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,

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

Rappe-Rabe-Kaxiras-Joanopoulos

- The correction functions satisfy the following conditions.

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

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

- α_1 and α_2 are determined by the conditions of the continuous first and second derivatives of RRKJ2 term at $r = r_\mathrm{c}$

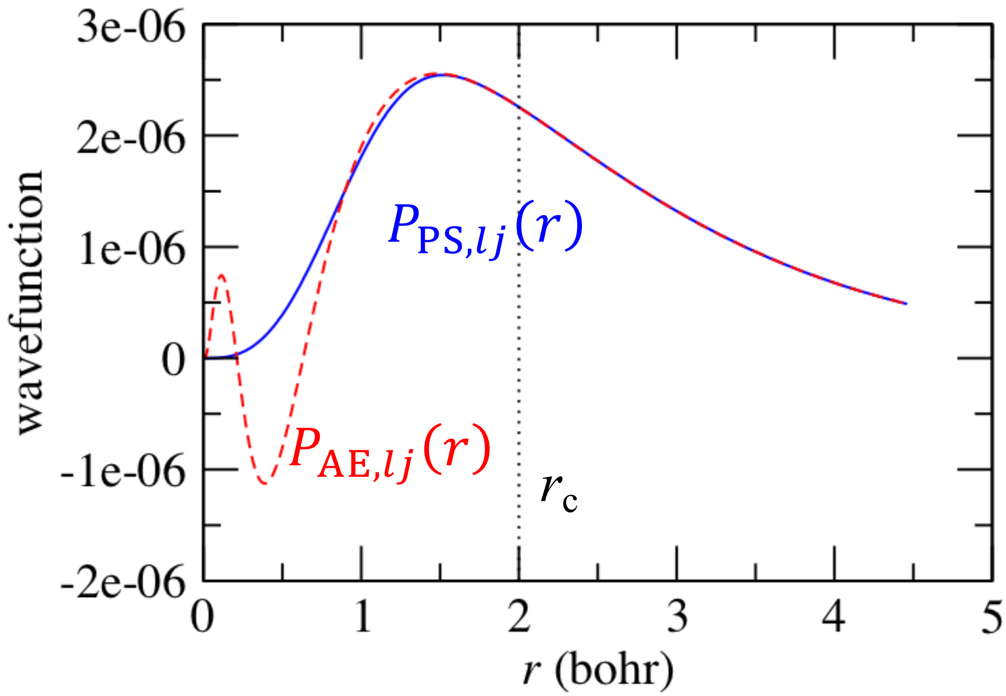
- α_3 and α_4 are determined by the conditions of the continuous third and fourth derivatives of $P_{\mathrm{PS}.lj}(r)$ at $r = r_\mathrm{c}$

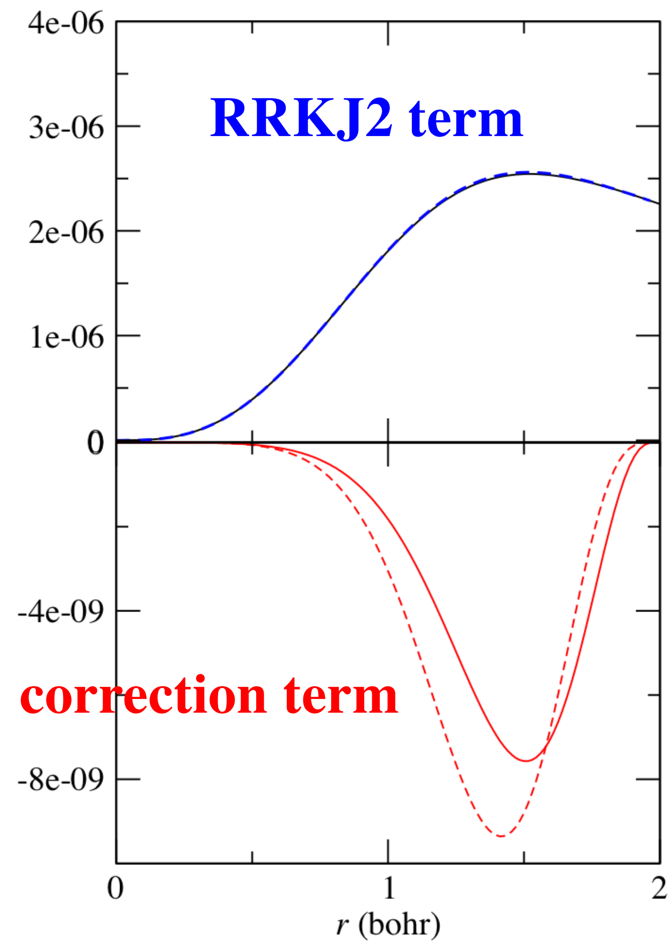
Index

- $(n,\ l)$ = quantum numbers
- j = reference number // using several reference energies improves transferability

