMFT} = \Phi_{GW}(G(\mathbf{r}, \mathbf{r}')) + \Phi_{DMFT}(G_{loc}) - \Phi_{GW}(G_{loc}) \quad (2)$$

Because the GW-type of the diagrams appear in both GW and DMFT the local GW diagrams need to be subtracted.

We have thus defined the GW+DMFT approximation:

$$\Gamma[G(\mathbf{r}, \mathbf{r}')] = \text{Tr} \log G - \text{Tr}(\Sigma G) + \Phi_{GW}[G(\mathbf{r}, \mathbf{r}')] + \Phi_{DMFT}[G_{loc}] - \Phi_{GW}[G_{loc}]. \quad (3)$$

The functional is stationary and thus we have

$$\Sigma = \frac{\delta(\Phi_{GW} + \Phi_{DMFT} - \Phi_{DC})}{\delta G} = \Sigma_{GW} + \Sigma_{DMFT} - \Sigma_{DC} \quad (4)$$

where Σ_{DC} is the local-GW self-energy. It is the sum of all GW diagrams where propagator is G_{loc} .

We still did not define what is G_{loc} and what is U . There is no unique definition of these two quantities. However, physical motivation guides us to construct a sphere around each atom with active d or f orbital (usually called Muffin Thin sphere), and we use a projector to all angular momentum components inside the sphere

$$P(\mathbf{r}\mathbf{r}'; tLL') = Y_L(\hat{\mathbf{r}}_t)\delta(r_t - r'_t)Y_{L'}(\hat{\mathbf{r}}'_t). \quad (5)$$

We then have

$$G_{loc}(t, LL') = \int P(\mathbf{r}\mathbf{r}'; tLL')G(\mathbf{r}, \mathbf{r}')d\mathbf{r}d\mathbf{r}' \quad (6)$$

This is the local Green's function used in the above functional equations.

It turns out that we can not actually use the above defined $P(\mathbf{r}\mathbf{r}'; tLL')$ because it leads to non-causal DMFT equations. In practice, we construct a *separable* projector, which is very close to the projector defined above, but gives causal DMFT equations (see

arXiv:0907.0195 for details).

The quantity U is more difficult. We should use the screened Coulomb repulsion and not bare repulsion. This is because the wide bands, not considered in DMFT, screen the interaction very efficiently. For example, in atom U is of the order of 20 eV, while in the solid it is around 5 – 10 eV. How to account for this screening.

We first notice that U is the bare interaction with respect to orbitals included in the DMFT, but it is screened by the orbitals excluded in DMFT.

The quantity U is similar to the Weiss field on the one particle level. The Weiss field \mathcal{G}^0 is the bare propagator on the level of the impurity (local), but it includes non-local processes through the full Green's function.

Hence, it is a good idea to refresh our memory on the local *bare* propagator on the one particle level, to understand the procedure on the two particle level.

On the one particle level, we have $G(\mathbf{r}, \mathbf{r}')$, $G_0(\mathbf{r}, \mathbf{r}')$, G_{loc} . But none of them is the *bare* local propagator. We derived the DMFT equations in the previous lecture, and showed that G_{loc} should be identified with G_{imp} and Σ_{loc} should be identified with Σ_{imp} . Then the

solution of the impurity problem, which delivers Σ_{imp} , also gives us Σ_{loc} . We thus have

$$G_{loc} \equiv G_{imp} = (\mathcal{G}_{imp}^{0^{-1}} - \Sigma_{loc})^{-1} \quad (7)$$

The bare local propagator \mathcal{G}^0 is thus a different quantity than the non-interacting $G_0(\mathbf{r}, \mathbf{r}')$.

$$G_0^{-1}(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}')(\omega + \mu + \nabla^2 - V_{ext}(\mathbf{r})) \quad (8)$$

