Some notes on LAPW

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The LAPW basis takes the form:

$$\chi_{\mathbf{k}+\mathbf{K}}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i(\mathbf{k}+\mathbf{K})\mathbf{r}} = \frac{4\pi i^l}{\sqrt{V}} e^{i(\mathbf{k}+\mathbf{K})\mathbf{r}_\alpha} Y^*_{lm}(R(\hat{\mathbf{k}}+\hat{\mathbf{K}})) j_l(|\mathbf{k}+\mathbf{K}||\mathbf{r}-\mathbf{r}_\alpha|) Y_{lm}(R(\mathbf{r}-\mathbf{r}_\alpha)) \qquad interstitial \tag{1}$$

$$\chi_{\mathbf{k}+\mathbf{K}}(\mathbf{r}) = \left(a_{lm} u_l(|\mathbf{r}-\mathbf{r}_\alpha|) + b_{lm}\dot{u}_l(|\mathbf{r}-\mathbf{r}_\alpha|)\right) Y_{lm}(R(\hat{\mathbf{r}}-\hat{\mathbf{r}_\alpha})) \qquad MT-sphere \tag{2}$$

The matching condition at the MT-sphere S gives

$$\begin{pmatrix} u_l(S) & \dot{u}_l(S) \\ \frac{d}{dr}u_l(S) & \frac{d}{dr}\dot{u}_l(S) \end{pmatrix} \begin{pmatrix} a_{lm} \\ b_{lm} \end{pmatrix} = \frac{4\pi i^l}{\sqrt{V}} e^{i(\mathbf{k}+\mathbf{K})\mathbf{r}_\alpha} Y^*_{lm}(R(\hat{\mathbf{k}}+\hat{\mathbf{K}})) \begin{pmatrix} j_l(|\mathbf{k}+\mathbf{K}|S) \\ \frac{d}{dr} j_l(|\mathbf{k}+\mathbf{K}|S) \end{pmatrix} \tag{3}$$

with the solution

$$\begin{pmatrix} a_{lm} \\ b_{lm} \end{pmatrix} = \frac{4\pi i^l}{\sqrt{V}} e^{i(\mathbf{k}+\mathbf{K})\mathbf{r}_\alpha} Y^*_{lm}(R(\hat{\mathbf{k}}+\hat{\mathbf{K}})) \begin{pmatrix} \frac{d}{dr}\dot{u}_l(S) & -\dot{u}_l(S) \\ -\frac{d}{dr}u_l(S) & u_l(S) \end{pmatrix} \frac{1}{u_l(S)\frac{d}{dr}\dot{u}_l(S) - \dot{u}_l(S)\frac{d}{dr}u_l(S)} \begin{pmatrix} j_l(|\mathbf{k}+\mathbf{K}|S) \\ \frac{d}{dr} j_l(|\mathbf{k}+\mathbf{K}|S) \end{pmatrix} \tag{4}$$

The two solutions satisfy the following equations

$$\left(-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V_{KS}(r) - \varepsilon\right) r u_l(r) = 0 \tag{5}$$

$$\left(-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V_{KS}(r) - \varepsilon\right) r \dot{u}_l(r) = r u_l(r) \tag{6}$$

We multiply the first equation by $r\dot{u}_l(r)$ and the second by $ru_l(r)$ to obtain

$$\int_0^S dr \left\{ r\dot{u}_l(r) \left(-\frac{d^2}{dr^2}\right) r u_l(r) - r u_l(r) \left(-\frac{d^2}{dr^2}\right) r\dot{u}_l(r) \right\} = -\int_0^S dr r^2 u_l(r) u_l(r) \tag{7}$$

Integration by parts gives

$$\left[-r\dot{u}_l(r) \frac{d}{dr}\left(r u_l(r)\right) + r u_l(r) \frac{d}{dr}\left(r\dot{u}_l(r)\right) \right]_0^S = -1 \tag{8}$$

which finally leads to

$$\dot{u}_l(S)\frac{d}{dr}u_l(S) - u_l(S)\frac{d}{dr}\dot{u}_l(S) = \frac{1}{S^2} \tag{9}$$

We can than simplify the solution for a_{lm} and b_{lm} to

$$\begin{pmatrix} a_{lm} \\ b_{lm} \end{pmatrix} = \frac{4\pi i^l}{S^2\sqrt{V}} e^{i(\mathbf{k}+\mathbf{K})\mathbf{r}_\alpha} Y^*_{lm}(R(\hat{\mathbf{k}}+\hat{\mathbf{K}})) \begin{pmatrix} \dot{u}_l(S)\frac{d}{dr} j_l(|\mathbf{k}+\mathbf{K}|S) - \frac{d}{dr}\dot{u}_l(S) j_l(|\mathbf{k}+\mathbf{K}|S) \\ \frac{d}{dr}u_l(S) j_l(|\mathbf{k}+\mathbf{K}|S) - u_l(S)\frac{d}{dr} j_l(|\mathbf{k}+\mathbf{K}|S) \end{pmatrix} \tag{10}$$

This equation is implemented in Wien2k, and also in both dmft1 and dmft2 steps.

