Stress and variable cell optimization in OpenMX

- Purpose of the study
- Stress tensor in OpenMX
- Approximate Hessian by Schlegel
- Benchmark calculations
- Optimization of enthalpy
- Summary

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Purpose of the study

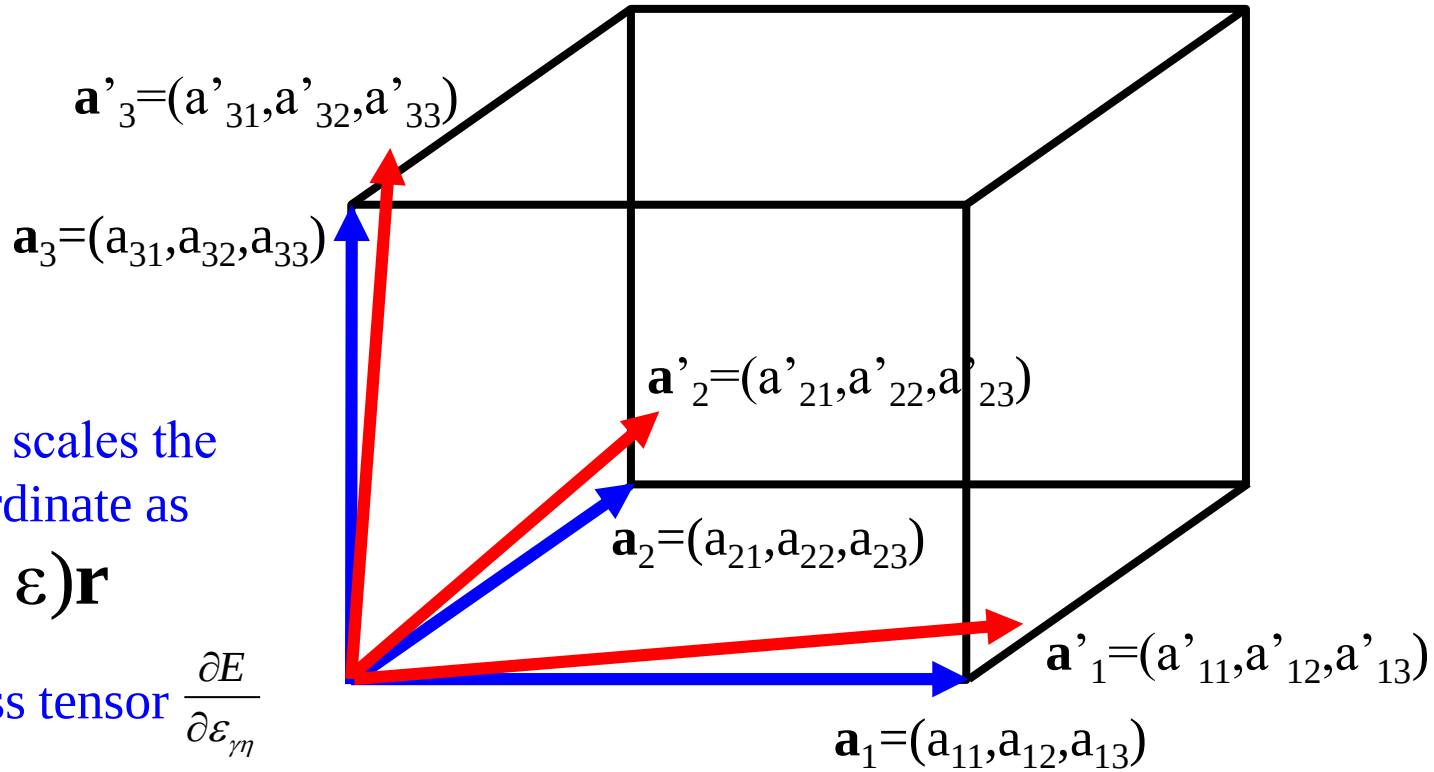
Done

- Full optimization of systems including internal coordinates and cell vectors
- Acceleration of optimization: reduction of iterative steps
- Optimization of the enthalpy: variable cell optimization under pressure

