物質科学のための計算数理 II
Numerical Analysis for Material Science II

12th: Density Functional Theory (5)
Dec. 25 (Tue)

Lecturer: Mitsuaki Kawamura (河村光晶)

Schedule (This semester W1, W2)

1. Sep. 28 (Fri) Guidance Y
2. Oct. 5 (Fri) Monte Carlo method O
3. Oct. 12 (Fri) Monte Carlo method O
4. Oct. 19 (Fri) Monte Carlo method O
5. Oct. 26 (Fri) Exact diagonalization Y
6. Nov. 2 (Fri) Exact diagonalization Y
7. Nov. 9 (Fri) Molecular dynamics O (1st report problem will be announced.)
8. Nov. 30 (Fri) Density functional theory K
9. Dec. 7 (Fri) Density functional theory K
10. Dec. 14 (Fri) Density functional theory K
11. Dec. 21 (Fri) Density functional theory K
12. Dec. 25 (Tue) Density functional theory K (遠隔講義室)
13. Jan. 11 (Fri) (2nd)Report problem K

※ Lecturers: Y … Yamaji, K … Kawamura, O… Ohgoe

Schedule in this section (DFT)

1. Nov. 30 (Fri) Standard DFT code
   - First-principles calculation and Density functional theory (Lecture)
   - One-body Schrödinger eq. for periodic system and Bloch theorem (L)
   - Numerical solution of Kohn-Sham (one-body Schrödinger) eq. (L)
   - Hands-on DFT code (Tutorial)
   - Version control system : Git (T)
2. Dec. 7 (Fri) Kohn-Sham eq.
   - Plane-wave basis and Pseudopotentials (L)
   - Iterative eigenvalue solution method (L & T)
3. Dec. 14 (Fri) Self-Consistent loop
   - Hartree potential (Poisson eq.), Atomic potential, XC potential
   - Update (Broyden's method)
   - Visualization of grid data (T)
4. Dec. 21 (Fri) Total Energy
   - Total energy
   - Brillouin-zone integral (Tetrahedron method)
   - Coulomb potential for periodic point charge (Ewald sum)
5. Dec. 25 (Tue) Advanced subjects for productive calculation (遠隔講義室)
   - Generalized gradient correction
   - Non-local pseudopotentials (Norm-conserving, ultrasoft, PAW)
   - Magnetism
6. Jan. 11 (Fri) Parctice

Today's Schedule

- Spin density functional theory
  - Collinear magnetism
  - Non-collinear magnetism
- Beyond local density approximation
  - Generalized gradient approximation
- Non-local pseudopotential
  - Norm conserving pseudopotential
  - Ultrasoft pseudopotential
  - Projector augmented wave (PAW)
  - Pseudopotential library

Density functional theory in non-spin polarized case

$$E[\rho] = \int d^3r \rho(\boldsymbol{r})\, v(\boldsymbol{r}) + E_{univ}[\rho]$$

$$E_{univ}[\rho] = T_{KS}[\rho] + \frac{1}{2}\iint d^3r d^3r' \frac{\rho(\boldsymbol{r})\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} + E_{XC}[\rho]$$

$$\left(-\frac{\boldsymbol{\nabla}^2}{2} + v_{KS}[\rho](\boldsymbol{r})\right)\varphi_n(\boldsymbol{r}) = \varepsilon_n \varphi_n(\boldsymbol{r}) \qquad v_{XC}[\rho](\boldsymbol{r}) \equiv \frac{\delta E_{XC}[\rho]}{\delta \rho(\boldsymbol{r})}$$

$$\rho(\boldsymbol{r}) = 2\sum_{n=1}^{N/2} |\varphi_n(\boldsymbol{r})|^2$$

Spin density functional theory

$$E[\rho_\uparrow, \rho_\downarrow] = \int d^3r \rho(\boldsymbol{r})\, v(\boldsymbol{r}) + E_{univ}[\rho_\uparrow, \rho_\downarrow]$$