Pseudo-Wave Function (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 eigen-energy) // default reference energy





Local Pseudo-potential

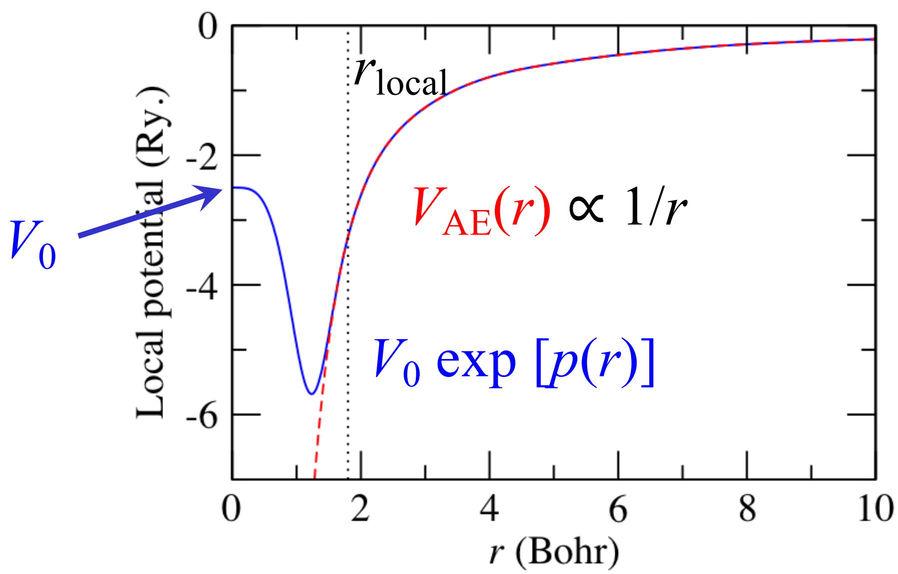
- We choose the following functions as a local potential:

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

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

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

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



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

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

- 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

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

Index

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

Generalized Eigen-equation

- We construct pseudo-potentials and functions given all-electron functions, $P_{\mathrm{AE},lj}$ and potentials, V_{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 eigen-equations given pseudo-potentials (V_{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 eigen-equations have the same eigen-energies as the AE eigen-energies and that the corresponding eigen-functions coincide with the AE eigen-functions outside the cutoff radius

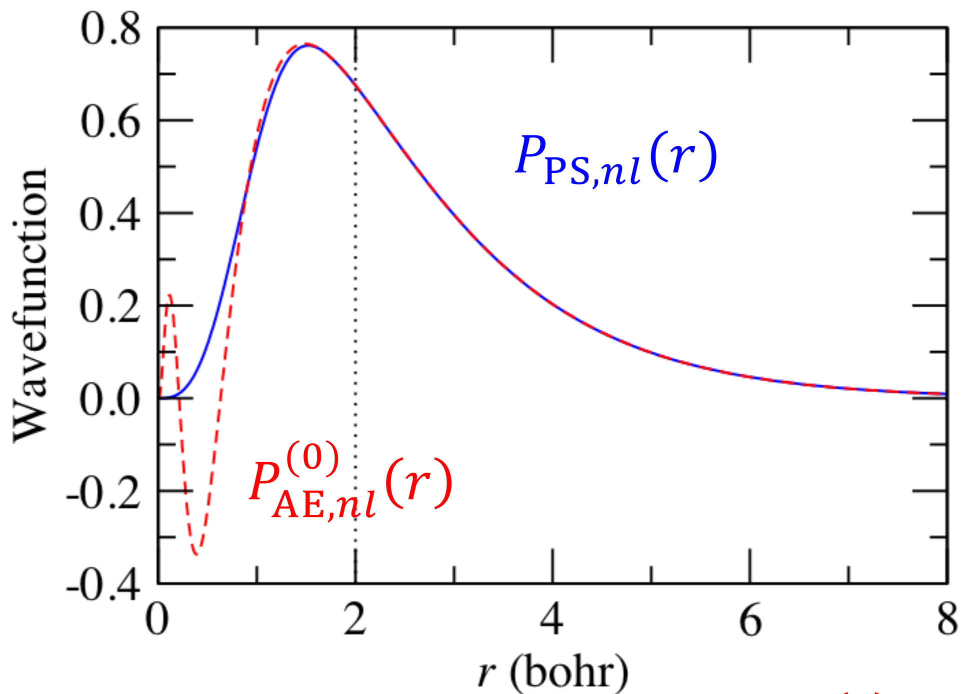
$$\varepsilon_{nl} = \varepsilon_{nl}^{(0)} \quad \text{and} \quad P_{\mathrm{PS},nl} = P_{\mathrm{AE},nl}^{(0)}\ (r > r_c)$$