Planned

- Molecular dynamics under NPT ensemble

Stress tensor and derivatives w.r.t cell vectors



Strain tensor ε scales the Cartesian coordinate as

$$\mathbf{r}' = (\mathrm{I} + \varepsilon)\mathbf{r}$$

Then, the stress tensor $\frac{\partial E}{\partial \varepsilon_{\gamma\eta}}$ can be related the energy derivative w.r.t. cell vectors $\frac{\partial E}{\partial a_{ij}}$ by

$$\frac{\partial E}{\partial a_{ij}} = \sum_{\gamma\eta} \frac{\partial \varepsilon_{\gamma\eta}}{\partial a_{ij}} \frac{\partial E}{\partial \varepsilon_{\gamma\eta}} = \sum_{\gamma} b_{\gamma i} \frac{\partial E}{\partial \varepsilon_{\gamma j}}$$

where

$$b = a^{-1}$$

Stress tensor in OpenMX

In OpenMX, the total energy is defined by

$$E_{\mathrm{tot}} = E_{\mathrm{kin}} + E_{\mathrm{na}} + E_{\mathrm{ec}}^{(\mathrm{NL})} + E_{\delta\mathrm{ee}} + E_{\mathrm{XC}} + E_{\mathrm{scc}}$$

Thus, at least there are six contributions to stress tensor.

$$\frac{\partial E_{tot}}{\partial \varepsilon_{\gamma\eta}} = \frac{\partial E_{kin}}{\partial \varepsilon_{\gamma\eta}} + \frac{\partial E_{\mathrm{na}}}{\partial \varepsilon_{\gamma\eta}} + \frac{\partial E_{\mathrm{ec}}^{(\mathrm{NL})}}{\partial \varepsilon_{\gamma\eta}} + \frac{\partial E_{\delta\mathrm{ee}}}{\partial \varepsilon_{\gamma\eta}} + \frac{\partial E_{\mathrm{XC}}}{\partial \varepsilon_{\gamma\eta}} + \frac{\partial E_{\mathrm{scc}}}{\partial \varepsilon_{\gamma\eta}}$$

- **The terms** are decomposed to derivatives of matrix elements and overlap stress, leading to rather straightforward analytic calculations.
- **The term** is analytically evaluated in reciprocal space.
- **The term** is analytically evaluated in real space with a carefully derived formula.

The computational time is almost the same as that for the force calculation.

Stress tensor for E_{kin}, E_{na}, and E_{ec}

The derivative of E_{kin} is given by

$$\frac{\partial E_{\mathrm{kin}}}{\partial \varepsilon_{\gamma\eta}} = \sum_{\sigma}\sum_{n}\sum_{i\alpha\, j\beta} \frac{\partial \rho^{(\mathbf{R}_n)}_{\sigma,i\alpha\, j\beta}}{\partial \varepsilon_{\gamma\eta}} \left\langle \chi_{i\alpha}(\mathbf{r}-\mathbf{t}_i)\middle|\hat{T}\middle|\chi_{j\beta}(\mathbf{r}-\mathbf{t}_i-\mathbf{R}_n)\right\rangle$$
$$+\sum_{\sigma}\sum_{n}\sum_{i\alpha\, j\beta} \rho^{(\mathbf{R}_n)}_{\sigma,i\alpha\, j\beta} \frac{\partial}{\partial \varepsilon_{\gamma\eta}} \left\langle \chi_{i\alpha}(\mathbf{r}-\mathbf{t}_i)\middle|\hat{T}\middle|\chi_{j\beta}(\mathbf{r}-\mathbf{t}_i-\mathbf{R}_n)\right\rangle$$

The latter derivatives can be transformed to the derivatives w.r.t. Cartesian coordinates:

$$\frac{\partial}{\partial \varepsilon_{\gamma\eta}} \left\langle \chi_{i\alpha}(\mathbf{r}-\mathbf{t}_i)\middle|\hat{T}\middle|\chi_{j\beta}(\mathbf{r}-\mathbf{t}_i-\mathbf{R}_n)\right\rangle = \left(\frac{\partial}{\partial t_i^{\gamma}} \left\langle \chi_{i\alpha}(\mathbf{r}-\mathbf{t}_i)\middle|\hat{T}\middle|\chi_{j\beta}(\mathbf{r}-\mathbf{t}_i-\mathbf{R}_n)\right\rangle \right) t^{\eta}_{ij,n}$$

where

$$\mathbf{t}_{ij,n} = \mathbf{t}_i - \mathbf{t}_j - \mathbf{R}_n$$

The former derivatives can be transformed to the overlap stress tensor:

