Theoretical Summary: DMFT+DFT with Wannier construction

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1 Derivative of Free Energy functional

Density Functional Theory (DFT) has great success among itinerant or fully gapped systems, but fails in strongly-correlated materials which consist of both itinerant and localized (read tight-binding) character. Particularly spectroscopy, lattice constants ,and band-gaps are grossly underestimated.

Kristjan Haule and Gheorghe Pascut (PRB, 2016) derive the general expression for Pulay forces in the most general case of frequency dependent Green's function. This means the matrix elements do not give a Hermitian operator, requiring a distinction between left and right eigenvectors.

In the formulation of Luttinger-Ward functionals, one can write down:

$$\frac{\delta\Gamma}{\delta R_\mu} = (\frac{\delta\Gamma[G]}{\delta R_\mu})|_G + \int dr_1 dr_2 \frac{\delta G(r_1, r_2)}{\delta R_\mu} (\frac{\delta\Gamma[G]}{\delta G(r_1, r_2)}) \tag{1}$$

The first term is the well-known Hellman force and the second vanishes under the condition that the functional Γ, is stationary with respect to the Green's function. This is true if our functional is the free energy.

The functional is written explicitly as:

$$\Gamma[G] = Tr[\ln(-G)] - Tr[(G_o^{-1} - G^{-1})G] + \Phi[G] + E_{nuc} \tag{2}$$

Here the trace is taken over all spatial and spin coordinates. The trace sums over frequencies as well in the dynamical case.

We enforce the Dyson equation:

$$\frac{\delta\Gamma}{\delta G} = G^{-1} - G_o^{-1} + \frac{\delta\Phi}{\delta G} \tag{3}$$

Using stationarity under variation

Taking the derivative will yield the term

$$
\begin{aligned}
&-Tr(G\tfrac{\partial G_o^{-1}}{\partial R_\mu}) \\
&= Tr(G(\delta V_{nuc})) = Tr((\delta V_{nuc})\tfrac{1}{\beta}\textstyle\sum_{\omega_n} G(i\omega_n) \\
&= Tr(\rho V_{nuc})
\end{aligned}
$$

This uses the fact that $G_o^{-1} = i\omega_n + \mu - T - V_{nuc}$ and the equivalence of the solid Green function to the statistical weight (read amplitude) of [propagation? revise later]

The Φ-term encapsulate all interactions and is approximated as follows:

$$
\Phi[G] = E_H[\rho] + E_{XC}[\rho] + \sum_{R_\mu} \Phi^{DMFT}[G^\mu_{loc}] - \Phi^{DC}[\rho^{DC}_{loc}] \tag{4}
$$

The Dyson equation now looks like:

$$
G^{-1} - G_o^{-1} + (V_H + V_{XC})\delta(r_1 - r_2)\delta(\tau - \tau') + \sum_{mm',R_\mu} \langle r_1|\phi^\mu_m\rangle \langle \phi^\mu_m| (\Sigma - V_{DC}) |\phi^\mu_{m'}\rangle \langle \phi^\mu_{m'}|r_2\rangle = 0 \tag{5}
$$

Upon substitution,

$$
G^{-1} = i\omega_n - T + \mu - V_{nuc} - V_H - V_{XC} - \sum_{mm',\mu} |\phi^\mu_m\rangle \langle \phi^\mu_m| (\Sigma - V_{DC}) |\phi^\mu_{m'}\rangle \langle \phi^\mu_{m'}| \tag{6}
$$

Writing in explicit form for the free energy, that is the differential of our functional Γ:

$$
\begin{aligned}
\mathscr{F} &= Tr[\ln(-G)] - Tr[(V_H + V_{XC})\rho] + E_H[\rho] \\
&+ E_{XC} + E_{nuc} \quad - Tr[(\Sigma - V_{DC}) \langle\phi| G |\phi\rangle] \\
&+ \sum_{R_\mu} \Phi^{DMFT}[G^\mu_{loc}] - \Phi^{DC}[\rho^\mu_{loc}] + \mu N
\end{aligned}
$$

Simplifying further by using eigenvalue equation:

$$\langle\psi_j|\,\hat{H}\,|\psi_k\rangle = \delta_{jk}\epsilon_{k,\omega_n,j} \tag{7}$$

In explicit form, we equate the terms:

$$\langle\psi_j|\,T{+}V_{nuc}{+}V_H{+}V_{XC}{+}\sum_{mm',\mu}|\phi^{\mu}_{m}\rangle\,\langle\phi^{\mu}_{m}|\,(\Sigma{-}V_{DC})\,|\phi^{\mu}_{m'}\rangle\,\langle\phi^{\mu}_{m'}|\,|\psi_k\rangle = \delta_{jk}\epsilon_{k,\omega_n,j} \tag{8}$$

Re-casting in terms of the solid's inverse Green function we further reduce to

$$\langle\psi_j|\,(-G^{-1}) + \mu + i\omega_n\,|\psi_k\rangle = \delta_{jk}\epsilon_{k,\omega_n,j} \tag{9}$$

