# Construction pseudo-potentials for the projector augmented-wave Method

## CSCI699 Assignment 2

## Make Your Own PAW Pseudopotentials

# I. Briefly describe

- Pseudo-wavefunction (RRKJ2)
- Local pseudo-potential
- Non-local operator and Overlap operator
- Generalized eigenequation
- Transferability
- Estimation of plane-wave cutoff energies

# Pseudo-wavefunction (RRKJ2)

- The pseudo-wavefunctions are defined by,

$$P_{\mathrm{PS},lj}(r) = \underbrace{\alpha_1 r\, j_l(q_1 r) + \alpha_2 r\, j_l(q_2 r)}_{\textbf{RRKJ2 term}} + \underbrace{\alpha_3 F_{lj}(r) + \alpha_4 \tilde{F}_{lj}(r)}_{\textbf{correction term}}$$

- The correction functions satisfy the bellowing conditions.

$$F_{lj}(r_\mathrm{c}) = F_{lj}^{(1)}(r_\mathrm{c}) = F_{lj}^{(2)}(r_\mathrm{c}) = 0, \quad F_{lj}^{(3)}(r_\mathrm{c}) = C_3, \quad F_{lj}^{(4)}(r_\mathrm{c}) = C_4$$

$$\tilde{F}_{lj}(r_\mathrm{c}) = \tilde{F}_{lj}^{(1)}(r_\mathrm{c}) = \tilde{F}_{lj}^{(2)}(r_\mathrm{c}) = \tilde{F}_{lj}^{(3)}(r_\mathrm{c}) = 0 \quad \tilde{F}_{lj}^{(4)}(r_\mathrm{c}) = \tilde{C}_4$$

- $\alpha_1$ and $\alpha_2$ are determined by the conditions of the continuous first and second derivatives of RRKJ2 term at $r = r_\mathrm{c}$

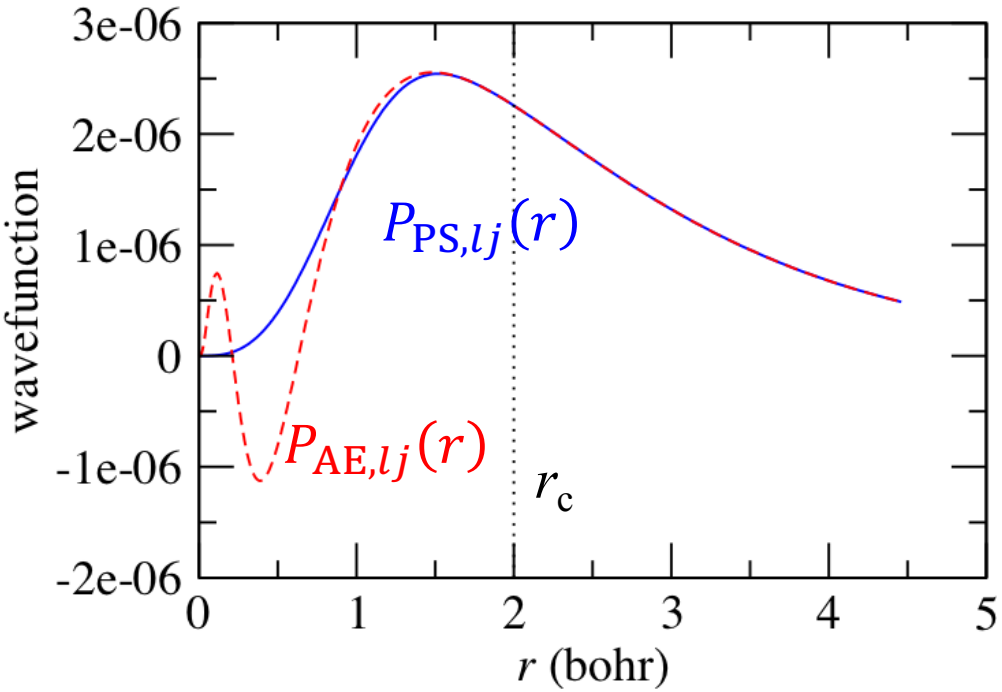
- $\alpha_3$ and $\alpha_4$ are determined by the conditions of the continuous third and fourth derivatives of $P_{\mathrm{PS}.lj}(r)$ at $r = r_\mathrm{c}$

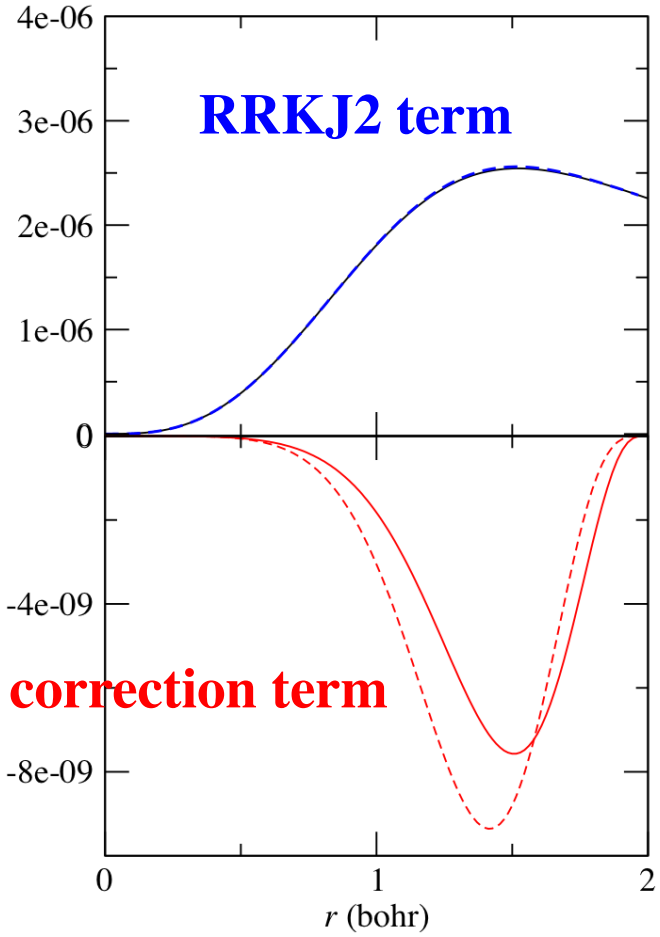
**Index**

- $(n,\ l)$ = quantum numbers
- $j$ = reference number

# Pseudo-wavefunction (RRKJ2)

- $P_{\mathrm{PS},lj}(r) = \underbrace{\alpha_1 r\, j_l(q_1 r) + \alpha_2 r\, j_l(q_2 r)}_{\textbf{RRKJ2 term}} + \underbrace{\alpha_3 F_{lj}(r) + \alpha_4 \tilde{F}_{lj}(r)}_{\textbf{correction term}}$
- $l = 3$ ($d$-orbital), $j = 0$ (all-electron eigenenergy)