$$\sum_{\sigma}\sum_{n}\sum_{i\alpha\, j\beta} \frac{\partial \rho^{(\mathbf{R}_n)}_{\sigma,i\alpha\, j\beta}}{\partial \varepsilon_{\gamma\eta}} \left\langle \chi_{i\alpha}(\mathbf{r}-\mathbf{t}_i)\middle|\hat{T}\middle|\chi_{j\beta}(\mathbf{r}-\mathbf{t}_i-\mathbf{R}_n)\right\rangle$$
$$= -\sum_{\sigma}\sum_{n}\sum_{i\alpha\, j\beta} E^{(\mathbf{R}_n)}_{\sigma,i\alpha\, j\beta} \frac{\partial S^{(\mathbf{R}_n)}_{i\alpha\, j\beta}}{\partial t_i^{\gamma}} t^{\eta}_{ij,n}$$

The energy terms, E_{na} and E_{ec}, can also be evaluated in a similar way.

Stress tensor for $E_{\delta ee}$

The derivative of $E_{\delta ee}$ is given by

$$\frac{\partial E_{\delta \mathrm{ee}}}{\partial \varepsilon_{\gamma\eta}} = \delta_{\gamma\eta}\int \delta n(\mathbf{r})\delta V_{\mathrm{H}}(\mathbf{r})d\mathbf{r} + \frac{1}{2}\int \frac{\partial \delta n(\mathbf{r})}{\partial \varepsilon_{\gamma\eta}}\delta V_{\mathrm{H}}(\mathbf{r})d\mathbf{r} + \frac{1}{2}\int \delta n(\mathbf{r})\frac{\partial \delta V_{\mathrm{H}}(\mathbf{r})}{\partial \varepsilon_{\gamma\eta}}d\mathbf{r}$$

The second term is given by

$$\begin{aligned}\frac{1}{2}\int \frac{\partial \delta n(\mathbf{r})}{\partial \varepsilon_{\gamma\eta}}\delta V_{\mathrm{H}}(\mathbf{r})d\mathbf{r} &= \frac{1}{2}\int_{\Omega}\delta V_{\mathrm{H}}\sum_{\sigma}\sum_{n}^{N}\sum_{i\alpha,j\beta}\left[\frac{\delta \rho^{(\mathbf{R}_n)}_{\sigma,i\alpha j\beta}}{\delta \varepsilon_{\gamma\eta}}\phi_{i\alpha}(\mathbf{r}-\mathbf{t}_i)\phi_{j\beta}(\mathbf{r}-\mathbf{t}_j-\mathbf{R}_n)\right.\\ &+\rho^{(\mathbf{R}_n)}_{\sigma,i\alpha j\beta}\left\{\nabla_{\gamma}\phi_{i\alpha}(\mathbf{r}-\mathbf{t}_i)(r^{\eta}-t_i^{\eta})\right\}\phi_{j\beta}(\mathbf{r}-\mathbf{t}_j-\mathbf{R}_n)\\ &\left.+\rho^{(\mathbf{R}_n)}_{\sigma,i\alpha j\beta}\phi_{i\alpha}(\mathbf{r}-\mathbf{t}_i)\left\{\nabla_{\gamma}\phi_{i\alpha}(\mathbf{r}-\mathbf{t}_i-\mathbf{R}_n)(r^{\eta}-t_i^{\eta}-R_n^{\eta})\right\}\right]\mathrm{d}\mathbf{r}\\ &-\frac{1}{2}\int_{\Omega}\delta V_{\mathrm{H}}\left\{\sum_{I}\nabla_{\gamma}n_I^{(a)}(\mathbf{r}-\mathbf{t}_I)(r^{\eta}-t_I^{\eta})\right\}\mathrm{d}\mathbf{r}\end{aligned}$$

The third term is given by

$$\frac{1}{2}\int \delta n(\mathbf{r})\frac{\partial \delta V_{\mathrm{H}}(\mathbf{r})}{\partial \varepsilon_{\gamma\eta}}d\mathbf{r} = 4\pi\int_{\Omega}\delta n(\mathbf{r})\sum_{\mathbf{G}}\delta n(\mathbf{G})\frac{G_{\gamma}G_{\eta}}{|\mathbf{G}|^4}\exp(i\mathbf{G}\cdot\mathbf{r})d\mathbf{r}$$

