

# Pseudopotential generation and test by the `ld1.x` atomic code: an introduction

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# Outline

- 1 All-electron radial equation
- 2 Norm-conserving pseudopotentials
  - The logarithmic derivative
  - Pseudopotential generation
  - Using the pseudopotential in the solid
  - Transferability tests
- 3 Fully separable pseudopotentials

## Spherical symmetry - I

The Kohn and Sham (KS) equation is (in atomic units):

$$\left[ -\frac{1}{2} \nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_H(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}).$$

For an atom  $V_{\text{ext}}(\mathbf{r}) = -Z/r$ , where  $Z$  is the nuclear charge and  $r = |\mathbf{r}|$ . Assuming a spherically symmetric charge density  $\rho(\mathbf{r}) = \rho(r)$ , one can show that the Hartree and exchange and correlation potentials are spherically symmetric too. In this hypothesis, the solutions of this equation have the form:

$$\psi_{nlm}(\mathbf{r}) = \frac{\psi_{nl}(r)}{r} Y_{lm}(\Omega_{\mathbf{r}}),$$

where  $(r, \Omega_{\mathbf{r}})$  are the spherical coordinates of  $\mathbf{r}$ .

## Spherical symmetry - II

Here  $n$ , the main quantum number, is a positive integer,  $0 \leq \ell \leq n - 1$  indicates the orbital angular momentum and  $-\ell \leq m \leq \ell$  its projection on a quantization axis.  $Y_{\ell m}(\Omega_{\mathbf{r}})$  are the spherical harmonics, eigenstates of  $\mathbf{L}^2$  and  $L_z$ :

$$\begin{aligned}\mathbf{L}^2 Y_{\ell m} &= \ell(\ell + 1) Y_{\ell m}, \\ L_z Y_{\ell m} &= m Y_{\ell m}.\end{aligned}$$

Inserting this solution in the KS equation, we obtain, for each value of  $\ell$ , an ordinary differential equation for  $\psi_{n\ell}(r)$ :

$$\left[ -\frac{1}{2} \frac{d^2}{dr^2} + \frac{\ell(\ell + 1)}{2r^2} + V_{KS}(r) \right] \psi_{n\ell}(r) = \epsilon_{n\ell} \psi_{n\ell}(r),$$

where  $V_{KS}(r) = V_{ext}(r) + V_H(r) + V_{xc}(r)$ .

## Spherical symmetry - III

The charge density is determined by the total number of electrons and by their distribution among the available orbitals defined by the occupation numbers  $f_{n\ell}$ . The maximum value of  $f_{n\ell}$  is 2, 6, 10, 14 for  $\ell = 0, 1, 2, 3$  (*s, p, d, f* states) respectively. Note that we assumed a spherically symmetric atom, so we cannot specify the occupation of a state with a given  $m$ . For open-shell configurations, a uniform distribution of electrons among the available orbitals is implicitly assumed. The charge density is:

$$\tilde{\rho}(r) = 4\pi r^2 \rho(r) = \sum_{n\ell} f_{n\ell} |\psi_{n\ell}(r)|^2.$$

## Spherical symmetry - IV

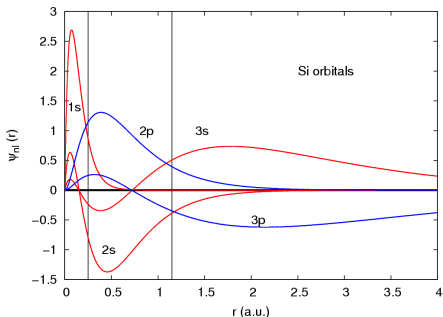
The radial equation is solved by the Numerov's method, discretizing the  $r$  coordinate by a logarithmic radial grid from  $r_{min}$  to  $r_{max}$ . The grid is:

$$r_i = \frac{1}{Z} e^{x_{min}} e^{(i-1)dx}, \quad i = 1, \dots, N_p.$$

From input, it is possible to change the default values of  $x_{min}$ ,  $dx$  and  $r_{max}$  but, usually, this is not needed.

