Self-Study Notes on "Soft self-consistent pseudopotentials (PP) in a generalized eigenvalue formalism PRB 1990 41 7892-7895."

Some derivation and comments are described in the footnote by Masahiro Yamamoto

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A new approach to the construction of first-principles pseudopotentials is described. The method allows transferability to be improved systematically while holding the cutoff radius fixed, even for large cutoff radii. Novel features are that the pseudopotential itself becomes charge-state dependent, the usual norm-conservation constraint does not apply, and a generalized eigenproblem is introduced. The potentials have a separable form well suited for plane-wave solid-state calculations, and show promise for application to first-row and transition-metal systems.

The development of first-principles norm-conserving pseudopotentials (PP) by Hamann, Schlüter, and Chiang[1] (HSC) and others[2,3] has paved the way to accurate calculations of solid-state properties within the local-density approximation using plane-wave basis functions.[4] However, the utility of this approach to systems containing highly localized valence orbitals (e.g., for first-row and transition-metal atoms) has been limited, because of the difficulty of representing the pseudo-wave-functions in a plane-wave basis. ...

Here, a new approach to the construction of first-principles PP is described, in which **a fully nonlocal PP is generated directly. It has the following desirable properties: (i) It takes the form of a sum of a few separable terms. (ii) It becomes local and vanishes outside the core. (iii) The scattering properties and their energy derivatives are, by construction, correct at several energies spanning the range of occupied states, and the transferability can be systematically improved by increasing the number of such energies. (iv) The normconserving constraint is removed so that the pseudo-wave-function can be constructed in such a way as to optimize smoothness. (v) The PP itself becomes involved in the self-consistent screening process, thereby improving transferability with respect to changes in charge configuration. Together, these features allow the cutoff radius to be increased without sacrificing transferability, even for "problem" cases such as 2p and d orbitals.**

The construction of the new PPs will be described in three stages. **In the first stage, I show that it is possible to arrive at a fully nonlocal KB-type PP by working with the wave function directly, bypassing the construction of a semilocal potential entirely.** Moreover, this can be done at an arbitrary energy ϵ_i, as suggested by Hamann.[12][1]

As usual, an AE calculation is carried out on a free atom in some reference configuration, Ieading to a screened potential $V_{\rm AE}(r)$. Cutoff radii r_{cl} and $r_c^{\rm loc}$ are chosen for the wave functions and local PP, respectively, and a diagnostic radius R is chosen large enough that all pseudo- and AE quantities agree at and beyond R. Some algorithm is used to generate a smooth local potential $V_{loc}(r)$ which approaches $V_{\rm AE}(r)$ beyond $r_c^{\rm loc}$. Now consider an AE wave function $\psi_i(\mathbf{r})$ of definite angular momentum Im, which is a solution of the Schrödinger equation, regular at t he origin, at an arbitrary energy ϵ_i:

$$[T + V_{\rm AE}(\mathbf{r})]\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r}) \tag{1}$$

Here i is a composite index, $i = \{\epsilon_i lm\}, T$ is the kinetic energy operator $-\frac{1}{2}\nabla^2$ and $V_{\rm AE}$ is the original reference screened potential, i .e., ψ_i is not determined self-consistently. (Atomic units are used throughout.) Despite the fact that ψ_i is, in general, non-normalizable. I adopt a bracket notation

$$(T + V_{\rm AE} - \epsilon_i)|\psi_i\rangle = 0 \tag{2}$$

as a stand-in for the previous equation. Quantities such as $\langle\psi_i|\psi_i\rangle$ are ill-defined, but I shall make use of the special notation $\langle\psi_i|\psi_i\rangle_R$ to denote the integral of $\psi_i^*(\mathbf{r})\psi_i(\mathbf{r})$ inside the sphere of radius R.

[1] Usually the radial schrödinger equation is solved using Adams-Moulton method from the origin $r = 0$ and from $\psi = 0, r = \infty$, and match them at the classical turning point. In the Hamann's paper ϵ_i is arbitrary chosen and using the outward Adams-Moulton method the radial wavefunction is solved. Thereby sometimes the wavefunction is divergent at $r \to \infty$.