To compute the projector, we need the overlap between a localized function $\phi(r)Y_L(\mathbf{r})$, and Kohn-Sham states

$$\mathcal{U}^{\mathbf{k},\mathbf{r}_\alpha}_{i,m} = \langle \phi_l Y_{lm} | \psi_{\mathbf{k}i} \rangle = \sum_{\mathbf{K}} C^{\mathbf{k}}_{i\mathbf{K}} \langle \phi_l(|\mathbf{r}-\mathbf{r}_\alpha|) Y_{lm}(R(\hat{\mathbf{r}}-\hat{\mathbf{r}}_\alpha)) | \chi_{\mathbf{k}+\mathbf{K}}(\mathbf{r}) \rangle \tag{11}$$

If function $\phi(r)$ extends sufficiently outside its MT-sphere, the overlap $\mathcal{U}_{i,m}^{\mathbf{k},\mathbf{r}_\alpha}$ will have non-zero contribution from all other MT-spheres. However, we will use only the envelope function outside its center sphere, because the increased charge in the neighboring spheres really should not be counted here as charge contribution to $\phi(r)$ function.

Therefore we have only two contributions. Inside MT-sphere we have

$$\langle \phi_l(|\mathbf{r}-\mathbf{r}_\alpha|) Y_{lm}(\hat{\mathbf{r}}-\hat{\mathbf{r}}_\alpha)|\chi_{\mathbf{k}+\mathbf{K}}(\mathbf{r})\rangle = \sum_\kappa a_{lm}^\kappa \int_0^S \phi(r) u_l^\kappa(r) r^2 dr \tag{12}$$

and outside MT-sphere we get

$$\langle \phi_l(|\mathbf{r}-\mathbf{r}_\alpha|) Y_{lm}(R(\hat{\mathbf{r}}-\hat{\mathbf{r}}_\alpha))|\chi_{\mathbf{k}+\mathbf{K}}(\mathbf{r})\rangle = \frac{4\pi i^l}{\sqrt{V}} e^{i(\mathbf{k}+\mathbf{K})\mathbf{r}_\alpha} Y_{lm}^*(R(\hat{\mathbf{k}}+\hat{\mathbf{K}})) \int_S^{S_2} \phi_l(r) j_l(|\mathbf{k}+\mathbf{K}|r) r^2 dr \tag{13}$$

I. FREE ENERGY AND TOTAL ENERGY

The equation for the total energy is

$$E = \mathrm{Tr}(H_0 G) + \frac{1}{2}\mathrm{Tr}(\Sigma G) - \Phi^{DC}[n_{loc}] + \Phi^H[\rho] + \Phi^{xc}[\rho] \tag{14}$$

where

$$H_0 = -\nabla^2 + \delta(\mathbf{r}-\mathbf{r}')V_{ext}(\mathbf{r})$$

We typically evaluate it in the following way

$$E = \mathrm{Tr}((-\nabla^2 + V_{ext} + V_H + V_{xc})G) + \frac{1}{2}\mathrm{Tr}(\Sigma G) - \Phi^{DC}[\rho_{loc}] - \mathrm{Tr}((V_H+V_{xc})\rho) + \Phi^H[\rho] + \Phi^{xc}[\rho] \tag{15}$$

Namely, we use the Green's function of the solid to evaluate:

$$E_1 = \mathrm{Tr}((-\nabla^2 + V_{ext} + V_H + V_{xc})G) - \mathrm{Tr}((V_H+V_{xc})\rho) + \Phi^H[\rho] + \Phi^{xc}[\rho] \tag{16}$$

and the impurity to evaluate

$$E_2 = \frac{1}{2}\mathrm{Tr}(\Sigma_{imp} G_{imp}) - \Phi^{DC}[\rho_{imp}] \tag{17}$$

