

Construction of Pseudo-potentials for the Projector Augmented- Wave (PAW) Method

PHYS 760 Assignment 2

Make Your Own PAW Pseudopotentials

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I. Background

- Pseudo-wave function (RRKJ2)
- Local pseudo-potential
- Nonlocal operator and overlap operator
- Generalized eigen-equation
- Transferability
- Estimation of plane-wave cutoff energies

Pseudo-Wave Function (RRKJ2)

- The pseudo-wave functions are defined by,

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

Rappe-Rabe-Kaxiras-Joanopoulos

RRKJ2 term

correction term

- The correction functions satisfy the following conditions.

$$F_{lj}(r_c) = F_{lj}^{(1)}(r_c) = F_{lj}^{(2)}(r_c) = 0, \quad F_{lj}^{(3)}(r_c) = C_3, \quad F_{lj}^{(4)}(r_c) = C_4$$
$$\tilde{F}_{lj}(r_c) = \tilde{F}_{lj}^{(1)}(r_c) = \tilde{F}_{lj}^{(2)}(r_c) = \tilde{F}_{lj}^{(3)}(r_c) = 0 \quad \tilde{F}_{lj}^{(4)}(r_c) = \tilde{C}_4$$

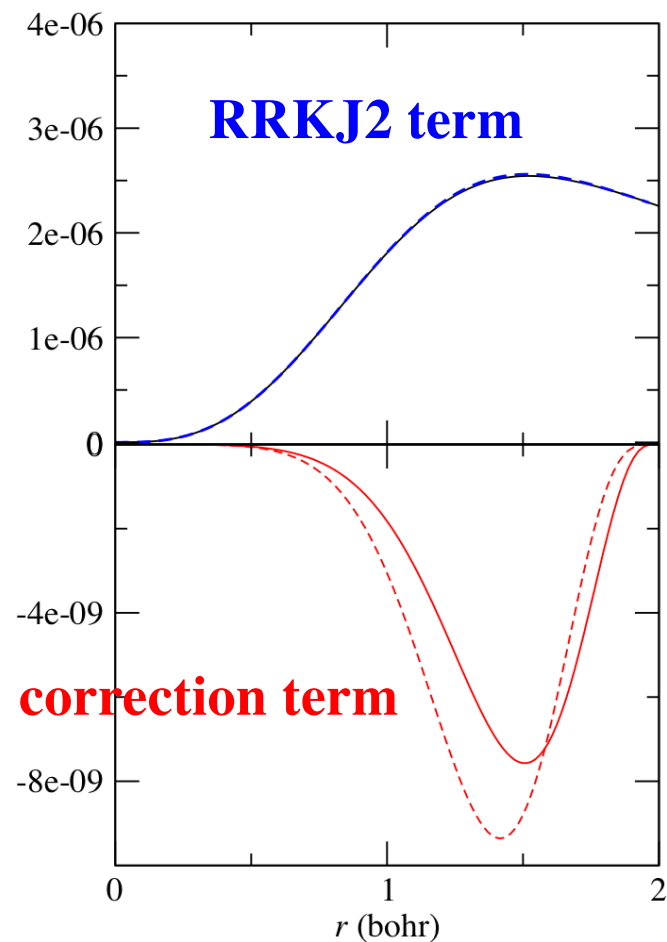
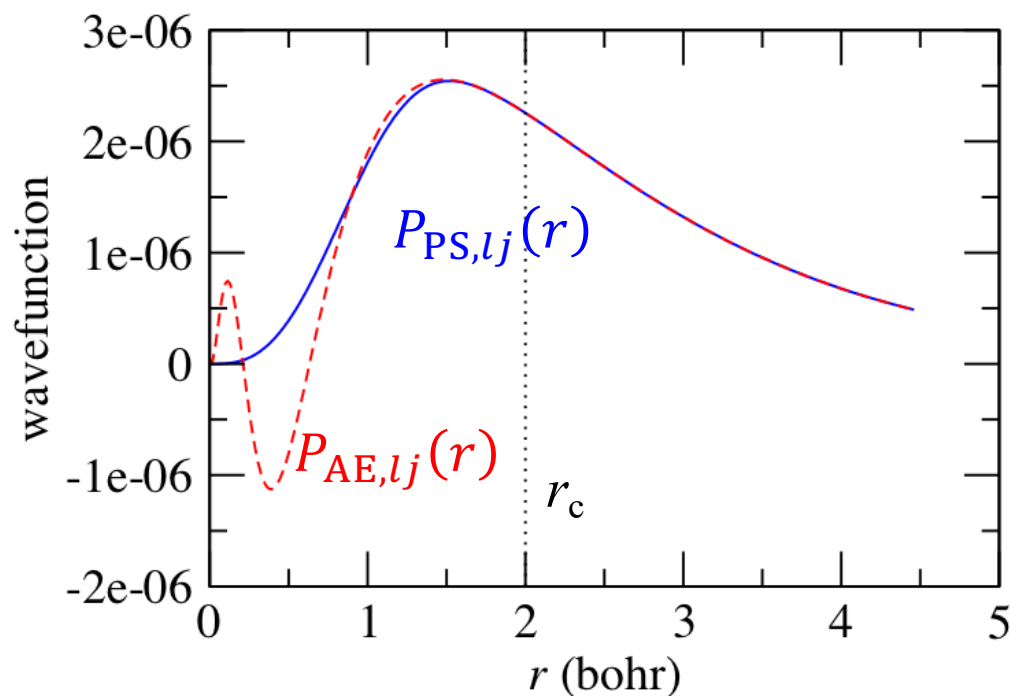
- α_1 and α_2 are determined by the conditions of the continuous first and second derivatives of **RRKJ2 term** at $r = r_c$
- α_3 and α_4 are determined by the conditions of the continuous third and fourth derivatives of $P_{\text{PS},lj}(r)$ at $r = r_c$