Index

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

Generalized Eigen-equation

- 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-wave function solved by the generalized eigen-energy.



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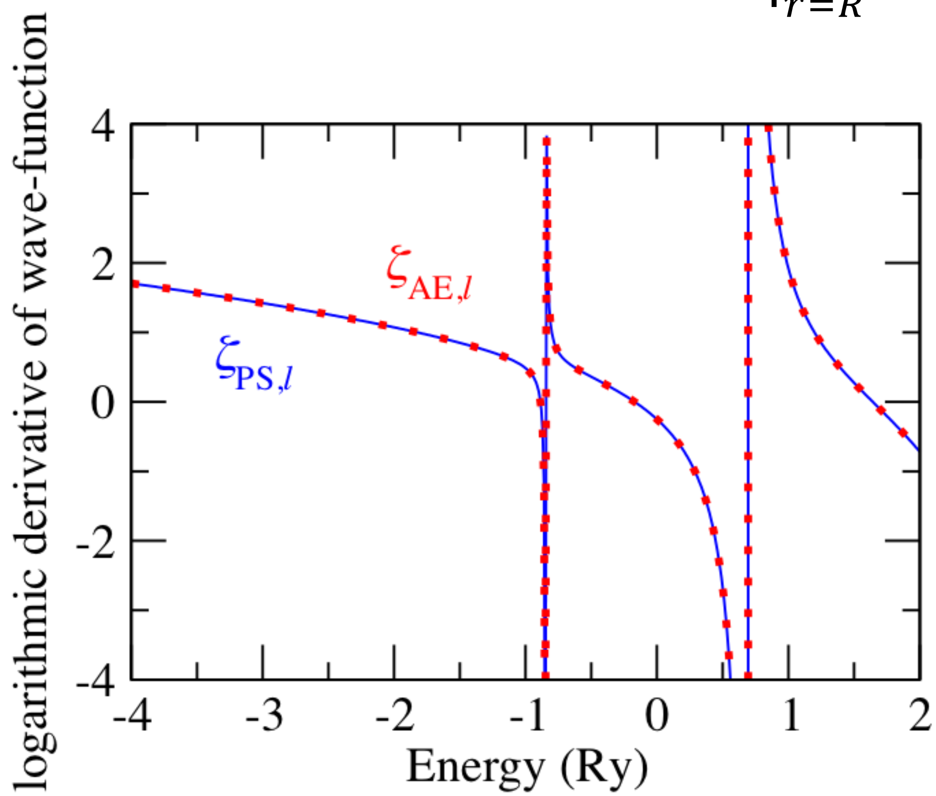
- (n, l) = quantum numbers
- j = reference number