Notice that $\frac{1}{2}\mathrm{Tr}(\Sigma_{imp}G_{imp})$ is not evaluated as a Matsubara sum, but we rather compute it from probabilities of atomic states, i.e.,

$$\frac{1}{2}\mathrm{Tr}(\Sigma_{imp}G_{imp}) = \sum_m P_m E_m - \sum_\alpha \varepsilon_{imp}^\alpha n_{imp}^\alpha \tag{18}$$

The free energy functional is

$$\Gamma[G] = \mathrm{Tr}\log G - \mathrm{Tr}\log((G_0^{-1} - G^{-1})G) + \Phi^H[\rho] + \Phi^{xc}[\rho] + \Phi^{DMFT}[G_{loc}] - \Phi^{DC}[\rho_{loc}] \tag{19}$$

hence stationarity gives

$$G^{-1} - G_0^{-1} + V_H + V_{xc} + \Sigma_{DMFT} - V_{dc} = 0 \tag{20}$$

and hence

$$F = \mathrm{Tr}\log G - \mathrm{Tr}(\Sigma G) + \mathrm{Tr}(V_{dc}\rho_{loc}) + \Phi^{DMFT}[G_{loc}] - \Phi^{DC}[\rho_{loc}] - \mathrm{Tr}((V_H+V_{xc})\rho) + \Phi^H[\rho] + \Phi^{xc}[\rho] \tag{21}$$

Since F_{imp} contains Φ^{DMFT}, i.e,

$$F_{imp} = \mathrm{Tr}\log G_{imp} - \mathrm{Tr}(\Sigma_{imp}G_{imp}) + \Phi^{DMFT}[G_{imp}] \tag{22}$$

we can write

$$F = \mathrm{Tr}\log(G) - \mathrm{Tr}\log(G_{loc}) + F_{imp} + \mathrm{Tr}(V_{dc}\rho_{loc}) - \Phi^{DC}[\rho_{loc}] - \mathrm{Tr}((V_H+V_{xc})\rho) + \Phi^H[\rho] + \Phi^{xc}[\rho] \tag{23}$$

where

$$F_{imp} = E_{imp} - TS_{imp}$$

and

$$E_{imp} = \mathrm{Tr}((\Delta + \varepsilon_{imp} - \omega_n \frac{\partial \Delta}{\partial \omega_n})G_{imp}) + \frac{1}{2}\mathrm{Tr}(\Sigma_{imp} G_{imp}) - TS_{imp}$$

Hence

$$F + TS_{imp} = \mathrm{Tr}\log(G) - \mathrm{Tr}\log(G_{loc}) + \mathrm{Tr}((\Delta + \varepsilon_{imp} - \omega_n \frac{\partial \Delta}{\partial \omega_n})G_{imp}) + \frac{1}{2}\mathrm{Tr}(\Sigma_{imp} G_{imp}) + \mathrm{Tr}(V_{dc}\rho_{loc}) - \Phi^{DC}[\rho_{loc}] \\ -\mathrm{Tr}((V_H + V_{xc})\rho) + \Phi^H[\rho] + \Phi^{xc}[\rho] \quad (24)$$

which can also be cast into the form

$$F + TS_{imp} = \mathrm{Tr}\log(G) - \mathrm{Tr}\log(G_{loc}) + \mathrm{Tr}((\Delta - \omega_n \frac{\partial \Delta}{\partial \omega_n} + \varepsilon_{imp} + V_{dc})G_{loc}) + \frac{1}{2}\mathrm{Tr}(\Sigma_{imp} G_{imp}) - \Phi^{DC}[\rho_{imp}] \\ -\mathrm{Tr}((V_H + V_{xc})\rho) + \Phi^H[\rho] + \Phi^{xc}[\rho] \quad (25)$$

We thus compute the following quantities with the Green's function of the solid:

$$F_1 = \mathrm{Tr}\log(G) - \mathrm{Tr}\log(G_{loc}) + \mathrm{Tr}((\Delta - \omega_n \frac{\partial \Delta}{\partial \omega_n} + \varepsilon_{imp} + V_{dc})G_{loc}) - \mathrm{Tr}((V_H + V_{xc})\rho) + \Phi^H[\rho] + \Phi^{xc}[\rho] \quad (26)$$

and the following with the impurity:

$$F_2 = \frac{1}{2}\mathrm{Tr}(\Sigma_{imp} G_{imp}) - \Phi^{DC}[\rho_{imp}] - TS_{imp} \quad (27)$$

Notice that F_2 is similar to E_2 (except for the entropy term), hence E_{solid} and F_{solid} contain exactly the same Monte Carlo noise.