Index

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

Pseudo-Wave Function (RRKJ2)

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



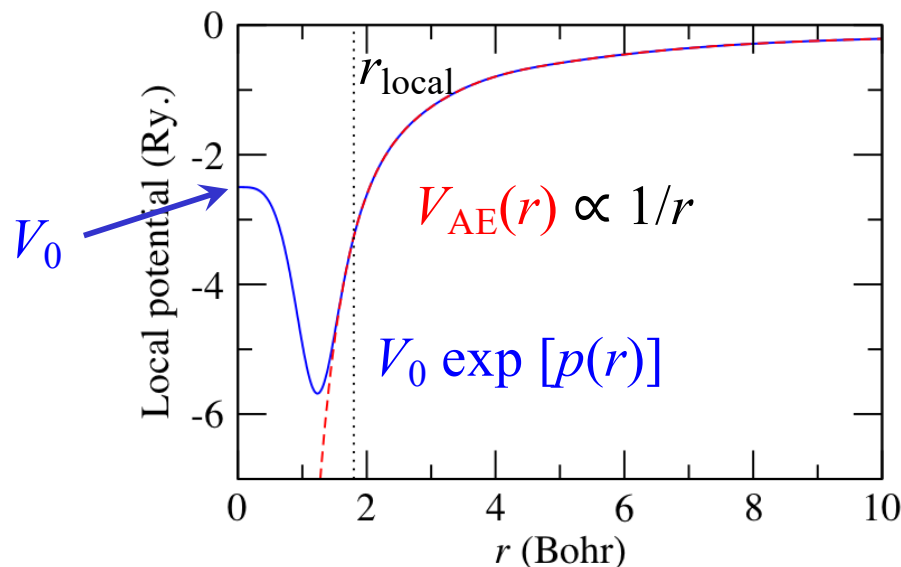
Local Pseudo-potential

- 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 $r = r_{\text{local}}$ ($m = 1, \dots, 4$)