The output of the calculation are the eigenvalues  $\epsilon_{nl}$ , the radial orbitals  $\psi_{nl}(r)$ , the charge density  $\tilde{\rho}(r)$ , and the total energy. For instance for Si, with  $Z = 14$  and the electron configuration  $1s^2 2s^2 2p^6 3s^2 3p^2$ , we obtain:

## An example: the Si atom within the LDA



n $l$	e(Ry)
1S 1( 2.00)	-130.3691
2S 1( 2.00)	-10.1489
2P 1( 6.00)	-7.0288
3S 1( 2.00)	-0.7966
3P 1( 2.00)	-0.3071

Etot = -576.383950 Ry

The orbitals can be divided into core and valence states according to the energy eigenvalues and the spatial localization about the nucleus. In Si, the 1s, 2s and 2p are core states while the 3s and 3p are valence states.

## Norm-conserving pseudopotentials - I

Let us now consider, for each orbital angular momentum  $\ell$ , the equation [1]:

$$\left[ -\frac{1}{2} \frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{2r^2} + V_{ps,\ell}(r) \right] \phi_\ell(r) = \epsilon_\ell \phi_\ell(r).$$

We would like to find an  $\ell$  dependent pseudopotential  $V_{ps,\ell}(r)$  with the following properties:

- 1) For each  $\ell$ , the lowest eigenvalue  $\epsilon_\ell$  coincides with the valence eigenvalue  $\epsilon_{n\ell}$  in the all-electron equation.  $n$  identifies the valence state.
- 2) For each  $\ell$ , it is possible to find a  $r_{c,\ell}$  such that  $\phi_\ell(r) = \psi_{n\ell}(r)$  for  $r > r_{c,\ell}$ .



## Norm-conserving pseudopotentials - II

The solution of the problem is not unique, and actually there are several recipes to construct a pseudopotential. First of all, it is convenient to note that at sufficiently large  $r$ ,  $V_{ps,\ell}(r)$  coincides with the all-electron potential because  $\phi_\ell(r) = \psi_{nl}(r)$  for  $r > r_{c,\ell}$  and  $\epsilon_\ell = \epsilon_{nl}$ . We can therefore choose a  $V_{eff}(r)$  such that  $V_{eff}(r) = V_{KS}(r)$  for  $r > r_{loc}$  and rewrite the radial equation in the form:

$$\left[ -\frac{1}{2} \frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{2r^2} + V_{eff}(r) + \Delta V_{ps,\ell}(r) \right] \phi_\ell(r) = \epsilon_\ell \phi_\ell(r).$$

Then suppose that we have a recipe to get a node-less  $\phi_\ell(r)$  for  $r < r_{c,\ell}$ . Then:

## Norm-conserving pseudopotentials - III

$$\Delta V_{ps,\ell}(r) = \frac{1}{\phi_\ell(r)} \left[ \epsilon_\ell + \frac{1}{2} \frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{2r^2} - V_{\text{eff}}(r) \right] \phi_\ell(r).$$

There are some guidelines to follow in the choice of the form of  $\phi_\ell(r)$  and one important condition. First of all the function must be as smooth as possible, with continuity of a certain number of derivatives at the matching point  $r_{c,\ell}$ . Then it is useful to search a function whose Fourier transform decays as rapidly as possible. However, the most important constraint is the norm-conserving condition [2] that is:

$$\int_0^{r_{c,\ell}} dr |\phi_\ell(r)|^2 = \int_0^{r_{c,\ell}} dr |\psi_{n,\ell}(r)|^2.$$

## The logarithmic derivative - I

In order to illustrate the importance of the norm-conserving condition, it is useful to define the concept of logarithmic derivative. Let us consider the two equations:

$$[T_\ell + V_{KS}(r)] \psi_\epsilon(r) = \epsilon \psi_\epsilon(r),$$

$$[T_\ell + V_{eff}(r) + \Delta V_{ps,\ell}(r)] \phi_\epsilon(r) = \epsilon \phi_\epsilon(r),$$

where we defined  $T_\ell = -\frac{1}{2} \frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{2r^2}$ . By construction, we know that at  $\epsilon = \epsilon_{n\ell}$ , the solution  $\phi_\epsilon(r)$  coincides with the  $\psi_\epsilon(r)$  for  $r > r_{c,\ell}$ . But what about the other energies? The transferability of the pseudopotential depends on the fact that  $\phi_\epsilon(r)$  reproduces  $\psi_\epsilon(r)$  for a certain range of energies about  $\epsilon_{n\ell}$ .