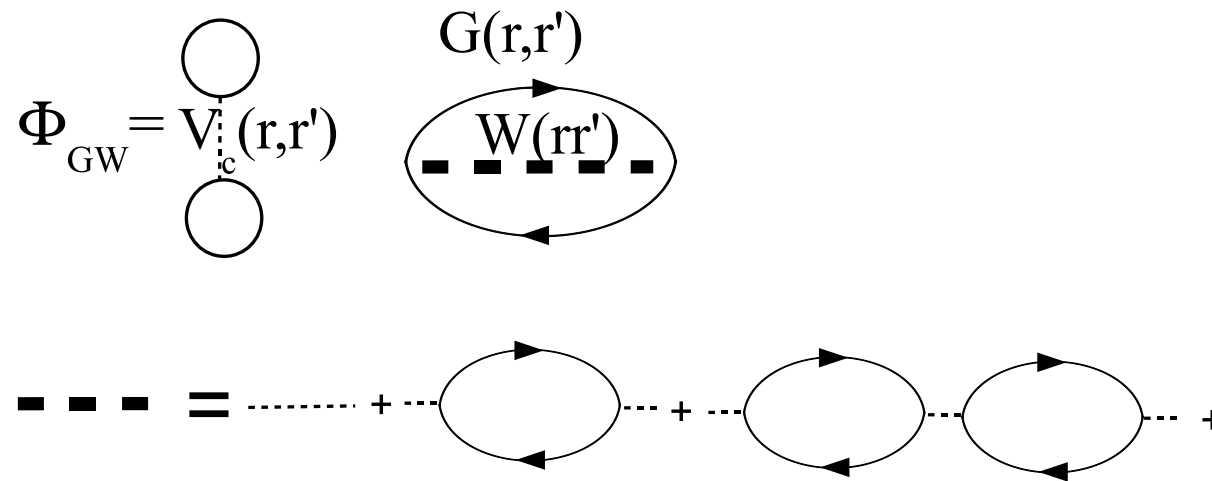
$$\mathcal{G}^{0^{-1}} = G_{loc}^{-1} + \Sigma_{loc} \quad (9)$$

$$G_{loc} = \int P_{loc}(\mathbf{r}\mathbf{r}')G(\mathbf{r}, \mathbf{r}')d\mathbf{r}d\mathbf{r}' \quad (10)$$

$$G^{-1}(\mathbf{r}, \mathbf{r}') = G_0^{-1}(\mathbf{r}, \mathbf{r}') - \Sigma \quad (11)$$

Rather than using the bare interaction $V_C(\mathbf{r}\mathbf{r}') = \frac{1}{|\mathbf{r}-\mathbf{r}'|}$, we can rewrite the fermionic problem in terms of the fully dressed (or screened) interaction $W(\mathbf{r}\mathbf{r}')$ and fully dressed Green's function $G(\mathbf{r}\mathbf{r}')$.

On the example of GW diagrams, the reformulated problem is



Clearly, the screened interaction also obeys the Dyson equation

$$W^{-1}(\mathbf{r}\mathbf{r}') = V^{-1}(\mathbf{r}\mathbf{r}') - \Pi(\mathbf{r}\mathbf{r}') \quad (12)$$

where $\Pi(\mathbf{r}\mathbf{r}')$ is the polarizability. In GW, this is just the bubble.

We thus have a set of parallel quantities on the one and the two particle level

name	one-particle	two particle
bare propagator	$G_0(\mathbf{r}\mathbf{r}')$	$V_c(\mathbf{r}\mathbf{r}') = \frac{1}{ \mathbf{r}-\mathbf{r}' }$
fully dressed propagator	$G(\mathbf{r}\mathbf{r}')$	$W(\mathbf{r}\mathbf{r}')$
self-energy/polarizability	$\Sigma(\mathbf{r}\mathbf{r}')$	$\Pi(\mathbf{r}\mathbf{r}')$
local propagator	G_{loc}	W_{loc}
Weiss-field/screened interaction	\mathcal{G}^0	U

On the two particle level, U is like the bare local propagator \mathcal{G}^0 on the one particle level, and $G_0(\mathbf{r}, \mathbf{r}')$ on the one particle level is like the bare Coulomb interaction $1/|\mathbf{r} - \mathbf{r}'|$ on the two particle level.

The DMFT equations on the two particle level (sometimes called extended-DMFT) are

$$U^{-1} = W_{loc}^{-1} + \Pi_{loc} \quad (13)$$

$$W_{loc}^t_{L_4 L_1; L_3 L_2} = \int P(\mathbf{r}\mathbf{r}, tL_4 L_1) W(\mathbf{r}\mathbf{r}') P(\mathbf{r}'\mathbf{r}', tL_3 L_2) d\mathbf{r}d\mathbf{r}' \quad (14)$$

and Π is local polarizability, which is equal to

$$\Pi_{loc}^t_{L_4 L_1; L_3 L_2}(\tau) = G_{loc}^t_{L_4 L_3}(\tau) G_{loc}^t_{L_1 L_2}(-\tau) \quad (15)$$

in GW approximation. In GW+DMFT, it should be computed self-consistently from the DMFT charge susceptibility (including vertex corrections).

