Total energy by DFT

$$E = E_{kin} + E_{ex} + E_{Hart} + E_{xc} + E_{cc} \quad \cdots\cdots (1)$$

$$E_{ex} = \int dr\, \rho(r) \sum_I V_{core}(r - r_I) \quad \cdots\cdots (2)$$

$$E_{Hart} = \frac{1}{2} \iint dr\, dr' \frac{\rho(r)\rho(r')}{|r - r'|} \quad \cdots\cdots (3)$$

$$E_{cc} = \frac{1}{2} \sum_{I,J} \frac{Z_I Z_J}{|\tau_I - \tau_J|} \quad \cdots\cdots (4)$$

The three terms can be reorganized as

$$
\begin{aligned}
& E_{ex} + E_{Hart} + E_{cc} \\
&= \int dr\, \rho(r) \sum_I V_{core}(r - \tau_I) + \int dr\, \rho(r) V_H^{(a)}(r) - \int dr\, \rho(r) V_H^{(a)}(r) \\
&\quad + \frac{1}{2} \int dr\, \rho(r) \left(V_H^{(a)}(r) + \delta V_H(r) \right) + \frac{1}{2} \int dr\, \rho^{(a)}(r) V_H^{(a)}(r) \\
&\quad - \frac{1}{2} \int dr\, \rho^{(a)}(r) V_H^{(a)}(r) + \frac{1}{2} \sum_{I,J} \frac{Z_I Z_J}{|\tau_I - \tau_J|} \\
&= \int dr\, n(r) \sum_I V_{na,I}(r - \tau_I) + \frac{1}{2} \int dr\, \delta n(r) \delta V_H(r) \\
&\quad + \frac{1}{2} \sum_{I,J} \left[\frac{Z_I Z_J}{|\tau_I - \tau_J|} - \int dr\, \rho_I^{(a)}(r) V_{H,J}^{(a)}(r) \right] \\
&= E_{na} + E_{see} + E_{scc} \quad \cdots\cdots (5)
\end{aligned}
$$

where

$$\rho(r) = \underbrace{\rho^{(a)}(r)}_{=\sum_I \rho_I^{(a)}(r)} + \delta\rho(r) \quad \cdots (6)$$

$$V_H^{(a)}(r) = \sum_I \int dr' \frac{\rho_I^{(a)}(r')}{|r-r'|} = \sum_I V_{H.I}^{(a)}(r) \quad \cdots (7)$$

$$\delta V_H(r) = \int dr \frac{\delta\rho(r)}{|r-r'|} \quad \cdots\cdots (8)$$

Thus, Eq. (1) can be rewritten as

$$E = E_{kin} + E_{na} + E_{see} + E_{xc} + E_{scc} \quad \cdots (9)$$

Now we consider KS eq. by

Index u contains k, band, spin.

$$(\hat{T} + V_{na} + \delta V_H + V_{xc})\varphi_u = \varepsilon_u \varphi_u \quad \cdots (10)$$

$$E_{kin} = \sum_u \langle \varphi_u | \hat{T} | \varphi_u \rangle = \underbrace{\sum_u \varepsilon_u}_{E_{band}} - \int dr\, \rho(r) V_{na}(r)$$

$$- \int dr\, \rho(r)\, \delta V_H(r)$$

$$- \int dr\, \rho(r) V_{xc}(r) \quad \cdots (11)$$

By inserting (11) into (9), we have

$$E = E_{band} + \underbrace{E_{see} - \int dr\, \rho(r)\, \delta V_H(r) + E_{xc} - \int dr\, \rho(r) V_{xc}(r) + E_{scc}}_{= E_{dc} + E_{cc}} \quad \cdots (12)$$

Here we remember the Harris functional.

$$E_{Harris} = E_{band}[\rho_{in}] + E_{dc}[\rho_{in}] + E_{cc} + O[(\delta\rho)^2] \quad \cdots\cdots (13)$$

The Harris functional allows us to calculate the total enery in an error of order $(\delta\rho)^2$.

So, we now consider to evaluate (12) using (13).

In (12), we can regard as $\rho^{(a)} = \rho_{in}$.

Then, (12) becomes

$$E = E_{band} + E_{xc} - \int dr\, \rho(r) V_{xc}(r) + E_{scc} \quad \cdots (14)$$

By using LDA or GGA for E_{xc} and V_{xc}, and focusing on the energetics of d-electrons, we can approximately evaluate as

$$E_{xc} \simeq \sum_I E_{xc}^{(I)}$$

$$\int dr\, \rho(r) V_{xc}(r) \simeq \sum_I \int dr\, \rho_I(r) V_{xc}^{(I)}(r) \quad \cdots (15)$$

The heat of formation per atom of alloy AB (equimolar) is given by

$$\Delta H = E_{AB} - \frac{1}{2} E_A - \frac{1}{2} E_B \longleftarrow (14)$$

$$\begin{aligned} &= E_{band}^{(AB)} + E_{xc}^{(AB)} - \int dr\, \rho^{(AB)} V_{xc}^{(AB)} + E_{scc}^{(AB)} \\ &\quad - \frac{1}{2} E_{band}^{(A)} - \frac{1}{2} E_{xc}^{(A)} + \frac{1}{2} \int dr\, \rho^{(A)} V_{xc}^{(A)} - \frac{1}{2} E_{scc}^{(A)} \\ &\quad - \frac{1}{2} E_{band}^{(B)} - \frac{1}{2} E_{xc}^{(B)} + \frac{1}{2} \int dr\, \rho^{(B)} V_{xc}^{(B)} - \frac{1}{2} E_{scc}^{(B)} \end{aligned} \quad \cdots (16)$$

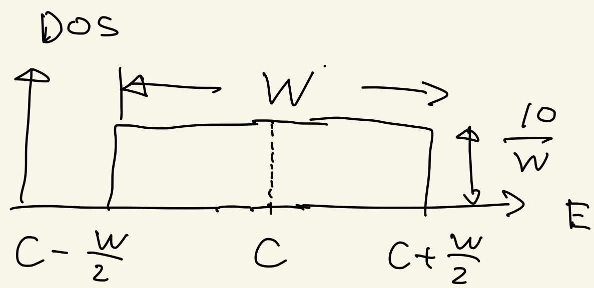
By using (15) and assuming that the screening in E_{scc} is perfect, we obtain

$$\Delta H = E_{band}^{(AB)} - \frac{1}{2} E_{band}^{(A)} - \frac{1}{2} E_{band}^{(B)} \quad \text{---- (17)}$$

Eq. (17) is the starting point of Pettifor's paper.