Stress tensor for E_{xc}

The derivative of E_{xc} is given by

$$\frac{\partial E_{\mathrm{XC}}}{\partial \varepsilon_{\gamma\eta}} = \delta_{\gamma\eta} E_{\mathrm{xc}} + \Delta V \sum_{\sigma}\sum_{p} \frac{\partial f_{\mathrm{xc}}}{\partial n_p^{(\sigma)}} \frac{\partial n_p^{(\sigma)}}{\partial \varepsilon_{\gamma\eta}} + \Delta V \sum_{\sigma}\sum_{p} \frac{\partial f_{\mathrm{xc}}}{\partial |\, n_p^{(\sigma)} \,|} \frac{\partial |\, n_p^{(\sigma)} \,|}{\partial \nabla n_p^{(\sigma)}} \bullet \frac{\partial \nabla n_p^{(\sigma)}}{\partial \varepsilon_{\gamma\eta}} + \text{PCC term}$$

The second term contributes the overlap stress tensor, and third term can be evaluated as

$$\Delta V \sum_{\sigma}\sum_{p} \frac{\partial f_{\mathrm{xc}}}{\partial |\, n_p^{(\sigma)} \,|} \frac{\partial |\, n_p^{(\sigma)} \,|}{\partial \nabla n_p^{(\sigma)}} \bullet \frac{\partial \nabla n_p^{(\sigma)}}{\partial \varepsilon_{\gamma\eta}} = -\Delta V \sum_{\sigma}\sum_{p} \nabla \bullet A_p^{\sigma} \frac{\partial n_p^{\sigma}}{\partial \varepsilon_{\gamma\eta}} - \Delta V \sum_{\sigma}\sum_{p} \frac{\partial n_p^{\sigma}}{\partial x_{\gamma}} A_{p,\eta}^{\sigma}$$

where $$A_p^{\sigma} = \frac{\partial f_{\mathrm{xc}}}{\partial |\, n_p^{(\sigma)} \,|} \frac{\partial |\, n_p^{(\sigma)} \,|}{\partial \nabla n_p^{(\sigma)}}$$

The last term is given by

$$\text{PCC term} = \Delta V \sum_{\sigma}\sum_{p} v_{\mathrm{xc}}^{\sigma} \frac{\partial \underline{n}_p^{(\sigma)}}{\partial \varepsilon_{\gamma\eta}} - \Delta V \sum_{\sigma}\sum_{p} \frac{\partial \underline{n}_p^{(\sigma)}}{\partial x_{\gamma}} A_{p,\eta}^{\sigma}$$

Approximate Hessian by Schlegel

Schlegel proposed a way of constructing an approximate Hessian. A force constant for every pair of elements is fitted to the following formula, where dataset were constructed by B3LYP calculations.

$$F = \frac{A}{(r - B)^3}$$

H.B. Schlegel, Theoret. Chim. Acta (Berl.) 66, 333 (1984); J.M. Wittbrodt and H.B. Schlegel, J. Mol. Struc. (Theochem) 398-399, 55 (1997).

Parameter *B* for Badger's rule computed at the B3LYP level of theory

Period	1 H	2 Li–F	3 Na–Cl	4 K–Br	5 Rb–I	6 Cs–At
1	– 0.2573	0.3401	0.6937	0.7126	0.8335	0.9491
2		0.9652	1.2843	1.4725	1.6549	1.7190
3			1.6925	1.8238	2.1164	2.3185
4				2.0203	2.2137	2.5206
5					2.3718	2.5110