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

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-wave functions

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



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

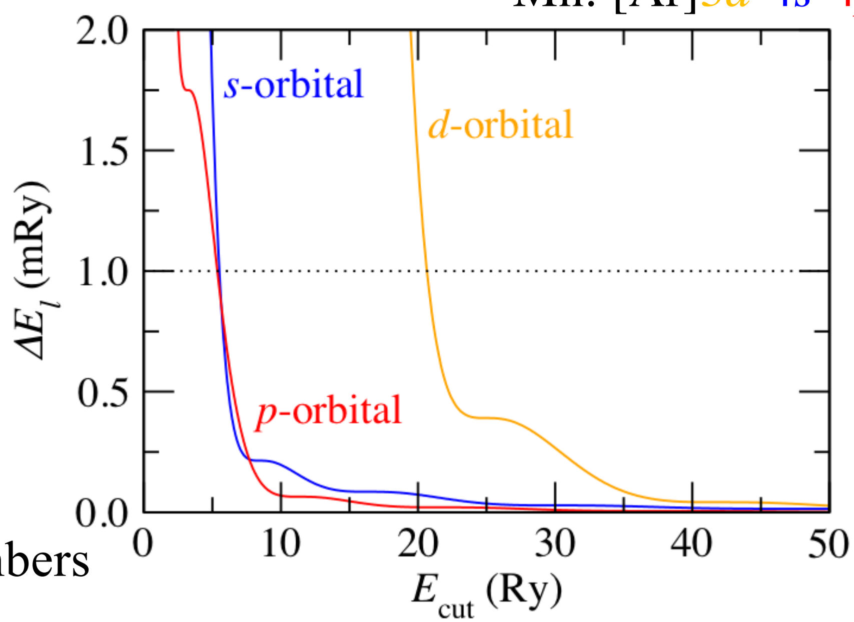
An error in the total energy associated with the cutoff energy, E_{cut} for the pseudo-wavefunctions is estimated as,

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

where,

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

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



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

- 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

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

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

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

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

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

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)

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

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

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

- 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.

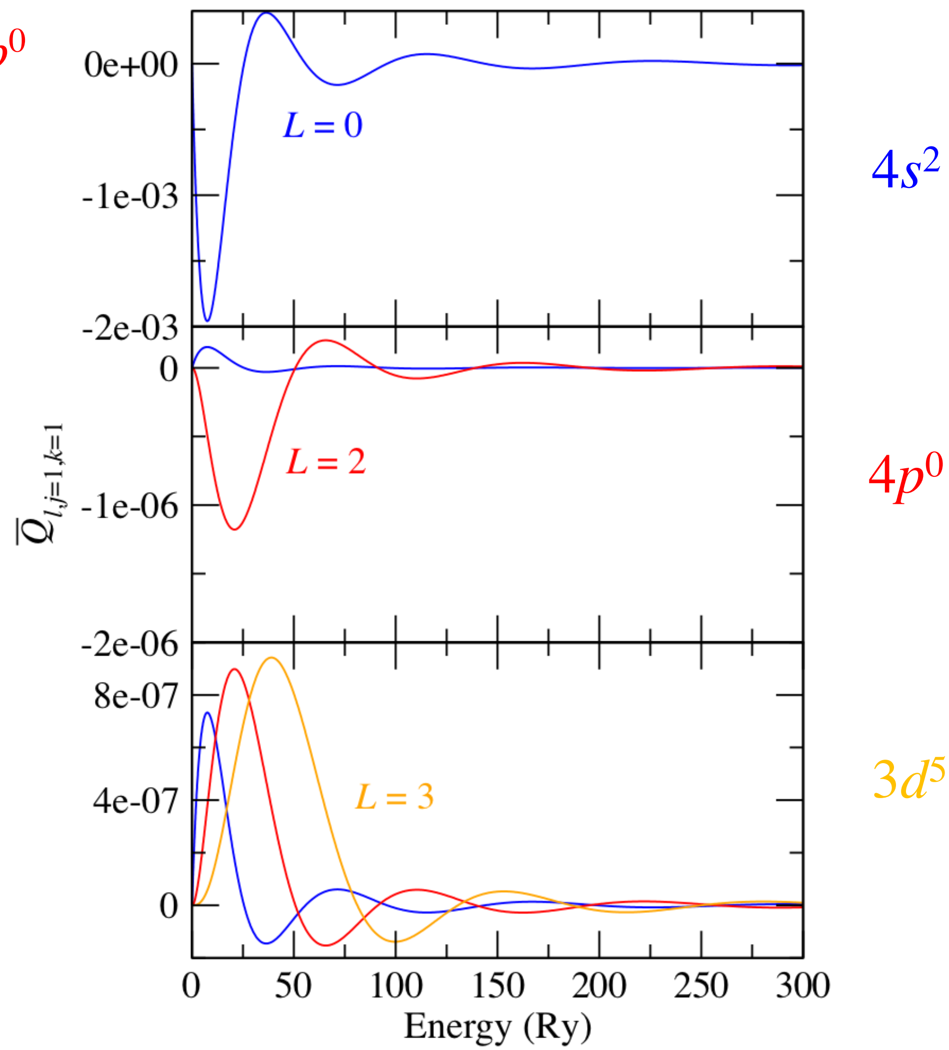
Index

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

Estimation of Plane-wave Cutoff Energies ($E_{\text{cut}}^{\text{dens}}$)

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

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

START

Input data

atomic number, valence, reference, cutoff radius *etc*.

