Appendix B

PSEUDO-POTENTIAL

Since the electronic structures of solids were calculated by the DFT, a number of efforts to reduce the computational time has been performed. The pseudo-potential method is one of such efforts. This method replace core electrons and a strong Coulomb potential of an atomic nucleus by an effective pseudo-potential. The core electron wave functions of an atom are not changed essentially if the atom is placed different chemical environment. On the other hand, the physical and chemical properties of solids and molecules depend on the valence electrons to a much greater extent than on the core electrons. In this sense, the core electrons, the valence electrons and the strong Coulomb potential of the atom are replaced by the weaker pseudo-potential and the pseudo valence electrons. The pseudo valence electrons experience the true potential outside the core region and experience the weaker pseudo-potential inside the core region. The fact that the pseudo-potential is weaker than the true potential inside the core region is crucial for the calculation with a plane wave basis set. Expanding the wave functions into plane waves is one of the simple formalisms to calculate the electronic structures. The enormous number of plane waves is required to expand the tightly bound core wave functions or the valence wave functions in the core region, which oscillate rapidly. This is an obstacle to increase the computational efficiency. For this reason, the plane wave basis formalism is not suitable for the all-electron calculations. Therefore, the plane wave basis set calculation is usually performed in combination with the pseudo-potential. Introducing the pseudo-potential, the core electrons are removed. In addition, the pseudo-potential is constructed in such a way that the radial part of the pseudo wave function does not have the node inside the core region. Consequently, the number of the plane waves to expand the wave function is sufficiently reduced.

B.1 Hydrogen Atom

At first, we investigate the electron in the central force field: The hydrogen atom. The Schrödinger equation for the radial part of the wave function is derived. The Schrödinger equation of the one-electron in the central force potential $V(r)$ is

$$\left[-\frac{1}{2}\nabla^2 + V(r) \right] \Phi(\mathbf{r}) = E\Phi(\mathbf{r}). \tag{B.1}$$

In the spherical coordinates, the Laplacian becomes

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\Lambda = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\Lambda,$$ (B.2)

where

$$\Lambda = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}.$$ (B.3)

When we write the wave function Φ as a product of the radial part and the angular part:

$$\Phi(r,\theta,\varphi) \equiv R(r)Y(\theta,\varphi),$$ (B.4)

the angular part does not depend on the $V(r)$ and represented by the spherical harmonics, which satisfies

$$\Lambda Y_{n\ell}(\theta,\varphi) = -\ell(\ell+\ell)Y_{n\ell}(\theta,\varphi).$$ (B.5)

On the other hand, the equation for the radial part is

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} - \frac{1}{r}\frac{d}{dr} + \frac{\ell(\ell+\ell)}{2r^2} + V(r)\right]R_{n\ell}(r) = ER_{n\ell}(r).$$ (B.6)

Setting $R_{n\ell}(r) \equiv \dfrac{\chi_{n\ell}(r)}{r}$, we can eliminate the term of the first derivative, $i.e.$

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} + \frac{\ell(\ell+\ell)}{2r^2} + V(r)\right]\chi_{n\ell}(r) = E\chi_{n\ell}(r)$$ (B.7)

$$\Longleftrightarrow \quad \left[-\frac{1}{2}\frac{d^2}{dr^2} + \frac{\ell(\ell+\ell)}{2r^2} + V(r)\right]rR_{n\ell}(r) = ErR_{n\ell}(r).$$ (B.8)

This is the Schrödinger equation for the radial part.

B.2 Pseuodo-Potential

In this next subsection, the Kohn-Sham equation for the radial part is considered and the construction scheme of the pseudo-potential is given.

Within the DFT, assuming a spherical screening, the Kohn-Sham equation for the radial part is

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} + \frac{\ell(\ell+\ell)}{2r^2} + v_{\text{eff}}(r)\right]rR_{n\ell}(r) = \varepsilon_{n\ell}rR_{n\ell}(r),$$ (B.9)

where the $v_{\text{eff}}(r)$ is the one-electron effective potential:

$$v_{\text{eff}}(r) = v(r) + \int\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + v_{\text{xc}}(r).$$ (B.10)

The density is obtained by a summation of the squares of occupied wave functions.

The pseudo potential is constructed in order to satisfy following conditions [93].