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



Non-local Operator and Overlap Operator

- Local function

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

- Basis function

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

- Augmentation charge

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

- Nonlocal 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

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

Index

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- j, k = reference number

Generalized Eigenequation

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

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

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

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

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

- And make sure that generalized eigen-equations have the same eigen-energies as the AE eigen-energies and that the corresponding eigenfunctions coincide with the AE eigenfunctions outside the cutoff radius

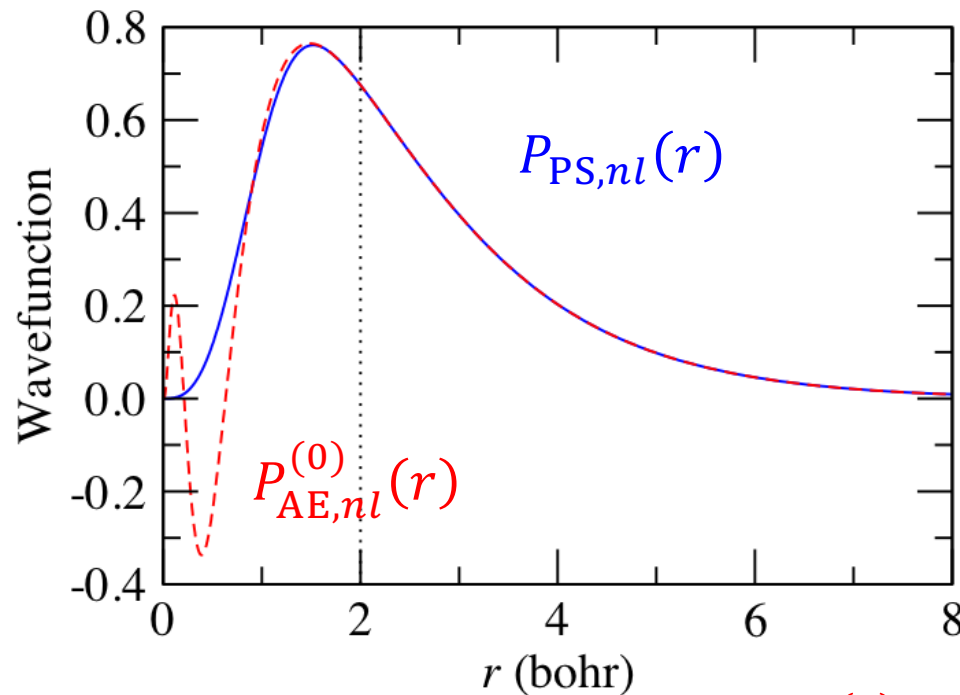
$$\varepsilon_{nl} = \varepsilon_{nl}^{(0)} \quad \text{and} \quad P_{\text{PS},nl} = P_{\text{AE},nl}^{(0)} \quad (r > r_c)$$

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Generalized Eigen-equation

- 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 eigen-energy.



