Relation between SCF convergence and response function

According to

Warren E. Pickett, Comp. Phys. Rep. 9, 115 (1989).

we will relate the SCF convergence and response function below.

The simple linear mixing scheme is given by

$$n_{i+1}^{in} = \alpha n_i^{out} + (1-\alpha) n_i^{in} = n_i^{in} + \alpha (n_i^{out} - n_i^{in}) \quad \text{---- (1)}$$

From (9.21), we have

$$n_i^{out}(r) = n_{KS}(r) + \int dr' \left(\hat{\chi}(r,r') + \overset{\delta(r-r')}{1}\right)\left(n_i^{in}(r') - n_{KS}(r')\right) \quad \text{--- (2)}$$

In short, we express Eq. (2) as

$$n_i^{out} = n_{KS} + (\hat{\chi}+1)(n_i^{in} - n_{KS}) \quad \text{---- (3)}$$

Inserting (3) to (1), we obtain

$$n_{i+1}^{in} = n_i^{in} + \alpha \left[\overbrace{n_{KS} + (\hat{\chi}+1)(n_i^{in} - n_{KS})}^{n_i^{out}} - n_i^{in} \right]$$

$$= n_i^{in} + \alpha \left[n_{KS} + \hat{\chi}(n_i^{in} - n_{KS}) + n_i^{in} - n_{KS} - n_i^{in} \right]$$

$$= n_i^{in} + \alpha \hat{\chi}(n_i^{in} - n_{KS}) = (1+\alpha\hat{\chi}) n_i^{in} - \alpha \hat{\chi} n_{KS}$$

$$\boxed{n_{i+1}^{in} = (\overset{\delta(r-r')}{1} + \alpha\hat{\chi}) n_i^{in} - \alpha \hat{\chi} n_{KS}} \quad \text{----- (4)}$$

e.g. $n_2^{in} = (1+\alpha\hat{\chi}) n_1^{in} - \alpha \hat{\chi} n_{KS}$

$$n_3^{in} = (1+\alpha\hat{\chi}) n_2^{in} - \alpha \hat{\chi} n_{KS} = (1+\alpha\hat{\chi})^2 n_1^{in} - (1+\alpha\hat{\chi}) \alpha \hat{\chi} n_{KS} - \alpha \hat{\chi} n_{KS}$$

In general

$$n_k^{in} = (1+\alpha\hat{\chi})^{k-1} n_1^{in} - \left[\sum_{i=0}^{k-2} (1+\alpha\hat{\chi})^i \right] \alpha \hat{\chi} n_{KS} \quad \text{----- (5)}$$

Remembering the definition of $\tilde{\chi}$,

$$\tilde{\chi}(r,r') + 1 = \int dr'' \, \underset{\uparrow \, D.3}{\chi_0(r,r'')} \, \underset{\uparrow \, (9.12)}{K(r'',r')} \quad \text{----} \quad (6)$$

(D.3) $$\chi_0(r,r') = \frac{\delta n(r)}{\delta V_{eff}(r')} = \sum_{i=1}^{occ} \sum_{j}^{empty} \frac{\psi_i^*(r)\psi_j(r)\psi_j^*(r')\psi_i(r')}{\varepsilon_i - \varepsilon_j} + c.c. \quad \text{----} \quad (7)$$

(9.12) $$K(r,r') = \frac{1}{|r-r'|} + \frac{\delta^2 E_{xc}}{\delta n(r)\delta n(r')} \quad \text{-----} \quad (8)$$

one can conclude that $\tilde{\chi}$ is always real.

Now, we introduce a set of orthonormal $\overbrace{\text{basis}}^{\text{real}}$ functions $\{q_a\}$

where $$\langle q_a | q_b \rangle = \delta_{ab} \quad \text{----} \quad (9)$$

Then, by using the closure relation, one can rewrite $\tilde{\chi}$ as

$$\tilde{\chi}(r,r') = \sum_{a,b} \langle r r' | q_a q_b \rangle \langle q_a(r) q_b(r') | \tilde{\chi}(r,r') \rangle$$

$$= \sum_{a,b} q_a(r) q_b(r') \langle q_a(r) q_b(r') | \tilde{\chi}(r,r') \rangle$$

$$= \sum_{a,b} q_a(r) \langle q_a(r) | \tilde{\chi}(r,r') | q_b(r') \rangle q_b(r)$$

$$= \sum_{a,b} q_a(r) V \Lambda V^T q_b(r') \quad \text{where} \quad \Lambda = V^T \chi V$$

eigen value matrix

$$\Lambda = \begin{pmatrix} \lambda_1 & & 0 \\ & \lambda_2 & \\ 0 & & \ddots \end{pmatrix}$$

eigen vector matrix

$$= \sum_a Q_a(r) \lambda_a Q_a(r') \quad \text{----} \quad (10)$$

where $$Q = q V \quad \text{---} \quad (11)$$

$$\langle Q_a | Q_b \rangle = \delta_{ab} \quad \text{---} \quad (12)$$

We return to Eq. (5).