Now a pseudo-wave-function ϕ_i is constructed, subject to the constraints that it join smoothly to ψ_i at r_{cl} and that it satisfy the norm-conserving property $\langle\phi_i|\phi_i\rangle_R = \langle\psi_i|\psi_i\rangle_R$. Since the wave function

$$|\chi_i\rangle = (\epsilon_i - T - V_{loc})|\phi_i\rangle \tag{3}$$

is local (it vanishes at and beyond R where $V_{\rm AE} = V_{\rm loc}$ and $\phi_i = \psi_i$), the nonlocal PP operator

$$V_{\rm NL} = \frac{|\chi_i\rangle\langle\chi_i|}{\langle\chi_i|\phi_i\rangle} \tag{4}$$

is well defined. It is straightforward to verify that ϕ_i is an eigenvector of $T + V_{\rm loc} + V_{\rm NL}$, [2] and that the scattering properties and their energy derivatives are correct at ϵ_i in the usual way (see below).

The second stage of the new PP scheme is arrived at by generalizing the previous construction to the case of two or more energies ϵ_i at which the scattering properties will be correct, as follows. For a given angular momentum l, some number (usually between one and three) of energies which span the energy of occupied states of a target (e.g., bulk crystal) calculation are chosen. Now the set of pseudo-wavefunctions $|\phi_i\rangle$ are constructed from the AE wave functions $|\psi_i\rangle$ as before, except that they should satisfy the generalized norm-conserving condition $Q_{ij} = 0$, where

$$Q_{ij} = \langle\psi_i|\psi_j\rangle_R - \langle\phi_i|\phi_j\rangle_R \tag{5}$$

Forming the matrix $B_{ij} = \langle\phi_i|\chi_j\rangle$ and defining a set of local wave functions

$$|\beta_i\rangle = \sum_j \left(B^{-1}\right)_{ji} |\chi_j\rangle \tag{6}$$

which are dual to the $|\phi_i\rangle$, the nonlocal PP operator can be chosen as

$$V_{\rm NL} = \sum_{i,j} B_{ij}|\beta_i\rangle\langle\beta_j| \tag{7}$$

Then it can easily be shown that $|\phi_i\rangle$ satisfies the secular equation $(H - \epsilon_i)|\phi_i\rangle = 0$, where $H = T + V_{\rm loc} + V_{\rm NL}$. [3]

I now show that the matrix B_{ij}, and therefore the operator $V_{\rm NL}$, are Hermitian when $Q_{ij} = 0$. Taking $u_i(r)/r$ to be the radial wave function associated with $\phi_i(r)$,

$$B_{ij} = \int_0^R dr u_i^*(r)\left[\epsilon_j + \frac{1}{2}\frac{d^2}{dr^2} - \frac{l(l+1)}{2r^2} - V_{\rm loc}(r)\right] u_j(r) \tag{8}$$

[4]

The expression for B^*_{ji} is identical except that ϵ_j is replaced by ϵ_i, and the derivative d^2/dr^2 acts to the left. [5] After one integration by parts on each expression,

$$\begin{aligned} B_{ij} - B^*_{ji} &= (\epsilon_j - \epsilon_i)\langle\phi_i|\phi_j\rangle_R \\ &+\frac{1}{2}[u_i^*(R)u_j'(R) - u_i^{*'}(R)u_j(R)] \end{aligned} \tag{9}$$

[6] A similar expression can be derived for the AE wave functions; subtracting this from the above equation, and noting that the pseudo- and AE wave functions and their derivatives match at R, one obtains

$$B_{ij} - B^*_{ji} = (\epsilon_i - \epsilon_j)Q_{ij} \tag{10}$$

which vanishes (i.e, Hermitian) when $Q_{ij} = 0$.