(I) The pseudo valence wave functions are generated by the pseudo-potential in such a way that the pseudo wave function has no node in the core region.

(II) The pseudo wave function $R_{n\ell}^{\text{PP}}(r)$ and the true all-electron wave function $R_{n\ell}^{\text{AE}}(r)$ must be identical beyond the cut-off radius of the pseudo-potential $r_{c\ell}$:

$$R_{n\ell}^{\text{PP}}(r) = R_{n\ell}^{\text{AE}}(r) \quad (r \geq r_{c\ell}).$$ (B.11)

(III) The norms of the $R_{n\ell}^{\rm PP}(r)$ and the $R_{n\ell}^{\rm AE}(r)$ in the range of $0 < r < r_{c\ell}$ must be equal [97]. (norm conservation)

$$\int_0^{r_{c\ell}} \left| R_{n\ell}^{\rm PP}(r) \right|^2 r^2 dr = \int_0^{r_{c\ell}} \left| R_{n\ell}^{\rm AE}(r) \right|^2 r^2 dr.$$ (B.12)

(IV) The $R_{n\ell}^{\rm PP}(r)$ and the $R_{n\ell}^{\rm AE}(r)$ yield the same eigenvalues.

$$\varepsilon_{n\ell}^{\rm PP} = \varepsilon_{n\ell}^{\rm AE}.$$ (B.13)

The pseudo-potential constructed to satisfy all conditions mentioned above is termed as the *norm-conserving pseudo-potential.*

When the pseudo wave functions is calculated, the screened pseudo-potential is obtained by solving Eq. (B.9) inversely:

$$V_{{\rm scr},n\ell}^{\rm PP}(r) = \varepsilon_{n\ell} - \frac{\ell(\ell+1)}{2r^2} + \frac{1}{2r R_{n\ell}^{\rm PP}(r)} \frac{d^2}{dr^2} [r R_{n\ell}^{\rm PP}(r)].$$ (B.14)

It is required that the $R_{n\ell}^{\rm PP}(r)$ has no node in order that the pseudo-potential has any singular point except at the origin. Furthermore, the $R_{n\ell}^{\rm PP}(r)$ and its first and second derivatives with respect to r must be continuous at $r_{c\ell}$ to ensure the pseudo-potential to be continuous. To eliminate the singularity of the pseudo-potential at the origin, the r^ℓ behavior is required to the pseudo wave function. When we substitute r^ℓ into the $R_{n\ell}^{\rm PP}(r)$ in Eq. (B.14), we find,

$$
\begin{aligned}
V_{{\rm scr},n\ell}^{\rm PP}(r) &= \varepsilon_{n\ell} - \frac{\ell(\ell+1)}{2r^2} + \frac{1}{2r \cdot r^\ell} \frac{d^2}{dr^2}[r \cdot r^\ell] \\
&= \varepsilon_{n\ell} - \frac{\ell(\ell+1)}{2r^2} + \frac{1}{2r^{\ell+1}} \cdot \ell(\ell+1) r^{\ell-1} \\
&= \varepsilon_{n\ell}.
\end{aligned}
$$ (B.15)

The term of r^{-2} is eliminated, followed by that the divergence at the origin is avoided.

This pseudo-potential contains the contribution from the valence electrons which depend on the environment. Eliminating this effect of the valence electrons from the pseudo-potential, we can generate an ionic pseudo-potential $V_{{\rm ion},n\ell}^{\rm PP}(r)$ which is not affected by the environment. The $V_{{\rm ion},n\ell}^{\rm PP}(r)$ is obtained by subtracting the Hartree term $V_H^{\rm PP}(r)$ and the exchange-correlation term $V_{\rm xc}^{\rm PP}(r)$ calculated from the pseudo valence wave functions from the $V_{{\rm scr},n\ell}^{\rm PP}(r)$:

$$V_{{\rm ion},n\ell}^{\rm PP}(r) = V_{{\rm scr},n\ell}^{\rm PP}(r) - V_H^{\rm PP}(r) - V_{\rm xc}^{\rm PP}(r).$$ (B.16)