$$E_{univ}[\rho_\uparrow, \rho_\downarrow] = T_{KS}[\rho] + \frac{1}{2}\iint d^3r d^3r' \frac{\rho(\boldsymbol{r})\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} + E_{XC}[\rho_\uparrow, \rho_\downarrow]$$

$$\left(-\frac{\boldsymbol{\nabla}^2}{2} + v_{KS,\sigma}[\rho_\uparrow, \rho_\downarrow](\boldsymbol{r})\right)\varphi_{n\sigma}(\boldsymbol{r}) = \varepsilon_{n\sigma}\varphi_{n\sigma}(\boldsymbol{r})$$

$$v_{XC,\sigma}[\rho_\uparrow, \rho_\downarrow](\boldsymbol{r}) \equiv \frac{\delta E_{XC}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\sigma(\boldsymbol{r})}$$

$$\rho_\sigma(\boldsymbol{r}) = \sum_{n=1}^{\infty} |\varphi_{n\sigma}(\boldsymbol{r})|^2 \theta(\varepsilon_F - \varepsilon_{n\sigma}) \qquad \rho(\boldsymbol{r}) = \sum_{\sigma=\uparrow,\downarrow} \rho_\sigma(\boldsymbol{r})$$

Exchange correlation energy

$$E_{XC}[\rho_\uparrow, \rho_\downarrow]$$

$$E_X[\rho_\uparrow, \rho_\downarrow] = \frac{E_X[2\rho_\uparrow] + E_X[2\rho_\downarrow]}{2}$$

The ″exchange″ effect acts only the same spin.

Local Spin Density Approximation (LSDA)

$$E_{XC}[\rho_\uparrow, \rho_\downarrow] \approx \int d^3r \left(\sum_{\sigma=\uparrow,\downarrow} \rho_\sigma(\boldsymbol{r}) \varepsilon_X\big(2\rho_\sigma(\boldsymbol{r})\big) + \rho(\boldsymbol{r}) \varepsilon_C\big(\rho(\boldsymbol{r}), \zeta(\boldsymbol{r})\big) \right)$$

$$\zeta = (\rho_\uparrow - \rho_\downarrow)/\rho$$

$$\varepsilon_C(\rho, \zeta) = \varepsilon_C(\rho, 0)\big(1 - f(\zeta)\big) + \varepsilon_C(\rho, 1) f(\zeta)$$

$$f(\zeta) \approx \frac{1}{2} \frac{(1+\zeta)^{4/3} + (1-\zeta)^{4/3} - 2}{2^{1/3} - 1}$$

Collinear and non-collinear spin

$\rho_\uparrow(\boldsymbol{r}), \rho_\downarrow(\boldsymbol{r})$ $\quad$ $\rho(\boldsymbol{r}), m_z(\boldsymbol{r})$

$\rho(\boldsymbol{r}), m_x(\boldsymbol{r}), m_y(\boldsymbol{r}), m_z(\boldsymbol{r})$

$$\begin{pmatrix} -\frac{\boldsymbol{\nabla}^2}{2} + v_{KS,\uparrow\uparrow}[\rho, \boldsymbol{m}](\boldsymbol{r}) & v_{KS,\uparrow\downarrow}[\rho, \boldsymbol{m}](\boldsymbol{r}) \\ v_{KS,\downarrow\uparrow}[\rho, \boldsymbol{m}](\boldsymbol{r}) & -\frac{\boldsymbol{\nabla}^2}{2} + v_{KS,\downarrow\downarrow}[\rho, \boldsymbol{m}](\boldsymbol{r}) \end{pmatrix} \begin{pmatrix} \varphi_{n\uparrow}(\boldsymbol{r}) \\ \varphi_{n\downarrow}(\boldsymbol{r}) \end{pmatrix} = \varepsilon_n \begin{pmatrix} \varphi_{n\uparrow}(\boldsymbol{r}) \\ \varphi_{n\downarrow}(\boldsymbol{r}) \end{pmatrix}$$

$$\hat{v}_H(\boldsymbol{r}) = \begin{pmatrix} v_H[\rho](\boldsymbol{r}) & 0 \\ 0 & v_H[\rho](\boldsymbol{r}) \end{pmatrix}$$