Again one may verify that $(d\ln u/dr)_R$ and its energy derivative match the corresponding AE quantities *at each* ϵ_i. Thus, by increasing the number of

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[2]

$$V_{\rm NL}|\phi_i\rangle = |\chi_i\rangle = (\epsilon_i - T - V_{loc})|\phi_i\rangle$$

then ϕ_i is an eigenvector of $T + V_{\rm loc} + V_{\rm NL}$. Then it is shown that the fully nonlocal KB-type PP can be obtained directly from $V_{\rm NL} = |\chi_i\rangle\langle\chi_i|/\langle\chi_i|\phi_i\rangle$.

[3] From the definition of $|\beta_i\rangle$

$$\begin{aligned} \sum_i B_{ik}|\beta_i\rangle &= \sum_{i,j}\left(B^{-1}\right)_{ji} B_{ik}|\chi_j\rangle \\ &= \sum_j \delta_{jk}|\chi_j\rangle = |\chi_k\rangle \\ |\chi_j\rangle &= \sum_i \underbrace{\langle\phi_i|\chi_j\rangle}_{B_{ij}}|\beta_i\rangle \end{aligned}$$

$$\begin{aligned} \langle\phi_k|\chi_j\rangle &= \sum_i \langle\phi_i|\chi_j\rangle\langle\phi_k|\beta_i\rangle \\ \text{then}\quad \langle\phi_k|\beta_i\rangle &= \delta_{ki} \\ V_{NL}|\phi_k\rangle &= \sum_{i,j}\langle\phi_i|\chi_j\rangle|\beta_i\rangle\langle\beta_j|\phi_k\rangle = \sum_i \langle\phi_i|\chi_k\rangle|\beta_i\rangle \\ &= \sum_i \langle\phi_i|\chi_k\rangle \sum_j \left(B^{-1}\right)_{ji}|\chi_j\rangle \\ &= \sum_{i,j} B_{ik}\left(B^{-1}\right)_{ji}|\chi_j\rangle \\ &= \sum_j \delta_{jk}|\chi_j\rangle = |\chi_k\rangle \\ &= (\epsilon_k - T - V_{loc})|\phi_k\rangle \end{aligned}$$

[4] In the central force field radial part of Schrödinger equation becomes

$$-\frac{\hbar^2}{2m}\left(\frac{d^2u}{dr^2} - \frac{l(l+1)}{r^2}u\right) + Vu = \epsilon u$$

[5]

$$B^*_{ji} = \langle\phi_j|\chi_i\rangle^* = \langle\chi_i|\phi_j\rangle$$

[6]

$$\begin{aligned} B_{ij} &= \int_0^R dr\epsilon_j u_i^*(r)u_j(r) + \frac{1}{2}\int_0^R dr u_i^*(r)u_j''(r) \\ &+ \int_0^R dr u_i^*(r)\left[-\frac{l(l+1)}{2r^2} - V_{\rm loc}(r)\right]u_j(r) \\ \int fg' &= fg - \int f'g \\ B_{ij} &= \epsilon_j\langle\phi_i|\phi_j\rangle_R + \frac{1}{2}u_i^*(r)u_j'(R) \end{aligned}$$

energies ϵ_i at which the construction is done, the scattering properties of the PP can be made to reproduce those of the AE potential with arbitrary accuracy over the energy range of interest. [13]

One could stop here, and still have a useful scheme. However, I now show that **the constraint $Q_{ij} = 0$ is unnecessary, if one is willing to adopt a generalized eigenvalue formalism in which an overlap operator appears.** In this third stage, I define a nonlocal overlap operator

$$S = 1 + \sum_{i,j} Q_{ij} |\beta_i\rangle\langle\beta_j| \quad (11)$$

and redefine the nonlocal potential operator to be

$$V_{\rm NL} = \sum_{i,j} D_{ij} |\beta_i\rangle\langle\beta_j| \quad (12)$$

where

$$D_{ij} = B_{ij} + \epsilon_j Q_{ij} \quad (13)$$

and Q_{ij} defined as before. Note that with these definitions,

$$\langle\phi_i|S|\phi_j\rangle_R = \langle\psi_i|\psi_j\rangle_R \quad (14)$$

[7] Then $|\psi_i\rangle$ is easily shown to be a solution of the generalized eigenvalue problem $(H - \epsilon_i S)|\phi_i\rangle = 0$. [8] Now it follows from Eqs. (5), (10), and (13) that Q and D are Hermitian matrices, even though B is not. Thus H and S are Hermitian operators. [9]