# Local pseudo-potential

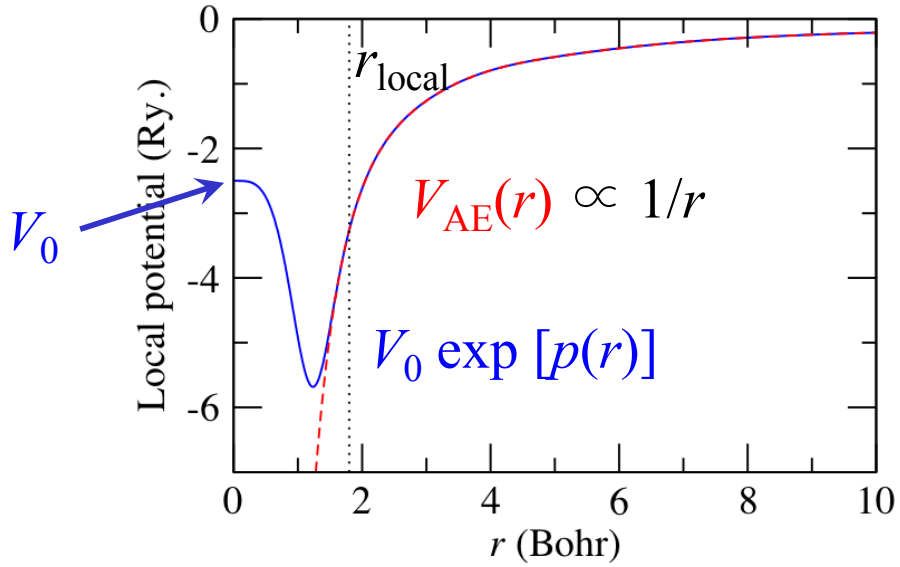
- We choose the following functions as a local potential:

$$V_{\text{local}}(r) = \begin{cases} V_0 \exp[p(r)] & r \le r_{\text{local}} \\ V_{\text{AE}}(r) & r > r_{\text{local}} \end{cases},$$

$$p(r) = \alpha_4 r^4 + \alpha_6 r^6 + \alpha_8 r^8 + \alpha_{10} r^{10} + \alpha_{12} r^{12}$$

- The coefficients $\{\alpha_{2i}\}$ are determined by the conditions of the continuous derivatives at $r = r_{\text{local}}$ ($m = 1, \ldots, 4$)

$$V_{\text{AE}}^{(m)}(r_{\text{local}}) = \frac{d^m}{dr^m}(V_0 \exp[p(r)])\Big|_{r=r_{\text{local}}}$$



# Non-local operator and Overlap operator

- Local function

$$|\chi_{lj}\rangle = \left(\varepsilon_{lj} - \hat{T} - V_{\text{local}}\right)\left|P_{\text{PS},lj}\right\rangle$$

- Basis function

$$|\beta_{lj}\rangle = \sum_k \left(\mathbf{B}_l^{-1}\right)_{kj}|\chi_{lk}\rangle, \quad B_{l,jk} = \langle P_{\text{PS},lj}|\chi_{lk}\rangle$$

- Augmentation charge

$$q_{l,jk}(r) = \langle P_{\text{AE},lj}|P_{\text{AE},lk}\rangle - \langle P_{\text{PS},lj}|P_{\text{PS},lk}\rangle$$

- Non-local operator

$$\hat{V}_{\text{NL}} = \sum_{l,j,k} D_{l,jk}|\beta_{lj}\rangle\langle\beta_{lk}|, \quad D_{l,jk} = B_{l,jk} + \varepsilon_{lk}q_{l,jk}$$

- Overlap operator

$$\hat{S} = 1 + \sum_{l,j,k} q_{l,jk}\left|\beta_{lj}\right\rangle\langle\beta_{lk}|$$

**Index**

- $(n,\ l)$ = quantum numbers
- $j,\ k$ = reference number

# Generalized eigenequation

- We construct pseudo-potentials and functions given all-electron functions, $P_{\mathrm{AE},lj}$ and potentials, $V_{\mathrm{AE}}$

$$P_{\mathrm{AE},lj} \text{ and } V_{\mathrm{AE}} \longrightarrow P_{\mathrm{PS},lj},\ V_{\mathrm{local}},\ \hat{V}_{\mathrm{NL}} \text{ and } \hat{S}$$

- Now, we solve generalized eigenequations given pseudo-potentials ($V_{\mathrm{local}}$, $\hat{V}_{\mathrm{NL}}$ and $\hat{S}$)

$$\left[\hat{T} + V_{\mathrm{local}}(r) + \hat{V}_{\mathrm{NL}}\right] P_{\mathrm{PS},nl}(r) = \varepsilon_{nl}\, \hat{S}\, P_{\mathrm{PS},nl}(r)$$

$$V_{\mathrm{local}},\ \hat{V}_{\mathrm{NL}} \text{ and } \hat{S} \longrightarrow \varepsilon_{nl} \text{ and } P_{\mathrm{PS},nl}$$

- And make sure that generalized eigenequations have the same eigenenergis as the AE eigenenergies and that the corresponding eigenfunctions coincide with the AE eigenfunctions outside the cutoff radius

$$\varepsilon_{nl} = \varepsilon_{nl}^{(0)} \quad \text{and} \quad P_{\mathrm{PS},nl} = P_{\mathrm{AE},nl}^{(0)} \ (r > r_c)$$