B.3 Norm-Conservation Condition

The pseudo-potential is constructed to satisfy the norm-conservation condition (norm-conserving pseudo-potential) [97]:

$$\int_0^{r_{c\ell}} \left| R_{n\ell}^{\rm PP}(r) \right|^2 r^2 dr = \int_0^{r_{c\ell}} \left| R_{n\ell}^{\rm AE}(r) \right|^2 r^2 dr.$$ (B.17)

This condition guarantees that the electrostatic potentials derived from the true electrons and pseudo electrons inside the core region are identical. Further, the norm-conservation condition

also assures that the scattering properties for the pseudo wave functions are identical to those of the ion and the core electrons for the true valence wave functions. This is because the norm within the core region can be written as [97]

$$-\frac{1}{2}\frac{\partial}{\partial\varepsilon_{n\ell}}\frac{\partial}{\partial r}\ln\left[R_{n\ell}(r)\right]\Big|_{r=r_{c\ell}} = \frac{1}{[rR_{n\ell}(r)]^2}\int_0^{r_{c\ell}}R_{n\ell}^2(r)r^2dr. \tag{B.18}$$

The norm-conservation condition is equivalent to that the energy derivative of the logarithmic derivative at $r_{c\ell}$ of both the pseudo wave functions and true wave functions are identical. The phase shift of scattering is derived from the logarithmic derivative of the wave function. Therefore, if the logarithmic derivative of the pseudo wave function and the true wave function are identical at $r_{c\ell}$,[1] the phase shift of the scattering by the pseudo-potential is correct. Furthermore, from Eq. (B.18), the first-order energy dependence of the phase shift is also correct. The norm-conserving pseudo-potential is capable ob describing the scattering properties of the ion in a variety atomic configurations.

The derivation of Eq. (B.18) is following.

The Schrödinger equation for the radial wave function is

$$\left[-\frac{1}{2}\frac{d^2}{dr^2}+\frac{\ell(\ell+\ell)}{2r^2}+v(r)\right]rR_{n\ell}(r) = \varepsilon_{n\ell}rR_{n\ell}(r), \tag{B.19}$$

where the $v(r)$ is the spherical potential. We define the logarithmic derivative of the $rR_{n\ell}(r)$ as $D(r)$:

$$D(r) \equiv \frac{\partial}{\partial r}\ln\{rR_{n\ell}(r)\} = \frac{\{rR_{n\ell}(r)\}'}{rR_{n\ell}(r)}. \tag{B.20}$$

The *prime* indicates the derivation with respect to the r. Thus, the Schrödinger equation (B.19) can be written as

$$D'(r) + D^2(r) = 2\left[v(r)+\frac{\ell(\ell+1)}{2r^2}-\varepsilon_{n\ell}\right]. \tag{B.21}$$

Differentiating this formula with respect to the $\varepsilon_{n\ell}$, we obtain,

$$\frac{\partial D'(r)}{\partial\varepsilon_{n\ell}}+\frac{\partial D^2(r)}{\partial\varepsilon_{n\ell}} = -2. \tag{B.22}$$

Using the relation valid for any function $f(r)$,

$$f'(r) + 2D(r)f(r) = \frac{1}{\{rR_{n\ell}(r)\}^2}\frac{d}{dr}\left[\{rR_{n\ell}(r)\}^2 f(r)\right], \tag{B.23}$$

the left hand side of Eq. (B.22) becomes

$$\left\{\frac{\partial D(r)}{\partial\varepsilon_{n\ell}}\right\}'+2D(r)\frac{\partial D(r)}{\partial\varepsilon_{n\ell}} = \frac{1}{\{rR_{n\ell}(r)\}^2}\frac{d}{dr}\left[\{rR_{n\ell}(r)\}^2\frac{\partial D(r)}{\partial\varepsilon_{n\ell}}\right]. \tag{B.24}$$

Thus, Eq. (B.22) can be written as,

$$\frac{1}{\{rR_{n\ell}(r)\}^2}\frac{d}{dr}\left[\{rR_{n\ell}(r)\}^2\frac{\partial D(r)}{\partial\varepsilon_{n\ell}}\right] = -2$$

$$\Longleftrightarrow\quad \frac{d}{dr}\left[\{rR_{n\ell}(r)\}^2\frac{\partial D(r)}{\partial\varepsilon_{n\ell}}\right] = -2\{rR_{n\ell}(r)\}^2. \tag{B.25}$$

---

[1] The pseudo wave functions are constructed to satisfy this condition.