$\hat{v}(\boldsymbol{r})$: Spin-orbit coupling

$\hat{v}_{XC}(\boldsymbol{r})$: Non-collinear spin texture

Beyond LDA : Generalized Gradient Approximation (GGA)

$$E_{XC}^{LDA}[\rho] \equiv \int d^3r \rho(\boldsymbol{r}) \varepsilon_{XC}\big(\rho(\boldsymbol{r})\big)$$

- Underestimate bandgaps
- Overestimate cohesive energy → Underestimate lattice constatnt
- Magnetic state of 3d metals (e.g. the ferromagnetic bcc structure of Fe does not become the most stable state.)

$$E_{XC}[\rho] \approx \int d^3r \rho(\boldsymbol{r}) \varepsilon_{XC}(\rho(\boldsymbol{r}), |\boldsymbol{\nabla}\rho(\boldsymbol{r})|)$$

Gradient expansion approximation (GEA) is not improved from LDA.

Gradient is large in practice → The expansion is not so appropriate.

Generalized Gradient approximation

- More flexible form
- Preserve known desired conditions.

GGA functional

$$E_{XC}^{GGA}[\rho] = \int d^3r \rho(\boldsymbol{r}) \varepsilon_X\big(\rho(\boldsymbol{r})\big) F_{XC}\big(\rho(\boldsymbol{r}), s(\boldsymbol{r})\big)$$

$$s \equiv \frac{|\boldsymbol{\nabla}\rho|}{2k_F\rho} = \frac{|\boldsymbol{\nabla}r_s|}{2(2\pi/3)^{1/3}r_s}$$

Fig. 8.1 of "Electronic Structure"
by R. M. Martin

Fig. 8.2 of "Electronic Structure"
by R. M. Martin

GGA XC potential

$$v_{XC}[\rho](\boldsymbol{r}) \equiv \frac{\delta E_{XC}[\rho]}{\delta \rho(\boldsymbol{r})} \qquad E_{XC}^{LDA/GGA}[\rho] \equiv \int d^3 r \rho(\boldsymbol{r}) \varepsilon_{XC}\big(\rho(\boldsymbol{r}), \boldsymbol{\nabla}\rho(\boldsymbol{r})\big)$$

$$v_{XC}^{LDA}(\boldsymbol{r}) = \varepsilon_{XC}\big(\rho(\boldsymbol{r})\big) + \rho(\boldsymbol{r}) \frac{d\varepsilon_{XC}(\rho)}{d\rho}$$

$$\delta E_{XC}^{GGA}[\rho] = \int d^3 r \left(\varepsilon_{XC} \delta\rho(\boldsymbol{r}) + \rho(\boldsymbol{r}) \frac{\partial \varepsilon_{XC}(\rho, \boldsymbol{\nabla}\rho)}{\partial \rho(r)} \delta\rho(\boldsymbol{r}) + \rho(\boldsymbol{r}) \frac{\partial \varepsilon_{XC}(\rho, \boldsymbol{\nabla}\rho)}{\partial \boldsymbol{\nabla}\rho(\boldsymbol{r})} \delta\boldsymbol{\nabla}\rho(\boldsymbol{r}) \right)$$

$$\hat{v}_{XC}^{GGA} = \varepsilon_{XC}\big(\rho(\boldsymbol{r}), \boldsymbol{\nabla}\rho(\boldsymbol{r})\big) + \rho(\boldsymbol{r}) \frac{\partial \varepsilon_{XC}(\rho, \boldsymbol{\nabla}\rho)}{\partial \rho(r)} + \rho(\boldsymbol{r}) \frac{\partial \varepsilon_{XC}(\rho, \boldsymbol{\nabla}\rho)}{\partial \boldsymbol{\nabla}\rho(\boldsymbol{r})} \cdot \boldsymbol{\nabla}$$