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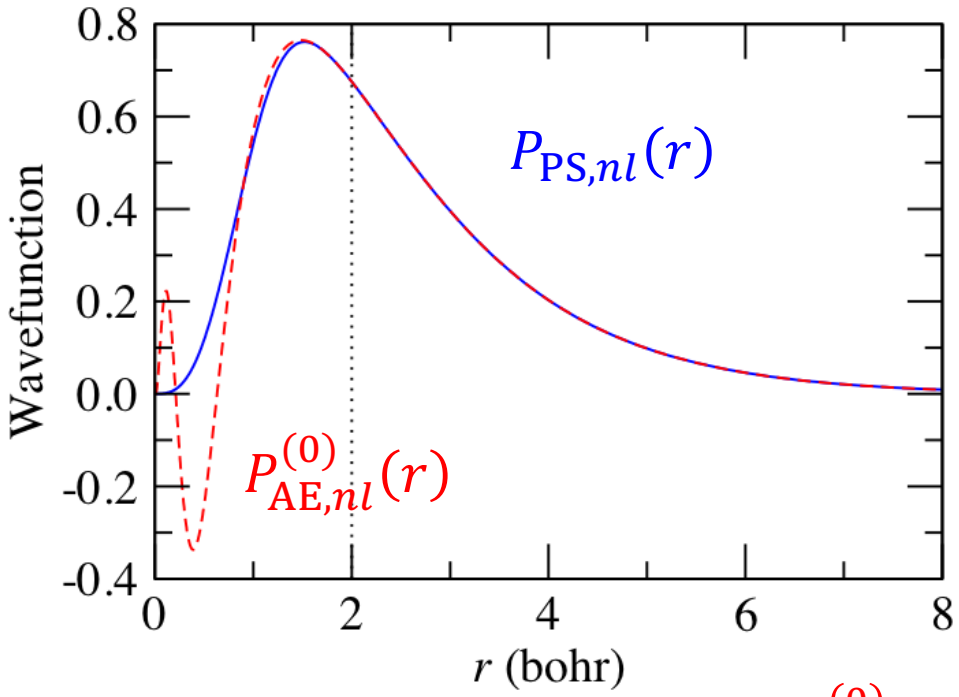
# Generalized eigenequation

- The normalized wavefuntions for 5*d* orbital.
- $P^{(0)}_{\mathrm{AE},nl}(r)$: the all electron wavefunction solved by the all electron Schrödinger equation
- $P_{\mathrm{PS},nl}(r)$: the pseudo-wavefunction solved by the generalized eigenenergy.




$$\varepsilon^{(0)}_{nl} = -0.8619636$$
$$\varepsilon_{nl} = -0.8619648$$

**Index**

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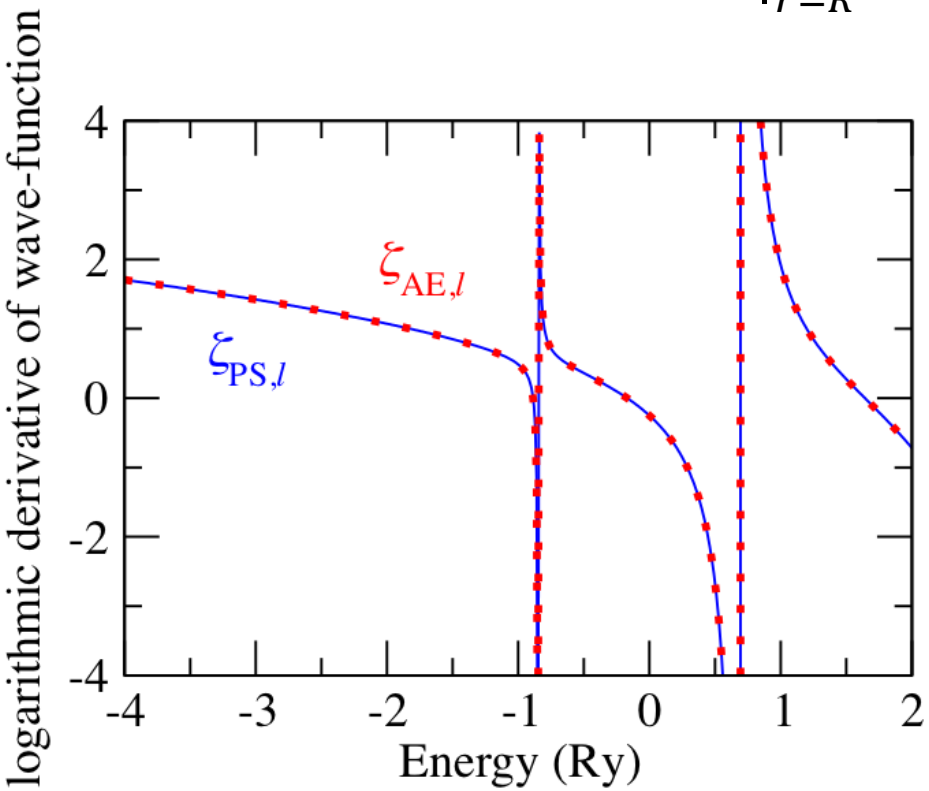
# Transferability

- A simple way to get a feeling for the transferability of a pseudo-potential is to compare logarithmic derivatives of all-electron and pseudo-wavefunction

$$\zeta_l(\varepsilon, R) = \frac{d}{dr}\left(\ln R_{nl}(r, \varepsilon)\right)\Big|_{r=R}$$

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# Estimation of plane-wave cutoff energies ($E_{\mathrm{cut}}$)