Integrating this formula from 0 to $r_{c\ell}$, we obtain

$$\int_0^{r_{c\ell}} \frac{d}{dr}\left[\{rR_{n\ell}(r)\}^2 \frac{\partial D(r)}{\partial \varepsilon_{n\ell}}\right] dr = -2 \int_0^{r_{c\ell}} R_{n\ell}^2(r) r^2 dr$$

$$\Longleftrightarrow \quad \{r_{c\ell}R_{n\ell}(r_{c\ell})\}^2 \left.\frac{\partial D(r)}{\partial \varepsilon_{n\ell}}\right|_{r=r_{c\ell}} = -2 \int_0^{r_{c\ell}} R_{n\ell}^2(r) r^2 dr$$

$$\Longleftrightarrow \quad \left.\frac{\partial D(r)}{\partial \varepsilon_{n\ell}}\right|_{r=r_{c\ell}} = -\frac{2}{\{r_{c\ell}R_{n\ell}(r_{c\ell})\}^2} \int_0^{r_{c\ell}} R_{n\ell}^2(r) r^2 dr. \qquad (B.26)$$

Further, the energy derivative in the left hand side are,

$$\frac{\partial}{\partial \varepsilon_{n\ell}} D(r) = \frac{\partial}{\partial \varepsilon_{n\ell}} \frac{\{rR_{n\ell}(r)\}'}{rR_{n\ell}(r)}$$

$$= \frac{\left\{\frac{\partial}{\partial \varepsilon_{n\ell}}(rR_{n\ell})'\right\} rR_{n\ell} - (rR_{n\ell})'\{\frac{\partial}{\partial \varepsilon_{n\ell}}(rR_{n\ell})\}}{\{rR_{n\ell}\}^2}$$

$$= \frac{\frac{\partial R'_{n\ell}}{\partial \varepsilon_{n\ell}} R_{n\ell} - R'_{n\ell}\frac{\partial R_{n\ell}}{\partial \varepsilon_{n\ell}}}{R_{n\ell}^2}$$

$$= \frac{\partial}{\partial \varepsilon_{n\ell}}\left[\frac{R'_{n\ell}}{R_{n\ell}}\right] = \frac{\partial}{\partial \varepsilon_{n\ell}} \frac{\partial}{\partial r} \ln R_{n\ell}(r). \qquad (B.27)$$

Therefore, Eq. (B.26) can be written as

$$-\frac{1}{2}\frac{\partial}{\partial \varepsilon_{n\ell}} \frac{\partial}{\partial r} \ln\left[R_{n\ell}(r)\right]\bigg|_{r=r_{c\ell}} = \frac{1}{[rR_{n\ell}(r)]^2} \int_0^{r_{c\ell}} R_{n\ell}^2 r^2 dr. \qquad (B.28)$$

Thus, Eq. (B.18) is derived.

B.4   Construction of Pseudo-Potentials

We discuss here the pseudo-potential construction procedure. At first, we must define the analytic function for the pseudo wave function inside the cut-off $r_{c\ell}$. This function must behave as r^ℓ near the origin as mentioned above. Along this line, Kerker introduced the pseudo wave function as [98]

$$R_{n\ell}^{\mathrm{PP}}(r) = \begin{cases} R_{n\ell}^{\mathrm{AE}}(r) & (r \ge r_{c\ell}) \\ r^\ell e^{p(r)} & (r < r_{c\ell}) \end{cases}, \qquad (B.29)$$

where the $p(r)$ is a polynomial of r:

$$p(r) = c_0 + c_2 r^2 + c_3 r^3 + c_4 r^4. \qquad (B.30)$$

The term of the first order which of r is not contained to avoid the singularity of the $V_{\mathrm{scr},n\ell}(r)$ at the origin.

Inserting Eq. (B.29) into Eq. (B.14), we obtain the screened pseudo-potential as

$$V_{\mathrm{scr},n\ell}(r) = \begin{cases} V_{\mathrm{AE}}(r) & (r \ge r_{c\ell}) \\ \varepsilon_{n\ell} + \dfrac{\ell+1}{r}p'(r) + \dfrac{p''(r) + [p'(r)]^2}{2} & (r < r_{c\ell}) \end{cases}, \qquad (B.31)$$

where the $V_{AE}(r)$ is the all-electron atomic screened potential. The $p'(r)$ and $p''(r)$ indicate the first and second derivatives with respect to r, respectively. If the $p(r)$ has the first power of r, the term $\dfrac{\ell+1}{r}p'(r)$ in the $V_{\mathrm{scr},n\ell}(r)$ diverge at the origin.