We recover the well-known form of Green's function:

$$\langle\psi_j|\,G\,|\psi_k\rangle = \frac{\delta_{jk}}{i\omega_n + \mu - \epsilon_{k,\omega_n,j}} \tag{10}$$

Summarily, the free energy functional in explicit and full form is:

$$\begin{aligned}\mathscr{F} = &-Tr[\ln(-i\omega_n - \mu + \epsilon_{k,\omega_n})]\\ &- Tr[(V_H + V_{XC})\rho] + E_H[\rho]] + E_{XC}[\rho] + E_{nuc}\\ &- Tr[(\Sigma - V_{DC}\,\langle\phi)|\,G\,|\phi\rangle)]\\ &+ \sum_{R_\mu}\Phi^{DMFT}[G^{\mu}_{loc} - \Phi^{DC}[\rho^{\mu}_{loc}] + \mu N\end{aligned} \tag{11}$$

Taking yet another differential with respect to a coordinate yields the force.

$$\delta\mathscr{F} = Tr[\frac{\delta\epsilon_{k,\omega_n} - \delta\mu}{i\omega_n + \mu - \epsilon_{k,\omega_n}}] - Tr[\rho(\delta V_H + \delta V_{XC})] - Tr[G_{loc}(\delta\Sigma - \delta V_{DC})] + \delta E_{nuc} + N\delta\mu \tag{12}$$

Note that

$$\delta(E_H + E_{XC}) = Tr[(V_H + V_{XC})\delta\rho]$$

and

$$\sum_{R_\mu} \delta\Phi^{DMFT}[G^\mu_{loc}] + \delta\Phi^{DC}[\rho^\mu_{loc}] = Tr[(\Sigma - V_{DC})\delta G_{loc}]$$

By number conservation, we can drop $\delta\mu$ terms. We can also equate the differential of the nuclear lattice's energy to the Hellman term and write:

$$\delta\mathscr{F} = Tr[\frac{\delta\epsilon_{k,\omega_n}}{i\omega_n + \mu - \epsilon_{k,\omega_n}}] - Tr[\rho\delta V_{KS}] - Tr[G_{loc}(\delta\Sigma - \delta V_{DC}] - \sum_\mu F^{HF}_\mu \delta R_\mu \tag{13}$$

Matching terms against the general expression for force, equation (1), we get

$$F^{Puly}_\mu = -Tr[\frac{1}{i\omega_n + \mu - \epsilon_{k,\omega_n}} \frac{\delta\epsilon_{k,\omega_n}}{\delta R_\mu}] + Tr[\rho\frac{\delta V_{KS}}{\delta R_\mu}] + Tr[G_{loc}(\frac{\delta(\Sigma - V_{DC})}{\delta R_\mu}] \tag{14}$$

However, for Dynamical Mean Field Theory (DMFT) the eigenvectors are generally frequency dependent. Therefore, we must distinguish between left and right eigenvectors. In consequence, this means $\hat{H}$ is not hermitian in general. This is equivalent to the physical screening of the Coulomb interaction.

We can set our notation as:

$$|\psi_{i\mathbf{k}\omega_n}\rangle = \sum_{\mathbf{K}} |\chi_K\rangle\, A^R_{K,i}\, \langle\psi_{j\mathbf{k}\omega_n}| = \sum_{\mathbf{K}} A^L_{K,i}\, \langle\chi_K| \tag{15}$$

To keep the derivation as general as possible, we must note that the coefficients inherit frequency and momentum dependence as well.

The general eigenvalue equation becomes:

$$\sum_{KK'} A^L[\hat{H}^{DFT} + \hat{V}^{DMFT}]A^R = \delta_{ij}\epsilon_{\mathbf{k}\omega_n,i} \tag{16}$$

Orthonormality is enforced still via:

$$\textstyle\sum_{KK'} A^L_{iK'}\hat{O}_{KK'}A^R_{Kj} = \delta_{ij}$$

where $\hat{O}_{KK'}$ is the overlap between eigenvectors $\langle\chi_K|\chi_{K'}\rangle$

The eigenvalue problem now reads:

$$\sum_{\mathbf{K}}(\overline{H}^{DFT} + \overline{V}^{DMFT})A^R = \sum \hat{O}_{\mathbf{K'K}}A^R_{\mathbf{K},i}\epsilon_{k,\omega_n,i}$$

We can eliminate the expression of $\delta\epsilon$ via enforcing the orthonormality prescribed before and differentiating the re-formulated eigenvalue problem

$$\delta(\overline{H}^{DFT}+\overline{V}^{DMFT})A^R+(H^{DFT}+V^{DMFT})\delta A^R = (\delta\hat{O})A^R\epsilon+\hat{O}(\delta A^R)\epsilon+\hat{O}A^R(\delta\epsilon) \tag{17}$$

Bra-ing against the left eigenvectors and using orthonormality definition $A^L_{iK'}\hat{O}A^R_{Kj} = \delta_{ij}$ as promised gives

$$A^L(\delta H^{DFT}+\delta V^{DMFT})A^R+A^L(H^{DFT}+V^{DMFT})\delta A^R = A^L(\delta\hat{O})A^R\epsilon+A^L\hat{O}(\delta A^R)\epsilon+(\delta\epsilon) \tag{18}$$