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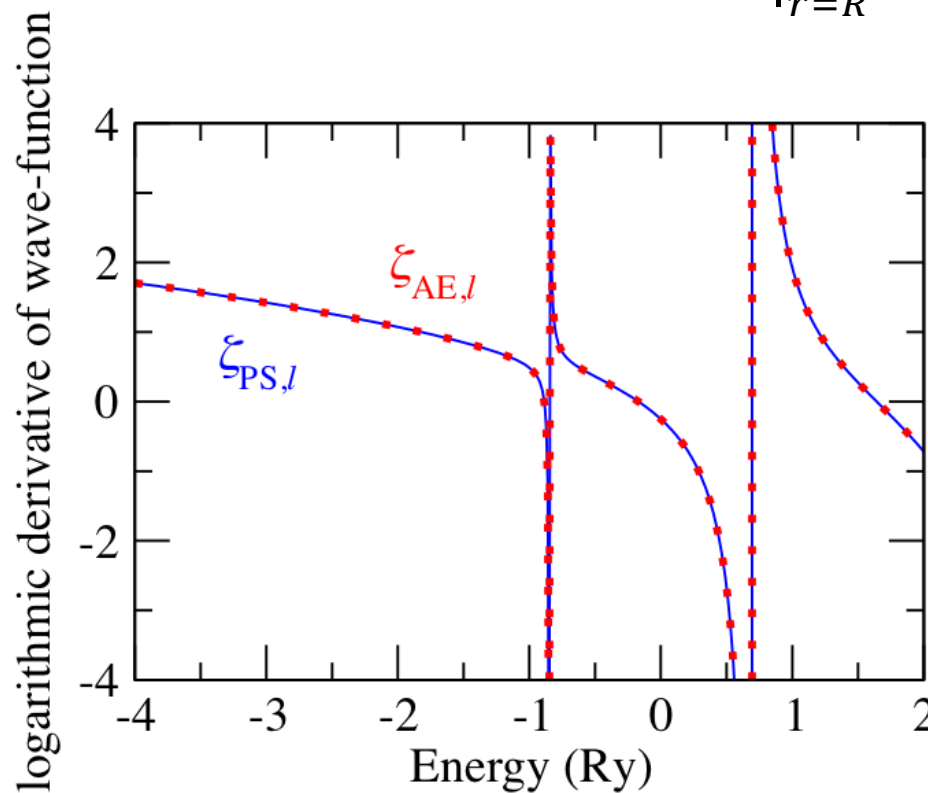
$$\epsilon_{nl}^{(0)} = -0.8619636$$

$$\epsilon_{nl} = -0.8619648$$

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-wave functions

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



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Estimation of Plane-wave Cutoff Energies (E_{cut})

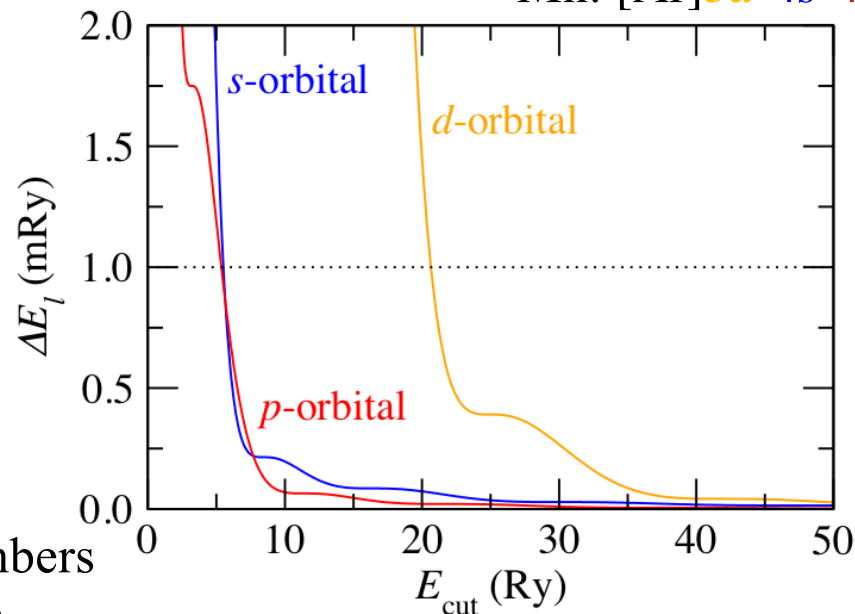
An error in the total energy associated with the cutoff energy, E_{cut} for the pseudo-wavefunctions is estimated as,

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

where,

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

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



Index

- (n, l) = quantum numbers
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Estimation of Plane-wave Cutoff Energies ($E_{\text{cut}}^{\text{dens}}$)

- 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 α_i are chosen by

$$\begin{aligned} \left. \frac{d}{dr} j_l(q_i r) \right|_{r=r_{\text{comp}}} &= 0 \\ g_l(r_{\text{comp}}) = \left. \frac{d^m}{dr^m} g_l(r) \right|_{r=r_{\text{comp}}} &= 0 \quad (m = 2, 3) \\ \int_0^{r_{\text{comp}}} g_l(r) r^{l+2} dr &= 1 \end{aligned}$$

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

$$r_{\text{comp}} = \frac{\max_{\text{reference}} r_c}{f_{\text{comp}}}, \quad 1.1 \leq f_{\text{comp}} \leq 1.6 \quad \left(\because r_{\text{comp}} < \max_{\text{reference}} r_c \right)$$

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)

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

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

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

- 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 .