The derivation of Eq. (B.31) is following.

We can obtain Eq. (B.31) by simply inserting Eq. (B.29) into Eq. (B.14). Only the case of $r < r_{c\ell}$ is discussed. The derivation in the case of $r \geq r_{c\ell}$ is obvious. At first, we differentiate twice the $R_{n\ell}^{\mathrm{PP}}(r)$ with respect to r:

$$
\begin{aligned}
\frac{d^2}{dr^2}[rR_{n\ell}^{\mathrm{PP}}(r)] &= \frac{d^2}{dr^2}[r^{\ell+1}e^{p(r)}] \\
&= \frac{d}{dr}[(\ell+1)r^\ell e^{p(r)} + r^{\ell+1}p'(r)e^{p(r)}] \\
&= r^{\ell-1}e^{p(r)}\left[\ell(\ell+1) + 2(\ell+1)rp'(r) + r^2\left\{[p'(r)]^2 + p''(r)\right\}\right]. \quad \text{(B.32)}
\end{aligned}
$$

Substituting Eqs. (B.32) and (B.29) into Eq. (B.14), we obtain,

$$
\begin{aligned}
V_{\mathrm{scr},n\ell}^{\mathrm{PP}}(r) &= \varepsilon_{n\ell} - \frac{\ell(\ell+1)}{2r^2} \\
&\quad + \frac{1}{2r^{\ell+1}e^{p(r)}}r^{\ell-1}e^{p(r)}\left[\ell(\ell+1) + 2(\ell+1)rp'(r) + r^2\left\{[p'(r)]^2 + p''(r)\right\}\right] \\
&= \varepsilon_{n\ell} - \frac{\ell(\ell+1)}{2r^2} + \frac{1}{2r^2}\left[\ell(\ell+1) + 2(\ell+1)rp'(r) + r^2\left\{[p'(r)]^2 + p''(r)\right\}\right] \\
&= \varepsilon_{n\ell} + \frac{\ell+1}{r}p'(r) + \frac{p''(r) + [p'(r)]^2}{2}. \quad \text{(B.33)}
\end{aligned}
$$

Thus Eq. (B.31) is derived in the case of $r < r_{c\ell}$.

Troullier and Martins generalized this procedure by increasing the order of $p(r)$ to investigate the pseudo-potential smoothness [93]. Furthermore, they proposed the additional condition that the second derivative of the $V_{\mathrm{scr},n\ell}(r)$ must be zero at the origin:

$$
V_{\mathrm{scr},n\ell}''(0) = 0. \quad \text{(B.34)}
$$

The $V_{\mathrm{scr},n\ell}(r)$ with this condition becomes flat near the origin. Troullier and Martins calculated the total energy of the diamond with the plane wave basis set. Among three cases that $V_{\mathrm{scr},n\ell}''(0)$ is positive, zero and negative, they compare the convergence of the total energy with respect to the cut-off energy of the plane wave basis set. It has been shown that the pseudo-potential satisfying Eq. (B.34) has good convergence properties.

The construction procedures of the pseudo-potential presented by Troullier and Martins is followings. They have increased the order of the $p(r)$ in Eq. (B.29):

$$
p(r) = c_0 + c_2 r^2 + c_4 r^4 + c_6 r^6 + c_8 r^8 + c_{10} r^{10} + c_{12} r^{12}. \quad \text{(B.35)}
$$

The 7 coefficients are determined from following 7 conditions (I)∼(VII).