We have thus fully defined the GW+DMFT equations. These equations are very challenging to implement. To date, we do not have a working code to fully carry out the set of equations specified above.

2 LDA+DMFT

Since LDA is such an accurate and fast method for weakly correlated materials, it is natural to use LDA instead of GW in the above equations, and use (almost) the same set of equations.

$$\Gamma[G] = \text{Tr} \ln(G) - \text{Tr}[\Sigma G] + \Phi_{LDA}[\rho] + \Phi_{DMFT}[G_{loc}] - \Phi_{DC}[G_{loc}] \quad (16)$$

where Tr runs over all space (orbitals, momenta) and time (frequency). The quantities appearing in the above functional are

$$G^{-1}(\mathbf{r}, \mathbf{r}') = [\omega + \mu + \nabla^2 - V_{ext}(\mathbf{r})] \delta(\mathbf{r} - \mathbf{r}') - \Sigma(\mathbf{r}, \mathbf{r}') \quad (17)$$

$$\Phi_{LDA}[\rho] = \Phi_H[\rho] + \Phi_{xc}[\rho] \quad (18)$$

$$\Sigma(\mathbf{r}, \mathbf{r}') = [V_H(\mathbf{r}) + V_{xc}(\mathbf{r})] \delta(\mathbf{r} - \mathbf{r}') + [\Sigma_{DMFT}(\mathbf{r}, \mathbf{r}') - E_{DC} \delta(\mathbf{r} - \mathbf{r}')] \rho$$

$$\rho = \widetilde{\text{Tr}}[G]$$

where $\widetilde{\text{Tr}}$ is trace over time only (not space), V_{ext} is the potentials due to ions, V_H, V_{XC} are the Hartree, and exchange-correlation potential, respectively. $\Phi_{DMFT}[G_{loc}]$ is the

sum of all local two particle irreducible skeleton diagrams constructed from G_{loc} , and the Coulomb repulsion U (screened by orbitals not contained in G_{loc}), and Φ_{DC} is the double counting functional.

The only quantity which is not very well defined in LDA+DMFT is the double-counting functional Φ_{DC} and $E_{DC} = \delta\Phi_{DC}/\delta n$.

In GW+DMFT, the double-counting is clear: all diagrams counted twice are the local GW diagrams. Since LDA is not a diagrammatic technique, we can not derive a double-counting correction.

We also need the Coulomb repulsion U , which one could compute from so called "constraint LDA". In practice, "constrained LDA" underestimates the "bare local interaction U ".

We thus carry out a GW calculation, where U is computed from the above defined method, namely, by computing

$$U^{-1} = W_{loc}^{-1} + \Pi_{loc}. \quad (20)$$

In this GW calculation, we also get the occupancy of the correlated orbital n_d . We can require that the *LDA + DMFT* must have the same occupancy of the correlated orbital as GW has. This uniquely determines the double counting.

In practice, it turns out that we can use a shortcut. In many materials the following "atomic formula" for the double counting is remarkably accurate

$$E_{DC} = U(n_d - 1/2) - J/2(n_d - 1) \quad (21)$$

which is the derivative of the atomic formula for the interacting energy

$$\Phi_{DC} = U \frac{n_d(n_d - 1)}{2} - J \frac{n_d(n_d - 2)}{4} \quad (22)$$

where U and J are two parameters that quite accurately parametrize the Coulomb repulsion.

Namely, the following parametrization is due to Slater, and he showed that when the orbitals are spherically symmetric, one has

$$U_{m_4 m_3 m_2 m_1} = \sum_k \frac{4\pi}{2k+1} F_{\{l\}}^k \langle Y_{lm_4} | Y_{k m_4 - m_1} | Y_{lm_1} \rangle \times \langle Y_{lm_3} | Y_{k m_2 - m_3}^* | Y_{lm_2} \rangle \quad (23)$$

where F^k are Slater integrals. For d materials, we have only $F^0 = U$, F^2 and F^4 , which are nonzero. It turns out that there is *almost* a fixed ratio between the two Slater integrals, namely, $F_2 = (14/1.625) J$ and $F_4 = (8.75/1.625) J$. Hence, we usually work with J , rather than F^2 , and F^4 .