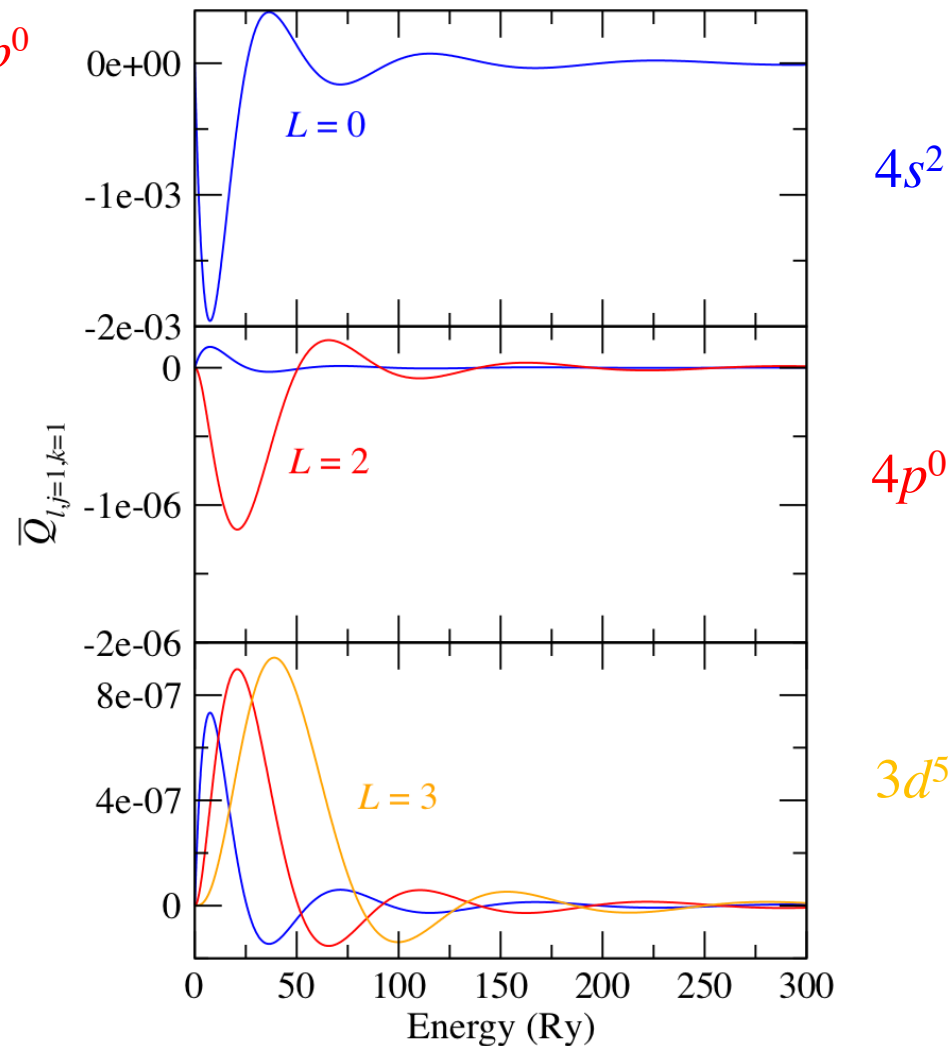
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Estimation of plane-wave cutoff energies ($E_{\text{cut}}^{\text{dens}}$)

