# Lecture VIII : The pseudopotential

## I.   KOHN-SHAM PROBLEM FOR AN ISOLATED ATOM

For a one-electron atom, the Coulombic potential, $V(\vec{r}) = V(r) = -Z/r$ is spherically symmetric. The solutions may then be split into a radial and an angular part

$$\psi_{nlm}(\vec{r}) = \psi_{nl}(r)Y_{lm}(\theta,\phi) = r^{-1}\phi_{nl}(r)Y_{lm}(\theta,\phi) \tag{1}$$

The last equality in Eq. 1 is given in order to simplify the spherically-symmetric Schrödinger equation and $Y_{lm}(\theta,\phi)$ are normalized spherical harmonics. The spherically-symmetric Schrödinger equation for principle quantum number $n$ can be reduced to the radial equation

$$-\frac{1}{2}\frac{d^2}{dr^2}\phi_{nl} + \left[\frac{l(l+1)}{2r^2} + V_{ext}(r) - \epsilon_{n,l}\right]\phi_{n,l} = 0. \tag{2}$$

In the Kohn-Sham approach to the many-particle system, the form of the single-particle equations are identical to the above radial Schrödinger equation, with an effective potential, $V_{eff}$ replacing the pure Coulomb potential. The substitution can be done directly provided $V_{eff}$ is also spherically symmetric. Let's see if that is the case :

- Density :

$$n(\vec{r}) = \sum_{n,l,m}^{\text{occ}} |\psi_{n,l,m}(r)|^2 = \sum_{n,l}^{\text{occ}}(2l+1)|\psi_{n,l}(r)|^2 = n(r) \tag{3}$$

- External potential : Ionic Coulomb potential

$$V_{ext}(\vec{r}) = -Z/r = V_{ext}(r) \tag{4}$$

- The Hartree potential

$$V_H(\vec{r}) = \int \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|}d\vec{r}'$$
$$= \int \frac{n(r')}{[(r - r'\cos\theta\sin\phi)^2 + (r'\cos\theta\sin\theta)^2 + (r'\sin\theta)^2]^{1/2}}r'^2 dr' d(\cos\theta)d\phi = V_H(r) \tag{5}$$

- The exchange-correlation potential

$$V_{xc}(\vec{r}) = \epsilon_{xc}[n(r)] + n(r)\frac{d\epsilon_{xc}}{dn}[n(r)] = V_{xc}(r) \tag{6}$$

- Total effective potential

$$V_{eff}(r) = V_{ext}(r) + V_H(r) + V_{xc}(r) \tag{7}$$

Thus the independent-particle Kohn-Sham states may be classified by the angular quantum numbers $L = l, m$. The one-particle equations are then analogous to the Schrödinger equation for the one-electron atom,

$$-\frac{1}{2}\frac{d^2}{dr^2}\phi_{nl} + \left[\frac{l(l+1)}{2r^2} + V_{eff}(r) - \epsilon_{n,l}\right]\phi_{n,l} = 0. \tag{8}$$

## II. THE PSEUDOPOTENTIAL IDEA

The concept of a *pseudopotential* is related to replacing the effects of the core electrons with an effective potential. The pseudopotential generation procedure starts with the solution of the atomic problem using the Kohn-Sham approach. Once the KS orbitals are obtained, we make an arbitrary distinction between *valence* and *core* states. The core states are assumed to change very little due to changes in the environment so their effect is replaced by a model potential derived in the atomic configuration and it is assumed to be *transferable*. The valence states are seen to oscillate rapidly close to the core regions. With the introduction of the new potential, the valence states are made smoother.

Let's now work out the pseudopotential transformation in its most general framework : Assume that we have a Hamiltonian $\hat{H}$, core states $\{|\chi_n\rangle\}$ and core eigenvalues $\{E_n\}$. We are looking at a single valence state $|\psi\rangle$ Let's replace the valence state by the smoother $|\phi\rangle$ and expand the remaining portion in terms of core states :

$$|\psi\rangle = |\phi\rangle + \sum_n^{\text{core}} a_n |\chi_n\rangle \tag{9}$$

Next, we take the inner product of Eq. 9 with one of the core states. Because the valence state has to be orthogonal to the core states, we have

$$\langle\chi_n|\psi\rangle = \langle\chi_n|\phi\rangle + \underbrace{\sum_n^{\text{core}} a_n\langle\chi_m|\chi_n\rangle}_{a_m} = 0 \tag{10}$$