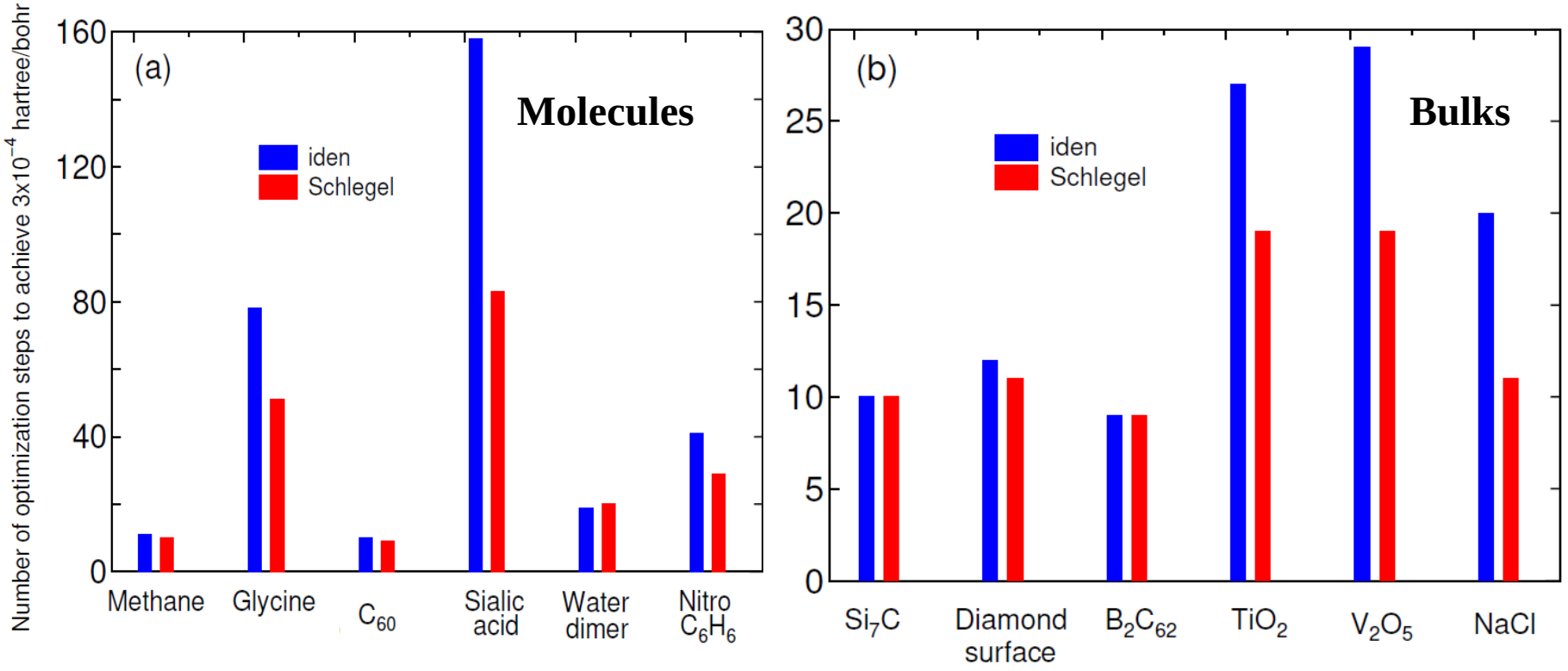
Suppose the total energy is given by the sum of pairwise potentials. Then, the derivatives lead to the following relation:

$$V_2 = \frac{1}{2}\sum_i \left(\sum_{Rn} \sum_j f(|r_i + R_n - r_j|) \right) \qquad H = BF$$

where B is the B-matrix of Wilson, H is the approximate Hessian in Cartesian coordinate.

Benchmark of the approximate Hessian in OpenMX

For both molecules and bulks, it is found that the Schlegel's method improves the convergence substantially.



Variable cell optimization

Initial Hessian:	Schlegel's method
Preconditioning:	RMM-DIIS
Hessian update:	BFGS
Update of positions:	Rational function (RF)

RF method

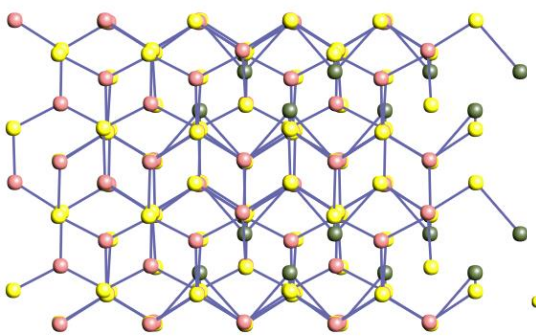
$$E = E_0 + \sum_i^{3N} \left(\frac{\partial E}{\partial x_i}\right)_0 (x_i - x_i^{(0)}) + \frac{1}{2}\sum_{i,j}^{3N} \left(\frac{\partial^2 E}{\partial x_i \partial x_j}\right)_0 (x_i - x_i^{(0)})(x_j - x_j^{(0)}) + \frac{1}{2}\lambda \sum_i^{3N} (x_i - x_i^{(0)})^2$$