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

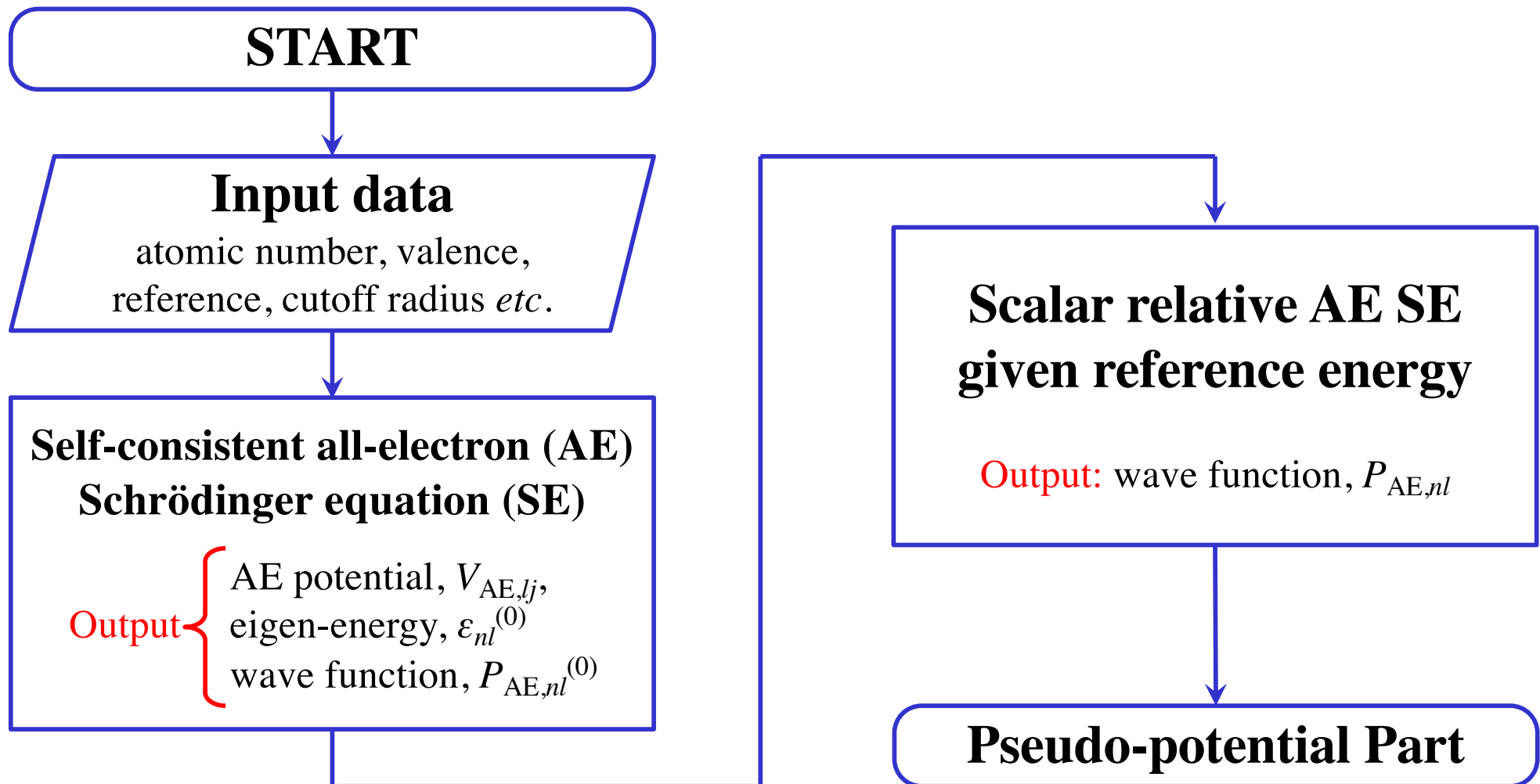
Mn: [Ar]3d⁵4s²4p⁰



II. Algorithm