We can determine these Slater integrals from the full GW matrix of interaction by the

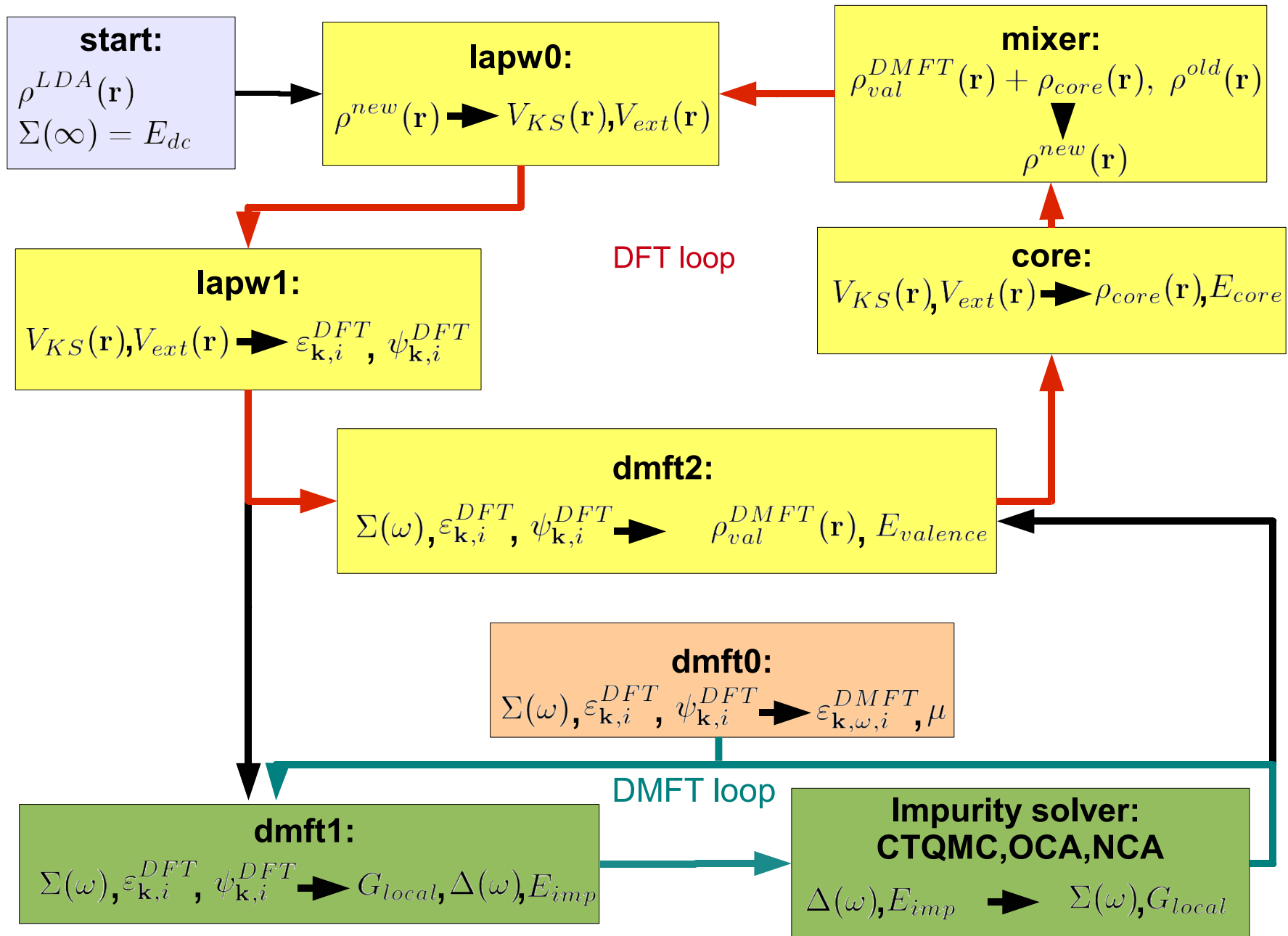
following projection

$$F_{\{l\}}^k = \sum_{m_1, m_2, m_3, m_4} \frac{1}{\mathcal{N}_{l,k}} \frac{4\pi}{2k+1} \langle Y_{lm_4} | Y_{k, m_4-m_1} | Y_{lm_1} \rangle \times U_{m_4 m_3 m_2 m_1}^{GW} \langle Y_{lm_3} | Y_{k, m_2-m_3}^* | Y_{lm_2} \rangle \quad (24)$$