But with our notation and choosing the $|\chi_K\rangle$ basis representation

$$A^L(H^{DFT} + V^{DMFT})A^R =$$

$$A^L\langle\chi_{K'}|(H^{DFT} + V^{DMFT})A^R|\chi_K\rangle = A^L\hat{O}A^R\epsilon$$

$$\implies (\delta\epsilon_{k\omega_n})_{ii} = \sum_{KK'} A^L_{iK'}[\delta H^{DFT}_{KK'} + \delta V^{DMFT}_{KK'}]A^R_{Ki} - A^L_{iK'}\delta\hat{O}_{KK'}A^R_{Ki}\epsilon_{k,\omega_n,i}$$

We can further decompose the coefficients of the DMFT eigenvectors a product between static Kohn-Sham (KS) components and the frequency dependent ones.

$$A^R_{Ki} = \sum_j A^o_{kj}(B^R_{\omega_n})_{ji}$$
$$A^L_{iK} = \sum_j (B^L_{\omega_n})_{ij} A^o_{jk}$$

Substituting into the Pulay force expression (eq. 11 or 12) yields,

$$\begin{aligned} - Tr[G^d B^L_{\omega_n}[A^{o\dagger}(\frac{\delta H^{DFT}}{\delta R_\mu} + \frac{\delta V^{DMFT}}{\delta R_\mu})A^o B^R_{\omega_n} - A^{o\dagger}\frac{\delta \hat{O}}{\delta R_\mu} A^o B^R_{\omega n}\epsilon_{k\omega_n}]] \\ + Tr[\rho \frac{\delta V^{KS}}{\delta R_\mu}] + Tr[G_{loc}\frac{\delta(\Sigma - V^{DC})}{\delta R_\mu}] \end{aligned} \tag{19}$$

Where G^d is the impurity Green's function of the form as before: $\frac{1}{i\omega_n + \mu - \epsilon_{k,\omega_n}}$ in the KS basis.

We can tidy up the notation by defining:

$$\tilde{\rho} = \frac{1}{\beta}\sum_{i\omega_n} B^R_{\omega_n}\frac{1}{i\omega_n + \mu - \epsilon_{k,\omega_n}} B^L_{\omega_n}$$
$$\widetilde{(\rho\epsilon)} = \frac{1}{\beta}\sum_{i\omega_n} B^R_{\omega_n}\frac{\epsilon_{k\omega_n}}{i\omega_n + \mu - \epsilon_{k,\omega_n}} B^L_{\omega_n}$$

We can also write down $\tilde{\rho}_{ij} = \langle \psi^o_i | \rho | \psi^o_j \rangle$ where ψ's are KS eigenvectors but ρ is the self-consistent charge density from DFT+DMFT treatment.

In the χ_K basis, the Green's function can be expressed as

$$\bar{G} = (A^o B^R_{\omega_n}\frac{1}{i\omega_n + \mu - \epsilon_{k,\omega_n}} B^L_{\omega_n} A^{o\dagger})_{KK'} \tag{20}$$

So that Pulay force is now

$$
\begin{aligned}
&- Tr[\widetilde{\rho} A^{o\dagger} \frac{\delta H^{DFT}}{\delta R_\mu} A^o - (\widetilde{\rho}\epsilon) A^{o\dagger} \frac{\delta \hat{O}}{\delta R_\mu} A^o] \\
&+ Tr[\rho \frac{\delta V^{KS}}{\delta R_\mu}] - Tr[\bar{G} \frac{\delta V^{DMFT}}{\delta R_\mu}] + Tr[G_{loc}(\frac{\delta(\Sigma - V_{DC})}{\delta R_\mu})]
\end{aligned}
$$

Expanding once again the differential of DMFT potential term $\frac{\delta V^{DMFT}}{\delta R_\mu}$, will read as

$$
\begin{aligned}
&\frac{1}{\beta} \sum_{i\omega_n, m'm, KK'} \bar{G_{KK'}} \delta(\langle \chi_{K'} | \phi_{m'} \rangle (\Sigma - V^{DC})_{mm'} \langle \phi_m | \chi_K \rangle \\
&= \frac{1}{\beta} \sum_{i\omega_n, m'm, KK'} \bar{G_{KK'}} (\Sigma - V^{DC})_{mm'} \delta(\langle \chi_{K'} | \phi_{m'} \rangle \langle \phi_m | \chi_K \rangle) \\
&\qquad\qquad + Tr[G_{loc}(\delta\Sigma - \delta V^{DC})]
\end{aligned}
$$

This yield the cancellation of $\delta\Sigma$ we anticipated from varying a stationary quantity and gives the general form for Pulay Force derived as:

$$
\begin{aligned}
&F_\mu^{Puly} = -Tr[\tilde{\rho} A^{0\dagger} \frac{\delta H^0}{\delta R_\mu} A^0 - \widetilde{\rho}\epsilon A^{0\dagger} \frac{\delta \hat{O}}{\delta R_\mu}] + Tr[\rho \frac{\delta V_{KS}}{\delta R_\mu}] \\
&- \frac{1}{\beta} \sum_{i\omega_n} \sum_{KK', m'm} \bar{G}_{KK'} (\Sigma - V_{DC})_{m'm} \frac{\delta(\langle \chi_{K'} | \phi_{m'} \rangle \langle \phi_m | \chi_K \rangle)}{\delta R_\mu}
\end{aligned}
$$