☆ Friedel model

DOS



$$U_{bond} = \int^{E_F} (E - C)\, n(E)\, dE \quad \text{---- (1)}$$

E_F can be determined as

$$N = \int_{C-\frac{W}{2}}^{E_F} \frac{10}{W}\, dE = \frac{10}{W}\left(E_F - C + \frac{W}{2}\right)$$

Num. of d-electrons

$$\rightarrow \quad E_F - C + \frac{W}{2} = \frac{W}{10} N \rightarrow E_F = \frac{W}{10} N + C - \frac{W}{2} \quad \text{--- (2)}$$

So, U_{bond} can be evaluated as

$$U_{bond} + NC = \int_{C-\frac{W}{2}}^{E_F} \frac{10}{W} \times E\, dE = \frac{10}{W} \times \frac{1}{2} \left[E^2\right]_{C-\frac{W}{2}}^{\frac{W}{10}N + C - \frac{W}{2}}$$

$$= \frac{5}{W}\left[\left(\frac{W}{10}N + C - \frac{W}{2}\right)^2 - \left(C - \frac{W}{2}\right)^2\right]$$

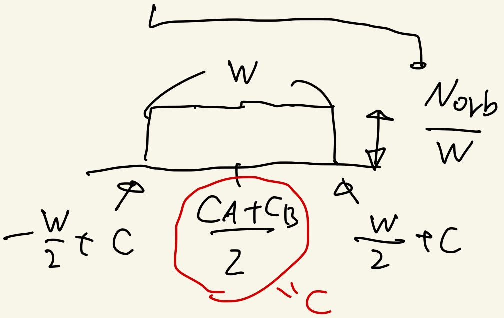
$$= \frac{5}{W}\left[\frac{W^2 N^2}{100} + \frac{W}{5} N \left(C - \frac{W}{2}\right)\right] = \frac{WN^2}{20} + NC - \frac{NW}{2}$$

$$U_{bond} = -N(10 - N)\frac{W}{20} \quad \text{---- (3)}$$

D.G. Pettifor, PRL 42, 846 (1979)

DOS of AB alloy.

$N_{orb} = 5 \times N_{atom}$



$$\frac{1}{N_{orb}}\int_{-\frac{W}{2}+C}^{\frac{W}{2}+C}(E-C)^2\times\frac{N_{orb}}{W}\,dE \quad \cdots\cdots (1)$$

$$x = E - C \rightarrow \frac{dx}{dE} = 1 \rightarrow dE = dx$$

$$= \int_{-\frac{W}{2}}^{\frac{W}{2}} x^2 \times \frac{1}{W}\,dE = \frac{1}{W}\left[\frac{1}{3}x^3\right]_{-\frac{W}{2}}^{\frac{W}{2}}$$

On the other hand

$$= \frac{1}{3W}\left(\frac{W^3}{8}+\frac{W^3}{8}\right) = \frac{W^2}{12} \quad \cdots\cdots (2)$$

$$(1) = \frac{1}{N_{orb}}\left[\int_{-\frac{W}{2}+C}^{\frac{W}{2}+C}E^2\frac{N_{orb}}{W}\,dE - 2C\int_{-\frac{W}{2}+C}^{\frac{W}{2}+C}E\frac{N_{orb}}{W}\,dE + C^2\int_{-\frac{W}{2}+C}^{\frac{W}{2}+C}\frac{N_{orb}}{W}\,dE\right]$$

$$= \frac{1}{N_{orb}}\left[\mathrm{Tr}(\mu_2) - 2C\,\mathrm{Tr}(\mu_1) + C\,\mathrm{Tr}(\mu_0)\right] \quad \cdots\cdots (3)$$

By considering (2) = (3), and changing $W \rightarrow W_{AB}$, we have

$$\frac{W_{AB}^2}{12} = \frac{1}{N_{orb}}\left[\mathrm{Tr}(\mu_2^{AB}) - 2C\,\mathrm{Tr}(\mu_1^{AB}) + C^2\,\mathrm{Tr}(\mu_0^{AB})\right] \quad \cdots (4)$$

If $C_A = C_B = C$, we have

$$\frac{W^2}{12} = \frac{1}{N_{orb}}\left[\mathrm{Tr}(\mu_2) - 2C\,\mathrm{Tr}(\mu_1) + C^2\,\mathrm{Tr}(\mu_0)\right] \quad \cdots\cdots (5)$$

$$\frac{1}{W}\int_{-\frac{W}{2}+C}^{\frac{W}{2}+C}E\,dE$$

$$\frac{1}{W}\left\{\frac{1}{2}E^2\right\}_{-\frac{W}{2}+C}^{\frac{W}{2}+C}$$

$$= \frac{1}{2W}\left(\left(\frac{W}{2}+C\right)^2 - \left(-\frac{W}{2}+C\right)^2\right)$$

$$= \frac{1}{2W}\left(\cancel{\frac{W^2}{4}} + WC + \cancel{C^2} - \cancel{\frac{W^2}{4}} + WC - \cancel{C^2}\right)$$

$$= C$$

The second moments can be written as

i,j are composite indices : site and orbital.

$$\mathrm{Tr}(\mu_2) = \sum_i\sum_j h_{ij}h_{ji} = \sum_i |h_{ii}|^2 + \sum_{i\neq j}|h_{ij}|^2$$

$$-\;\mathrm{Tr}(\mu_2^{AB}) = \sum_i\sum_j h_{ij}^{AB}h_{ji}^{AB} = \sum_i |h_{ii}^{AB}|^2 + \sum_{i\neq j}|h_{ij}|^2$$

Here is equivalent.