## The logarithmic derivative - II

In order to quantify the accuracy of the pseudopotential it is useful to define the logarithmic derivative at a point  $R$  close or slightly larger than  $r_{c,\ell}$ :

$$f_{\epsilon}(R) = \frac{d}{dr} \ln \phi_{\epsilon}(r) \Big|_{r=R}.$$

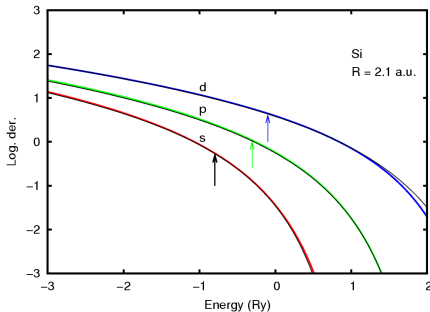
The following relationship links the derivative with respect to  $\epsilon$  of  $f_{\epsilon}(R)$  to the norm of the wavefunction up to  $R$ :

$$\phi_{\epsilon}^2(R) \frac{d}{d\epsilon} f_{\epsilon}(R) = 2 \int_0^R dr \phi_{\epsilon}^2(r)$$

so the norm-conserving condition guarantees that, at  $\epsilon_{nl}$ , the all-electron and pseudo logarithmic derivatives not only coincide but have also the same derivative with respect to the energy.

## The logarithmic derivative - III

The two logarithmic derivatives usually coincide for a quite extended range of energies, of the order of a few Rydberg making the pseudopotential concept quite useful in practice. Here is the example of the  $s$ ,  $p$  and  $d$  logarithmic derivatives for the Si atom (color: all-electron; black: pseudopotential) :



## Pseudopotential generation - I

In order to generate the pseudopotential we have to:

- 1 Choose the electronic configuration for the atom.
- 2 Define the core and valence states.
- 3 Choose the effective potential  $V_{eff}(r)$  and the radius  $r_{loc}$ .
- 4 For each  $\ell$  choose the function  $\phi_{\ell}(r)$  and  $r_{c,\ell}$ .

Points 1) and 2) are reasonably simple and one can find several suggestions and examples in the literature. Let's discuss points 3 and 4.

## Pseudopotential generation - II

In 1d1.x, there are two ways of choosing  $V_{eff}(r)$ .  $V_{eff}(r)$  can be taken as the sum of two spherical Bessel function for  $r \leq r_{loc}$ , so:

$$V_{eff}(r) = \begin{cases} V_{KS}(r) & \text{if } r \geq r_{loc} \\ a_1 j_0(q_1 r) + a_2 j_0(q_2 r) & \text{if } r \leq r_{loc} \end{cases},$$

where the parameters  $a_1$ ,  $a_2$ ,  $q_1$ ,  $q_2$  are chosen to have continuity of  $V_{eff}(r)$  and of its first two radial derivatives, or  $V_{eff}(r)$  can be calculated choosing  $\ell$  and solving the equation:

$$V_{eff}(r) = \frac{1}{\phi_\ell(r)} \left[ \epsilon_\ell + \frac{1}{2} \frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{2r^2} \right] \phi_\ell(r)$$

using one of the recipes described below for calculating  $\phi_\ell(r)$ .

## Pseudopotential generation - III

We start illustrating the Kerker method [3] for defining  $\phi_\ell(r)$ . Although this method is not implemented in `ld1.x`, it is the basis of the Troullier and Martins (TM) method. [3] In the Kerker method the wavefunction for  $r \leq r_{c,\ell}$  is given by the exponential of a polynomial multiplied by  $r^{\ell+1}$  which gives the correct behavior close to the origin:

$$\phi_\ell(r) = r^{\ell+1} e^{p(r)},$$

$$p(r) = \delta + \gamma r^2 + \beta r^3 + \alpha r^4,$$

where the four coefficients  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$  are chosen to have  $\phi_\ell(r)$  continuous with its two derivatives (three constraints) and to satisfy the norm-conserving condition (fourth constraint).