[7]

$$\begin{aligned}\langle\phi_i|S|\phi_j\rangle_R &= \langle\phi_i|\phi_j\rangle_R + \sum_{kl} Q_{kl} \underbrace{\langle\phi_i|\beta_k\rangle_R}_{\delta_{ik}} \underbrace{\langle\beta_l|\phi_j\rangle_R}_{\delta_{lj}} \\ &= \langle\phi_i|\phi_j\rangle_R + Q_{ij} = \langle\psi_i|\psi_j\rangle_R\end{aligned}$$

[8]

$$\begin{aligned}V_{\rm NL}|\phi_i\rangle &= \sum_{kl}(B_{kl} + \epsilon_l Q_{kl})|\beta_k\rangle \underbrace{\langle\beta_l|\phi_i\rangle}_{\delta_{li}} \\ &= \underbrace{\sum_k B_{ki}|\beta_k\rangle}_{\sum_{kn} B_{ki}B^{-1}_{kn}|\chi_n\rangle = |\chi_i\rangle} \\ &\quad + \sum_{kl} \epsilon_l Q_{kl}|\beta_k\rangle\langle\beta_l|\phi_i\rangle \\ &= |\chi_i\rangle + \underbrace{\epsilon_i}_{\delta_{li}} \sum_{kl} Q_{kl}|\beta_k\rangle\langle\beta_l|\phi_i\rangle \\ &= (\epsilon_i - T - V_{\rm loc})|\phi_i\rangle + \epsilon_i \sum_{kl} Q_{kl}|\beta_k\rangle\langle\beta_l|\phi_i\rangle \\ &= \left[\epsilon_i(1 + \sum_{kl} Q_{kl}|\beta_k\rangle\langle\beta_l|) - T - V_{\rm loc}\right]|\phi_i\rangle \\ &= (\epsilon_i S - T - V_{\rm loc})|\phi_i\rangle\end{aligned}$$

[9]

$$D^*_{ji} = B^*_{ji} + \epsilon_i Q^*_{ji} = B_{ij} - (\epsilon_i - \epsilon_j)Q_{ij} + \epsilon_i Q_{ij} = D_{ij}$$

Moreover, it follows from the identity that (from variational principle)

$$0 = \left[\frac{d}{d\epsilon}\langle\phi_\epsilon|T + V_{\rm loc} + V_{\rm NL} - \epsilon S|\phi_\epsilon\rangle_R\right]_{\epsilon=\epsilon_i} \quad (15)$$

that

$$-\frac{1}{2}u_i^2 \frac{d}{d\epsilon}\frac{d}{dr}\ln u_\epsilon(r)\Big|_R = \langle\phi_i|\phi_i\rangle_R + Q_{ii} = \langle\psi_i|\psi_i\rangle_R \quad (16)$$

(See Appendix) so that the matching of the AE and pseudologarithmic derivatives follows in the usual way.

The relaxation of the constraint $Q_{ij} = 0$ means that each ψ_i can be made into a pseudo-wave-function ϕ_i independently, with the *only constraint* being the matching of $\phi(r)$ to $\psi(r)$ at the cutoff radius. Thus it becomes possible to choose the cutoff radius to be *well beyond the radial wave-function maximum*, as illustrated in Fig. l. A consequence of this freedom is that a generalized eigenvalue problem has to be solved in the target solid-state calculation. However, within iterative approaches to the eigenvector problem, the time-dominant step is the multiplication of $H - \epsilon S$ by a trial vector $\phi_{n\mathbf{k}}$. In this case the operation count need hardly increase at all, because the identical form of the nonlocal parts of S and H allows them to be consolidated into a single operator. Incidentally, the current PP bears a formal resemblance to the original Phillips-Kleinman PP.[14] The latter can be cast in the form of Eqs. (11) and (12) (with the $|\beta_i\rangle$ being just the core orbitals), but does not have an adjustable cutoff radius.