$$n_k^{in} = (1+\alpha\hat{x})^{k-1} n_1^{in} - \left[\sum_{i=0}^{k-2}(1+\alpha\hat{x})^i\right]\alpha\hat{x}\, n_{ks} \quad \cdots\cdots (5)$$

If we write $(1+\alpha\hat{x})^{k-1} n_1^{in}$ explicitly, we see

$$(1+\alpha\hat{x})^{k-1} n_1^{in}$$

$$= \iint\cdots\int dr_1 dr_2 \cdots dr_{k-1} \left(\delta(r-r_1)+\alpha\hat{x}(r,r_1)\right)\left(\delta(r_1-r_2)+\alpha\hat{x}(r_1,r_2)\right)$$

$$\times \cdots\cdots \times \left(\delta(r_{k-2}-r_{k-1})+\alpha\hat{x}(r_{k-2},r_{k-1})\right) n_1^{in}(r_{k-1})$$

$$\cdots\cdots (13)$$

Noting

$$\delta(r-r') = \sum_a Q_a(r) Q_a(r') \quad \cdots\cdots (14)$$

and using Eq. (10), Eq. (13) can be rewritten as

$$(13) = \iint\cdots\int dr_1 dr_2 \cdots dr_{k-1} \left[\sum_{a_1} Q_{a_1}(r)(1+\alpha\lambda_{a_1}) Q_{a_1}(r_1)\right]\left[\sum_{a_2} Q_{a_2}(r_1)(1+\alpha\lambda_{a_2}) Q_{a_2}(r_2)\right]$$

$$\times \cdots \times \left[\sum_{a_{k-1}} Q_{a_{k-1}}(r_{k-2})(1+\alpha\lambda_{a_{k-1}}) Q_{a_{k-1}}(r_{k-1})\right] n_1^{in}(r_{k-1})$$

$$\cdots\cdots (15)$$

Using (12), we have

$$(13) = \sum_a Q_a(r)(1+\alpha\lambda_a)^{k-1}\langle Q_a | n_1^{in}\rangle \quad \cdots\cdots (16)$$

Similary, the second term of Eq. (5) can be written as

$$-\left[\sum_{i=0}^{k-2}(1+\alpha\hat{x})^i\right]\alpha\hat{x}\, n_{ks} = -\sum_{i=0}^{k-2}\sum_a Q_a(r)(1+\alpha\lambda_a)^i \alpha\lambda_a \langle Q_a | n_{ks}\rangle$$

$$\cdots\cdots (17)$$

Thus using Eqs. (16) and (17), we can rewrite Eq. (5) as

$$n_{in}^{k}(r) = \sum_a Q_a(r)(1+\alpha\lambda_a)^{k-1}\langle Q_a | n_1^{in}\rangle - \sum_a Q_a(r)\left[\sum_{i=0}^{k-2}(1+\alpha\lambda_a)^i\right]\alpha\lambda_a\langle Q_a | n_{ks}\rangle \quad \text{---} (18)$$

If $|1+\alpha\lambda_a| < 1$, we see

$$\lim_{k\to\infty}(1+\alpha\lambda_a)^{k-1} = 0 \quad \text{----} (19)$$

$$\lim_{k\to\infty}\sum_{i=0}^{k-2}(1+\alpha\lambda_a)^i = \frac{1}{1-(1+\alpha\lambda_a)} = \frac{-1}{\alpha\lambda_a} \quad \text{---} (20)$$

So, Eq. (18) becomes

$$\lim_{k\to\infty} n_{in}^{k}(r) = 0 - \sum_a Q_a(r)\times\left[\frac{-1}{\alpha\lambda_a}\right]\alpha\lambda_a\langle Q_a | n_{ks}\rangle$$

$$= \sum_a Q_a(r)\int dr'\, Q_a(r')\, n_{ks}(r')$$

$$= \int dr'\left[\sum_a Q_a(r)Q_a(r')\right]n_{ks}(r')$$

$$= \int dr'\,\delta(r-r')\,n_{ks}(r') = n_{ks}(r) \quad \text{----} (21)$$

From Eq. (21), it turns out that the simple mixing is convergent if $|1+\alpha\lambda| < 1$.

$$-1 < 1+\alpha\lambda < 1 \rightarrow -1 < 1+\alpha\lambda_{min} \rightarrow -2 < \alpha\lambda_{min}$$

$$1+\alpha\lambda_{max} < 1 \rightarrow \alpha\lambda_{max} < 0$$

Now we assume $\alpha > 0$. So in general $\lambda_a < 0$.

There fore. $-\frac{2}{\lambda_{min}} > \alpha \rightarrow \frac{2}{|\lambda_{min}|} > \alpha$ --- (22)