## Pseudopotential generation - IV

The Kerker recipe is quite simple and gives always node-less orbitals, but these orbitals are not optimized with respect to the number of plane waves required in the solid. Therefore the next two recipes are preferred. TM improves the Kerker method choosing a higher order polynomial:

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

There are now seven parameters, so that three additional constraints can be imposed. TM require that  $\phi_\ell(r)$  has also the third and fourth derivatives continuous, and that  $V_{eff}(r) + \Delta V_{ps,\ell}(r)$  has zero curvature at the origin, a condition that they find particularly useful to reduce the required cut-off energy in the solid.

## Pseudopotential generation - V

The Rappe, Rabe, Kaxiras and Joannopoulos (RRKJ) method [4] is an alternative to the TM method. In this method  $\phi_\ell(r)$  is expanded into spherical Bessel functions of order  $\ell$  for  $r \leq r_{c,\ell}$ :

$$\phi_\ell(r) = \sum_{i=1}^3 \alpha_i r j_\ell(q_i r).$$

The parameters  $q_i$  are determined so that the  $r j_\ell(q_i r)$  have the same logarithmic derivative as  $\psi_{nl}(r)$  at  $r_{c,\ell}$ . Using three functions, four conditions as in the Kerker method can be satisfied. The RRKJ orbitals are quite efficient requiring a low cut-off energy in the solid. However, the orbitals are not guaranteed to be node-less and sometimes the allowed values of  $r_{c,\ell}$  are too restricted.

## Using the pseudopotential in the solid - I

In order to use the pseudopotential in the solid we have to subtract from  $V_{eff}(r)$  the Hartree and exchange and correlation potentials.

$$V_{loc}(r) = V_{eff}(r) - V_H(r) - V_{xc}(r).$$

Usually only the valence atomic charge is used to calculate  $V_H(r)$  and  $V_{xc}(r)$ . This however can introduce a significant error if there is a large overlap of the core and valence charge. In this case it is also possible to use the total charge  $\rho_c(r) + \rho_v(r)$  in the calculation of  $V_{xc}(r)$ . The technique is known as nonlinear core correction. In order to improve the plane wave convergence a pseudized version of  $\rho_c(r)$  is generally used for  $r \leq r_{core}$ .

## Using the pseudopotential in the solid - II

$V_{loc}(r)$  behaves as  $-Z_V/r$  for large  $r$ , while  $\Delta V_{ps,l}(r)$  is localized and goes to zero for  $r \geq \max(r_{loc}, r_{c,l})$ . In order to apply the nonlocal part of the potential, that is different for different  $\ell$ , we use projectors into subspaces of well defined  $\ell$ :

$$P_\ell = \sum_{m=-\ell}^{m=\ell} |Y_{\ell m}\rangle \langle Y_{\ell m}|.$$

## Using the pseudopotential in the solid - III

Therefore the resulting potential is nonlocal (actually it is called semilocal because it is local in the radial variable and nonlocal in the angular variables). We can write:

$$\begin{aligned}
 V_{ps}(\mathbf{r}, \mathbf{r}') &= \sum_I V_{loc}^I(|\mathbf{r} - \mathbf{R}_I|) \delta(\mathbf{r} - \mathbf{r}') \\
 &+ \sum_I \sum_{lm} \Delta V_{ps,\ell}^I(|\mathbf{r} - \mathbf{R}_I|) \delta(|\mathbf{r} - \mathbf{R}_I| - |\mathbf{r}' - \mathbf{R}_I|) \\
 &\times Y_{\ell m}(\Omega_{\mathbf{r}-\mathbf{R}_I}) Y_{\ell m}^*(\Omega_{\mathbf{r}'-\mathbf{R}_I}).
 \end{aligned}$$

Note that  $V_{loc}(\mathbf{r})$  is applied to all angular momenta larger than  $\ell_{max}$ , the maximum angular momentum included in the nonlocal part.