Since LAPW and PAW are essentially plane wave techniques, and both in the interstitial region we will focus on the localized terms, in our case the Wannier projector changes. The authors go on to note that although within their Muffin-Tin they have an atomic coordinate dependence, that is R_μ, in phase factor the basis is still plane-wave which allows for rigid-shift approximation. This is valid because although their is charge deformation due to atomic displacement, the Fourier composition is unchanged due to the origin-less nature of the basis set.

The phase factor $e^{i(K+k)R_\mu}$ is trivial and yield the well known Hankel-like

functions, which satisfy the condition:

$$\frac{\delta(\langle\chi_{K'}|\phi_{m'}\rangle\langle\phi_m|\chi_K\rangle)}{\delta R_\mu} = i(K-K^{'})\langle\chi_{K'}|\phi_{m'}\rangle\langle\phi_m|\chi_K\rangle \tag{21}$$

Focusing on the Wannier projection $|\phi\rangle$

$$\phi_R = \frac{1}{\sqrt{N}}\sum_k e^{-ik\cdot R}\psi_k \tag{22}$$

$$\psi_k = e^{ik\cdot r}u_k(r) \tag{23}$$

An earlier implementation by Leonov, Anisimov and Vollhardt calculates linear response of LDA+DMFT formalism within total energy functional:

$$\begin{aligned} E &= E_{LDA}[\rho] + \langle\hat{H}_{LDA}\rangle - \sum_{m,k}\epsilon_{m,k}^{LDA} \\ &+ \frac{1}{2}\sum_{imm',\sigma\sigma'} U_{mm'}^{\sigma\sigma'}\langle\hat{n}_{im\sigma}\hat{n}_{im'\sigma'}\rangle - E_{DC} \end{aligned} \tag{24}$$

At low temperature calculations, the total versus the free energy should be comparable. The quantities calculated from this are strictly not variational but nevertheless we week to quantify the difference in a system such as $LaNiO_3$. Note that in this case $E_{DC} = \frac{1}{2}\sum_{imm',\sigma\sigma'} U_{mm'}^{\sigma\sigma'}\langle\hat{n}_{im\sigma}\rangle\langle\hat{n}_{im'\sigma'}\rangle$ which is equivalent to minimizng the double-occupancy matrix's second moment, aka the fluctuations. The justification for this kind of neglect remains unclear to the author at this time.

They go on to evaluate the correlation induced displacement via calculating the force as:

$$F_s = F^s_{LDA} - \delta_s \langle \hat{H}_{LDA} \rangle + \sum_{m,k} \delta_s \epsilon^{LDA}_{m,k}$$
$$- \frac{1}{2} \sum_{imm',\sigma\sigma'} U^{\sigma\sigma'}_{mm'} \delta_s \langle \hat{n}_{im\sigma} \hat{n}_{im'\sigma'} \rangle$$
$$- \frac{1}{2} \sum_{imm',\sigma\sigma'} U^{\sigma\sigma'}_{mm'} (\delta_s \langle \hat{n}_{im\sigma} \rangle) \langle \hat{n}_{im'\sigma'} \rangle + \langle \hat{n}_{im\sigma} \rangle (\delta_s \langle \hat{n}_{im'\sigma'} \rangle)$$

Per usual, Hellman force term is present and on-site repulsion parameter U is taken to be constant. The second term is the Hellman term within the Wannier representation, which will include the typical first order changes as well as the change in amplitudes (read Green function) on the position:

$$\delta_s \langle \hat{H}_{LDA} \rangle = \langle \delta_s \hat{H}_{LDA} \rangle + Tr \sum_{\mathbf{k}, i\omega_n} \hat{H}^{\mathbf{k}}_{LDA} \delta_s \hat{G}_{\mathbf{k}}(i\omega_n) e^{i\omega_n 0+} \tag{25}$$

the derivative of the local Green function is:

$$\delta_s \hat{G}_{\mathbf{k}}(\omega) = \hat{G}_{\mathbf{k}}(\omega)[\delta_s \hat{H}^{\mathbf{k}}_{LDA} + \delta_s \hat{\Sigma}(\omega) - \delta_s \mu] \hat{G}_{\mathbf{k}}(\omega) \tag{26}$$

By taking the substitution that $\delta G = \delta \frac{1}{argument} = -\frac{1}{arg^2} \cdot \delta(arg)$

Forces due to Coulomb repulsions here will be approximated as the derivative of the Migdal-Galitskii formula, yielding

$$F^s_U = -\frac{1}{2} Tr \sum_{i\omega_n} [\delta_s \hat{\Sigma}(i\omega_n) \hat{G}(i\omega_n) + \hat{\Sigma}(i\omega_n) \delta_s \hat{G}(i\omega_n)] e^{i\omega_n 0+} \tag{27}$$

while again using a constant Coulomb and Hund parameters (U,J). Enforcing number conservation to calculate the change in chemical potention μ, The independent variables needed are only $\delta \hat{H}_{LDA}$ and $\delta \hat{\Sigma}$. Per usual, this means we need another equation to solve self-consistently.