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

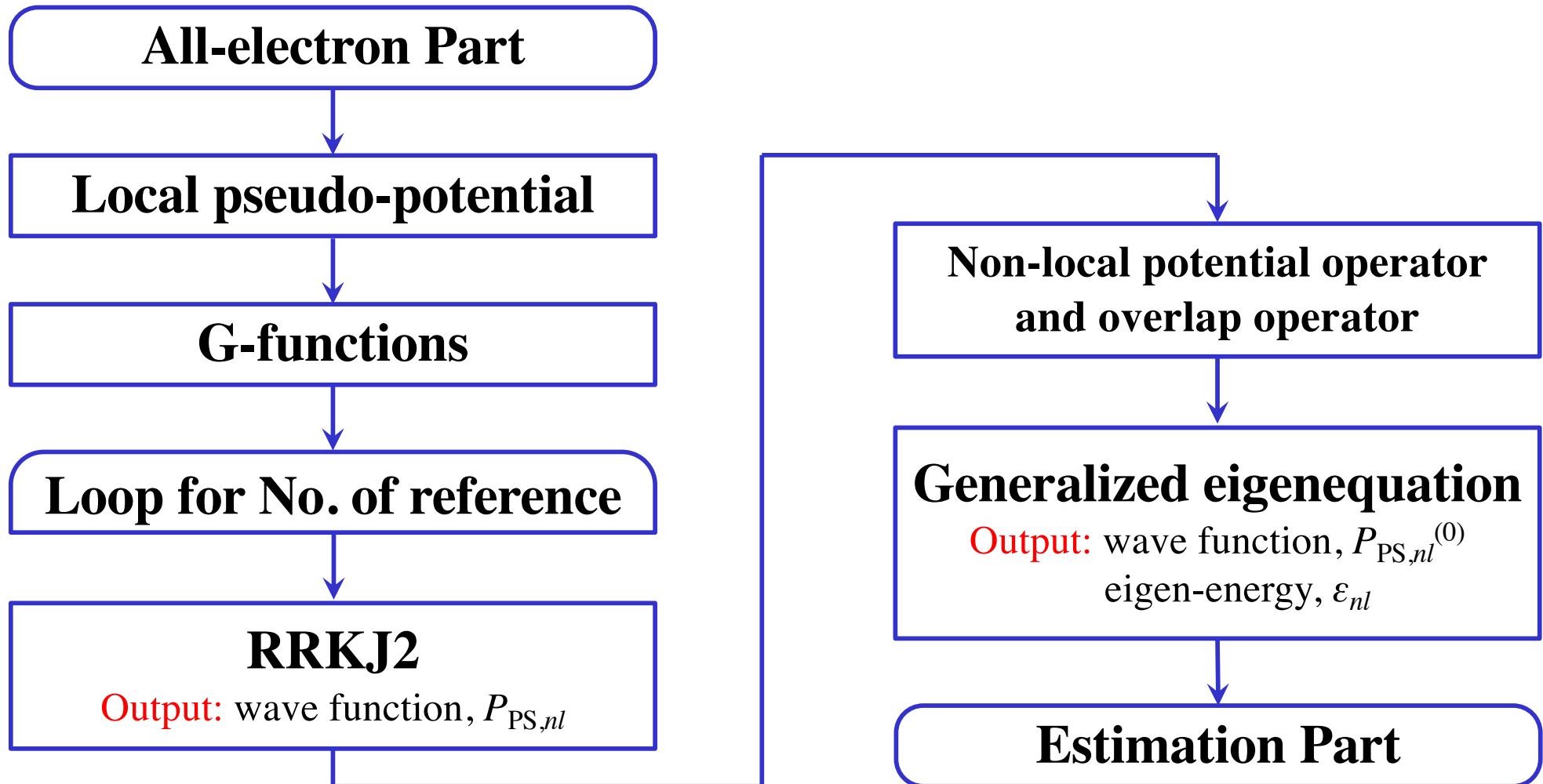
Algorithm (1) – All-electron Calculation