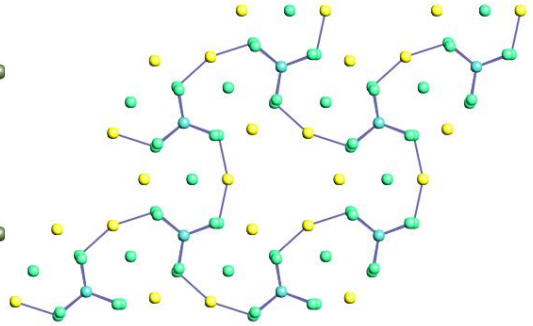
It is very important to construct the initial Hessian including internal coordinates, cell vectors, and the cross term for fast and stable convergence.

$$H = BF = \begin{pmatrix} Int & Int - Cell \\ Cell - Int & Cell \end{pmatrix}$$

Benchmark calculations of RFC5

For 785 crystals (mostly sulfides) , the full optimization by RFC5 were performed by Mr. Miyata, Ph.D student in JAIST, as computational screening in searching good thermoelectric materials





The optimization criterion: 10^{-4} Hartree/bohr

The histogram shows the number of systems among 785 systems as a function of the number of iterations to achieve the convergence

Optimization of the enthalpy

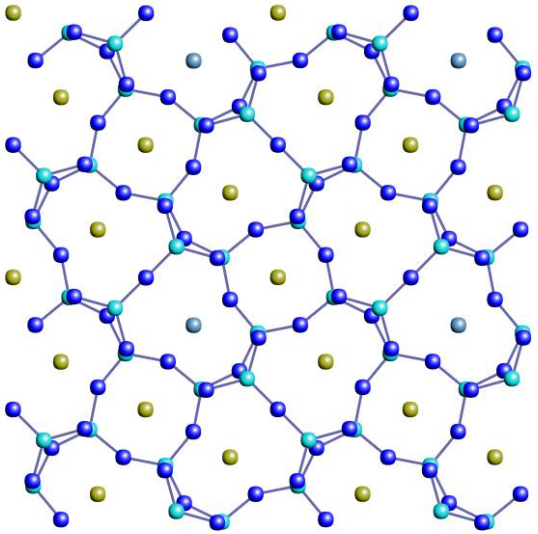
Under an external pressure *p*, the structural optimization can be performed by minimizing the enthalpy defined with

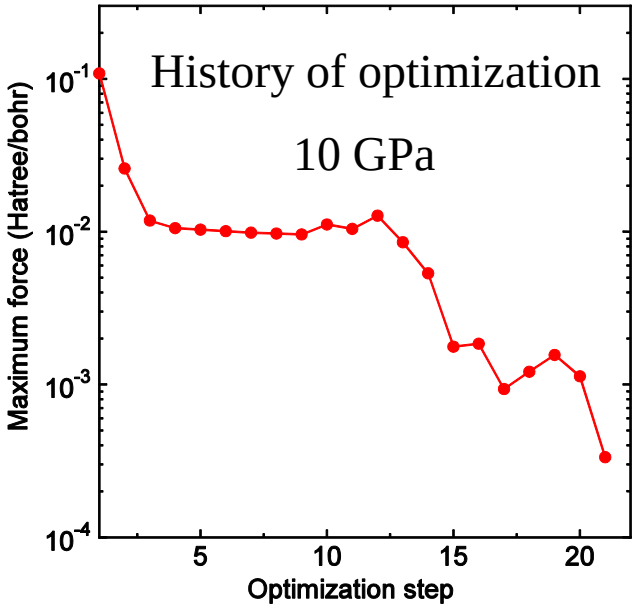
$$H = E + pV$$

The stress tensor is easily calculated by

$$\frac{\partial H}{\partial \varepsilon_{\gamma\eta}} = \frac{\partial E}{\partial \varepsilon_{\gamma\eta}} + p\frac{\partial V}{\partial \varepsilon_{\gamma\eta}} = \frac{\partial E}{\partial \varepsilon_{\gamma\eta}} + pV\delta_{\gamma\eta}$$

$La_3Si_6N_{11}$: Ce_{2c}





Summary

- We have derived an analytic formula of stress tensor and implemented the stress tensor in OpenMX.
- Acceleration of optimization has been achieved by introducing an approximate Hessian by Schlegel, which is effective to reduce the number of iterative steps.
- It is found from benchmark calculations of 785 systems that most of systems converge around 20-40 iterations.
- Optimization of the enthalpy was implemented, enabling variable cell optimization under pressure.