In a self-consistent calculation, the "deficit" of valence charge in the core region associated with a pseudo-wave-function such as that of Fig.1 will have to be restored. The solutions of the generalized eigenvalue problem should be normalized according to

$$\langle\phi_{n\mathbf{k}}|S|\phi_{n'\mathbf{k}}\rangle = \delta_{nn'}, \quad (17)$$

which is automatic in the usual methods of solution. Taken together with Eq. (14). Eq. (17) ensures that the pseudosolution has the same amplitude as the AE one at and beyond R. To make up the charge deficit, the valence charge density is defined to be

$$n_v(\mathbf{r}) = \sum_{n\mathbf{k}} \phi^*_{n\mathbf{k}}(\mathbf{r})\phi_{n\mathbf{k}}(\mathbf{r}) + \sum_{ij} \rho_{ij} Q_{ij}(\mathbf{r}) \quad (18)$$

where

$$\rho_{ij} = \sum_{n\mathbf{k}} \langle\beta_i|\phi_{n\mathbf{k}}(\mathbf{r})\rangle\langle\phi_{n\mathbf{k}}(\mathbf{r})|\beta_j\rangle, \quad (19)$$

$$Q_{ij}(\mathbf{r}) = \psi^*_i(\mathbf{r})\psi_j(\mathbf{r}) - \phi^*_i(\mathbf{r})\phi_j(\mathbf{r}) \quad (20)$$

It follows from Eqs. (11) and (17) that $\int d^3\mathbf{r} n_v(\mathbf{r}) = N_v$, exactly, where N_v, is the number of valence electrons in the unit cell.

***** The treatment of D in the following chapter was corrected in their 1993 paper. K. Laasonen et al. PRB, 47, 10142, 1993. *****

In order to make a variational theory, the total energy

$$\begin{aligned} E_{\rm tot} &= \langle\phi_{n\mathbf{k}}| \left[T + V_{\rm loc}^{\rm ion} + \sum_{ij} D_{ij}^{\rm ion} |\beta_i\rangle\langle\beta_j| \right] |\phi_{n\mathbf{k}}\rangle \\ &+ E_{\rm H}[n_v] + E_{\rm xc}[n_c + n_v] \end{aligned} \quad (21)$$

is to be minimized subject to the constraint (17). Here n_c is a frozen-core density included to improve transferability.[15]

Defining

$$V_{\rm Hxc}(\mathbf{r}) = V_{\rm H}^{[n_v]}(\mathbf{r}) + V_{\rm xc}^{[n_v]+[n_c]}(\mathbf{r}) \quad (22)$$

$$D_{ij}^{\rm Hxc} = \int d\mathbf{r} V_{\rm Hxc}(\mathbf{r}) Q_{ij}(\mathbf{r}) \quad (23)$$

the secular equation becomes

$$(T + V_{\rm loc} + V_{\rm NL} - \epsilon_{n\mathbf{k}} S)|\phi_{n\mathbf{k}}\rangle = 0 \quad (24)$$

with V_{NL} and S given by Eqs. (11)-(13), $V_{\rm loc} = V_{\rm loc}^{\rm ion} + V_{\rm Hxc}$, and $D_{ij} = D_{ij}^{ion} + D_{ij}^{\rm Hxc}$. The $V_{\rm loc}^{\rm ion}$ and $D_{ij}^{\rm ion}$ must be obtained by unscreening the $V_{\rm loc}$ and D_{ij} of the generating atomic configuration in the usual way. .. The dependence of D_{ij} upon n_v through $V_{\rm Hxc}$ implies that the PP itself must be updated as part of the self-consistent screening process.

....

In conclusion, it is hoped that the present method will allow PPs to be applied to first-row atom and transition-metal systems using modest plane-wave cutoffs for the first time.