$\delta \hat{H}_{LDA}$ is calculated within LDA linear-response (Vanilla perturbation theory) within DFT package VASP. Only the Wannier projections are used to

weight against all Bloch bands, including the overlaps between Wannier orbitals. *Note that this requires the subspace is complete and the Bloch window sufficient to capture all changes*

Formally this is writte as:

$$(\delta_s \hat{H}^{\mathbf{k}}_{LDA})_{nm} = \sum_{i=N_a}^{N_b} \langle \phi_n | \psi_{ik} \rangle \langle \psi_{ik} | \phi_m \rangle \cdot (\delta_s V^{KS}_{ik} + \delta_s V^{HXC}_{ik}) \tag{28}$$

To calculate $\delta\Sigma$, a functional derivative is taken of the impurity Green function (the authors of the paper neglected double-counting corrections since the term is second order in total) and extract the formula

$$\delta\hat{G}(\tau_{12}) = -\hat{\chi}(\tau_{1234})\delta\hat{\mathcal{G}}^{-1}(\tau_{34}) \tag{29}$$

where χ can be sampled via the impurity solver through explicit summation over Matusbara frequencies, and the self-consistency is closed by enforcing Dyson equation per usual. Namely $\delta_s\hat{\mathcal{G}}^{-1} = \delta_s\hat{G}^{-1} + \delta_s\hat{\Sigma}$

The argument we would like to use is neglecting $\delta\Sigma$ term completely in the spirit that if indeed at low temperature total Energy functional can be well equated to the Free energy, then the scheme of Leonov, Anisimov, and Vollhardt should be valid with the benefit of Haule and Pascut's argument that susceptibility (i.e second order derivatives) have total cancellation.

The $\delta\epsilon$ term entails computing the projector dependence on ionic shifts

$$\frac{\delta(\langle \chi_{K'} | \phi_{m'} \rangle \langle \phi_m | \chi_K \rangle)}{\delta R_\mu} \tag{30}$$

2 Linear Response within DFPT formalism

I would like to briefly review the adiabatic approximation, the infamous *Born-Oppenheimer Approximation*, which asserts the nuclei in a solid-state system are essentially stationary due to their 2000 times heavier mass compared to the electrons. This decouples the vibrational degrees of freedom from the electronic ones, yielding a simplified Schrödinger equation:

$$(-\sum_I \frac{\hbar^2}{2M_I}\frac{\partial^2}{\partial \mathbf{R}_I^2} + E(\mathbf{R}))\Phi(\mathbf{R}) = \varepsilon\Phi(\mathbf{R}) \tag{31}$$

Where index I runs over the nuclei, M is their respective masses, and so on. In this approximation the kinetic energy of the nuclei are strictly zero, the ion-ion potential is fixed, and the only interesting terms are the kinetic energies of the electrons, their mutual repulsive potential, and the attractive potential towards the background nuclei as in:

$$H_{BO}(\mathbf{R}) = -\frac{\hbar^2}{2m}\sum_i \frac{\partial^2}{\partial \mathbf{r}_i^2} + \frac{e^2}{2}\sum_{i\neq j}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{iI}\frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + E_N(\mathbf{R}) \tag{32}$$

Where lower-case i index runs over electrons now. Equilibrium condition is the usual:

$$\mathbf{F}_I \equiv -\frac{\partial E(\mathbf{R})}{\partial \mathbf{R}_I} = 0 \tag{33}$$

Under the general conditions of *linear response*, or the harmonic regime, the well-known secular equation reads:

$$det\left|\frac{1}{\sqrt{M_I M_J}}\frac{\partial^2 E(\mathbf{R})}{\partial \mathbf{R}_I \partial \mathbf{R}_J} - \omega^2\right| = 0 \tag{34}$$

Where ω is the frequency of oscillation for given torsion (if $i \neq j$) or normal (if $i = j$) directions.

Hellman (1937) and Feynman (1939) derived their correspondence equation of force in quantum mechanical systems as

$$\frac{\partial E_\lambda}{\partial \lambda} = \langle \psi_\lambda | \frac{\partial H_\lambda}{\partial \lambda} | \psi_\lambda \rangle \tag{35}$$

Substituting in the Born-Oppenheimer Hamiltonian and using product-rule yields:

$$\mathbf{F}_I = - \langle \psi(\mathbf{R}) | \frac{\partial H_{BO}(\mathbf{R})}{\partial \mathbf{R}_I} | \psi_(\mathbf{R}) \rangle \tag{36}$$

There are only two terms which concern the nuclei-coordinates. In the limit of many electrons, let the sums become integrals and this entails:

$$\mathbf{F}_I = - \int n_{\mathbf{R}}(\mathbf{r}) \frac{\partial V_{\mathbf{R}}(\mathbf{r})}{\partial \mathbf{R}_I} d\mathbf{r} - \frac{\partial E_N(\mathbf{R})}{\partial \mathbf{R}_I} \tag{37}$$

Where the potential V is the electron-nuclei interaction, with dependence on both spatial $\mathbf{r}$ coordinates and nucleic $\mathbf{R}$ site-coordinates.