## Transferability tests - I

The energy range in which the logarithmic derivatives coincide give an estimate of the pseudopotential quality. However, the logarithmic derivative is calculated at fixed charge density. Before using the pseudopotential in the solid, we can check its transferability on the atom by predicting the eigenvalues and the total energy of atomic configurations different from the reference one used for the generation. We can also check spin-polarized atomic configurations. An accuracy of a few mRy on the eigenvalues of atomic configurations that differ in energy up to a few Ry from the reference configuration is within the possibilities of the method. As an example, in Si, we can check the configuration  $3s^1 3p^3$  and the spin-polarized configuration  $3s^2 3p^2$ . We find:

## Transferability tests - II

n	l	s	f_nl	e_AE (Ry)	e_PS (Ry)	diff
1	0	3S	1( 2.00)	-0.79663	-0.79663	0.00000
2	1	3P	1( 2.00)	-0.30705	-0.30705	0.00000
Etot =		-576.383950 Ry,		-288.191975 Ha,	-7842.102455 eV	
Etotps =		-9.254121 Ry,		-4.627060 Ha,	-125.908713 eV	
1	0	3S	1( 1.00)	-0.85139	-0.85190	0.00051
2	1	3P	1( 3.00)	-0.34907	-0.34898	-0.00009
dEtot_ae =		0.496095 Ry				
dEtot_ps =		0.496377 Ry,		Delta E=	-0.000282 Ry	
1	0	3S	1( 1.00)	-0.83109	-0.83154	0.00045
2	1	3P	1( 2.00)	-0.33829	-0.33867	0.00038
1	0	3S	2( 1.00)	-0.72857	-0.72723	-0.00134
2	1	3P	2( 0.00)	-0.24627	-0.24521	-0.00106
dEtot_ae =		-0.044949 Ry				
dEtot_ps =		-0.045683 Ry,		Delta E=	0.000733 Ry	

## Fully separable pseudopotentials - I

The semilocal form of the pseudopotential is not very efficient for practical calculations. It requires to keep in memory the matrix  $\langle \mathbf{k} + \mathbf{G} | V_{ps} | \mathbf{k} + \mathbf{G}' \rangle$  that becomes rapidly big for large systems and matrix-vector multiplications to apply it to the wavefunctions. It is convenient to write the nonlocal part of the pseudopotential in the fully separable form [5]:

$$V_{NL}(\mathbf{r}, \mathbf{r}') = \sum_l \sum_{\ell m} E_l^l \langle \mathbf{r} | \beta_l^l Y_{\ell,m}^l \rangle \langle \beta_l^l Y_{\ell,m}^l | \mathbf{r}' \rangle.$$

In this way we can keep in memory only the vectors  $\langle \mathbf{k} + \mathbf{G} | \beta_l^l Y_{\ell,m}^l \rangle$  which are the Fourier transform of  $\langle \mathbf{r} | \beta_l^l Y_{\ell,m}^l \rangle$  and to apply the nonlocal pseudopotential by doing a few scalar products with the vectors which represent the wavefunction.



## Fully separable pseudopotentials - II

In the atom, we can define  $\beta_\ell(r) = \Delta V_{ps,\ell}(r)\phi_\ell(r)$  and  $E_\ell = [\int_0^\infty dr \phi_\ell(r)\Delta V_{ps,\ell}(r)\phi_\ell(r)]^{-1}$  so that the fully separable potential:

$$V_{NL} = E_\ell |\beta_\ell\rangle \langle \beta_\ell|$$

has the following property:

$$\langle r | V_{NL} | \phi_\ell \rangle = \Delta V_{ps,\ell}(r) \phi_\ell(r).$$

As a consequence, the equation

$$[T_\ell + V_{eff}(r)] \Phi_\ell(r) + \langle r | V_{NL} | \Phi_\ell \rangle = \epsilon \Phi_\ell(r)$$

has  $\epsilon_\ell$  as an eigenvalue and  $\phi_\ell(r)$  as an eigenfunction.

## Fully separable pseudopotentials - III

Note that this is an integro-differential equation, so although the node-less function  $\phi_\ell(r)$  is an eigenfunction with eigenvalue  $\epsilon_\ell$ , there is no guarantee that this is the lowest energy eigenvalue. Actually states with some nodes with energies below the node-less solution are known as *ghost states* and must be carefully avoided in the pseudopotential construction. They can be detected as peaks present only in the pseudo logarithmic derivative and can usually be removed by changing  $V_{eff}(r)$  or  $r_{c,\ell}$ .

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