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,

\[ P_{PS,lj}(r) = \alpha_1 r \, j_l(q_1 r) + \alpha_2 r \, j_l(q_2 r) + \alpha_3 F_{lj}(r) + \alpha_4 \tilde{F}_{lj}(r) \]

**RRKJ2 term**

**correction term**

• The correction functions satisfy the following conditions.

\[ F_{lj}(r_c) = F_{lj}^{(1)}(r_c) = F_{lj}^{(2)}(r_c) = 0, \quad F_{lj}^{(3)}(r_c) = C_3, \quad F_{lj}^{(4)}(r_c) = C_4 \]

\[ \tilde{F}_{lj}(r_c) = \tilde{F}_{lj}^{(1)}(r_c) = \tilde{F}_{lj}^{(2)}(r_c) = \tilde{F}_{lj}^{(3)}(r_c) = 0 \quad \tilde{F}_{lj}^{(4)}(r_c) = \tilde{C}_4 \]

• \( \alpha_1 \) and \( \alpha_2 \) are determined by the conditions of the continuous first and second derivatives of **RRKJ2 term** at \( r = r_c \)

• \( \alpha_3 \) and \( \alpha_4 \) are determined by the conditions of the continuous third and fourth derivatives of \( P_{PS,lj}(r) \) at \( r = r_c \)

Index

• \((n, l)\) = quantum numbers

• \( j \) = reference number
Pseudo-wavefunction (RRKJ2)

- \[ P_{PS,lj}(r) = \alpha_1 r j_1(q_1 r) + \alpha_2 r j_1(q_2 r) + \alpha_3 F_{lj}(r) + \alpha_4 \tilde{F}_{lj}(r) \]

  \[ \text{RRKJ2 term} \quad \text{correction term} \]

- \( l = 3 \) (d-orbital), \( j = 0 \) (all-electron eigenenergy)
Local pseudo-potential

- We choose the following functions as a local potential:
  \[ V_{\text{local}}(r) = \begin{cases} 
  V_0 \exp[p(r)] & r \leq r_{\text{local}} \\
  V_{\text{AE}}(r) & r > r_{\text{local}}
  \end{cases} \]
  \[ p(r) = \alpha_4 r^4 + \alpha_6 r^6 + \alpha_8 r^8 + \alpha_10 r^{10} + \alpha_12 r^{12} \]

- The coefficients \( \{\alpha_{2i}\} \) are determined by the conditions of the continuous derivatives at \( r = r_{\text{local}} \) (\( m = 1, \ldots, 4 \))
  \[ V^{(m)}_{\text{AE}}(r_{\text{local}}) = \left. \frac{d^m}{dr^m} \left( V_0 \exp[p(r)] \right) \right|_{r=r_{\text{local}}} \]
Non-local operator and Overlap operator

- Local function
  \[ |\chi_{lj}\rangle = (\varepsilon_{lj} - \hat{T} - V_{\text{local}}) |P_{PS,lj}\rangle \]

- Basis function
  \[ |\beta_{lj}\rangle = \sum_k (B_l^{-1})_{kj} |\chi_{lk}\rangle, \quad B_{l,jk} = \langle P_{PS,lj} |\chi_{lk}\rangle \]

- Augmentation charge
  \[ q_{l,jk}(r) = \langle P_{AE,lj} |P_{AE,lk}\rangle - \langle P_{PS,lj} |P_{PS,lk}\rangle \]

- Non-local operator
  \[ \hat{V}_{NL} = \sum_{l,j,k} D_{l,jk} |\beta_{lj}\rangle \langle \beta_{lk}|, \quad D_{l,jk} = B_{l,jk} + \varepsilon_{lk} q_{l,jk} \]

- Overlap operator
  \[ \hat{S} = 1 + \sum_{l,j,k} q_{l,jk} |\beta_{lj}\rangle \langle \beta_{lk}| \]

Index
- \((n, l)\) = quantum numbers
- \(j, k\) = reference number
Generalized eigenequation

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

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

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

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

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

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

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

Index
- $(n, l) = \text{quantum numbers}$
- $j = \text{reference number}$
Generalized eigenequation

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

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

\[ \varepsilon_{nl}^{(0)} = -0.8619636 \]
\[ \varepsilon_{nl} = -0.8619648 \]
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

\[ \zeta_l(\varepsilon, R) = \frac{d}{dr} \ln R_{nl}(r, \varepsilon) \bigg|_{r=R} \]

Index
- \((n, l)\) = quantum numbers
- \(j\) = reference number
Estimation of plane-wave cutoff energies ($E_{\text{cut}}$)

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

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

where,

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

Index
- $(n, l) =$ quantum numbers
- $j =$ reference number
Estimation of plane-wave cutoff energies ($E_{\text{cut}}^{\text{dens}}$)

- Firstly, we define the compensation functions called G-function
  
  $g_l(r) = \alpha_1 j_l(q_1 r) + \alpha_2 j_l(q_2 r) + \alpha_3 F_{lj}(r) + \alpha_4 \tilde{F}_{lj}(r)\quad \text{original term by Kresse}$