$$v_{XC}^{GGA}(\boldsymbol{r}) = \varepsilon_{XC}\big(\rho(\boldsymbol{r}), \boldsymbol{\nabla}\rho(\boldsymbol{r})\big) + \rho(\boldsymbol{r}) \frac{\partial \varepsilon_{XC}(\rho, \boldsymbol{\nabla}\rho)}{\partial \rho(r)} - \boldsymbol{\nabla} \left(\rho(\boldsymbol{r}) \frac{\partial \varepsilon_{XC}(\rho, \boldsymbol{\nabla}\rho)}{\partial \boldsymbol{\nabla}\rho(\boldsymbol{r})} \right)$$

$$v_{XC}^{GGA}(\boldsymbol{r}_i) = \varepsilon_{XC} + \rho \frac{\partial \varepsilon_{XC}}{\partial \rho} + \sum_j \rho(\boldsymbol{r}) \frac{\partial \varepsilon_{XC}(\rho, \boldsymbol{\nabla}\rho)}{\partial \boldsymbol{\nabla}\rho(\boldsymbol{r})} \frac{\boldsymbol{\nabla}\rho(\boldsymbol{r})}{|\boldsymbol{\nabla}\rho(\boldsymbol{r})|} C_{ji}$$

$$\boldsymbol{\nabla}\rho(\boldsymbol{r}_i) = \sum_j \rho(\boldsymbol{r}_i)\, C_{ij}$$

Beyond LDA : Hybrid functional

Coupling constant integral (adiabatic connection) form

$$E_{XC}[\rho] = \int_0^1 d\lambda \left(\left\langle \Psi_\lambda \left| \frac{1}{2} \sum_{n,n'=1}^{N} \frac{1}{|\boldsymbol{r}_n - \boldsymbol{r}_{n'}|} \right| \Psi_\lambda \right\rangle - E_H[\rho] \right)$$

$$\lambda = 1 \quad E_X^{Fock} = -\frac{1}{2} \sum_{n,n'}^{N/2} \iint d^3r d^3r' \frac{\varphi_n^*(\boldsymbol{r}) \varphi_{n'}^*(\boldsymbol{r}') \varphi_{n'}(\boldsymbol{r}) \varphi_n(\boldsymbol{r}')}{|r - r'|}$$

$$\lambda = 0 \quad E_{XC}^{GGA}[\rho]$$

$$E_{XC} = \frac{E_X^{Fock} + E_{XC}}{2}$$

$$\hat{v}_X^{Fock} \varphi_n(\boldsymbol{r}) = -\sum_{n'}^{N/2} \varphi_{n'}(\boldsymbol{r}) \int d^3r' \frac{\varphi_{n'}^*(\boldsymbol{r}') \varphi_n(\boldsymbol{r}')}{|r - r'|}$$

For PW basis, it can be done with FFT. $O\left(N_k^2 N_b^2 N_{PW} \log N_{PW}\right)$

Beyond LDA : Other functional

- van der Waals functional

$$E_{XC}[\rho] = \iint d^3r d^3r' \rho(\boldsymbol{r}) g(\boldsymbol{r}-\boldsymbol{r}') \rho(\boldsymbol{r}')$$

Organic solid
Graphite (layer distance)
Mirror potential for surface

- DFT+U

$$E_{XC}[\rho] = E_{XC}^{GGA} + \sum_{\tau a} \rho_{\tau a} \rho_{\tau a} U_{\tau a} - E_{DC}$$

- meta-GGA

$$E_{XC}[\rho] = \int d^3r \rho(\boldsymbol{r}) \varepsilon_{XC}\big(\rho(\boldsymbol{r}), |\boldsymbol{\nabla}\rho(\boldsymbol{r})|, t(r)\big)$$