$$\mathrm{Tr}(\mu_2) - \mathrm{Tr}(\mu_2^{AB}) = \sum_i\left(|h_{ii}|^2 - |h_{ii}^{AB}|^2\right) = N_{orb}\left(\frac{C_A+C_B}{2}\right)^2 - \frac{N_{orb}}{2}C_A^2 - \frac{N_{orb}}{2}C_B^2$$

$$= N_{orb}\left(\frac{1}{4}C_A^2 + \frac{1}{2}C_AC_B + \frac{1}{4}C_B^2 - \frac{1}{2}C_A^2 - \frac{1}{2}C_B^2\right)$$

$$= N_{orb}\left(-\frac{1}{4}C_A^2 + \frac{1}{2}C_AC_B - \frac{1}{4}C_B^2\right) = -\frac{1}{4}N_{orb}\left(C_A^2 - 2C_AC_B + C_B^2\right)$$

$$-\frac{1}{4}N_{orb}(C_A - C_B)^2$$

Appendix

Lehman represention

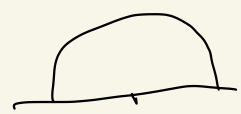
$$G(Z) = \int_{-\infty}^{\infty} dE \, \frac{g(E)}{Z - E} \qquad \text{---} \; (A1)$$

Taking account of

$$(Z-E)^{-1} = Z^{-1}\left(1 - \frac{E}{Z}\right)^{-1} = \sum_{p}^{\infty} \frac{E^p}{Z^{p+1}} \qquad \text{for } \left|\frac{E}{Z}\right| < 1$$

One obtain $$G(Z) = \sum_{p}^{\infty} \frac{\mu_p}{Z^{p+1}} \qquad \text{----} \; (A2)$$

where



$$\mu_p = \int dE \, E^p g(E) = -\frac{1}{\pi} \, \mathrm{Im} \int_{-\infty}^{\infty} dE \, E^p G(E + i0^+) \quad \cdots \; (A3)$$

$$E^p g_{ij}(E) = \langle i | \varphi(E) \rangle E^p \langle \varphi(E) | j \rangle$$

$$(H^p)_{ij} = \langle i | \left(\sum_{i_1} |\varphi_{i_1}\rangle \varepsilon_{i_1} \langle \varphi_{i_1}| \right) \left(\sum_{i_2} |\varphi_{i_2}\rangle \varepsilon_{i_2} \langle \varphi_{i_2}| \right)$$

$$\cdots \left(\sum_{i_{p-1}} |\varphi_{i_{p-1}}\rangle \varepsilon_{i_{p-1}} \langle \varphi_{i_{p-1}}| \right) \left(\sum_{i_p} |\varphi_{i_p}\rangle \varepsilon_{i_p} \langle \varphi_{i_p}| \right)$$

$$= \langle i | \left[\sum_{i_1} |\varphi_{i_1}\rangle \varepsilon_{i_1}^p \langle \varphi_{i_1}| \right] | j \rangle$$

$$= \int dE \, \langle i | \varphi(E) \rangle \langle \varphi(E) | j \rangle$$

Thus $$\mu_p = -\frac{1}{\pi} \int_{-\infty}^{\infty} dE \, E^p G(E + i0^+) = H^p$$

There fore, $\mathrm{Tr}\left(\mathcal{U}_2^{AB}\right) = \mathrm{Tr}\left(\mathcal{U}_2\right) + \frac{1}{4} N_{orb}\left(C_A - C_B\right)^2$ .... (6)

Noting $\mathrm{Tr}\left(\mathcal{U}_1^{AB}\right) = N_{orb}\left(\frac{C_A + C_B}{2}\right)$, $\mathrm{Tr}\left(\mathcal{U}_1\right) = N_{orb}\left(\frac{C_A + C_B}{2}\right)$ .... (7)

We have $\mathrm{Tr}\left(\mathcal{U}_0^{AB}\right) = \mathrm{Tr}\left(\mathcal{U}_0\right) = N_{orb}$

from (4) $N_{orb} \times \frac{W_{AB}^2}{12} = \mathrm{Tr}\left(\mathcal{U}_2\right) + \frac{1}{4} N_{orb}\left(C_A - C_B\right)^2 - 2 N_{orb} \frac{(C_A + C_B)}{2} \times \frac{(C_A + C_B)}{2} + N_{orb}\left(\frac{C_A + C_B}{2}\right)^2$

$= \mathrm{Tr}\left(\mathcal{U}_2^{(AB)}\right) + \frac{1}{4} N_{orb}\left(C_A - C_B\right)^2 - N_{orb} \frac{(C_A + C_B)^2}{4}$

from (5) $N_{orb} \times \frac{W^2}{12} = \mathrm{Tr}\left(\mathcal{U}_2\right) - 2 N_{orb} \frac{(C_A + C_B)}{2} \times \frac{(C_A + C_B)}{2} + N_{orb}\left(\frac{C_A + C_B}{2}\right)^2 = \mathrm{Tr}\left(\mathcal{U}_2\right) - N_{orb} \frac{(C_A + C_B)^2}{4}$ ...(9)

(8) − (9) leads to

$$N_{orb} \times \left(\frac{W_{AB}^2}{12} - \frac{W^2}{12}\right) = \frac{1}{4} N_{orb}\left(C_A - C_B\right)^2 \quad \text{---- (10)}$$

$$\rightarrow \boxed{\frac{W_{AB}^2}{12} = \frac{W^2}{12} + \frac{1}{4}\left(C_A - C_B\right)^2} \quad \text{..... (11)}$$

Therefore, we obtain (5) in Pettifor's paper

$$W_{AB}^2 = W^2 + 3\left(C_A - C_B\right)^2$$

$$W_{AB}^2 = \left(1 + \frac{3(C_A - C_B)^2}{W^2}\right) W^2$$

$$\boxed{W_{AB} = \left[1 + 3\left(\frac{C_A - C_B}{W}\right)^2\right]^{\frac{1}{2}} W} \quad \text{----- (12)}$$