(I) The norm within the cut-off $r_{c\ell}$ must be conserved:

$$
\ln\left[\int_0^{r_{c\ell}} |r^\ell e^{p(r)}|^2 r^2 dr\right] = \ln\left[\int_0^{r_{c\ell}} |R_{n\ell}^{\mathrm{AE}}(r)|^2 r^2 dr\right]
$$

$$
\Longleftrightarrow \quad 2c_0 + \ln\left[\int_0^{r_{c\ell}} r^{2(\ell+1)}e^{2(p(r)-c_0)}dr\right] = \ln\left[\int_0^{r_{c\ell}} |R_{n\ell}^{\mathrm{AE}}(r)|^2 r^2 dr\right]. \quad \text{(B.36)}
$$

The $R_{n\ell}^{\mathrm{PP}}(r)$ and its first four derivatives must be continuous at $r_{c\ell}$. These conditions are imposed for continuity of the $V_{\mathrm{scr},n\ell}(r)$ and its first two derivatives at $r_{c\ell}$. These conditions are represented explicitly as followings.

(II)

$$p(r_{c\ell}) = \ln\left[\frac{P(r_{c\ell})}{r_{c\ell}^{\ell+1}}\right],\tag{B.37}$$

where $P(r) \equiv rR_{n\ell}^{\mathrm{AE}}(r)$.

(III)

$$p'(r_{c\ell}) = \frac{P'(r_{c\ell})}{P(r_{c\ell})} - \frac{\ell+1}{r_{c\ell}}\tag{B.38}$$

(IV)

$$p''(r_{c\ell}) = 2V_{\mathrm{AE}}(r_{c\ell}) - 2\varepsilon_{n\ell} - \frac{2(\ell+1)}{r_{c\ell}}p'(r_{c\ell}) - [p'(r_{c\ell})]^2.\tag{B.39}$$

We used Eq. (B.31) to derive this condition.

(V)

$$p^{(3)}(r_{c\ell}) = 2V_{\mathrm{AE}}'(r_{c\ell}) + \frac{2(\ell+1)}{r_{c\ell}^2}p'(r_{c\ell}) - \frac{2(\ell+1)}{r_{c\ell}}p''(r_{c\ell}) - 2p'(r_{c\ell})p''(r_{c\ell}).\tag{B.40}$$

(VI)

$$\begin{aligned}p^{(4)}(r_{c\ell}) = {} & 2V_{\mathrm{AE}}''(r_{c\ell}) - \frac{4(\ell+1)}{r_{c\ell}^3}p'(r_{c\ell}) + \frac{4(\ell+1)}{r_{c\ell}^2}p''(r_{c\ell}) \\ & - \frac{2(\ell+1)}{r_{c\ell}}p^{(3)}(r_{c\ell}) - 2[p''(r_{c\ell})]^2 - 2p'(r_{c\ell})p^{(3)}(r_{c\ell}).\end{aligned}\tag{B.41}$$

The $p^{(3)}(r)$ and $p^{(4)}(r)$ indicate the third and forth derivatives with respect to r.

(VII) The second derivative of the $V_{\mathrm{scr},n\ell}(r)$ is zero at the origin. This condition yields

$$c_2^2 + c_4(2\ell + 5) = 0.\tag{B.42}$$

From these 7 conditions, we can obtain the pseudo wave function. Finally, the screened pseudo-potential is derived from the pseudo wave function by using Eq. (B.31).

The derivations of Eqs. (B.37)–(B.42) are followings.

Equation (B.37) is derived from the continuity condition of $R_{n\ell}^{\mathrm{PP}}(r)$ at $r_{c\ell}$, i.e.

$$R_{n\ell}^{\mathrm{PP}}(r_{c\ell}) = r_{c\ell}^\ell e^{p(r_{c\ell})} = R_{n\ell}^{\mathrm{AE}}(r_{c\ell}).\tag{B.43}$$

Therefore, we obtain

$$p(r_{c\ell}) = \ln\frac{R_{n\ell}^{\mathrm{AE}}(r_{c\ell})}{r_{c\ell}^\ell} = \ln\frac{P(r_{c\ell})}{r_{c\ell}^{\ell+1}},\tag{B.44}$$

where $P(r) \equiv rR_{n\ell}^{\mathrm{AE}}(r)$.