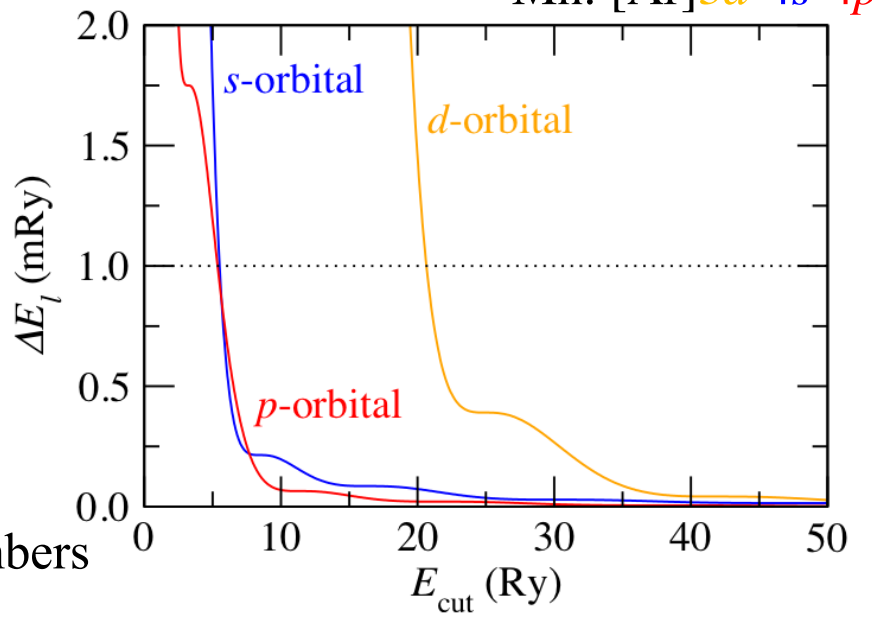
An error in the total energy associated with the cutoff energy, $E_{\mathrm{cut}}$ for the pseudo-wavefunctions is estimated as,

$$\Delta E_l(E_{\mathrm{cut}}) = \int_{\sqrt{E_{\mathrm{cut}}}}^{\infty} q^2 \left|\bar{P}^{(0)}_{\mathrm{PS},nl}(q)\right|^2 \, dq$$

where,

$$\bar{P}^{(0)}_{\mathrm{PS},nl}(q) = \sqrt{\frac{2}{\pi}} \int_0^{\infty} P^{(0)}_{\mathrm{PS},nl}(r)\, j_l(qr)\, qr \; dr$$

Mn: [Ar]$3d^5 4s^2 4p^0$

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# Estimation of plane-wave cutoff energies ($E_{\mathrm{cut}}^{\mathrm{dens}}$)

- Firstly, we define the compensation functions called G-function

$$g_l(r) = \underbrace{\alpha_1 j_l(q_1 r) + \alpha_2 j_l(q_2 r)}_{\text{original term by Kresse}} + \underbrace{\alpha_3 F_{lj}(r) + \alpha_4 \tilde{F}_{lj}(r)}_{\text{correction term}}$$

- The coefficients $q_i$ and $\alpha_i$ are chosen by

$$\left.\frac{d}{dr} j_l(q_i r)\right|_{r=r_{\mathrm{comp}}} = 0$$

$$g_l(r_{\mathrm{comp}}) = \left.\frac{d^m}{dr^m} g_l(r)\right|_{r=r_{\mathrm{comp}}} = 0 \quad (m = 2, 3)$$

$$\int_0^{r_{\mathrm{comp}}} g_l(r)\, r^{l+2}\, dr = 1$$

- We use a ratio $f_{\mathrm{comp}}$ to define the cutoff radius $r_{\mathrm{comp}}$:

$$r_{\mathrm{comp}} = \frac{\max\limits_{\mathrm{reference}} r_{\mathrm{c}}}{f_{\mathrm{comp}}}, \quad 1.1 \le f_{\mathrm{comp}} \le 1.6 \quad \left(\because\ r_{\mathrm{comp}} < \max_{\mathrm{reference}} r_{\mathrm{c}}\right)$$

# Estimation of plane-wave cutoff energies ($E_{\mathrm{cut}}^{\mathrm{dens}}$)

- G-function

$$g_l(r) = \alpha_1 j_l(q_1 r) + \alpha_2 j_l(q_2 r) + \alpha_3 F_{lj}(r) + \alpha_4 \tilde{F}_{lj}(r)$$

- Augmentation function (radial direction)

$$Q_{l,jk}(r) = r^2 g_l(r) \int_0^{r_c} \left[ P_{\mathrm{AE},lj}(r) P_{\mathrm{AE},lk}(r) - P_{\mathrm{PS},lj}(r) P_{\mathrm{PS},lk}(r) \right] r^l \, dr$$

- Next, we estimate the augmentation functions and their Fourier components:

$$\bar{Q}_{l,jk}^{L}(q) = q^2 \int_0^{\infty} Q_{l,jk}(r) \; j_L(qr) \, dr \quad (L = 0, 2, \ldots\ldots, 2l)$$

- The cutoff energy for the electron density is estimated from $\bar{Q}_{l,jk}^{L}(q)$. But we need not estimate $\bar{Q}_{l,jk}^{L}(q)$ for all references. $j = k = 1$ should be fine for each $l$.

**Index**

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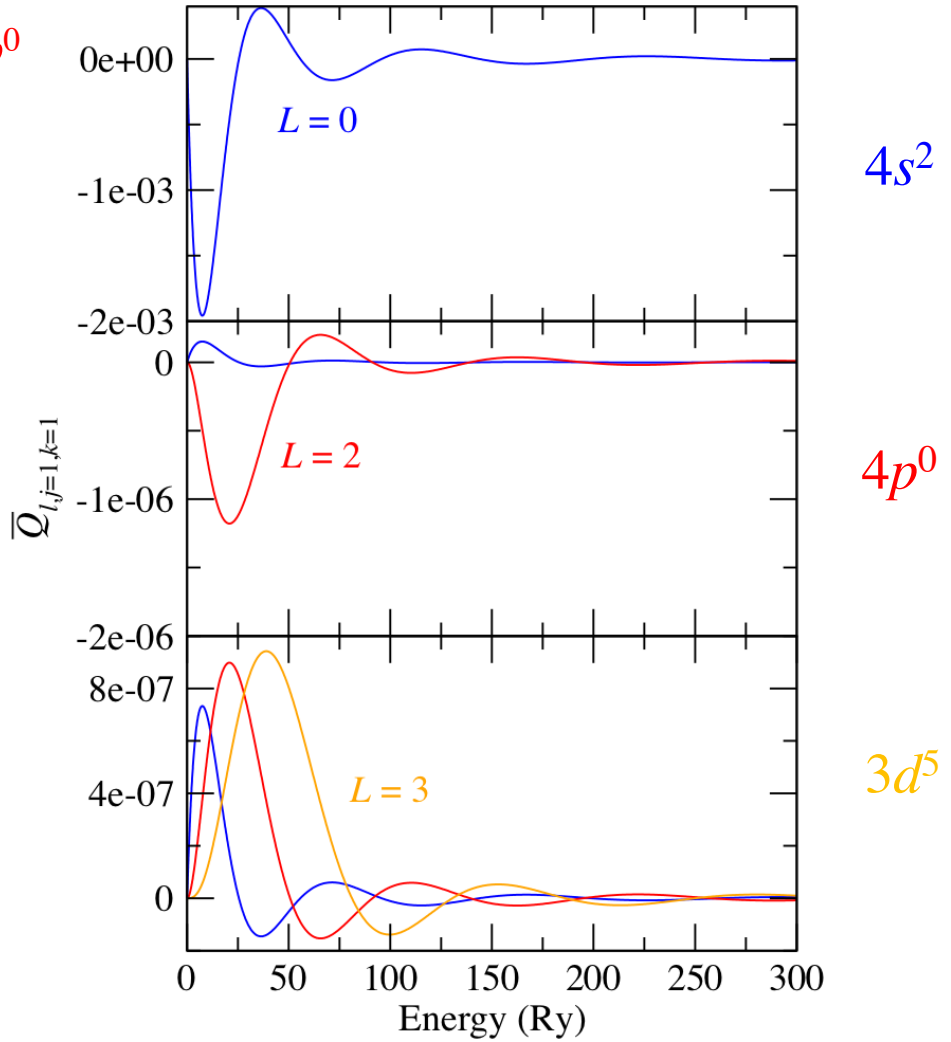
# Estimation of plane-wave cutoff energies ($E_{\mathrm{cut}}^{\mathrm{dens}}$)