(6) in Pettifor's paper

Noting $(1 + x)^{\frac{1}{2}} = 1 + \frac{1}{2}x + O(x^2)$

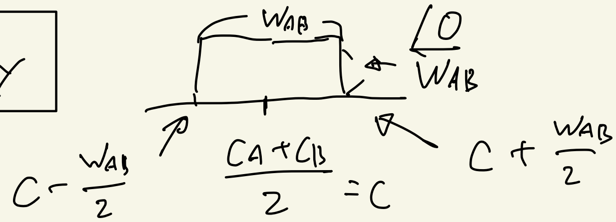
We have $W_{AB} \simeq W + \frac{3}{2} W \left(\frac{C_A - C_B}{W}\right)^2$ ------ (13)

Now we return to ΔH defined by

$$\Delta H = \int^{E_F} E\, n_{AB}(E)\, dE - \frac{1}{2}\int^{E_F^A} E\, n_A(E)\, dE - \frac{1}{2}\int^{E_F^B} E\, n_B(E)\, dE$$

---- (14)

AB alloy



$$\bar N = \int_{C-\frac{W_{AB}}{2}}^{E_F} \frac{10}{W_{AB}}\, dE = \frac{10}{W_{AB}}\Big[E\Big]_{C-\frac{W_{AB}}{2}}^{E_F}$$

$$= \frac{10}{W_{AB}}\left(E_F - C + \frac{W_{AB}}{2}\right) = \frac{10}{W_{AB}}E_F - \frac{10}{W_{AB}}C + 5 \quad \cdots (15)$$

$$\rightarrow \quad \frac{10}{W_{AB}}E_F = \bar N + \frac{10}{W_{AB}}C - 5$$

$$E_F = \bar N \frac{W_{AB}}{10} + C - \frac{W_{AB}}{2} \quad \cdots\cdots (16)$$

We evaluate the first term in Eq. (14).

$$\int_{C-\frac{W_{AB}}{2}}^{E_F} E\,\frac{10}{W_{AB}}\,dE = \frac{10}{W_{AB}}\left[\frac{1}{2}E^2\right]_{C-\frac{W_{AB}}{2}}^{E_F}$$

$$= \frac{5}{W_{AB}}\left[\left(\frac{\bar N W_{AB}}{10} + \underbrace{C - \frac{W_{AB}}{2}}_{a}\right)^2 - \left(\underbrace{C-\frac{W_{AB}}{2}}_{a}\right)^2\right]$$

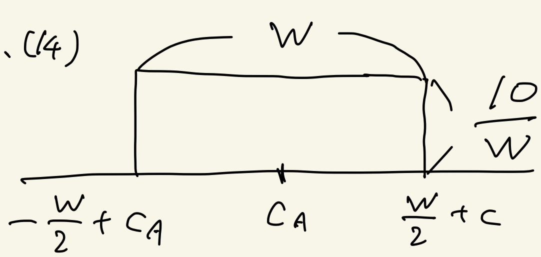
$$= \frac{5}{W_{AB}}\left[\frac{\bar N^2 W_{AB}^2}{100} + \frac{\bar N W_{AB}}{5}\left(C-\frac{W_{AB}}{2}\right) \cancel{+ a^2 - a^2}\right]$$

$$= \frac{\bar N^2 W_{AB}}{20} + \bar N\left(C - \frac{W_{AB}}{2}\right) = \left(\frac{\bar N^2}{20} - \frac{\bar N}{2}\right)W_{AB} + \bar N C$$

$$= \left(\frac{\bar N^2}{20} - \frac{\bar N}{2}\right)W\left(1+\frac{3}{2}\left(\frac{C_A-C_B}{W}\right)^2\right) + \bar N C \quad \cdots\cdots (17)$$

We calculate the second term in Eq. (14)

$$\frac{1}{2}\int^{E_F^A} E\, n_A(E)\, dE$$



Let's determine E_F^A at first.

$$N_A = \int_{-\frac{W}{2}+C_A}^{E_F^A} \frac{10}{W} dE = \frac{10}{W}\left[E\right]_{-\frac{W}{2}+C_A}^{E_F^A}$$

$$= \frac{10}{W}\left(E_F^A + \frac{W}{2} - C_A\right) = \frac{10}{W}E_F^A + 5 - \frac{10}{W}C_A$$

$$\frac{10}{W}E_F^A = N_A + \frac{10}{W}C_A - 5$$

$$E_F^A = N_A\frac{W}{10} + C_A - \frac{W}{2}$$

$$\frac{1}{2}\int_{-\frac{W}{2}+C_A}^{E_F^A} E \times \frac{10}{W} dE = \frac{5}{W}\left[\frac{1}{2}E^2\right]_{C_A-\frac{W}{2}}^{E_F^A}$$

$$= \frac{5}{2W}\left[\left(N_A\frac{W}{10} + C_A - \frac{W}{2}\right)^2 - \left(C_A - \frac{W}{2}\right)^2\right]$$

$$= \frac{5}{2W}\left[N_A^2\frac{W^2}{100} + \frac{N_AW}{5}\left(C_A - \frac{W}{2}\right)\right]$$

$$= \frac{N_A^2W}{40} + \frac{N_A}{2}\left(C_A - \frac{W}{2}\right) = \left(\frac{N_A^2}{40} - \frac{N_A}{4}\right)W + \frac{N_AC_A}{2} \quad \cdots (18)$$

As well, we can caculate as

$$\frac{1}{2}\int_{-\frac{W}{2}+C_B}^{E_F^B} E \times \frac{10}{W} dE = \left(\frac{N_B^2}{40} - \frac{N_B}{4}\right)W + \frac{N_BC_B}{2} \quad \cdots (19)$$

From (17), (18), and (19), one can evaluate ΔH_0 as constant volume case.