Kinetic energy density (Relates to $\boldsymbol{\nabla}^2\rho(\boldsymbol{r})$)

Modern pseudopotential

Concept of modern pseudopotential : Orthogonalized Plane Wave (OPW)

$$\left(-\frac{\nabla^2}{2}+v_{KS}\right)|\varphi_n\rangle=\varepsilon_n|\varphi_n\rangle$$

$$|\varphi_n\rangle\equiv|\tilde{\varphi}_n\rangle-\sum_c|\phi_c\rangle\langle\phi_c|\tilde{\varphi}_n\rangle$$

$$\langle\phi_c|\phi_{c'}\rangle=\delta_{cc'}$$

$$\langle\phi_c|\varphi_n\rangle=0$$

$$\left(-\frac{\nabla^2}{2}+v_{KS}\right)|\phi_c\rangle=\varepsilon_c|\phi_c\rangle$$

$$\left(-\frac{\nabla^2}{2}+v_{KS}\right)\left(|\tilde{\varphi}_n\rangle-\sum_c|\phi_c\rangle\langle\phi_c|\tilde{\varphi}_n\rangle\right)=\varepsilon_n\left(|\tilde{\varphi}_n\rangle-\sum_c|\phi_c\rangle\langle\phi_c|\tilde{\varphi}_n\rangle\right)$$

$$\left(-\frac{\nabla^2}{2}+v_{KS}-\sum_c|\phi_c\rangle\langle\phi_c|\right)|\tilde{\varphi}_n\rangle=\varepsilon_n\left(1-\sum_c|\phi_c\rangle\langle\phi_c|\right)|\tilde{\varphi}_n\rangle$$

$$\left\langle\tilde{\varphi}_n\left|1-\sum_c|\phi_c\rangle\langle\phi_c|\right|\tilde{\varphi}_{n'}\right\rangle=\delta_{nn'}$$

Norm conserving pseudopotential

What is the good pseudopotential (PS)

- Only requires small cutoff for plane wave. ↔ Shallow
- Reproduce the result of the all-electron (AE) calculation at various cases (atoms, molecule, solid, ...) → Transferability