We now write the right-hand side of Eq. 10 in terms of the pseudofunction, $|\phi\rangle$

$$|\psi\rangle = |\phi\rangle - \sum_n \langle\chi_n|\phi\rangle|\chi_n\rangle \tag{11}$$

Applying the Hamiltonian onto the expression in Eq. 11, we get

$$\hat{H}|\phi\rangle + \sum_n^{\text{core}} (E - E_n)|\chi_n\rangle\langle\chi_n|\phi\rangle = E|\phi\rangle \tag{12}$$

As a result, the smooth, pseudowavefunction satisfies an effective equation with the same eigenenergy of the real valence wavefunction. In the case of isolated atoms, the indices $n$ corresponds to the combined index $nlm_l$ including the principal quantum number $n$, the angular momentum quantum number $l$ and the magnetic quantum number $m_l$. However, since the potential does not include any terms (such as $\vec{L}\cdot\vec{S}$ coupling) that lift the $m_l$ degeneracy, we include in what follows only $n$ and $l$. The reason why the $l$-degeneracy is broken instead will become clear later on. Eq. 12 may then be written as an eigenvalue equation for the smooth *pseudo wavefunction* as

$$\left(\hat{H} + \hat{V}_{nl}\right)|\phi\rangle = E|\phi\rangle \tag{13}$$

where the extra potential $\hat{V}_{nl}$ depends on $l$ due to spherical symmetry and its effect is localized to the core. Since $E > E_n$ by definition, it is a repulsive potential and it partially cancels the effect of the attractive Coulombic potential. The resulting potential is then a much weaker one than the original potential. This shows that the eigenstates of this new potential are smoother.

## III. NORM-CONSERVING PSEUDOPOTENTIALS

In order to ensure the optimum smoothness and transferability Hamann, Schlüter and Chiang (Phys Rev Lett **43** 1494 (1979)) came up with four criteria that the pseudopotentials are expected to obey in the *reference configuration* (i.e. the atomic configuration for which the pseudopotential is generated.) :

1. All-electron and pseudo eigenvalues agree for the reference configuration.

$$\hat{H}|\psi_{nl}^{AE}\rangle = \epsilon_{nl}|\psi_{nl}^{AE}\rangle \tag{14}$$

$$\left(\hat{H} + \hat{V}_{nl}\right)|\psi_{nl}^{PS}\rangle = \epsilon_{nl}|\psi_{nl}^{PS}\rangle \tag{15}$$

$$\tag{16}$$

2. AE and PS wavefunctions agree beyond a certain cutoff, $r_c$.

$$\psi_{nl}^{AE}(r) = \psi_{nl}^{PS}(r) \quad \text{for} \quad r \geq r_c \tag{17}$$

3. Real and pseudo norm squares integrated from 0 to $R$ for all $R < r_c$ agree.

$$\int_0^R |\phi_{nl}^{AE}|^2 r^2 dr = \int_0^R |\phi_{nl}^{PS}|^2 r^2 dr \tag{18}$$

4. The logarithmic derivatives and the energy derivative of the logarithmic derivative agree for all $R < r_c$.

$$\left[ (r\phi^{AE}(r))^2 \frac{d}{dE} \frac{d}{dr} \ln \phi^{AE}(r) \right]_R = \left[ (r\phi^{PS}(r))^2 \frac{d}{dE} \frac{d}{dr} \ln \phi^{PS}(r) \right]_R \tag{19}$$

Items 1 and 2 are obvious. Item 3 is necessary so that by Gauss' theorem, outside the *core region* where $r < r_c$, the electrostatic potential is identical for the real and pseudo wavefunctions. Finally, 4 is necessary in order to improve transferability, reproducing phase shifts of the real potential in the scattering sense. When we go from an atom to a different environment such as a solid or a molecule, the eigenvalues change. A pseudopotential satisfying this item reproduces these changes to linear order. Using the Friedel sum rule, one can show that item 4 is implied by item 3.