$$(17) = \left(\frac{\bar{N}^2}{20} - \frac{\bar{N}}{2}\right)W\left(1 + \frac{3}{2}\left(\frac{C_A - C_B}{W}\right)^2\right) + \bar{N}C$$

$$\Delta H_0 = (17) - (18) - (19)$$

$$= \underbrace{\left(\frac{\bar{N}^2}{20} - \frac{\bar{N}}{2}\right) w \left(1 + \frac{3}{2}\left(\frac{C_A - C_B}{w}\right)^2\right)}_{A} + \bar{N}C - \underbrace{\left(\frac{N_A^2}{40} + \frac{N_B^2}{40} \cancel{- \frac{N_A}{4} - \frac{N_B}{4}}\right) w}_{B} - \frac{N_A C_A}{2} - \frac{N_B C_B}{2}$$

$$\frac{1}{2}\left(\frac{N_A + N_B}{2}\right)$$

$$\frac{\bar{N}^2}{20} = \frac{1}{20}\left(\frac{N_A + N_B}{2}\right)^2 = \frac{1}{80}\left(N_A^2 + 2N_A N_B + N_B^2\right)$$

$$A = \frac{\bar{N}^2}{20} w + \frac{3}{40} w \bar{N}^2 \left(\frac{\Delta C}{w}\right)^2 - \frac{\bar{N} w}{2} - \frac{3}{4} \bar{N} w \left(\frac{\Delta C}{w}\right)^2$$

$$= \frac{w}{80}\left(N_A^2 + 2N_A N_B + N_B^2\right) + \frac{3}{40} w \bar{N}^2 \left(\frac{\Delta C}{w}\right)^2 - \cancel{\frac{\bar{N} w}{2}} - \frac{3}{4} \bar{N} w \left(\frac{\Delta C}{w}\right)^2$$

$$A + B = -\frac{w}{80} \underbrace{\left(N_A^2 - 2N_A N_B + N_B^2\right)}_{(\Delta N)^2} + \frac{3}{40} w \bar{N}^2 \left(\frac{\Delta C}{w}\right)^2 - \frac{3}{4} \bar{N} w \left(\frac{\Delta C}{w}\right)^2$$

Also,

$$\bar{N}C - \frac{N_A C_A}{2} - \frac{N_B C_B}{2} = \left(\frac{N_A + N_B}{2}\right) \times \left(\frac{C_A + C_B}{2}\right) - \frac{N_A C_A}{2} - \frac{N_B C_B}{2}$$

$$= \frac{1}{4}\left(N_A C_A + N_A C_B + N_B C_A + N_B C_B\right) - \frac{N_A C_A}{2} - \frac{N_B C_B}{2}$$

$$= \frac{1}{4}\left(-N_A C_A + N_A C_B + N_B C_A - N_B C_B\right)$$

$$= -\frac{1}{4}\left(N_A - N_B\right)\left(C_A - C_B\right) = -\frac{1}{4} \Delta N \Delta C$$

Thus, we have

$$\boxed{\Delta H_0 = -\frac{w}{80}(\Delta N)^2 - \frac{1}{4}\Delta N \Delta C - \frac{3}{40}\bar{N}(10 - \bar{N}) w \left(\frac{\Delta C}{w}\right)^2} \quad \cdots\cdots (20)$$

Next, we consider the change of volume.

AB alloy V $\qquad V = \alpha l^3 \rightarrow \frac{dV}{dl} = 3\alpha l^2$

$\Delta V = 3\alpha l^2 \Delta l \rightarrow \Delta l = \frac{\Delta V}{3\alpha l^2}$

A V_A

B V_B

(per atom)

$$\boxed{h = \beta l^{-5}} \rightarrow \frac{dh}{dl} = -5\beta l^{-6}$$

$$\Delta h = -5\beta l^{-6} \times \Delta l$$

$$= -5\beta l^{-6} \times \frac{\Delta V}{3\alpha l^2} = -\frac{5\beta}{3\alpha} l^{-8} \Delta V$$

$$\Delta h = -\frac{5}{3}\left(\beta \ell^{-5}\right) \times \frac{1}{(\alpha \ell^{3})} \Delta V = -\frac{5}{3}\frac{h}{V}\Delta V \quad \cdots\cdots (21)$$

From (5)

$$N_{orb}\frac{W^2}{12} = \mathrm{Tr}(\mathcal{U}_2) - 2C\,\mathrm{Tr}(\mathcal{U}_0) + C^2\,\mathrm{Tr}(\mathcal{U}_0) \to \mathrm{Tr}(\mathcal{U}_2) = N_{orb}\frac{W^2}{12} + 2C\,\mathrm{Tr}(\mathcal{U}_1) - C^2\,\mathrm{Tr}(\mathcal{U}_0)$$

$$\left[\mathrm{Tr}(\mathcal{U}_1) = \frac{C_A + C_B}{2},\quad \mathrm{Tr}(\mathcal{U}_0) = N_{orb},\quad \mathrm{Tr}(\mathcal{U}_2) = \sum_i |h_{ii}|^2 + \sum_{i\neq j}|h_{ij}|^2\right]$$

$$\frac{d\,\mathrm{Tr}\,\mathcal{U}_2}{dV} = 2\sum_{i\neq j} h_{ij}\frac{d h_{ij}}{dV} = 2\sum_{i\neq j} h_{ij}\left(-\frac{5}{3}\frac{h_{ij}}{V}\right) = -\frac{10}{3V}\sum_{i\neq j}|h_{ij}|^2 = -\frac{10}{3V}\left(\mathrm{Tr}\,\mathcal{U}_2 - \sum_i |h_{ii}|^2\right)$$

$$= -\frac{10}{3V}\left(\mathrm{Tr}\,\mathcal{U}_2 - N_{orb}C^2\right) \quad \cdots\cdots (22)$$

$$\frac{\partial}{\partial V}\left(\frac{W^2}{12}\right) = \frac{2}{12}W\frac{\partial W}{\partial V} = \frac{1}{N_{orb}}\frac{\partial\,\mathrm{Tr}\,\mathcal{U}_2}{\partial V} \to \frac{\partial W}{\partial V} = \frac{6}{W N_{orb}}\frac{\partial\,\mathrm{Tr}\,\mathcal{U}_2}{\partial V} = \frac{6}{W N_{orb}}\left(-\frac{10}{3V}\left(\mathrm{Tr}\,\mathcal{U}_2 - N_{orb}C^2\right)\right)$$

$$\frac{\partial W}{\partial V} = -\frac{20}{W V N_{orb}}\left(\mathrm{Tr}\,\mathcal{U}_2 - N_{orb}C^2\right) \to \Delta W = -\frac{20}{W V N_{orb}}\left(\mathrm{Tr}\,\mathcal{U}_2 - N_{orb}C^2\right)\Delta V = -\frac{\cancel{20}\,\cancel{10}\,5}{\cancel{W}V}\left(\frac{W^{\cancel{2}}}{\cancel{12}\,\cancel{6}\,3} + C^2 - C^2\right)\Delta V$$