Required conditions for PS atomic orbital

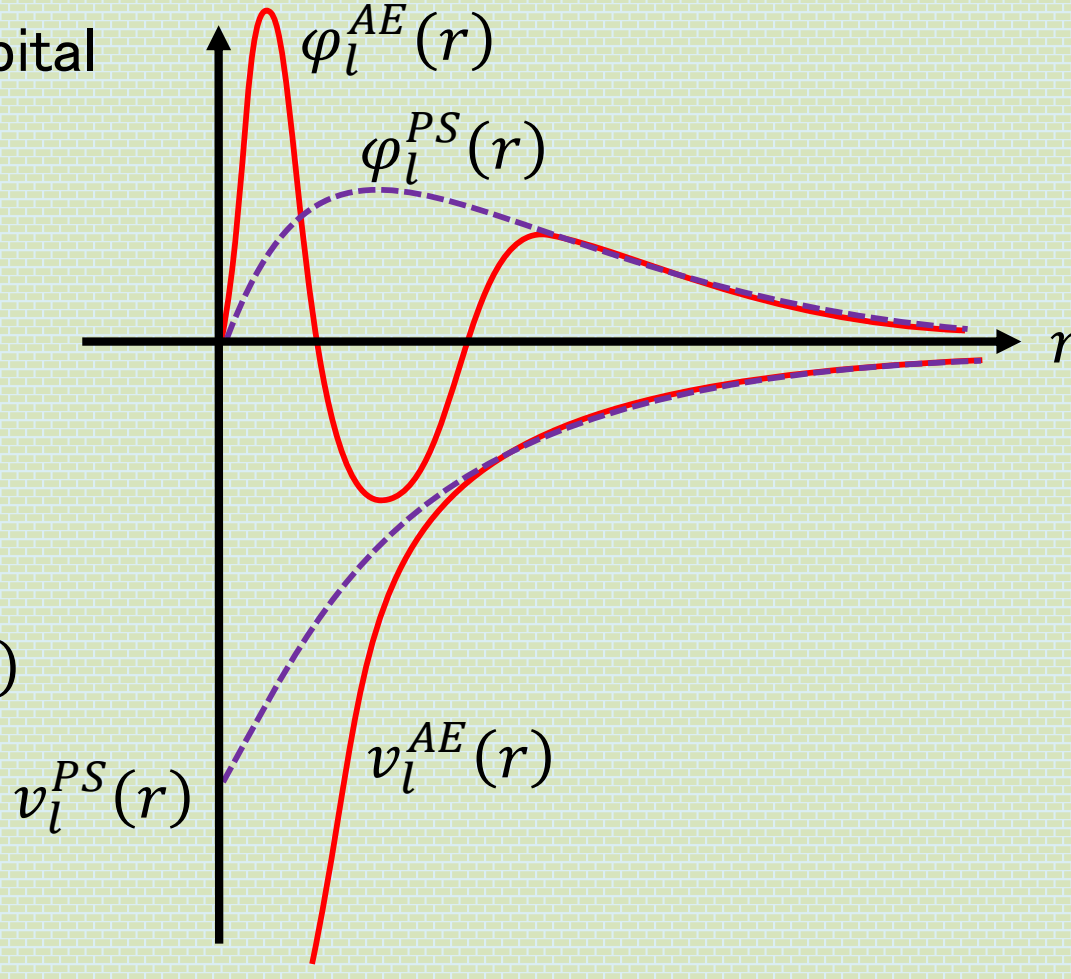
- $\varepsilon_l^{PS} = \varepsilon_l^{AE}$ at the atomic case.
- $\varphi_l^{PS}(r_c) = \varphi_l^{AE}(r_c)$
- $D_l^{PS}(r_c, \varepsilon) = D_l^{AE}(r_c, \varepsilon)$

$$D_l(r, \varepsilon_l) \equiv r \frac{d}{dr} \ln \varphi_l(r)$$

- $\frac{d}{d\varepsilon} D_l^{PS}(r_c, \varepsilon) = \frac{d}{d\varepsilon} D_l^{AE}(r_c, \varepsilon)$

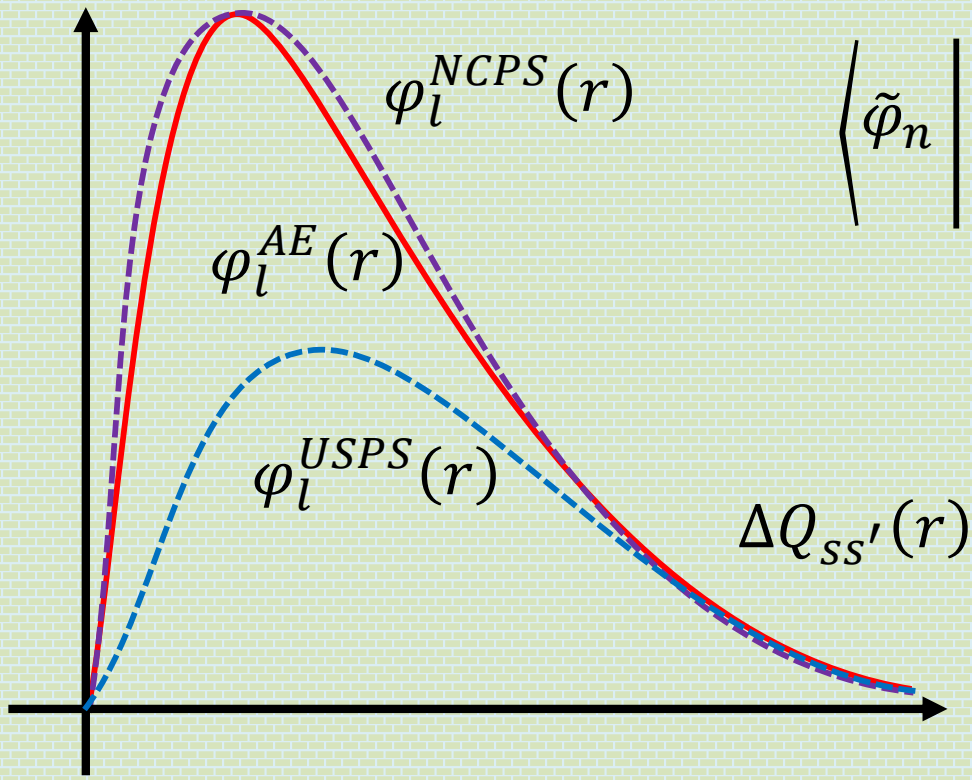
$$\int_0^{r_c} dr r^2 \, \varphi_l^{PS}(r) = \int_0^{r_c} dr r^2 \, \varphi_l^{AE}(r)$$

