Pulay Charge Mixing

10/2/03

– Fixed-point charge mapping

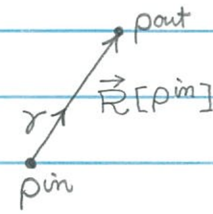
$$\rho^{in}(\mathbf{r}) \longmapsto v(\mathbf{r}) \longmapsto \{\psi_i(\mathbf{r})\} \longmapsto \rho^{out}(\mathbf{r}) \tag{1}$$

(Charge density residual)

$$R[\rho^{in}] \equiv \rho^{out}[\rho^{in}] - \rho^{in} \tag{2}$$

(Steepest descent)

$$\rho^{in} \longleftarrow \rho^{in} + \underset{\text{RSCMIX}}{\gamma} R[\rho^{in}] \tag{3}$$



– Pulay mixing

Store the previous $\overset{\text{NITRHO}}{n}$ input charge densities ρ_i^{in} $(i=1,\dots,n)$ with residuals $R[\rho_i^{in}]$.

Consider a linear mixing

$$\rho^{in} = \sum_{i=1}^{n} \alpha_i \rho_i^{in} \tag{4}$$

with the charge-conservation constraint

$$\sum_{i=1}^{n} \alpha_i = 1 \tag{5}$$

We approximate the residual of the linearly-mixed density as

$$R[\rho^{in}] = R\Big[\sum_i \alpha_i \rho_i^{in}\Big] \simeq \sum_i \alpha_i R[\rho_i^{in}] \tag{6}$$

We determine $\{\alpha_i\}$ to minimize the norm of the residual

$$\mathcal{R} = \langle R[\rho^{in}] \,|\, R[\rho^{in}] \rangle = \int d\mathbf{r}\, R(\mathbf{r}) R(\mathbf{r}) \tag{7}$$

– Constrained minimize : Lagrange multiplier

$$\mathcal{H}^* = \langle R[\rho^{in}] | R[\rho^{in}] \rangle - \lambda \left(\sum_{i=1}^{n} \alpha_i - 1 \right) \tag{8}$$

$$= \sum_{i=1}^{n} \sum_{j=1}^{n} \alpha_i \underbrace{\langle R[\rho_i^{in}] | R[\rho_j^{in}] \rangle}_{\equiv A_{ij}} \alpha_j - \lambda \left(\sum_{i=1}^{n} \alpha_i - 1 \right) \tag{9}$$

$$= \sum_{i=1}^{n} \sum_{j=1}^{n} \alpha_i A_{ij} \alpha_j - \lambda \left(\sum_{i=1}^{n} \alpha_i - 1 \right) \tag{10}$$

where

$$A_{ij} = \langle R[\rho_i^{in}] | R[\rho_j^{in}] \rangle \tag{11}$$

$$\frac{\partial \mathcal{H}^*}{\partial \alpha_i} = \sum_j A_{ij} \alpha_j + \sum_j \alpha_j \underbrace{A_{ji}}_{\overset{\text{III}}{A_{ij}}} - \lambda = 0$$

$$\therefore 2 \sum_j A_{ij} \alpha_j = \lambda \tag{12}$$

$\sum_i A^{-1}_{ki} \times$ Eq. (12)

$$2 \sum_i \underbrace{\sum_j A^{-1}_{ki} A_{ij}}_{\delta_{kj}} \alpha_j = \lambda \sum_i A^{-1}_{ki}$$

$$\therefore \alpha_k = \frac{\lambda}{2} \sum_i A^{-1}_{ki} \tag{13}$$

The Lagrange multiplier is determined to satisfy the constraint,

$$\sum_k \alpha_k = \frac{\lambda}{2} \sum_{ki} A^{-1}_{ki} = 1$$

$$\therefore \frac{\lambda}{2} = \frac{1}{\sum_{ki} A^{-1}_{ki}} \tag{14}$$

Substituting Eq. (14) to (13),

$$\alpha_i = \frac{\sum_{j=1}^{n} A^{-1}_{ij}}{\sum_{k=1}^{n}\sum_{j=1}^{n} A^{-1}_{kj}} \tag{15}$$

– Pulay mixing algorithm

$$\left\{\begin{array}{lll} \overset{\text{NRHOP}}{n} = \max(icg, N_{itrho}) & & \\ \rho_i^{in}(\mathbf{r}) & (i = 1, \dots, n) & \rightarrow \text{RHOP}(-M_{shlp}:M_{shup}^{3}, N_{itrho}) \\ R[\rho_i^{in}] & (i = 1, \dots, n) & \rightarrow \text{RRHO}(-M_{shlp}:M_{shup}^{3}, N_{itrho}) \end{array}\right.$$

Compute $\underset{\rightarrow \text{ARES}(N_{itrho}, N_{itrho})}{A_{ij}} = \langle R[\rho_i^{in}] | R[\rho_j^{in}] \rangle = \int d\mathbf{r}\, R[\mathbf{r}; \rho_i^{in}] R[\mathbf{r}; \rho_j^{in}]$

invert $A_{ij} \rightarrow A^{-1}_{ij}$ → ARESI(N_{itrho}, N_{itrho})

$\underset{\text{ALMIX}}{\alpha_i} = \sum_{j=1}^{n} A^{-1}_{ij} \Big/ \underbrace{\sum_{k=1}^{n}\sum_{j=1}^{n} A^{-1}_{kj}}_{\text{aIRES\_SUM}}$

$$\rho^{in} = \sum_{i=1}^{n} \alpha_i \rho_i^{in}$$

$$\rho^{in} \longleftarrow \rho^{in} + \gamma \overbrace{R[\rho^{in}]}^{\simeq \sum_i \alpha_i R[\rho_i^{in}]}$$

$$= \sum_{i=1}^{n} \alpha_i \left\{ \rho_i^{in} + \gamma R[\rho_i^{in}] \right\} \tag{16}$$