In order to generate a norm-conserving pseudopotential, we must follow the steps below :

1. Solve the all-electron atomic system.

2. Decide which of the states are to be taken as core and which are to be taken as valence.

3. Generate the pseudopotentials, $V_{nl}(r)$, for the valence states. There are several methods for doing that. We describe here the method due to Kerker. In this method, we assume a parametrized analytical function for the core region. The analytic form chosen by Kerker is $\phi_{nl}^{PS}(r) = e^{p(r)}$, where $p(r)$ is a fourth-order polynomial matching the true solution and its various derivatives at $r_c$.

4. Once we have a form for the pseudowavefunction, invert the Schrödinger equation, yielding

$$V_{nl,total}(r) = \epsilon - \left[ \frac{l(l+1)}{2r^2} - \frac{\frac{d^2}{dr^2}\phi_{nl}^{PS}(r)}{\phi_{nl}^{PS}(r)} \right] \tag{20}$$

Keep in mind that we are dealing with $\phi(r)$, which is defined by $\psi(r) = r\phi(r)$.

5. The potential $V_{l,total}(r)$ found by inversion of the Schrödinger equation is not only the ionic potential that we want, but includes also contributions from the Hartree and exchange-correlation terms. We must therefore subtract these two contributions.

$$V_{nl}(r) = V_{l,total}(r) - V_{Hxc}^{PS}(r) \tag{21}$$

where the Hartree and xc contributions are computed for the pseudowavefunctions. This operation is called *unscreening*.

There is no unique way to determine the $V_{nl}$'s. There are two opposing considerations :

1. Good transferability $\Rightarrow$ small $r_c$.

2. Large $r_c$ $\Rightarrow$ smoother pseudopotentials.

A good pseudopotential is one that strikes a balance between these two contraints.

Although the generation procedure is similar, the form of the pseudopotential may be assumed differently depending on considerations such as ease of computation, accuracy etc. In the following subsections, we shall see two different ways of forming norm-conserving pseudopotentials. Keep in mind that these pseudopotentials are formed within the atomic configuration and then exported to the solid with the hope of decent transferability.

An actual example of the construction of the pseudopotential can be seen in Fig. 1 for the radial parts of 2S and 2P orbitals of the element B. The agreement of the wavefunctions after the cutoff radius $r_c$ is evident.
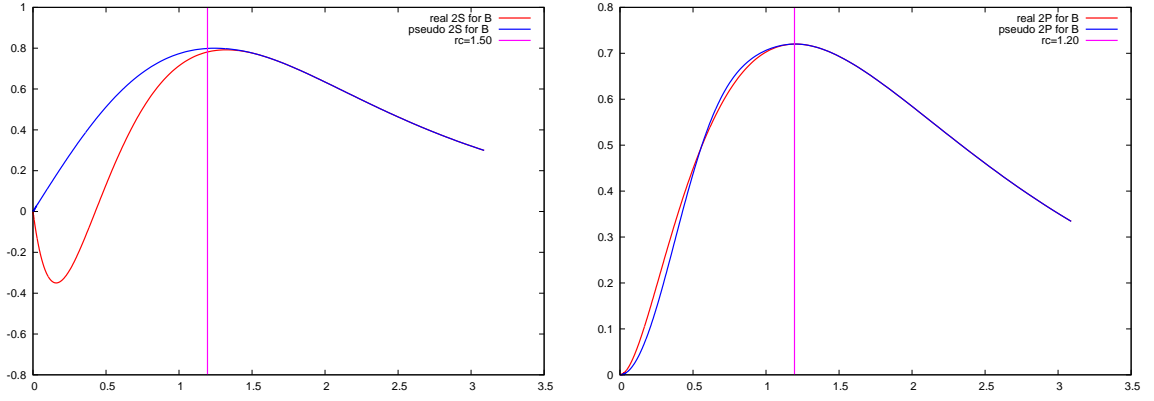
FIG. 1: Semilog plot of the real and pseudo wavefunctions for 2S (a) and 2P (b) orbitals of B.

## A. Semilocal pseudopotentials

Since a model pseudopotential replaces the potential of a nucleus, it is spherically symmetric and each angular momentum $l$ may be treated separately. This leads to the *nonlocal*, i.e. $l$-dependent model pseudopotentials $V_{nl}(r)$. Thus, the general form of a pseudopotential may be written in the *semilocal* form as

$$\hat{V}_{SL} = \sum_{lm} |Y_{lm}\rangle V_{nl}(r) \langle Y_{lm}|. \tag{22}$$

Here the angular and the radial parts are separated due to spherical symmetry and the $Y_{lm}$'s are there because any function that depends upon angles only may be written as an expansion. This form is called semilocal because it is nonlocal only in the angular coordinates and it's local in the radial coordinate.