- The coefficients $q_i$ and $\alpha_i$ are chosen by
  
  $\frac{d}{dr} j_l(q_i r) \bigg|_{r=r_{\text{comp}}} = 0$

  $g_{l}(r_{\text{comp}}) = \frac{d^m}{dr^m} g_{l}(r) \bigg|_{r=r_{\text{comp}}} = 0 \quad (m = 2, 3)$

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

- We use a ratio $f_{\text{comp}}$ to define the cutoff radius $r_{\text{comp}}$:
  
  $r_{\text{comp}} = \frac{\max \text{ reference}}{f_{\text{comp}}} r_c, \quad 1.1 \leq f_{\text{comp}} \leq 1.6 \quad (\because r_{\text{comp}} < \max \text{ reference } r_c)$
Estimation of plane-wave cutoff energies ($E_{\text{cut}}^{\text{dens}}$)

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

- Next, we estimate the augmentation functions and their Fourier components:
  \[ \bar{Q}_{l,jk}^L(q) = q^2 \int_0^{\infty} Q_{l,jk}(r) j_L(qr) \, dr \quad (L = 0, 2, ..., 2l) \]

- 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**
- $(n, l) =$ quantum numbers
- $j =$ reference number
Estimation of plane-wave cutoff energies ($E_{\text{cut}}^{\text{dens}}$)

- $\bar{Q}_{L,j,k}^{L}(q) = q^2 \int_{0}^{\infty} Q_{L,j,k}(r) j_{L}(qr) \, dr \quad (L = 0, 2, \ldots, 2l)$

Mn: [Ar]$3d^54s^24p^0$

![Graph showing energy levels for Mn with $3d^5$, $4s^2$, and $4p^0$ orbitals]
II. Algorithm

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

START

Input data
atomic number, valence, reference, cutoff radius etc.

Self-consistent all-electron (AE) Schröedinger equation (SE)

Output
AE potential, $V_{AE, lj}$, eigenenergy, $\varepsilon_{nl}^{(0)}$, wavefunction, $P_{AE, nl}^{(0)}$

Scalar relative AE SE given reference energy

Output: wavefunction, $P_{AE, nl}$

Pseudo-potential Part

Index
• $(n, l) = \text{quantum numbers}$
• $j = \text{reference number}$
Algorithm (2) – Pseudo-potential

All-electron Part

Local pseudo-potential

G-functions

Loop for No. of reference

RRKJ2
Output: wavefunction, $P_{PS,nl}$

Non-local potential operator and overlap operator

Generalized eigenequation
Output: wavefunction, $P_{PS,nl}^{(0)}$

eigenenergy, $\varepsilon_{nl}$

Estimation Part

Index
- $(n, l) =$ quantum numbers
- $j =$ reference number
Algorithm (3) – Estimation

Pseudo-potential Part

Estimate charge density

Estimation of plane-wave cutoff energies

Check for transferability

Loop for No. of reference

Output data

END

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'
• **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)
  - [He], [Ne], [Ar], [Kr], [Xe], [Rn]
  - : (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

\[ W(Z = 74) : [\text{Xe}] 4f^{14}5d^46s^2 \]

**frozen shell**
\((k = 0)\)

**construct PP**
\((k = 1)\)

\[ 4f^{14} \Rightarrow n^l_{\text{wnlj}} \]

\( n\) and \( l\) are quantum numbers

\[ n_{\text{ljc}} = 100n + 10l + k \]
Input file (2)

- **Input parameter**
  - (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)
      - [-0.1d0 2.6d0 2.6d0]: (ref, rus, rnc)
      - [2]: (iref) No. of reference ...... 6s orbital
      - [-0.7d0 2.7d0 2.7d0]: (ref, rus, rnc)
    - 2: (iref) No. of reference ...... 6p orbital
      - [-0.7d0 2.7d0 2.7d0]: (ref, rus, rnc)

No. of reference (iref) = 1 ...... $\varepsilon_{l_k=1} = \varepsilon_{AE, nl}$
No. of reference (iref) = 2 ...... $\varepsilon_{l_k=1} = \varepsilon_{AE, nl}, \varepsilon_{l_k=2} = \text{ref}$

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

![Graph showing wavefunctions](image)
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 $E_{\text{cut}}$
  - |-- D_Pae.dat ....... AE wavefunctions given reference energies
  - |-- D_Pus.dat ....... PS wavefunctions given reference energies
  - |-- D_Pus,nl.dat ....... Normalized 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**

• **Norm-conserving pseudo-potential**

• **RRKJ pseudo-potential**

• **Ultrasoft pseudo-potential**

• **Projector augmented wave**

• **Estimation of plane-wave cutoff energies**
CSCI699 Assignment 2
Make Your Own PAW Pseudopotentials

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


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 \( E_{\text{cut}} \) 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 \( E_{\text{cut}}^{\text{dens}} \) for the electron density, \( i.e., \) Eq. (4.3) in Sugahara et al.

Due: Wednesday, March 5, 2018