

# Charge Mixing Methods: Ver. 1.0

Taisuke Ozaki, RCIS, JAIST

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## 1 Simple mixing

A simple scheme of mixing charge densities is to mix the input matrix and the output density matrix at the last  $n$ th SCF step as

$$\rho_{n+1}^{(\text{in})} = \alpha \rho_n^{(\text{in})} + (1 - \alpha) \rho_n^{(\text{out})}, \quad (1)$$

where  $\alpha$  is a mixing parameter, and the optimum choice strongly depends on the system under study. After mixing the density matrix, the corresponding charge density is easily evaluated.

## 2 RMM-DIIS for density matrix

A more efficient scheme beyond the simple mixing method is the residual minimization method in the direct inversion of iterative subspace (RMM-DIIS) [1, 2]. By defining a residual  $R$ :

$$R_n \equiv \rho_n^{(\text{out})} - \rho_n^{(\text{in})}, \quad (2)$$

we assume that the residual  $\bar{R}_{n+1}$  at the next  $(n + 1)$ th SCF step can be estimated by a linear combination of  $\{R_m\}$

$$\bar{R}_{n+1} = \sum_{m=n-(p-1)}^n \alpha_m R_m, \quad (3)$$

where  $\alpha_m$  is found by minimizing  $\langle \bar{R}_n | \bar{R}_n \rangle$  with a constraint  $\sum_{m=n-(p-1)}^n \alpha_m = 1$ . According to Lagrange's multiplier method,  $F$  is defined by

$$\begin{aligned} F &= \langle \bar{R}_{n+1} | \bar{R}_{n+1} \rangle - \lambda \left( 1 - \sum_m \alpha_m \right), \\ &= \sum_{m,m'} \alpha_m \alpha_{m'} \langle R_m | R_{m'} \rangle - \lambda \left( 1 - \sum_m \alpha_m \right). \end{aligned} \quad (4)$$

Considering  $\frac{\partial F}{\partial \alpha_k} = 0$  and  $\frac{\partial F}{\partial \lambda} = 0$ , an optimum set of  $\{\alpha\}$  can be found by solving the following linear equation:

$$\begin{pmatrix} \langle R_{n-(p-1)} | R_{n-(p-1)} \rangle & \cdots & \cdots & 1 \\ \cdots & \cdots & \cdots & 1 \\ \cdots & \cdots & \langle R_n | R_n \rangle & \cdots \\ 1 & 1 & \cdots & 0 \end{pmatrix} \begin{pmatrix} \alpha_{n-(p-1)} \\ \alpha_{n-(p-1)+1} \\ \vdots \\ \frac{1}{2} \lambda \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 1 \end{pmatrix}. \quad (5)$$

An optimum choice of the input density matrix  $\rho_{n+1}^{(\text{in})}$  may be obtained by the set of coefficients  $\{\alpha\}$  as

$$\rho_{n+1}^{(\text{in})} = \sum_{m=n-(p-1)}^n \alpha_m \rho_m^{(\text{in})}. \quad (6)$$

### 3 Kerker mixing in momentum space

After Fourier-transforming the difference charge density  $\delta n(\mathbf{r})$  by

$$\delta \tilde{n}(\mathbf{q}_{\mathbf{p}'}) = \frac{1}{N_1 N_2 N_3} \sum_{\mathbf{p}} \delta n(\mathbf{r}_{\mathbf{p}}) e^{-i\mathbf{q}_{\mathbf{p}'} \cdot \mathbf{r}_{\mathbf{p}}}, \quad (7)$$

$\delta \tilde{n}(\mathbf{q})$  can be mixed in a simple mixing [3]:

$$\delta \tilde{n}_{n+1}^{(\text{in})}(\mathbf{q}) = \alpha w(\mathbf{q}) \delta \tilde{n}_n^{(\text{in})}(\mathbf{q}) + (1 - \alpha w(\mathbf{q})) \delta \tilde{n}_n^{(\text{out})}(\mathbf{q}) \quad (8)$$

with the Kerker factor  $w(\mathbf{q})$ .

$$w(\mathbf{q}) = \frac{|\mathbf{q}|^2}{|\mathbf{q}|^2 + q_0^2}, \quad (9)$$

where  $q_0 = \gamma|\mathbf{q}_{\text{min}}|$ , and  $\mathbf{q}_{\text{min}}$  is the  $\mathbf{q}$  vector with the minimum magnitude except 0-vector in the FFT. Since the charge sloshing tends to be introduced by charge components with a small  $\mathbf{q}$  vector, it is found that  $w(\mathbf{q})$  is effective for avoiding the charge sloshing. The back transformation of the mixed charge density in momentum space gives the charge density in real space as

$$\delta n(\mathbf{r}_{\mathbf{p}}) = \sum_{\mathbf{p}'} \delta \tilde{n}(\mathbf{q}_{\mathbf{p}'}) e^{i\mathbf{q}_{\mathbf{p}'} \cdot \mathbf{r}_{\mathbf{p}}}. \quad (10)$$

### 4 RMM-DIIS in momentum space

By defining the residual vector  $R(\mathbf{q})$  in momentum space,

$$R_n(\mathbf{q}) \equiv \rho_n^{(\text{out})}(\mathbf{q}) - \rho_n^{(\text{in})}(\mathbf{q}), \quad (11)$$

and the norm with the Kerker metric as:

$$\langle R_m | R_{m'} \rangle \equiv \sum_{\mathbf{q}} \frac{R_m^*(\mathbf{q}) R_{m'}(\mathbf{q})}{w(\mathbf{q})}, \quad (12)$$

we can apply the RMM-DIIS to the charge density mixing in momentum space with a care for the charge sloshing [4]. The procedure of finding an optimum charge density is same as in the RMM-DIIS for the density matrix.

## References

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- [3] G. P. Kerker, *Phys. Rev. B* **23**, 3082 (1981).
- [4] G. Kresse and J. Furthmeuller, *Phys. Rev. B.* **54**, 11169 (1996).