Charge Mixing Methods: Ver. 1.0

Taisuke Ozaki, RCIS, JAIST

August 20, 2007

1 Simple mixing

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

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

where α 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:

$$R_n \equiv \rho_n^{(\mathrm{out})} - \rho_n^{(\mathrm{in})}, \tag{2}$$

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 $\{R_m\}$

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

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

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

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:

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

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

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

3 Kerker mixing in momentum space

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

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

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

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

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

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

where $q_0 = \gamma|\mathbf{q}_{\mathrm{min}}|$, and $\mathbf{q}_{\mathrm{min}}$ 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

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

4 RMM-DIIS in momentum space

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

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

and the norm with the Kerker metric as:

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

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

[1] P. Csaszar and P. Pulay, J. Mol. Struc. **114**, 31 (1984).

[2] F. Eckert, P. Pulay, and H.-J. Werner, J. Comp. Chem. **18**, 1473 (1997).

[3] G. P. Kerker, Phys. Rev. B **23**, 3082 (1981).

[4] G. Kresse and J. Furthmeuller, Phys. Rev. B. **54**, 11169 (1996).