$$\Delta W = -\frac{5W}{3V}\Delta V \quad \cdots\cdots (23) \longrightarrow \Delta W = -\frac{5W}{3\bar{V}}\Delta V$$

$$2\bar{V} = \Delta V_A + \Delta V_B + V_A + V_B$$

$$\bar{V} = \frac{\Delta V_A + \Delta V_B}{2} + \frac{V_A + V_B}{2}$$

$$=$$

$$\Delta V_A = \bar{V} - V_A, \qquad \Delta V_B = \bar{V} - V_B$$

$$\bar{V} = \Delta V_A + V_A, \qquad \bar{V} = \Delta V_B + V_B$$

$$0 = \Delta V_A - \Delta V_B + \Delta V$$

$$\Delta V_A - \Delta V_B = -\Delta V$$

For (18) and (19), we change $W \to W + \Delta W$

Then, the energy change is given by

$$-\left(\frac{N_A^2}{40} - \frac{N_A}{4}\right)\Delta W_A - \left(\frac{N_B^2}{40} - \frac{N_B}{4}\right)\Delta W_B$$

$$= \left(\frac{N_A^2}{40} - \frac{N_A}{4}\right)\times\left(\frac{5W}{3\bar{V}}\Delta V_A\right) + \left(\frac{N_B^2}{40} - \frac{N_B}{4}\right)\times\left(\frac{5W}{3\bar{V}}\Delta V_B\right)$$

$$= \frac{W}{24\bar{V}}\left(N_A^2 - 10N_A\right)\times\left(\bar{V} - V_A\right) + \frac{W}{24\bar{V}}\left(N_B^2 - 10N_B\right)\times\left(\bar{V} - V_B\right)$$

$$= \frac{W}{24\bar{V}}\left(N_A^2\bar{V} - N_A^2 V_A - 10N_A\bar{V} + 10N_A V_A + N_B^2\bar{V} - N_B^2 V_B - 10N_B\bar{V} + 10N_B V_B\right)$$

$$= \frac{W}{24\bar{V}}\left[\left(N_A^2 + N_B^2\right)\bar{V} - 10\left(N_A + N_B\right)\bar{V} - \left(N_A^2 - 10N_A\right)V_A - \left(N_B^2 - 10N_B\right)V_B\right] \quad \cdots (24)$$

If we assume $\bar{V} = \frac{1}{2}(V_A + V_B)$, Vegard's law, we have

$$= \frac{W}{24\bar{V}}\left[\frac{1}{2}\left(N_A^2 + N_B^2\right)\left(V_A + V_B\right) - 5\left(N_A + N_B\right)\left(V_A + V_B\right) - \left(N_A^2 - 10N_A\right)V_A - \left(N_B^2 - 10N_B\right)V_B\right]$$

$$= \frac{W}{24\bar{V}}\Big(\tfrac{1}{2}N_A^2V_A + \tfrac{1}{2}N_A^2V_B + \tfrac{1}{2}N_B^2V_A + \tfrac{1}{2}N_B^2V_B - 5N_AV_A - 5N_AV_B - 5N_BV_A - 5N_BV_B$$

$$- N_A^2V_A \qquad - N_B^2V_B \quad + 10N_AV_A \qquad + 10N_BV_B\Big)$$

$$= \frac{W}{24\bar{V}}\Big(-\tfrac{1}{2}N_A^2V_A + \tfrac{1}{2}N_A^2V_B + \tfrac{1}{2}N_B^2V_A - \tfrac{1}{2}N_B^2V_B + 5N_AV_A - 5N_AV_B - 5N_BV_A + 5N_BV_B\Big)$$

$$= \frac{W}{24\bar{V}}\Big[-\tfrac{1}{2}(N_A^2 - N_B^2)V_A + \tfrac{1}{2}(N_A^2 - N_B^2)V_B + 5(N_A - N_B)V_A - 5(N_A - N_B)V_B\Big]$$

$$= \frac{W}{24\bar{V}}\Big[-\tfrac{1}{2}(N_A^2 - N_B^2)(V_A - V_B) + 5(N_A - N_B)(V_A - V_B)\Big]$$

$$= -\frac{W}{24\bar{V}}\Big[\overbrace{(N_A - N_B)}^{\Delta N}\overbrace{\frac{(N_A + N_B)}{2}}^{\bar{N}}\Delta V + 5\Delta N\Delta V\Big]$$

$$= -\frac{W}{24\bar{V}}(5 - \bar{N})\Delta N\Delta V \qquad \cdots\cdots (25)$$

(size factor)

Thus, the contribution by the volume change becomes

$$\boxed{\Delta H_s = -\frac{W}{24}(5 - \bar{N})\Delta N\frac{\Delta V}{\bar{V}}} \qquad \cdots\cdots (26)$$

$$\boxed{\Delta H_0 = -\frac{W}{80}(\Delta N)^2 - \frac{1}{4}\Delta N\Delta C - \frac{3}{40}\bar{N}(10 - \bar{N})\,w\left(\frac{\Delta C}{w}\right)^2} \cdots\cdots (20)$$

If we replace in (20) by

$$\Delta C = -\hbar\,\Delta N \qquad \cdots\cdots (27)$$

we have

$$\Delta H_0 = \Big(-\frac{W}{80} + \frac{1}{4}\hbar - \frac{3}{40}\bar{N}(10 - \bar{N})\frac{\hbar^2}{W}\Big)(\Delta N)^2$$

$$= \frac{1}{4}W\Big[-\frac{1}{20} + \frac{\hbar}{W} - \frac{3}{10}\bar{N}(10 - \bar{N})\frac{\hbar^2}{W}\Big](\Delta N)^2$$

where $\hat{\hbar} = \dfrac{\hbar}{w}$

$$= \boxed{\frac{1}{4}w\Big[\big(\hat{\hbar} - \frac{1}{20}\big) - \frac{3}{10}\hat{\hbar}^2\bar{N}(10 - \bar{N})\Big]\Delta N^2} \cdots (28)$$

$$\boxed{\Delta H_s = -\frac{W}{24}(5-\bar{N})\Delta N \frac{\Delta V}{\bar{V}}} \quad \cdots\cdots (26)$$