$$v_l^{PS}(r) = v_l^{AE}(r) - v_{HXC}[\rho^{PS}](r)$$



Ultrasoft pseudopotential and partial core correction

Problem : Norm-conserving condition for 1s (H), 2p (B,C,...), 3d(Ti,V,...), 4f, ...



$$\left\langle \tilde{\varphi}_n \middle| 1 + \sum_{s,s'} \Delta Q_{ss'} |\beta_s\rangle\langle\beta_{s'}| \middle| \tilde{\varphi}_{n'} \right\rangle = \delta_{nn'}$$

$$\Delta Q_{ss'} = \int_0^{r_c} dr\, \Delta Q_{ss'}(r)$$

$$\Delta Q_{ss'}(r) = \varphi_s^{AE*}(r)\varphi_{s'}^{AE}(r) - \varphi_s^{PS*}(r)\varphi_{s'}^{PS}(r)$$

Partial core correction (nonlinear core correction)

$$v_{XC}[\rho_c + \rho_v] \neq v_{XC}[\rho_c] + v_{XC}[\rho_v]$$

$$v_l^{PS}(r) = v_l^{AE}(r) - v_{HXC}[\rho^{PS}](r) - v_{XC}[\rho_{pc}]$$

$$v_{XC} = v_{XC}[\rho_{PS} + \rho_{pc}]$$

Projector augmented wave

Orthogonalized Plane Wave (OPW) again

$$|\varphi_n\rangle \equiv |\tilde{\varphi}_n\rangle - \sum_c |\phi_c\rangle\langle\phi_c|\tilde{\varphi}_n\rangle = \hat{T}|\tilde{\varphi}_n\rangle$$

The final equation form is the same as US pseudopotential, but ..

- We can obtain true KS orbital rather than the pseudo orbitals
- (Very ?) slightly different result for the magnetic system.

Pseudopotential library for QE

Although we can generate PS by ourselves ...

→ Huge effort !