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

Output
- AE potential, $V_{\mathrm{AE},lj}$,
- eigen-energy, $\varepsilon_{nl}^{(0)}$
- wave function, $P_{\mathrm{AE},nl}^{(0)}$

Scalar relative AE SE given reference energy

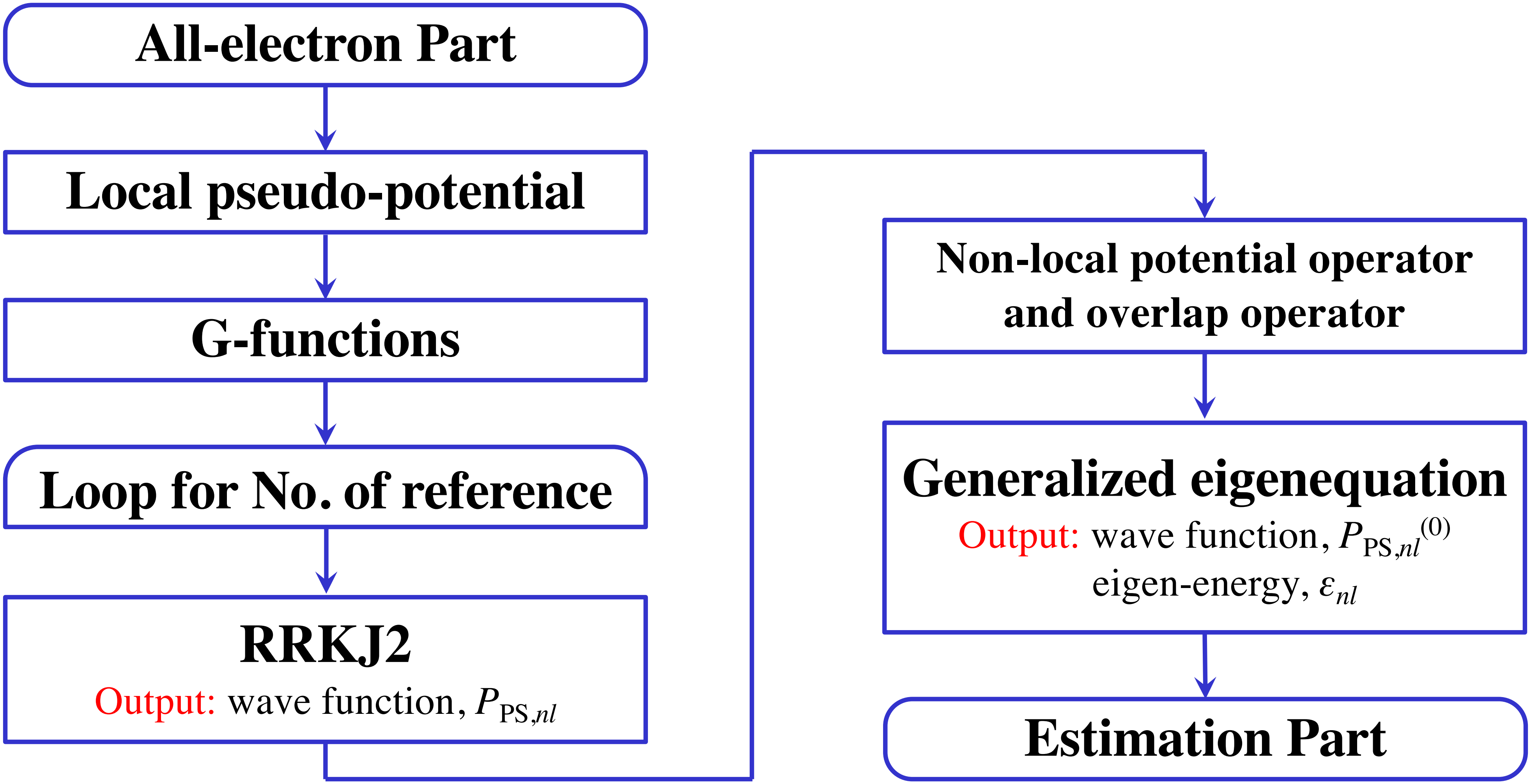
Output: wave function, $P_{\mathrm{AE},nl}$