Although conceptually simple, semilocal pseudopotentials create a severe problem in the planewave basis representation due to the form of the nonlocal part. This can be seen by considering a particular matrix element of the pseudopotential and using a lot of straighforward but tedious algebra

$$\langle \vec{q}|\hat{V}_{SL}|\vec{q}'\rangle = \frac{1}{\Omega} \sum_{lm} \int \int e^{-i\vec{q}\cdot\vec{r}} Y_{lm}^*(\theta,\phi) V_{nl}(r) Y_{lm}(\theta,\phi) e^{i\vec{q}'\cdot\vec{r}'} r^2 \, d\Omega \, d\Omega' \, dr \tag{23}$$

where $\vec{r}' = (r, \theta', \phi')$. Notice the fact that we calculate a single integral over the radial component $r$ but two integrals over the angles because the nonlocal part of the pseudopotential is in the form of *projectors* instead of a regular function as for the radial coordinate. In order to make use of their orthonormality, we expand the planewaves in the integral in Eq. 23 in terms of spherical harmonics

$$e^{i\vec{q}\cdot\vec{r}} = 4\pi \sum_{lm} i^l j_l(qr) Y_{lm}^*(\hat{q}) Y_{lm}(\hat{r}) \tag{24}$$

where $j_l(qr)$ are spherical Bessel functions and $\hat{q}$ and $\hat{r}$ denote the angles associated with the vectors $\vec{q}$ and $\vec{r}$. Substituting Eq. 24 into Eq. 23 we have

$$\langle \vec{q}|\hat{V}_{NL}|\vec{q}'\rangle = \frac{(4\pi)^2}{\Omega} \sum_{lm} \sum_{l'm'} \sum_{l''m''} \int (-i)^{l'} i^{l''} j_{l'}(qr) j_{l''}(q'r) Y_{l'm'}(\hat{q}) Y_{l''m''}^*(\hat{q}') V_{nl}(r) r^2 \, dr \times$$

$$\underbrace{\int Y_{l'm'}^*(\hat{r}') Y_{lm}(\hat{r}') \, d\Omega'}_{\delta_{ll',mm'}} \underbrace{\int Y_{lm}^*(\hat{r}) Y_{l''m''}(\hat{r}) d\Omega}_{\delta_{ll'',mm''}} \tag{25}$$

where we have used the orthonormality of spherical harmonics as mentioned before. When the delta functions are imposed the two sums over $lm$ and $l'm'$ are gone and the only indices that remain are $l$ and $m$. Next in order to deal with the remaining spherical harmonics, we utilize the *summation theorem for spherical harmonics*.

$$\sum_m Y_{lm}(\hat{q}) Y_{lm}^*(\hat{q}') = \frac{2l+1}{4\pi} P_l(\cos\theta_{\vec{q}\vec{q}'}) \tag{26}$$

where $P_l$ is the generalized Legendre polynomial and $\theta_{\vec{q}\vec{q}'}$ is the angle between the two wavevectors $\vec{q}$ and $\vec{q}'$. Putting everything together the expectation value in Eq. 25 becomes

$$\langle \vec{q} | \hat{V}_{NL} | \vec{q}' \rangle = \frac{4\pi}{\Omega} \sum_l (2l+1) \int j_l(qr) j_l(q'r) P_l(\cos\theta_{\vec{q}\vec{q}'}) V_l(r) \, r^2 \, dr \tag{27}$$

As seen in Eq. 27, the semilocal pseudopotential mixes planewaves with different $\vec{q}$ vectors. This means that if we have $N_{pw}$ planewaves in the basis that we choose we have to evaluate $N_{pw}^2$ such integrals as in Eq. 27, which brings a large computational load. In their seminal work Kleinman and Bylander (*Physical Review Letters*, **48**, 1425) proposed a different scheme for composing the angular momentum-dependent part of the pseudopotential such that the number of integrals to be calculated could be reduced from $N_{pw}^2$ to just $N_{pw}$. This form is called the *fully nonlocal form* and we shall see how it is formed in the next section.