If we replace in (26) by

$$V = V_0\left[1 + \alpha(N - N_0)^2\right] \quad \cdots\cdots (27)$$

we can calculate as

$$V_A = V_0\left[1 + \alpha(N_A - N_0)^2\right]$$

$$V_B = V_0\left[1 + \alpha(N_B - N_0)^2\right]$$

$$\Delta V = V_A - V_B = \alpha V_0\left[(N_A - N_0)^2 - (N_B - N_0)^2\right]$$

$$= \alpha V_0\left(N_A^2 - 2N_A N_0 + \cancel{N_0^2} - N_B^2 + 2N_B N_0 - \cancel{N_0^2}\right)$$

$$= \alpha V_0\left[(N_A - N_B)(N_A + N_B) - 2N_0(N_A - N_B)\right]$$

$$= \alpha V_0 (N_A - N_B)(N_A + N_B - 2N_0)$$

$$= \alpha V_0 \Delta N \times 2\left(\frac{N_A + N_B}{2} - N_0\right) = \alpha V_0 \Delta N \times 2\bar{N}$$

$$\bar{V} = \frac{1}{2}(V_A + V_B)$$

$$= \frac{1}{2}V_0\left[2 + \alpha\left((N_A - N_0)^2 + (N_B - N_0)^2\right)\right]$$

$$= \frac{1}{2}V_0\left[2 + \alpha\left(N_A^2 - 2N_A N_0 + N_0^2 + N_B^2 - 2N_B N_0 + N_0^2\right)\right]$$

$$= \frac{1}{2}V_0\left[2 + \alpha\left((N_A + N_B)^2 \underbrace{- 2N_A N_B}_{???} - 2N_A N_0 - 2N_B N_0 + 2N_0^2\right)\right]$$

For virtual cyrstal approximation (VCA),

we assume the band width W,

$\frac{C_A+C_B}{2}$

the band center $C = \frac{C_A+C_B}{2}$, and all the sites

Based on Eq.(5) we focus on a single site.

$$\frac{W^2}{12} = \frac{1}{5}\left[\sum_\alpha (\mu_2)_{i\alpha i\alpha} - 2C\sum_\alpha (\mu_1)_{i\alpha i\alpha} + C^2 \sum_\alpha (\mu_0)_{i\alpha i\alpha}\right]$$

$$= \frac{1}{5}\sum_\alpha (\mu_2)_{i\alpha i\alpha} - \frac{2C}{\cancel{5}} \times \cancel{5}\left(\frac{C_A+C_B}{2}\right) + \frac{C^2}{5}\times 5$$

$$= \frac{1}{5}\sum_\alpha (\mu_2)_{i\alpha i\alpha} - 2\left(\frac{C_A+C_B}{2}\right)^2 + \left(\frac{C_A+C_B}{2}\right)^2$$

$$= \frac{1}{5}\sum_\alpha (\mu_2)_{i\alpha i\alpha} - \left(\frac{C_A+C_B}{2}\right)^2 \quad \cdots\cdots (28)$$

Next, we consider the site disorder with volume change.

Site A

$$\frac{W_{AB,A}^2}{12} = \frac{1}{5}\left[\sum_\alpha (\mu_2)^{(A)}_{i\alpha i\alpha} - 2C\sum_\alpha (\mu_1)^{(A)}_{i\alpha i\alpha} + C^2\sum_\alpha (\mu_0)^{(A)}_{i\alpha i\alpha}\right]$$

$$= \frac{1}{5}\sum_\alpha (\mu_2)^{(A)}_{i\alpha i\alpha} - \frac{2C}{5}\times 5$$

ダメ。まず Trace でやった方が良い。

(5) より。

$$\frac{W^2}{12} = \frac{1}{N_{orb}}\left[\mathrm{Tr}(\mu_2) - 2C\,\mathrm{Tr}(\mu_1) + C^2\,\mathrm{Tr}(\mu_0)\right]$$

$$= \frac{1}{N_{orb}}\mathrm{Tr}(\mu_2) - \left(\frac{C_A+C_B}{2}\right)^2 \quad \cdots\cdots (29)$$

Site disorder に対して

$$\frac{W_{AB}^2}{12} = \frac{1}{N_{orb}}\left[\mathrm{Tr}(\mu_2^{(AB)}) - 2C\,\mathrm{Tr}(\mu_1^{(AB)}) + C^2\,\mathrm{Tr}(\mu_0^{(AB)})\right]$$

$$\frac{W_{AB}^2}{12} = \frac{1}{N_{orb}} \mathrm{Tr}\left(\mathcal{U}_2^{(AB)}\right) - \left(\frac{C_A + C_B}{2}\right)^2 \quad \cdots\cdots (30)$$

$\bar{V} = \frac{V_A + V_B}{2}$ に対するもの

(30) − (29) leads to

$$\frac{W_{AB}^2}{12} - \frac{W^2}{12} = \frac{1}{N_{orb}} \left[\mathrm{Tr}\left(\mathcal{U}_2^{(AB)}\right) - \mathrm{Tr}\left(\mathcal{U}_2\right) \right] \quad \cdots\cdots (31)$$

$$\mathrm{Tr}(\mathcal{U}_2) = \sum_i \sum_j h_{ij} h_{ji} = \sum_i |h_{ii}|^2 + \sum_{i \neq j} |h_{ij}|^2$$

$$= N_{orb} \left(\frac{C_A + C_B}{2}\right)^2 + \sum_{i \neq j} |h_{ij}(l_0)|^2$$

$$= N_{orb} \left(\frac{C_A + C_B}{2}\right)^2 + \mathrm{Tr}(\mathcal{U}_2) - N_{orb} C^2 \quad \cdots\cdots (32)$$

$$\mathrm{Tr}\left(\mathcal{U}_2^{(AB)}\right) = \sum_{ij} h_{ij}^{(AB)} h_{ji}^{(AB)} = \sum_i |h_{ii}^{(AB)}|^2 + \sum_{i \neq j} |h_{ij}^{(AB)}|^2 = \frac{N_{orb}}{2} C_A^2 + \frac{N_{orb}}{2} C_B^2 + \sum_{i \neq j} |h_{ij}^{(AB)}|^2 \quad \cdots\cdots (33)$$

$$= \frac{N_{orb}}{2} C_A^2 + \frac{N_{orb}}{2} C_B^2 + \sum_{i \neq j} \left(|h_{ij}^{(AB)}(l_0)|^2 + 2 h_{ij}^{(AB)}(l_0) \frac{\partial h_{ij}^{(AB)}(l_0)}{\partial V} \Delta V \right)$$