1 Appendix

Derivation of logarithmic derivative(Harrison, Solid State Theory)

1.1 Norm-concerving pseudopotential case

$$\begin{aligned} \epsilon R_l &= -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} R_l + V(r) R_l + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2} R_l \\ (\epsilon+\delta\epsilon) R_l' &= -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} R_l' + V(r) R_l' + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2} R_l' \end{aligned}$$

If we apply R_l' to lhs of the first equation and R_l to lhs of the second equation and integral from 0 to R

$$\begin{aligned} -\delta\epsilon \int_0^R dr 4\pi r^2 R_l' R_l &= -\frac{4\pi\hbar^2}{2m}\left(\int_0^R R_l' \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} R_l \right. \\ &\left. - \int_0^R R_l \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} R_l' \right) \end{aligned}$$

Here we assume $V(r)$ had no ϵ dependence. Using partial integral

$$\begin{aligned} -\delta\epsilon \int_0^R dr 4\pi r^2 R_l' R_l &= -\frac{4\pi\hbar^2}{2m}\left(\left[R_l' r^2 \frac{\partial R_l}{\partial r} \right]_0^R \right. \\ &\left. - \int_0^R dr \frac{\partial R_l'}{\partial r} r^2 \frac{\partial R_l}{\partial r} \right) \\ &- \left[R_l r^2 \frac{\partial R_l'}{\partial r} \right]_0^R - \int_0^R dr \frac{\partial R_l}{\partial r} r^2 \frac{\partial R_l'}{\partial r} \Bigg) \\ &= -\frac{4\pi\hbar^2}{2m}\left(R_l' r^2 \frac{\partial R_l}{\partial r} - R_l r^2 \frac{\partial R_l'}{\partial r} \right)_R \end{aligned}$$

$$R_l' = R_l + \frac{\partial R_l}{\partial \epsilon}\delta\epsilon$$

$$\begin{aligned} -\delta\epsilon \int_0^R dr 4\pi r^2 (R_l + \frac{\partial R_l}{\partial\epsilon}\delta\epsilon) R_l &= -\frac{4\pi\hbar^2}{2m}\left((R_l + \frac{\partial R_l}{\partial\epsilon}\delta\epsilon) r^2 \frac{\partial R_l}{\partial r} \right. \\ &\left. - R_l r^2 \frac{\partial (R_l + \frac{\partial R_l}{\partial\epsilon}\delta\epsilon)}{\partial r} \right)_R \\ -\delta\epsilon \int_0^R dr 4\pi r^2 (R_l^2 + R_l \frac{\partial R_l}{\partial\epsilon}\delta\epsilon) &= -\frac{4\pi\hbar^2}{2m}\delta\epsilon \left(r^2 \frac{\partial R_l}{\partial\epsilon}\frac{\partial R_l}{\partial r} - r^2 R_l \frac{\partial^2 R_l}{\partial\epsilon\partial r} \right)_R \end{aligned}$$

If we pick up the first-order of $\delta\epsilon$

$$\begin{aligned} \int_0^R dr r^2 R_l^2 &= \frac{\hbar^2}{2m} R^2 \left(\frac{\partial R_l}{\partial\epsilon}\frac{\partial R_l}{\partial r} - R_l \frac{\partial^2 R_l}{\partial\epsilon\partial r} \right) \\ &= \frac{\hbar^2}{2m} R^2 R_l^2 \left(R_l^{-2} \frac{\partial R_l}{\partial\epsilon}\frac{\partial R_l}{\partial r} - R_l^{-1}\frac{\partial^2 R_l}{\partial\epsilon\partial r} \right) \\ &= -\frac{\hbar^2}{2m} R^2 R_l^2 \frac{\partial}{\partial\epsilon}\left(R_l^{-1}\frac{\partial R_l}{\partial r} \right) \\ &= -\frac{\hbar^2}{2m} R^2 R_l^2 \frac{\partial}{\partial\epsilon}\frac{\partial}{\partial r} \ln R_l \end{aligned}$$