## B. The Kleinman-Bylander Transformation

The difficulty with the semilocal pseudopotentials above is that due to the locality in the radial coordinate there is a single radial variable for both planewaves while the angular part is nonlocal and the integrals related to each angular coordinate may be evaluated separately. The fully nonlocal formulation includes the radial part in the projectors thereby separating the integral related to each projector. The starting point for the transformation is the usual semilocal form explained above where the local radial part is given by $V_l$. We then find the pseudowavefunctions in the atomic configuration, $\phi_l^{PS}$ corresponding to this pseudopotential. Using these wavefunctions, we construct a new pseudopotential who is composed of a local part, $V_L$, which is a completely arbitrary function that has the long-range behavior of the real potential and a nonlocal part $V_{NL}$, which is the remaining part of the pseudopotential. After the subtraction of the local part, the nonlocal part is left behind localized in the core region. The nonlocal part is then given by

$$\hat{V}_{NL} = \sum_l \hat{V}_l^{NL} = \sum_{lm} \frac{|\hat{V}_l^{SL}\phi_{lm}^{PS}\rangle\langle\phi_{lm}^{PS}\hat{V}_l^{SL}|}{\langle\phi_{lm}^{PS}|\hat{V}_l|\phi_{lm}^{PS}\rangle} \tag{28}$$

This particular form is chosen such that its action on a pseudowavefunction yields the same result as the action of the semilocal form

$$\hat{V}_l^{NL}|\phi_{lm}^{PS}\rangle = \hat{V}_l^{SL}|\phi_{lm}^{PS}\rangle \tag{29}$$

In order to see this, let's apply this operator on the pseudowavefunction

$$\hat{V}_l^{NL}|\phi_{lm}^{PS}\rangle = \frac{|\hat{V}_l^{SL}\phi_{lm}^{PS}\rangle\langle\phi_{lm}^{PS}|\hat{V}_l^{SL}|\phi_{lm}^{PS}\rangle}{\langle\phi_{lm}^{PS}|\hat{V}_l|\phi_{lm}^{PS}\rangle} = \hat{V}_l^{SL}|\phi_{lm}^{PS}\rangle \tag{30}$$

In the planewave representation, an arbitrary matrix element of the Kleinman-Bylanderized pseudopotential is

$$\langle \vec{q} | \hat{V}_l^{NL} | \vec{q}' \rangle = \frac{\langle\vec{q}|\hat{V}_l\phi_{lm}^{PS}\rangle\langle\hat{V}_l\phi_{lm}^{PS}|\vec{q}'\rangle}{\langle\phi_{lm}^{PS}|\hat{V}_l|\phi_{lm}^{PS}\rangle}. \tag{31}$$

The two integrals in Eq. 31 do not share any common integral variables and may thus be performed separately. One could then compute $N_{PW}$ such integrals, i.e. $\langle\vec{q}|\hat{V}_l\phi_{lm}^{PS}\rangle$ in advance and calculate the appropriate product $\langle\vec{q}|\hat{V}_l\phi_{lm}^{PS}\rangle\langle\hat{V}_l\phi_{lm}^{PS}|\vec{q}'\rangle$ for each $\vec{q}, \vec{q}'$ pair.

## IV. ULTRASOFT PSEUDOPOTENTIALS

In 1990, Vanderbilt (see *Physical Review B*, **41**, 7892) proposed a new and radical method for generating pseudopotentials by relaxing the norm-conservation constraint. Pseudopotentials generated in this way (due to their softness) require a much smaller planewave cutoff and thus a much smaller number of planewaves. For this reason they are usually called *ultrasoft pseudopotentials*.

First let's see how ultrasoft pseudopotential is integrated into the Kohn-Sham equations and then see how it is generated. The total energy in the presence of ultrasoft pseudopotentials is written as

$$E_e = \sum_i \sum_i \langle \phi_i | -\frac{1}{2}\nabla^2 + V_{NL} |\phi_i\rangle + \frac{1}{2}\int\int d\vec{r}d\vec{r}' \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} + E_{xc}[n] + \int d\vec{r}V_{loc}(\vec{r})n(\vec{r}) \tag{32}$$

where the Hartree, exchange-correlation, local and kinetic terms have the usual form. The nonlocal part of the pseudopotential instead is given in terms of a new set of projection operators as

$$V_{NL} = D_{nm}^{(0)}|\beta_n^I\rangle\langle\beta_m^I| \tag{33}$$

where the superscript $I$ indicates that the projector is centered on atom $I$.