Here $\mathcal{N}_{l,0} = (2l+1)^2$, $\mathcal{N}_{l=2,k=1} = 5(2/7)^2$ and $\mathcal{N}_{l=2,k=2} = (10/21)^2$.

We have just defined the LDA+DMFT method. Provided we have an accurate impurity solver for d and/or f orbitals, we can carry out the above defined set of equations. This set of equations are nowadays quite routinely solved for many correlated materials.

3 Wien2K+DMFT schemes



dmft1

$$\Sigma(\omega), \varepsilon_{\mathbf{k},i}^{DFT}, \psi_{\mathbf{k},i}^{DFT} \longrightarrow G_{local}, \Delta(\omega), E_{imp}$$

projector: $P(\mathbf{r}\mathbf{r}', \tau LL') \approx Y_L(\hat{\mathbf{r}}_\tau) \delta(r_\tau - r'_\tau) Y_{L'}^*(\hat{\mathbf{r}}'_\tau)$

self-energy
in KS base: $\bar{\Sigma}_{\mathbf{k},ij}(\omega) = \sum_{\tau, L_1 L_2} P_{\mathbf{k}\tau}(ji, \tau L_2 L_1) (\Sigma_{L_1 L_2}^\tau(\omega) - E_{dc}^\tau)$

DMFT self-consistency condition:

$$G_{local}^\tau{}_{LL'} = \sum_{\mathbf{k}ij} P_{\mathbf{k}\tau}(ij, LL') \left[(i\omega + \mu - \epsilon_{\mathbf{k}} - \bar{\Sigma}_{\mathbf{k}}(\omega))^{-1} \right]_{ji}$$

$$= \left[\frac{1}{i\omega - E_{imp}^\tau - \Sigma^\tau(\omega) - \Delta^\tau(\omega)} \right]_{LL'}$$

dmft2

$$\Sigma(\omega), \varepsilon_{\mathbf{k},i}^{DFT}, \psi_{\mathbf{k},i}^{DFT} \rightarrow \rho_{val}^{DMFT}(\mathbf{r}), E_{valence}$$

projector: $P(\mathbf{r}\mathbf{r}', \tau L L') \approx Y_L(\hat{\mathbf{r}}_\tau) \delta(r_\tau - r'_\tau) Y_{L'}^*(\hat{\mathbf{r}}'_\tau)$

self-energy in KS base: $\bar{\Sigma}_{\mathbf{k},ij}(\omega) = \sum_{\tau, L_1 L_2} P_{\mathbf{k}\tau}(ji, \tau L_2 L_1) (\Sigma_{L_1 L_2}^\tau(\omega) - E_{dc}^\tau)$

DMFT eigenvalues: $(-\nabla^2 + V_{KS}(\mathbf{r}) + \bar{\Sigma}_{\mathbf{k}}(\omega)) \psi_{\mathbf{k}\omega_n i}(\mathbf{r}) = \varepsilon_{\mathbf{k}\omega_n i}^{DMFT} \psi_{\mathbf{k}\omega_n i}(\mathbf{r})$

The chemical potential: $N_{val} = T \sum_{\omega_n, i} \frac{1}{i\omega_n + \mu - \varepsilon_{\mathbf{k}\omega_n i}}$

Valence charge density:

$$\rho_{val}^{DMFT} = \sum_{\mathbf{k}, ij} \psi_{\mathbf{k}i}^{DFT}(\mathbf{r}) \times T \sum_{\omega_n} \left[(i\omega_n + \mu - \epsilon_{\mathbf{k}} - \bar{\Sigma}_{\mathbf{k}}(\omega))^{-1} \right]_{ij} \times \psi_{\mathbf{k}j}^{DFT}(\mathbf{r})$$

total energy contribution: $E_{valence} = \text{Tr}((-\nabla^2 + V_{KS})\rho_{val}^{DMFT})$