1.2 In the case of ultra-soft PP

$$\begin{aligned} \phi_l &= R_l Y_{lm}, \quad R_l = \frac{u_l}{r} \\ (H - \epsilon_l S)|\phi_l\rangle &= 0 \\ \langle\phi_l'|\epsilon S|\phi_l\rangle_R &= \langle\phi_l'|T + V_{\rm loc} + V_{\rm NL}|\phi_l\rangle_R \\ \langle\phi_l|(\epsilon+\delta\epsilon)S|\phi_l'\rangle_R &= \langle\phi_l|T + V_{\rm loc} + V_{\rm NL}|\phi_l'\rangle_R \\ \langle\phi_l'|S|\phi_l\rangle_R &= \langle\phi_l|S|\phi_l'\rangle_R \\ S &= 1 + \sum_{i,j} Q_{ij}|\beta_i\rangle\langle\beta_j| \\ \langle\phi_l'|V_{\rm NL}|\phi_l\rangle_R &= \langle\phi_l|V_{\rm NL}|\phi_l'\rangle_R \\ \sum_{ij} D_{ij}\langle\phi_l'|\beta_i\rangle\langle\beta_j|\phi_l\rangle|_R &= \sum_{ij} D_{ij}\langle\phi_l|\beta_i\rangle\langle\beta_j|\phi_l'\rangle|_R \\ -\delta\epsilon\langle\phi_l|S|\phi_l'\rangle_R &= \langle\phi_l'|T|\phi_l\rangle_R - \langle\phi_l|T|\phi_l'\rangle_R \\ \epsilon_l S R_l Y_{lm} &= -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} R_l Y_{lm} + V\phi_l - \frac{\hbar^2}{2m}\frac{\Lambda}{r^2} Y_{lm} R_l \\ \epsilon S R_l Y_{lm} &= -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} R_l Y_{lm} + V_{\rm loc}(r) R_l Y_{lm} \\ &+ \frac{\hbar^2 l(l+1)}{2mr^2} Y_{lm} R_l + V_{\rm NL} R_l Y_{lm} \\ \langle\phi_l|S|\phi_l'\rangle_R &= \langle\phi_l|(1 + \sum_{i,j} Q_{ij}|\beta_i\rangle\langle\beta_j|)|\phi_l'\rangle_R \\ &= \langle\phi_l|\phi_l'\rangle_R + \sum_{i,j} Q_{ij}\langle\phi_l|\beta_i\rangle\langle\beta_j|\phi_l'\rangle_R \end{aligned}$$

$$\begin{aligned} -\delta\epsilon\langle\phi_l|S|\phi_l'\rangle_R &= -\frac{2\pi\hbar^2}{m}\left(\int_0^R R_l' \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} R_l \right. \\ &- \left. \int_0^R R_l \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} R_l' \right) \end{aligned}$$

Here we assume $V(r)$ had no ϵ dependence. Using partial integral

$$-\frac{\delta\epsilon m}{2\pi\hbar^2}\langle\phi_l|S|\phi_l'\rangle_R = -\left[R_l' r^2 \frac{\partial R_l}{\partial r} \right]_0^R + \int_0^R dr \frac{\partial R_l'}{\partial r} r^2 \frac{\partial R_l}{\partial r}$$

$$
\begin{aligned}
&+ \quad \left[R_l r^2 \frac{\partial R_l'}{\partial r} \right]_0^R - \int_0^R dr \frac{\partial R_l}{\partial r} r^2 \frac{\partial R_l'}{\partial r} \\
&= \quad - \left(R_l' r^2 \frac{\partial R_l}{\partial r} - R_l r^2 \frac{\partial R_l'}{\partial r} \right)_R \\
R_l' &= \quad R_l + \frac{\partial R_l}{\partial \epsilon} \delta\epsilon
\end{aligned}
$$