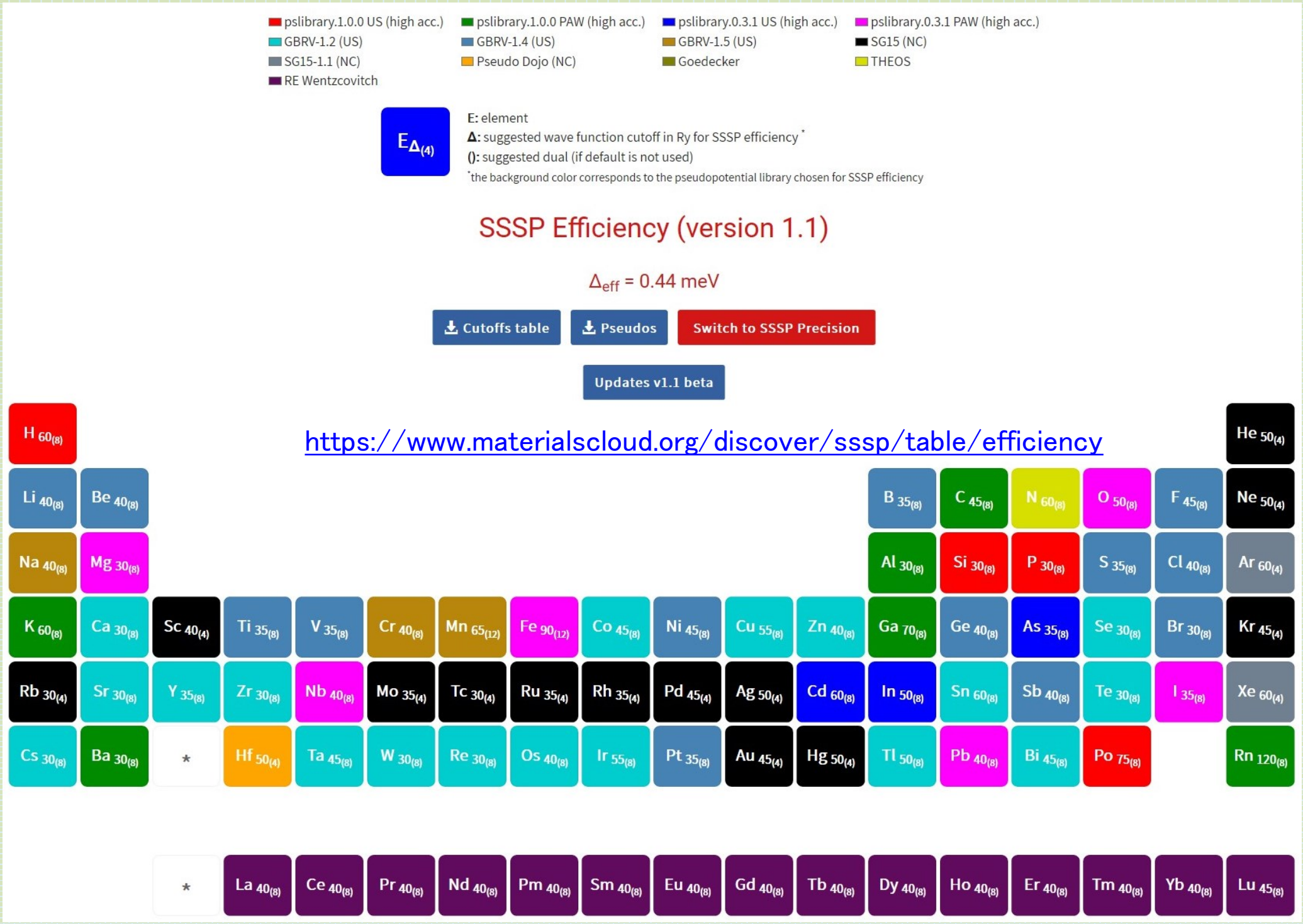
Good pseudopotential

- Requires small cutoff energy
- Well verified (compared with the AE results)
- Partial core correction
- Semicore (becomes harder)

Pseudopotential libraries

- SG15 library
  - http://www.quantum-simulation.org/potentials/sg15_oncv/
  - Norm conserving pseudopotential
- PS library
  - https://www.quantum-espresso.org/pseudopotentials
  - QE official
- Standard Solid State library (SSSP)
  - https://www.materialscloud.org/discover/sssp/table/efficienc
  - Strictly verified

Standard Solid State Pseudopotentials



Today's summary

- Magnetics system
  - Spin density functional theory
  - Local Spin Density Approximation (LSDA)
  - Collinear and non-collinear magnetism
- Beyond LDA
  - Generalized Gradient Approximation
  - Hybrid functional
  - VdW, DFT+U