Differentiating a second time to obtain force constants, the so-called Hessian yields:

$$\frac{\partial^2 E(\mathbf{R})}{\partial \mathbf{R}_I \partial \mathbf{R}_J} \equiv \int \frac{\partial n_{\mathbf{R}}(r)}{\partial \mathbf{R}_J} \frac{\partial V_{\mathbf{R}}(r)}{\partial \mathbf{R}_I} dr + \int n_{\mathbf{R}}(r) \frac{\partial^2 V_{\mathbf{R}}(r)}{\partial \mathbf{R}_I \partial \mathbf{R}_J} dr + \frac{\partial^2 E_N(\mathbf{R})}{\partial \mathbf{R}_I \partial \mathbf{R}_J} \tag{38}$$

Note that the linear response of ground-state charge density, $\frac{\partial n_{\mathbf{R}(r)}}{\partial \mathbf{R}}$, is needed to compute the Hessian

Analagously we may apply this sort of analysis to *density functional theory*, the formalism set down by Kohn-Hohenberg-Sham which maps the quantum many-fermion problem to an effective potential and charge density function. Of course the condition of number conservation is enforced such that the charge

density integrates to an integer number of electrons in the system.

This *universal functional* takes the form of:

$$E[n] = F[n] + \int n(r)V(r)dr \tag{39}$$

where $V(\mathbf{r})$ is the external potential due to the lattice background

This subtle but powerful reformulation of quantum many-body problems lies in the fact that physically real properties are uniquely determined by the ground-state charge density. It does not matter the specific electron-electron interactions as long as one can calculate the charge profile as function of spatial coordinates, as opposed to dealing with the basis set of N electrons, each having their own x, y, z coordinates (a problem with scaling of 3N degrees of freedom)

The scheme goes to the independent electron picture, defining:

$$F[n] = T_0[n] + \frac{e^2}{2}\int \frac{n(\mathbf{r})n(\mathbf{r}^{'})}{|\mathbf{r}-\mathbf{r}^{'}|}d\mathbf{r}d\mathbf{r}^{'} + E_{xc}[n] \tag{40}$$

Where $T_0[n]$ is the ground-state density distribution in the absence of electron-electron interaction, the second term being the Coulomb repulsion (with a division of 2 to remove double-counting the same spatial coordinate pair $\langle r, r^{'}\rangle$. The third term $E_{xc}[n]$ is the *exchange-correlation* energy, a term which encapsulates the remaining constraints and interactions on the charge density profile. This includes constraints such as Pauli-exlusion, magnetic ordering, etc. It is no coincidence that it is largely the spin degree of freedom which provides additional exchange-correlation for the self-interacting part of density profile.

However we may go back to Schrödinger equation by differentiating this functional with respect to the density profile to obtain the effective field that will yield this yet unknown charge profile.

$$V_{SCF} = V(r) + e^2 \int \frac{n(r^{'})}{|r - r^{'}|} dr^{'} + v_{xc}(r)$$

$$v_{xc}(r) \equiv \frac{\delta E_{xc}}{\delta n(r)}$$

Thus allowing a self-consistent scheme to calculate $n(r)$ and V_{SCF}, SCF standing for *self-consistent field*

Given the effective potential, the noninteracting kinetic energy functional T_0 wouldn't have to be solved and one is left with a one-particle like Schrodinger equation to be solved. The ground state and noninteracting kinetic-energy fucntional would be solved in terms of so called *Kohn-Sham orbitals*

$$n(\mathbf{r}) = 2 \sum_{n=1}^{N/2} |\psi_n(\mathbf{r})|^2 \tag{41}$$

$$T_0[n] = -2 \frac{\hbar^2}{2m} \sum_{n=1}^{N/2} \int \psi_n^*(\mathbf{r}) \frac{\partial^2 \psi_n(\mathbf{r})}{\partial \mathbf{r}^2} d\mathbf{r} \tag{42}$$

Where ψ are the auxiliary Kohn-Sham orbitals and this is in the case of no magnetic order, hence the divison by 2 in the summation in accommodating two electrons of opposite spin per orbital

Although there is complication due to the potential depending on its own eigenfunctions implicitly through the charge density, once explicit form of the exchange-correlation energy is written then it will be susceptible to solution through self-consistent methods.