Pseudo-potential Part

Index

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

Algorithm (2) – Pseudo-potential



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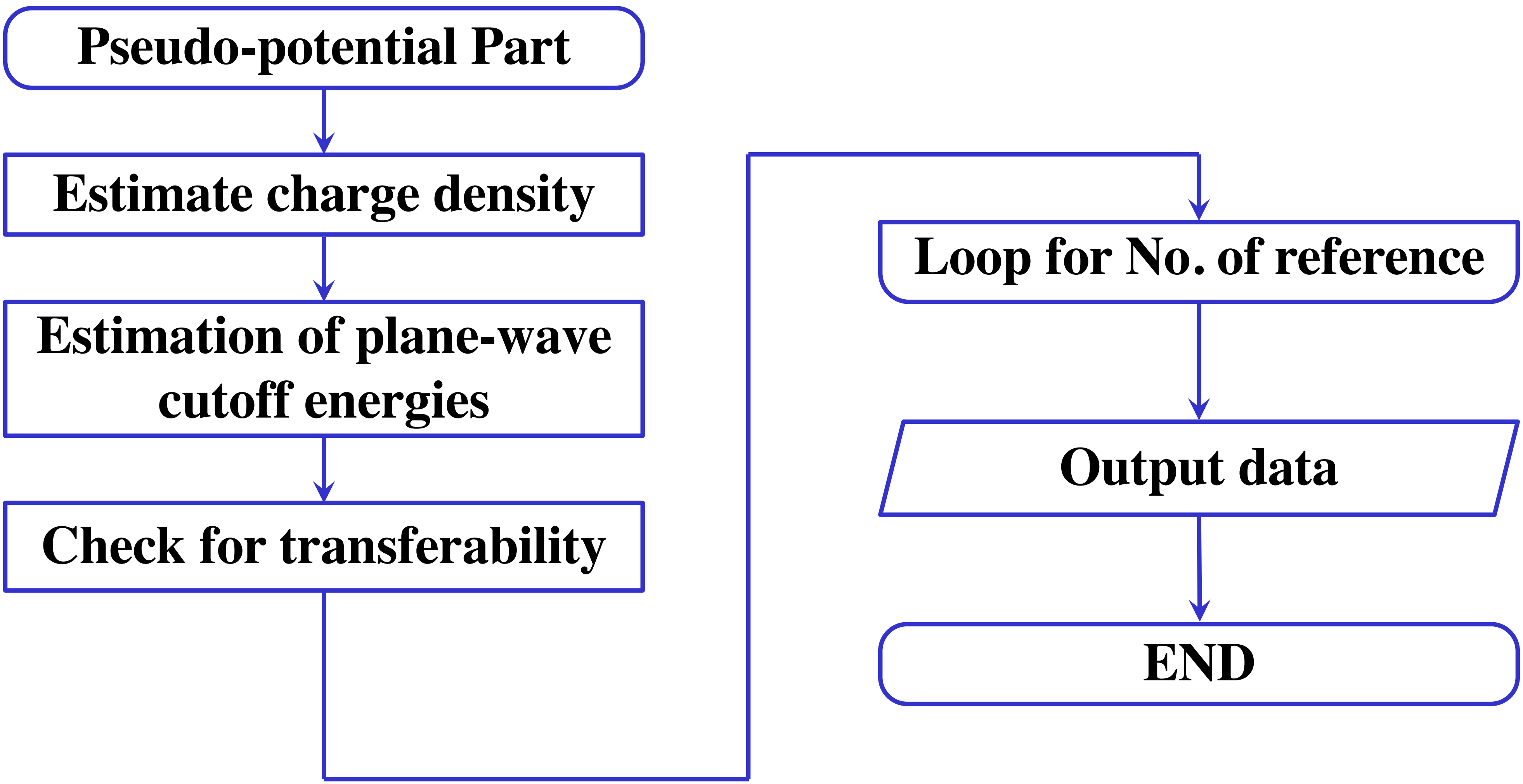
Algorithm (3) – Estimation



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