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

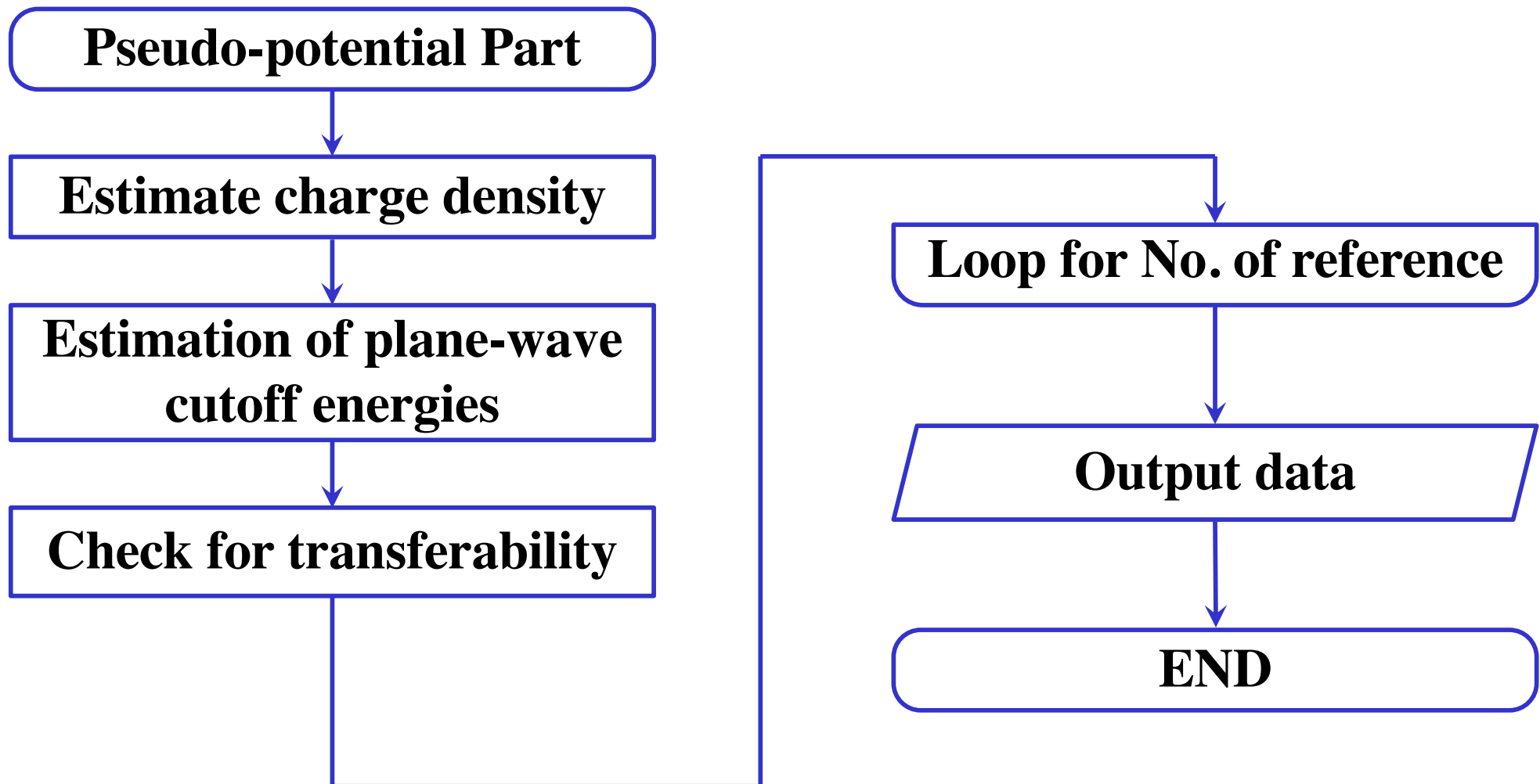
Algorithm (2) – Pseudo-potential



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

Algorithm (3) – Estimation



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- (n, l) = quantum numbers
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