Differentiating Eq. (B.44) with respect to r, we obtain

$$
\begin{aligned}
p'(r_{c\ell}) &= \left. \frac{d}{dr} \ln\left[\frac{P(r)}{r^{\ell+1}}\right] \right|_{r=r_{c\ell}} \\
&= \frac{P'(r_{c\ell})/r_{c\ell}^{\ell+1} - (\ell+1)P(r_{c\ell})/r_{c\ell}^{\ell+2}}{P(r_{c\ell})/r_{c\ell}^{\ell+1}} \\
&= \frac{P'(r_{c\ell})}{P(r_{c\ell})} - \frac{\ell+1}{r_{c\ell}}.
\end{aligned}
\tag{B.45}
$$

Thus, Eq. (B.38) is derived.

Equation (B.39) is calculated from Eq. (B.31). Since the $V_{\text{scr},n\ell}(r)$ is also continuous at $r_{c\ell}$, we obtain

$$
\varepsilon_{n\ell} + \frac{\ell+1}{r_{c\ell}}p'(r_{c\ell}) + \frac{p''(r_{c\ell}) + [p'(r_{c\ell})]^2}{2} = V_{\text{AE}}(r_{c\ell}).
\tag{B.46}
$$

Equation (B.39) is derived by solving this formula with respect to the $p''(r_{c\ell})$.

Equations (B.40) and (B.41) are derived by differentiating Eq. (B.39) once and twice with respect to r, respectively.

Equation (B.42) is derived from the condition that the second derivatives of the pseudo-potential must be zero at the origin. Using Eq. (B.31), we calculate the $V''_{\text{scr},n\ell}(0)$. Differentiating the $V_{\text{scr},n\ell}(r)$ with respect r, we obtain

$$
\begin{aligned}
V'(r) &= -\frac{\ell+1}{r^2}p'(r) + \frac{\ell+1}{r}p''(r) + \frac{1}{2}\left\{p^{(3)}(r) + 2p'(r)p''(r)\right\} \\
V''(r) &= 2\frac{\ell+1}{r^3}p'(r) - 2\frac{\ell+1}{r^2}p''(r) + \frac{\ell+1}{r}p^{(3)}(r) \\
&\quad + \frac{1}{2}\left\{p^{(4)}(r) + 2[p''(r)]^2 + 2p'(r)p^{(3)}(r)\right\}.
\end{aligned}
\tag{B.47}
$$

From Eq. (B.30), the following formulae are derived:

$$
p'(r) = 2c_2 r + 4c_4 r^3 + 6c_6 r^5 \cdots,
\tag{B.48}
$$

$$
p''(r) = 2c_2 + 12c_4 r^2 + 30c_6 r^4 \cdots,
\tag{B.49}
$$

$$
p^{(3)} = 24c_4 r + 120c_6 r^3 \cdots,
\tag{B.50}
$$

$$
p^{(4)} = 24c_4 + 360c_6 r^2 \cdots.
\tag{B.51}
$$

Inserting these formulae into Eq. (B.47) and set $r = 0$, the $V''(r)$ becomes

$$
\begin{aligned}
V''(r=0) &= \left[2\frac{\ell+1}{r^3}p'(r) - 2\frac{\ell+1}{r^2}p''(r) + \frac{\ell+1}{r}p^{(3)}(r)\right]_{r=0} \\
&\quad + \frac{1}{2}p^{(4)}(r=0) + [p''(r=0)]^2 + p'(r=0)p^{(3)}(r=0) \\
&= (\ell+1)\left[\frac{2}{r^3}(2c_2 r + 4c_4 r^3 + 6c_6 r^5 \cdots) - \frac{2}{r^2}(2c_2 + 12c_4 r^2 + 30c_6 r^4 \cdots)\right. \\
&\quad \left. + \frac{1}{r}(24c_4 r + 120c_6 r^3 \cdots)\right]_{r=0} + \frac{1}{2}(24c_4) + [2c_2]^2 \\
&= (\ell+1)[8c_4] + \frac{1}{2}(24c_4) + [2c_2]^2 \\
&= 8\ell c_4 + 20c_4 + 4c_2^2.
\end{aligned}
\tag{B.52}
$$

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Therefore, the condition $V''_{\mathrm{scr},n\ell}(0) = 0$ yields Eq. (B.42):

$$V''_{\mathrm{scr},n\ell}(0) = 0$$

$$\Longleftrightarrow \quad 4[(2\ell + 5)c_4 + c_2^2] = 0$$

$$\Longleftrightarrow \quad c_2^2 + (2\ell + 5)c_4 = 0. \tag{B.53}$$