A remarkabley accurate and simple approximation to this exchange-correlation energy is the *local-density approximation*, known as LDA. A physically intuitve ansatz that penalizes high frequency fluctuations in small volumes. The exchange-correlation energy and potential are written as:

$$E_{xc}[n] = \int \epsilon_{xc}(n)|_{n=n(\mathbf{r})} n(\mathbf{r}) d\mathbf{r} \tag{43}$$

$$v_{xc}[n](\mathbf{r}) = (\epsilon_{xc}(n) + n\frac{d\epsilon_{xc}(n)}{dn}) \tag{44}$$

3 Linear Response for DMFT

In general and written explicitly, linear response will yield for the ground-state energy:

$$\frac{\partial E}{\partial \lambda_i} = \int \frac{\partial V_{\lambda_i}(\mathbf{r})}{\partial \lambda_i} n_\lambda(\mathbf{r}) d\mathbf{r} \tag{45}$$

$$\frac{\partial^2 E}{\partial \lambda_i \partial \lambda_j} = \int \frac{\partial^2 V_{\lambda_i}(\mathbf{r})}{\partial \lambda_i \partial \lambda_j} n_\lambda(\mathbf{r}) d\mathbf{r} + \int \frac{\partial n_\lambda(\mathbf{r})}{\partial \lambda_i} \frac{\partial V_{\lambda(\mathbf{r})}}{\partial \lambda_j} d\mathbf{r} \tag{46}$$

But the calculation of the charge density's perturbation in terms of the wave function results in first order as:

$$\Delta n(\mathbf{r}) = 4Re \sum_{n=1}^{N/2} \psi_n^*(\mathbf{r}) \Delta\psi_n(\mathbf{r}) \tag{47}$$

where $\Delta^\lambda F \equiv \sum_i \frac{\partial F_\lambda}{\partial \lambda_i} \Delta\lambda_i$ denotes a total change of the respective quantity.

Although implementation is linear, the self-consistency scheme extrapolates the first order difference to all order as long as the changes are adiabatic or weak. The condition is written as

$$(H_{SCF} - \epsilon_n) |\Delta\psi_n\rangle = -(\Delta V_{SCF} - \Delta\epsilon_n) |\psi_n\rangle \tag{48}$$

where

$$H_{SCF} \equiv -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mathbf{r}^2} + V_{SCF}(\mathbf{r}) \tag{49}$$

$$\Delta\epsilon = \langle\psi_n|\Delta V_{SCF}|\psi_n\rangle \tag{50}$$

And the correction to the wavefunctions themselves ψ are the off-diagonal

corrections as in standard perturbation theory.

$$\Delta\psi_n(\mathbf{r}) = \sum_{m\neq n} \psi_m(\mathbf{r}) \frac{\langle\psi_m|\Delta V_{SCF}|\psi_n\rangle}{\epsilon_n - \epsilon_m} \tag{51}$$

$$\Delta n(\mathbf{n}) = 4\sum_{n=1}^{N/2}\sum_{m\neq n} \psi_n^*\psi_m(\mathbf{r}) \frac{\langle\psi_m|\Delta V_{SCF}|\psi_r\rangle}{\epsilon_n - \epsilon_m} \tag{52}$$

Contributions from occupied state transfers will cancel each other over the summation in equation (52) above due to hermiticity. Physically this also makes sense as transfer from occupied to unoccupied states, so called excitations, are the quantities of interest and among the initially unmixed Hamiltonians, all transfers obey sum rules [is this garbage?]

This implies for equation (48) that there exist null eigenvalues for the linear operator. Here we note that the linear response only depends on the terms that couple unoccupied to occupied bands. This allows us to only calculate among the projection of the linear correction to the occupied manifold onto the empty one.

We can denote projector operators P_c & P_ν, the empty and occupied state projectors respectively, and rewrite equation (52) as

$$\left(H_{SCF} + \alpha P_\nu - \epsilon_n\right)|\Delta\psi_n\rangle = -P_c\Delta V_{SCF}\,|\psi_n\rangle \tag{53}$$

Of course in real calculations, orthonormality is ensured among the states upon setup and so projector operators P_ν is redundant.

The main motivation for linear reponse formalism is the construction of phonon spectra. One can also avoid building a large supercell as in finite-difference calculations. This is due to the ability to decompose the linear response linearly via Fourier transforms. Perturbations of different wavelengths are decoupled and so phonon frequencies at any arbitrary wave vector $\mathbf{q}$ can be

calculated with scaling independent of the frequency.

Decomposing ΔV_{SCF} yields:

$$\Delta V_{SCF} = (\mathbf{r}) = \sum_{\mathbf{q}} \Delta v^{\mathbf{q}}_{SCF}(\mathbf{r}) e^{i\mathbf{q}\cdot\mathbf{r}} \tag{54}$$

This allows equation (53) to be rewritten as

$$\begin{aligned}(H^{\mathbf{k}+\mathbf{q}}_{SCF} + \alpha \sum_{\nu'} |\psi^{\mathbf{k}+\mathbf{q}}_{\nu'}\rangle \langle\psi^{\mathbf{k}+\mathbf{q}}_{\nu'}| - \epsilon^{\mathbf{k}}_{\nu}) |\Delta\psi^{\mathbf{k}+\mathbf{q}}_{\nu}\rangle \\ = -[1 - \sum_{\nu'} |\psi^{\mathbf{k}+\mathbf{q}}_{\nu'}\rangle \langle\psi^{\mathbf{k}+\mathbf{q}}_{\nu'}|]\Delta v^{\mathbf{q}}_{SCF} |\psi^{\mathbf{k}}_{\nu}\rangle\end{aligned}$$