- $\bar{Q}_{l,jk}^{L}(q) = q^2 \int_0^\infty Q_{l,jk}(r)\; j_L(qr)\, dr \quad (L = 0, 2, \ldots\ldots, 2l)$

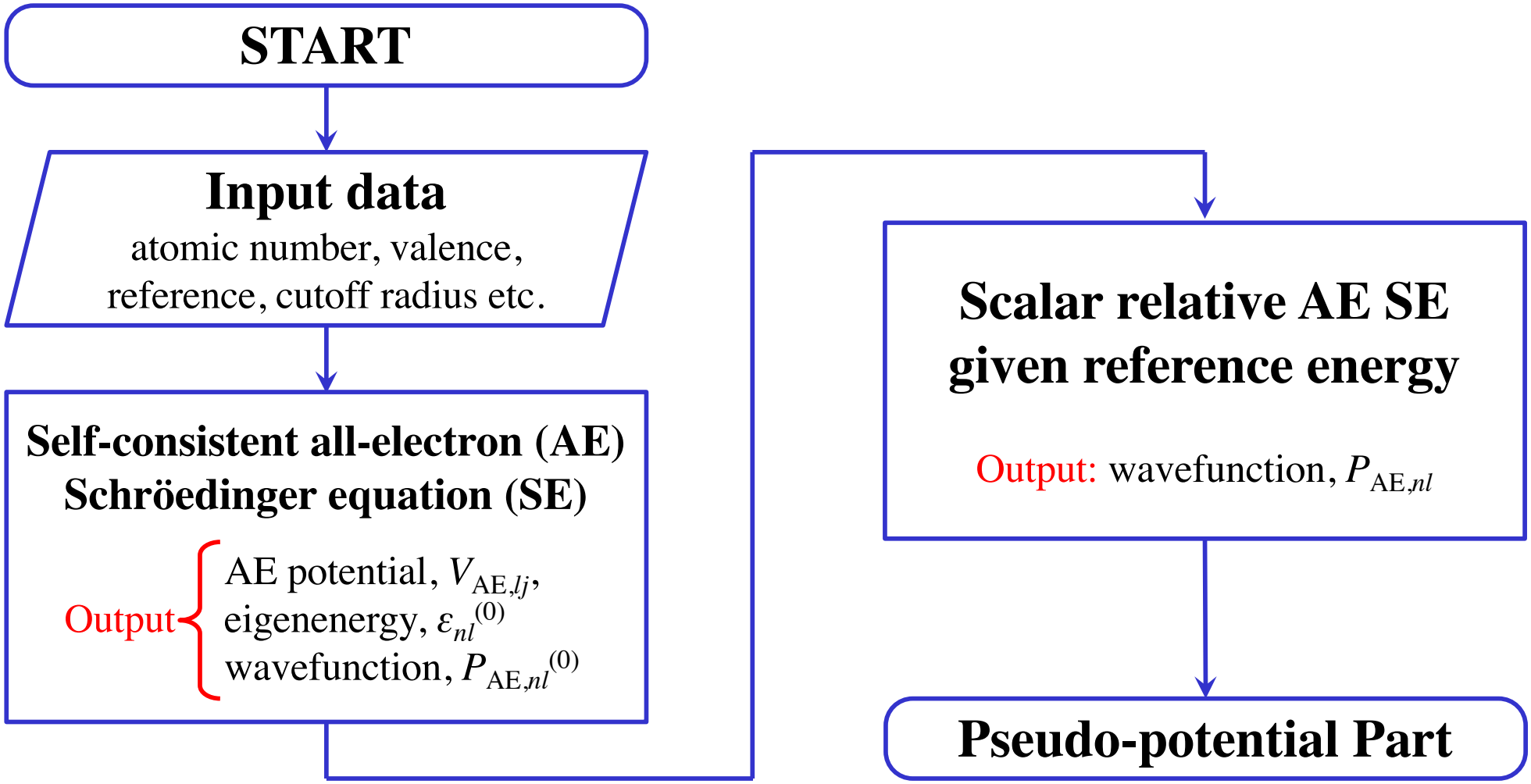
Mn: [Ar]$3d^5 4s^2 4p^0$



# II. Algorithm

- Algorithm (1) – All-electron calculation
- Algorithm (2) – Pseudo-potential
- Algorithm (3) – Estimation

