Charge Mixing Methods: Ver. 1.0

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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 nth SCF step as

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

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:

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

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 $\sum_{m=n-(p-1)}^{n} \alpha_m = 1$. According to Lagrange's multiplier method, F is defined by

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

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:

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

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

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

3   Kerker mixing in momentum space

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

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

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

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

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

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

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

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

4   RMM-DIIS in momentum space

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

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

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

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

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