$h_{ij}^{(AB)}(l_0) = h_{ij}(l_0) = h_{ij}$

$$= \frac{N_{orb}}{2} C_A^2 + \frac{N_{orb}}{2} C_B^2 + \sum_{i \neq j} \left[|h_{ij}(l_0)|^2 + 2 h_{ij}(l_0) \left(-\frac{5}{3} \frac{h_{ij}}{V} \right) \Delta V \right]$$

$$= \frac{N_{orb}}{2} C_A^2 + \frac{N_{orb}}{2} C_B^2 + \sum_{i \neq j} \left[|h_{ij}|^2 - \frac{10}{3V} |h_{ij}|^2 \Delta V \right]$$

注意
VCA と SD は
h_{ij} $(i \neq j)$ は同じ
h_{ij} $(i = j)$ は異なる
ことに注意せよ

$$= \frac{N_{orb}}{2} C_A^2 + \frac{N_{orb}}{2} C_B^2 + \frac{3V - 10\Delta V}{3V} \sum_{i \neq j} |h_{ij}|^2$$

$$= \frac{N_{orb}}{2} C_A^2 + \frac{N_{orb}}{2} C_B^2 + \left(1 - \frac{10}{3} \frac{\Delta V}{V}\right) \left[\mathrm{Tr}(\mathcal{U}_2) - N_{orb} C^2 \right] \quad \cdots\cdots (33)$$

VCA

(32) と (33) を用いて、

$$\mathrm{Tr}\left(\mathcal{U}_2^{(AB)}\right) - \mathrm{Tr}(\mathcal{U}_2) = \frac{N_{orb}}{2} C_A^2 + \frac{N_{orb}}{2} C_B^2 - \frac{10\Delta V}{3V} \left[\mathrm{Tr}(\mathcal{U}_2) - N_{orb} C^2 \right] - N_{orb} \left(\frac{C_A + C_B}{2}\right)^2$$

$$= \frac{N_{orb}}{4} C_A^2 - \frac{N_{orb}}{2} C_A C_B + \frac{N_{orb}}{4} C_B^2 - \frac{10\Delta V}{3V}\left[\mathrm{Tr}(\mathcal{U}_2) - N_{orb} C^2 \right]$$

$$= \frac{1}{4} N_{orb} (C_A - C_B)^2 - \frac{10\Delta V}{3V}\left[\mathrm{Tr}(\mathcal{U}_2) - N_{orb} C^2 \right] \quad \cdots\cdots (34)$$

(34) に (31) を代入して、

$$\frac{W_{AB}^2}{12} - \frac{W^2}{12} = \frac{1}{N_{orb}}\left[\mathrm{Tr}\left(\mathcal{U}_2^{(AB)}\right) - \mathrm{Tr}\left(\mathcal{U}_2\right) \right] \cdots\cdots (31)$$

we have

$$\frac{W_{AB}^2}{12} = \frac{W^2}{12} + \frac{1}{4}(C_A - C_B)^2 + \frac{10\Delta V}{3V} C^2 - \frac{10\Delta V}{3V N_{orb}} \mathrm{Tr}(\mathcal{U}_2) \cdots\cdots (35)$$

(29) を思い出して、

$$\frac{W^2}{12} = \frac{1}{N_{orb}} \mathrm{Tr}(\mathcal{U}_2) - \left(\frac{C_A + C_B}{2} \right)^2 \quad \cdots\cdots (29)$$

$$\frac{1}{N_{orb}} \mathrm{Tr}(\mathcal{U}_2) = \frac{W^2}{12} + C^2$$

(35) を書き直すと、

$$\frac{W_{AB}^2}{12} = \frac{W^2}{12} + \frac{1}{4}(C_A - C_B)^2 + \frac{10\Delta V}{3V} C^2 - \frac{10\Delta V}{3V}\left(\frac{W^2}{12} + C^2 \right)$$

$$= \left(1 - \frac{10\Delta V}{3V}\right)\frac{W^2}{12} + \frac{1}{4}(C_A - C_B)^2 \quad \cdots\cdots (36)$$

ここでの W は VCA のそれ。$V = \dfrac{V_A + V_B}{2}$ である。

W_0 とかくべき　　　V_0 とかくべき

$\Delta V < 0$ の場合、W_{AB} は大きくなる。

$$W_{AB} = \left[1 - \frac{10\Delta V}{3V} + 3\left(\frac{\Delta C}{W} \right)^2 \right]^{\frac{1}{2}} W$$

Noting $(1+x)^{\frac{1}{2}} = 1 + \frac{1}{2}x + o(x^2)$

$$W_{AB} \simeq \left[1 - \frac{5\Delta V}{3V} + \frac{3}{2}\left(\frac{\Delta C}{W} \right)^2 \right] W \quad \cdots\cdots (37)$$

(16) と (17) の導出を参照して。

$$\int_{C-\frac{W_{AB}}{2}}^{E_F} E\,\frac{10}{W_{AB}}\,dE = \left(\frac{\bar{N}^2}{20} - \frac{\bar{N}}{2}\right)W_{AB} + \bar{N}C$$

$\Delta V = V_{AB} - \frac{V_A + V_B}{2}$ ← (26)の ΔVとは意味が違う

$$= \frac{\bar{N}}{20}(\tilde{N} - 10)\left[1 - \frac{5\Delta V}{3V} + \frac{3}{2}\left(\frac{\Delta C}{W}\right)^2\right]W + \bar{N}C \quad \cdots\cdots (38)$$