# Algorithm (1) – All-electron calculation




**Index**

- $(n,\ l)$ = quantum numbers
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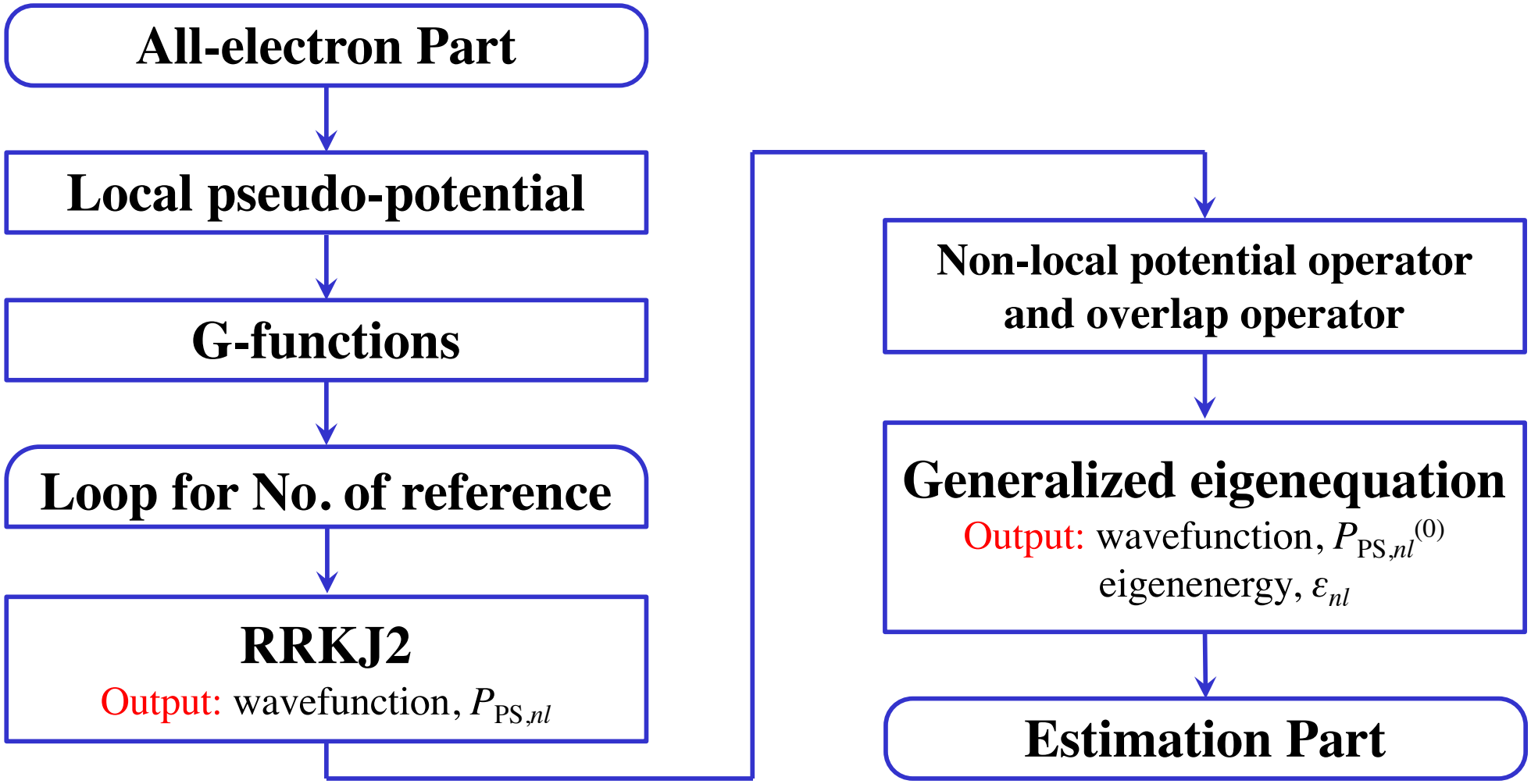
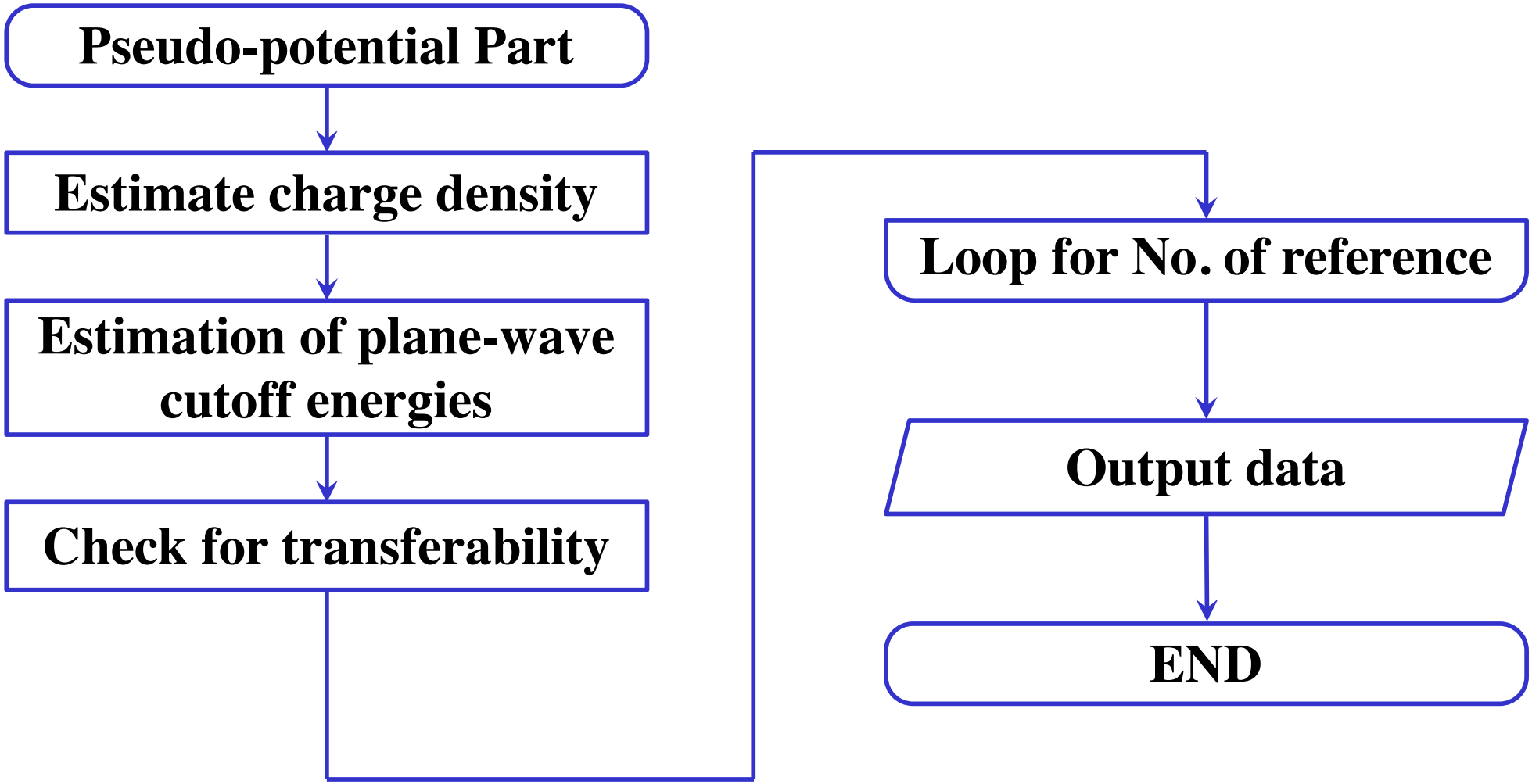
# Algorithm (2) – Pseudo-potential