The linear charge response is similarly simple to calculate as

$$\Delta n^{\mathbf{q}}_{\nu}(\mathbf{r}) = 4 \sum_{\mathbf{k}\nu} u^{\mathbf{k}*}_{\nu}(\mathbf{r}) \Delta u^{\mathbf{k}+\mathbf{q}}_{\nu}(\mathbf{r}) \tag{55}$$

And the response of the self-consistent potential similarly decomposed as:

$$\begin{aligned}\Delta v^{\mathbf{q}}_{SCF}(\mathbf{r}) = \Delta v^{\mathbf{q}}(\mathbf{r}) + e^2 \int \frac{\Delta n^{\mathbf{q}}(r')}{|r - r'|} e^{-i\mathbf{q}\cdot(r-r')} dr' \\ + \frac{dv_{xc}(n)}{d\mathbf{n}})|_{n=n(r)} \Delta n^{\mathbf{q}}(r)\end{aligned}$$

Per usual, the space is complete and basis orthonormal. Therefore calculations on the components are trivial, as is well known that Fourier frequencies become multiplication under transformation to k-space from derivatives in real space. And so although all components/modes have to be checked, the implementation is simple enough and scales well enough that this is still considered the standard.

All of these assumptions are in some way to maintain Bloch's theorem, because dealing with lattice-periodic functions is simple. It is possible that other bases are better suited but this would entail a systematic categorization of what boundary conditions would use which bases functions (There are some cases

where Legendre functions and so-called intermediate representations exhibit superior calculational performance, but again under very specific conditons and symmetries) [Need to understand Saitama group, Julich group... what did they do and why? Clock is ticking].

Within the framework of DMFT, the calculation of self-energy is now taken into account to treat strong correlation in the form of Hubbard repulsion term. Namely we start from the total energy functional:

$$E \equiv E_{LDA}[\rho] + \langle \hat{H}_{LDA} \rangle - \sum_{m,k} \epsilon^{LDA}_{m,k} + \frac{1}{2} \sum_{imm',\sigma\sigma'} U^{\sigma\sigma'}_{mm'} \langle \hat{n}_{im\sigma} \hat{n}_{im'\sigma'} \rangle - E_{DC} \quad (56)$$

The $\hat{H}_{LDA}$ is the effective low-energy Hamiltonian obtained from LDA band structure that is projected onto a localized atomic basis, in our case Wannier orbitals. The full LDA component is subtracted in the same window once replaced, the $\sum \epsilon$-term, and traditional Hubbard term which penalizes double-occupation. The double-counting term E_{DC} is taken to be the average Coulomb repulsion proportional instead to $\langle \hat{n}_{im\sigma} \rangle \langle \hat{n}_{im'\sigma'} \rangle$

The first order derivative yields terms:

$$\delta_\lambda \langle \hat{H}_{LDA} \rangle = \langle \delta_\lambda \hat{H}_{LDA} \rangle + Tr \sum_{\mathbf{k}, i\omega_n} \hat{H}^{\mathbf{k}}_{LDA} \delta_\lambda \hat{G}_{\mathbf{k}}(i\omega_n) e^{i\omega_n 0+} \quad (57)$$

$$(\delta_s \hat{H}^{\mathbf{k}}_{LDA})_{nm} = \sum_{i=N_a}^{N_b} \langle \phi_n | \psi_{ik} \rangle \langle \psi_{ik} | \phi_m \rangle \cdot (\delta_s V^{KS}_{ik} + \delta_s V^{HXC}_{ik}) \quad (58)$$

To calculate $\delta\Sigma$, a functional derivative is taken of the impurity Green function (the authors of the paper neglected double-counting corrections since the term is second order in total) and extract the formula

$$\delta\hat{G}(\tau_{12}) = -\hat{\chi}(\tau_{1234})\delta\hat{\mathcal{G}}^{-1}(\tau_{34}) \tag{59}$$

where χ can be sampled via the impurity solver through explicit summation over Matusbara frequencies, and the self-consistency is closed by enforcing Dyson equation per usual. Namely $\delta_s\hat{\mathcal{G}}^{-1} = \delta_s\hat{G}^{-1} + \delta_s\hat{\Sigma}$

To round this out explicitly, I believe the scheme was to equate:

$$-\hat{\chi}(\tau_{1234})\delta\hat{\mathcal{G}}^{-1}(\tau_{34}) = \delta_s\hat{G}_{\mathbf{k}}(\omega) = \hat{G}_{\mathbf{k}}(\omega)[\delta_s\hat{H}^{\mathbf{k}}_{LDA} + \delta_s\hat{\Sigma}(\omega) - \delta_s\mu]\hat{G}_{\mathbf{k}}(\omega) \tag{60}$$

Where χ can be sampled directly in Matsubara space in CTQMC solver, $\delta_\lambda\hat{H}_{LDA}$ is calculable as weighted by overlaps of correlated orbitals on DFPT, and $\delta_\lambda\mu$ amounts to a constant off-set.