The norm-conserving condition is relaxed by introducing a generalized orthonormality condition through the overlap matrix $S$

$$\langle \phi_i | S | \phi_j \rangle = \delta_{ij} \tag{34}$$

where

$$S = 1 + \sum_{nm,I} q_{nm}|\beta_n^I\rangle\langle\beta_m^I| \tag{35}$$

with $q_{nm} = \int d\vec{r}Q_{nm}(\vec{r})$. Because the norm-conserving condition is now relaxed, the electronic density needs to be *augmented* in order to preserve the correct number of electrons. The new density is then

$$n(\vec{r}) = \sum_i \left[ |\phi_i(\vec{r})|^2 + \sum_{nm,I} Q_{nm}^I(\vec{r})\langle\phi_i|\beta_n^I\rangle\langle\beta_m^I|\phi_i\rangle \right] \tag{36}$$

In order to verify that the density as given in Eq. 36 integrates to the correct number of electrons, consider

$$\int n(\vec{r})d\vec{r} = \sum_i \left[ \int |\phi_i(\vec{r})|^2 + \sum_{nm,I} \int d\vec{r}Q_{nm}^I(\vec{r})\langle\phi_i|\beta_n^I\rangle\langle\beta_m^I|\phi_i\rangle \right]$$
$$= \sum_{ij} \delta_{ij} \left[ \langle\phi_i|\phi_j\rangle + \sum_{nm,I,j} \delta_{ij}q_{nm}\langle\phi_i|\beta_n^I\rangle\langle\beta_m^I|\phi_j\rangle \right]$$
$$\equiv \sum_{ij}\delta_{ij}\langle\phi_i|S|\phi_j\rangle = \sum_{ij}\delta_{ij}\delta_{ij} = \sum_i\delta_{ii} = \sum_i 1 = N_v \tag{37}$$

where $N_v$ stands for the number of valence electrons in the system.

The new form of the density, although it gives us the flexibility to create softer pseudopotentials, inevitably makes the Kohn-Sham equations more complex. The functional derivative of the density with respect to the orbitals is

$$\frac{\delta n(\vec{r}')}{\delta\phi_i^*(\vec{r})} = \phi_i(\vec{r})\delta(\vec{r} - \vec{r}') + \sum_{nm,I} Q_{nm}^I(\vec{r}')\beta_n^I(\vec{r})\langle\beta_m^I|\phi_i\rangle. \tag{38}$$

Utilizing Eq. 38 and Eq. 32 we arrive at the modified Kohn-Sham equations

$$\frac{\delta E_e}{\delta\phi_i^*} = \int d\vec{r}' \frac{\delta E_e}{\delta n(\vec{r}')}\frac{\delta n(\vec{r}')}{\delta\phi_i^*(\vec{r})} = \left[ -\frac{1}{2}\nabla^2 + V_{eff} + \left( D_{nm}^{(0)} + \int d\vec{r}'V_{eff}(\vec{r}')Q_{nm}(\vec{r}') \right)|\beta_n^I\rangle\langle\beta_m^I| \right]|\phi_i\rangle. \tag{39}$$

where $V_{eff}$ is the regular potential

$$V_{eff} = V_H + V_{loc} + V_{xc}. \tag{40}$$

As easily seen in Eq. 39, unlike norm-conserving pseudopotentials, the coefficients of the projectors in the nonlocal part of the pseudopotential gets updated in a self-consistent manner at every iteration. This introduces a slight overhead to the calculation but the gain in the planewave expansion surpasses the loss thus introduced.

Now, we take a step back and see the justification and generation of such a radical implementation. The generation of ultrasoft potentials start out in the same way as norm-conserving pseudopotentials. For a given species, the atomic

Kohn-Sham system is solved self-consistently, resulting in the screened all-electron potential, $V_{AE}$. Then for each angular momentum channel, a few energy values, $\epsilon_{l\tau}$ are chosen ($\tau$=number of such energies, usually max 3). For the $V_{AE}$ already obtained, the Schrödinger equation is found

$$[T + V_{AE}]|\psi_n(r)\rangle = \epsilon_n|\psi_n\rangle(r) \tag{41}$$

where $n$ is a composite index holding $l$ for the angular momentum quantum number, $m$ for the projection and $\tau$. In the general case, $\psi_n$ is not going to be normalizable but we use the bra-ket notation anyway.