**Index**

- $(n, l)$ = quantum numbers
- $j$ = reference number

# Algorithm (3) – Estimation




**Index**

- $(n, l)$ = quantum numbers
- $j$ = reference number

# III. How to use

- **Directory structure**
- **Jupyter Notebook on hpc**
- **Compilation of atm**
- **Input file**
- **Output file**

# Directory structure

- QXMD_Course/src/atm/

```
|-- atm*            ......  Executable file
|-- Atm/†           ......  Directory for compile
|-- data/†          ......  Output data for AE wavefunctions
|-- in7.dat         ......  Input file
|-- Makefile
`-- Sources/        ......  Original source
```

† These directories are made automatically after compiling.

- QXMD_Course/src/atm/Sources/

```
|-- ae.f90          ......  All-electron calculations
|-- ecut.f90        ......  Estimation of plane-wave cutoff energies
|-- ftmain.f90      ......  Main program
|-- funcs.f90       ......  Definition of functions
|-- Makefile
|-- pp.f90          ......  Pseudo-potential calculations
|-- trans.f90       ......  Check for transferability
|-- vloc.f90        ......  Local pseudo-potential
`-- vxc.f90         ......  Exchange and correlation energy functional
```

# Jupyter Notebook on hpc

- **How to install**

```
$ source /usr/usc/python/3.6.0/setup.sh
$ pip3 install jupyter --user
```

- **How to use**

Start the notebook in no-browser mode and specify a port (different from any other port on the server). My port is 8800.

```
$ ~/.local/bin/jupyter notebook --no-browser --port=8800
```

Create an ssh tunnel to the corresponding server and binding remote port

```
$ ssh -N -f -L 127.0.0.1:8800:127.0.0.1:8800 username@hpc-login3.usc.edu
```

Open your internet browser and type in

```
http://localhost:8800/?token=sometoken
```

- **Notation:**

```
$ COMMAND      ......  execute on hpc
$ COMMAND      ......  execute on your local machine
```

# Compilation of atm

1. **Prepare**

```
$ source /usr/usc/intel/default/setup.sh
$ cd QXMD_Course/
$ git stash
$ git pull
$ cd src/atm/
```

2. **Compile**

```
$ make ifort        ..... specify the fortran compiler
mkdir Atm
mkdir data
sed "s/^#IFORT#//" Sources/Makefile > Atm/Makefile
$ make atm          ..... compile
```

# Compilation of atm

```
$ make atm
cd Atm;  make atm
make[1]: Entering directory `QXMD_Course/src/atm/Atm'
cp ../Sources/ftmain.f90 ./ftmain.F90
ifort -c  ftmain.F90
ftmain.F90(1344): remark #8291: Recommended relationship between field width 'W' and the
number of fractional digits 'D' in this edit descriptor is 'W>=D+7'.
   2005 FORMAT(A2,I5,' (',D16.10,' )  ',10A8)
--------------------------^
cp ../Sources/funcs.f90  ./funcs.F90
ifort -c  funcs.F90
cp ../Sources/input.f90  ./input.F90
ifort -c  input.F90
cp ../Sources/vxc.f90    ./vxc.F90
ifort -c  vxc.F90
cp ../Sources/ae.f90     ./ae.F90
ifort -c  ae.F90
cp ../Sources/vloc.f90   ./vloc.F90
ifort -c  vloc.F90
cp ../Sources/pp.f90     ./pp.F90
ifort -c  pp.F90
cp ../Sources/ecut.f90   ./ecut.F90
ifort -c  ecut.F90
cp ../Sources/trans.f90  ./trans.F90
ifort -c  trans.F90
Loading atm ...
ifort ftmain.o funcs.o input.o vxc.o ae.o vloc.o pp.o ecut.o trans.o -o atm
mv atm ..
done
make[1]: Leaving directory `QXMD_Course/src/atm/Atm'
```

Successful in compiling

# Input file (1)

- **Input file:**
  Input file is '`in7.dat`'. And '`in7.dat`' is read from '**`*pseudo-potentials`**' to '**`* (end)`**'.

- **Input parameter**

```
(atomic number)              :
   74.d0                     : (zatm)   atomic number
    1.d0                     : (xion)   valence ion
(closed shell)               :
[Xe]                         : (clshl)    [He], [Ne], [Ar], [Kr], [Xe], [Rn]
                             : (nclshl) =  1,    3,    5,    8,   11,   15
(configuration)              :
     4                       : No. of orbitals - No. of closed orbitals
   430  14.d0                : (nljc, wnlj) orbital & No. of electrons  4f14
   521   4.d0                : (nljc, wnlj) orbital & No. of electrons  5d4
   601   1.d0                : (nljc, wnlj) orbital & No. of electrons  6s1
   611   0.d0                : (nljc, wnlj) orbital & No. of electrons  6p0
```

$\mathrm{W}(Z=74) : [\mathrm{Xe}]\ 4f^{14}5d^{4}6s^{2}$

frozen shell ($k=0$) — construct PP ($k=1$)