$$
\begin{aligned}
\text{lhs} &= -\delta\epsilon \int_0^R dr 4\pi r^2 R_l (R_l + \frac{\partial R_l}{\partial \epsilon}\delta\epsilon) \\
&\quad -\delta\epsilon \sum_{i,j} Q_{ij} \langle \phi_l | \beta_i \rangle \langle \beta_j | \phi_l + (\partial\phi_l/\partial\epsilon)\delta\epsilon \rangle_R \\
\text{rhs} &= -\frac{2\pi\hbar^2}{m} \left((R_l + \frac{\partial R_l}{\partial \epsilon}\delta\epsilon) r^2 \frac{\partial R_l}{\partial r} - R_l r^2 \frac{\partial (R_l + \frac{\partial R_l}{\partial \epsilon}\delta\epsilon)}{\partial r} \right)_R \\
&= -\frac{2\pi\hbar^2}{m} \delta\epsilon \left(r^2 \frac{\partial R_l}{\partial \epsilon} \frac{\partial R_l}{\partial r} - r^2 R_l \frac{\partial^2 R_l}{\partial \epsilon \partial r} \right)_R
\end{aligned}
$$

If we pick up the first-order of $\delta\epsilon$

$$
\begin{aligned}
\text{lhs} &= \int_0^R dr 4\pi r^2 R_l^2 + \sum_{ij} Q_{ij} \delta_{li} \delta_{lj} = \int_0^R dr 4\pi r^2 R_l^2 + Q_{ll} \\
&= \langle \phi_l | \phi_l \rangle_R + Q_{ll} = \langle \psi_l | \psi_l \rangle_R \\
\text{rhs} &= \frac{2\pi\hbar^2}{m} R^2 \left(\frac{\partial R_l}{\partial \epsilon} \frac{\partial R_l}{\partial r} - R_l \frac{\partial^2 R_l}{\partial \epsilon \partial r} \right) \\
&= \frac{2\pi\hbar^2}{m} R^2 R_l^2 \left(R_l^{-2} \frac{\partial R_l}{\partial \epsilon} \frac{\partial R_l}{\partial r} - R_l^{-1} \frac{\partial^2 R_l}{\partial \epsilon \partial r} \right) \\
&= -\frac{2\pi\hbar^2}{m} R^2 R_l^2 \frac{\partial}{\partial \epsilon} \left(R_l^{-1} \frac{\partial R_l}{\partial r} \right) \\
&= -\frac{2\pi\hbar^2}{m} R^2 R_l^2 \frac{\partial}{\partial \epsilon} \frac{\partial}{\partial r} \ln R_l
\end{aligned}
$$

2 References

1. D. R. Hamann, M. Schluter and C. Chiang, Phys. Rev. Lett. 43, 1494 (1979).

2. G. Kerker, J. Phys. C 13, L189 (1980).

3. A. Zunger and M. L. Cohen, Phys. Rev. B 18, 5449 (1978); and, 20, 4082 (1979).

4. W. E. Pickett, Comput. Phys. Rep. 9, 115 (1989).

5. D. Vanderbilt, Phys. Rev. B 32, 8412 (1985).

6. A. M. Rappe, K. M. Rabe, E. Kaxiras and J. D. Joannopoulos, Phys. Rev. B 41, 1227 (1990).

7. R. Car and M. Parrinello, Phys. Rev. Lett. 55, 2471 (1985).

8. R. Natarajan and D. Vanderbilt, J. Comput. Phys. 82, 218 (1989).

9. I. Stich, R. Car, M. Parrinello and S. Baroni, Phys. Rev. B 39, 4997 (1989).

10. X. Gonze, J. P. Vigneron and J.-P. Michenaud, J. Phys. Condens. Matter 1, 525 (1989).

11. L. Kleinman and D. M. Bylander, Phys. Rev. Lett. 48, 1425 (1982).

12. D. R. Hamann, Phys. Rev. B 40, 2980 (1989).

13. For an alternative approach, see E. L. Shirley, D. C. Allan, R. M. Martin and J. D. Joannopoulos, Phys. Rev. B 40, 3652 (1989).

14. J. C. Phillips and L. Kleinman, Phys. Rev. 116, 287 (1959).

15. S. G. Louie, S. Froyen and M. L. Cohen, Phys. Rev. B 26, 1738 (1982).

16. G. B. Bachelet, D. R. Hamann and M. Schluter, Phys. Rev. B 26, 4199 (1982).