Next, we choose *three* cutoff radii :

1. A smooth local ($l$-independent) potential is created which matches $V_{AE}(r)$ after the radius $r_c^{loc}$.

2. A second cutoff radius, $r_{cl}$, is chosen for each angular momentum channel and a pseudowavefunction, $\phi_n$ is constructed which matches the real wavefunction $\psi_n$ at $r_{cl}$.

3. Finally a diagnostic radius $R$ is chosen which is slightly larger than the maximum of the maximum of all the $r_{cl}$ and $r_C^{loc}$.

Then new orbitals are formed that satisfy

$$|\chi_n\rangle = (\epsilon_n - T - V_{loc})|\phi_n\rangle \tag{42}$$

which are zero beyond $R$.

Next, an auxiliary matrix of inner products

$$B_{nm} = \langle\phi_n|\chi_m\rangle \tag{43}$$

and the projectors necessary for the definition of the nonlocal part of the potential

$$|\beta_n\rangle = \sum_m (B^{-1})_{mn}|\chi_m\rangle \tag{44}$$

are defined.

While determining the pseudowavefunctions mentioned above, norm-conservation has not been imposed. We thus define a set of generalized *augmentation functions*

$$Q_{nm}(\vec{r}) = \psi_n^*(\vec{r})\psi_m(\vec{r}) - \phi_n^*(\vec{r})\phi_m(\vec{r}) \tag{45}$$

and the related *augmentation charges*

$$q_{nm} = \langle\psi_n|\psi_m\rangle_R - \langle\phi_n|\phi_m\rangle_R. \tag{46}$$

where the subscript $R$ denotes an integration within the cutoff radius, R. With all these descriptions, we can verify that the pseudowavefunctions $|\phi_n\rangle$ obey the equation

$$\left(\hat{T} + V_{loc} + \sum_{nm} D_{nm}|\beta_n\rangle\langle\beta_m|\right)|\phi_i\rangle = \epsilon_i\left(1 + \sum_{nm} q_{nm}|\beta_n\rangle\langle\beta_m|\right)|\phi_i\rangle \tag{47}$$

where $D_{nm} = B_{nm} + \epsilon_m q_{nm}$. In order to prove the central equation Eq. 47, let's look at

$$\left(\sum_{nm} B_{nm}|\beta_n\rangle\langle\beta_m|\right)|\phi_i\rangle = \sum_{nm} B_{nm}\sum_l (B^{-1})_{ln}|\chi_l\rangle\sum_k (B_{km}^{-1})^* \underbrace{\langle\chi_k|phi_i\rangle}_{B_{ik}^*}$$

$$= \sum_{ml}|\chi_l\rangle\sum_n (B^{-1})_{ln}B_{nm}\sum(B_{ik}(B^{-1})_{km})$$

$$= \sum_{ml}\delta_{lm}\delta_{im}|\chi_l\rangle = |\chi_i\rangle = (\epsilon_i - \hat{T} - V_{loc})|\phi_i\rangle \tag{48}$$

Sustituting Eq. 48 into Eq. 47 completes the proof.

Thus the fundamental equation of the pseudopotential theory has been satisfied, that is pseudowavefunctions that satisfy the same equation as the real wavefunctions have been found. These pseudopotentials, however, may be proven to satisfy, instead of being orthonormal in the usual sense, satisfy a generalized orthonormality equation through an overlap matrix

$$S = 1 + \sum_{nm} q_{nm} |\beta_n\rangle\langle\beta_m| \tag{49}$$

Once the $D_{nm}$ are obtained, the local part and the nonlocal coefficients of the bare pseudopotential are obtained through a descreening procedure

$$V_{loc}^{ion} = V_{loc} - V_H - V_{xc} \tag{50}$$

$$D_{nm}^{(0)} = D_{nm} - \int d\vec{r}' V_{loc}(\vec{r}') n(\vec{r}') \tag{51}$$

While generating pseudopotentials, we don't enforce norm conservation. This allows us to increase the cutoff radii to larger values. This convenient fact however brings about the necessity of defining a separate planewave cutoff for the density because as seen in the expression in Eq. 36, the density now has a smooth part and a sharp part. This sharp part needs to be expressed using planewaves that have high frequencies, i.e. a plane wave cutoff that is typically several times the planewave cutoff used to express the wavefunctions.