$4f^{14} \Rightarrow nl$`wnlj`

`nljc` $= 100n + 10l + k$

$n$ and $l$ are quantum numbers

# Input file (2)

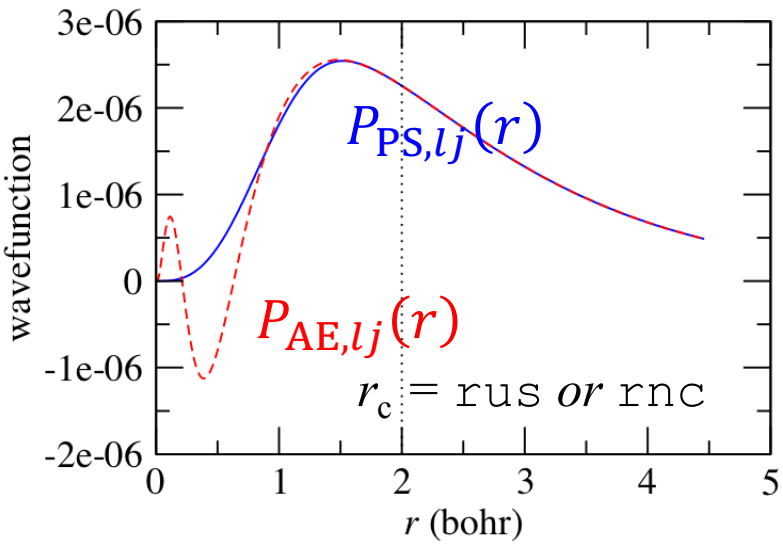
- **Input parameter**

W($Z = 74$) : [Xe] $4f^{14}5d^{4}6s^{2}6p^{0}$

```
(pseudo-potential)          :
    3                       : (methodpp) = 2:USPP, 3:PAW
(valence)                   :
    3                       : (nval)  No. of valence  (No. of k = 1)
 [  2                       : (iref)  No. of reference  ......  5d orbital
 [ -1.5d0   2.0d0    2.0d0  : (ref, rus, rnc)
 [  2                       : (iref)  No. of reference  ......  6s orbital
 [ -0.1d0   2.6d0    2.6d0  : (ref, rus, rnc)
 [  2                       : (iref)  No. of reference  ......  6p orbital
 [ -0.7d0   2.7d0    2.7d0  : (ref, rus, rnc)
```

No. of reference (`iref`) = 1 ..... $\varepsilon_{lk=1} = \varepsilon_{\mathrm{AE},nl}$
No. of reference (`iref`) = 2 ..... $\varepsilon_{lk=1} = \varepsilon_{\mathrm{AE},nl}$, $\varepsilon_{lk=2} =$ `ref`

`rus` and `rnc` are cutoff radii for USPP/PAW and NCPP



# Output file

- QXMD_Course/src/atm/

```
|-- D_beta.dat        ......  Basis functions
|-- D_chiae.dat       ......  Logarithmic derivative of AE wavefunctions
|-- D_chi.dat         ......  Local functions
|-- D_chil.dat        ......  Logarithmic derivative of PS wavefunctions
|-- D_delE.dat        ......  Error in energy associated with E_cut
|-- D_Pae.dat         ......  AE wavefunctions given reference energies
|-- D_Pus.dat         ......  PS wavefunctions given reference energies
|-- D_Pus,nl.dat      ......  Normilized PS wavefunctions by GEE
|-- D_Qbar.dat        ......  Fourier components of augmentation functions
|-- D_Q_L=0.dat       ......  Augmentation functions (L = 0)
|-- D_Q_L=2.dat       ......  Augmentation functions (L = 2)
|-- D_Q_L=4.dat       ......  Augmentation functions (L = 4)
|-- ele.dat           ......  Core charge density
|-- out_W             ......  Log file
|-- vloc.dat          ......  Local pseudo-potential
|-- W_A.wps           ......  Conditions to construct PP (for qxmd)
|-- W_D5.ae           ......  AE wavefunctions (for qxmd)
|-- W_D5.pwf          ......  PS wavefunctions from GEE (for qxmd)
|-- W_D5.wps          ......  PS wavefunctions given reference energies (for qxmd)
|-- W_local           ......  Local pseudo-potential (for qxmd)
`-- W_val             ......  Valence and core charge density (for qxmd)
```

# Reference

- **General information**
  Sugahara *et al*., *Phys. Rep. Kumamoto Univ*. **12**, 279 (2006)

- **Norm-conserving pseudo-potential**
  Troullier *et al*., *Phys. Rev. B* **43**, 1993 (1991); Hamann *et al*., *Phys. Rev. lett*. **43**, 1494 (1979)

- **RRKJ pseudo-potential**
  Rappe etal., Phys. Rev. B 41, 1227 (1990)

- **Ultrasoft pseudo-potential**
  Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990); Laasonen *et al*., *Phys. Rev. B* **47**, 10142 (1993)
  *cf*. Kresse *et al*., *Phys. Rev. B* **59**, 1758 (1999)

- **Projector augmented wave**
  Kresse *et al*., *Phys. Rev. B* **59**, 1758 (1999); Blöchl, *Phys. Rev. B* **50**, 17953 (1994)

- **Estimation of plane-wave cutoff energies**
  Kresse *et al*., *J. Phys. Condens. Matter* **6**, 8245 (1994); Laasonen *et al*., *Phys. Rev. B* **47**, 10142 (1993)

# CSCI699 Assignment 2
# Make Your Own PAW Pseudopotentials

Construct a projector-augmented wave (PAW) psudopotentials for the 5d, 6s and 6p orbitals of tungsten (W, atomic number $Z = 74$) using the ATM program in the class GitHab repository, https://github.com/USCCACS/QXMD_Course.

Submit the following plots, based on discussions in Sugahara *et al*., *Phys. Rep. Kumamoto Univ*. **12**, 279 (2006) [http://cacs.usc.edu/education/cs699/SugaharaUSPP-Kumamoto06.pdf].

1. All-electron and pseudo wave functions as a function of radius for each of the three angular momenta (5d, 6s, 6p).
2. Estimated error as a function of the cutoff energy $E_{\mathrm{cut}}$ for pseudowave functions, *i.e*., Eq. (4.1) in Sugahara *et al*.
3. Fourier components of the augmentation functions for the three angular momenta as a function of the cutoff energy $E_{\mathrm{cut}}^{\mathrm{dens}}$ for the electron density, *i.e*., Eq. (4.3) in Sugahara *et al*.

**Due: Wednesday, March 5, 2018**