

Modern pseudopotentials: an introduction

Andrea Dal Corso

SISSA and DEMOCRITOS
Trieste (Italy)

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Modern pseudopotentials: an overview

Modern pseudopotentials are constructed on the isolated atom. The radial Kohn and Sham equations are first solved for all the electrons. Then the orbitals are divided into core and valence, and for the valence orbitals a pseudopotential that reproduces the all-electron results is calculated.

Modern pseudopotentials are divided in three types:

- Norm-conserving pseudopotentials
- Ultrasoft pseudopotentials
- The projector augmented-wave data sets

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:

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

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 ℓ , 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

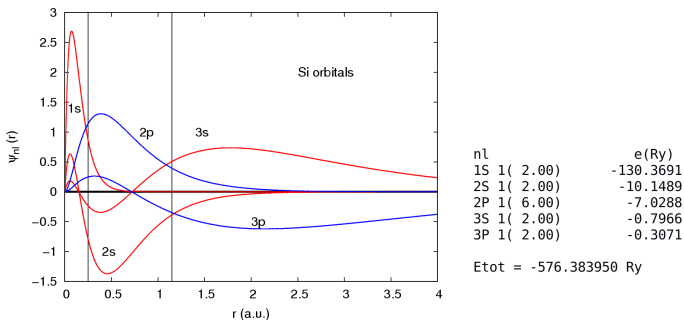
The radial equation is solved by the Numerov's method, discretizing the r coordinate by a logarithmic radial grid from r_{min} to r_{max} . The grid is:

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

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 $\epsilon_{n\ell}$, the radial orbitals $\psi_{n\ell}(r)$, 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



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 ℓ , 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 ℓ dependent pseudopotential $V_{ps,\ell}(r)$ with the following properties:

- 1) For each ℓ , the lowest eigenvalue ϵ_ℓ coincides with the valence eigenvalue $\epsilon_{n\ell}$ in the all-electron equation. n identifies the valence state.
- 2) For each ℓ , 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

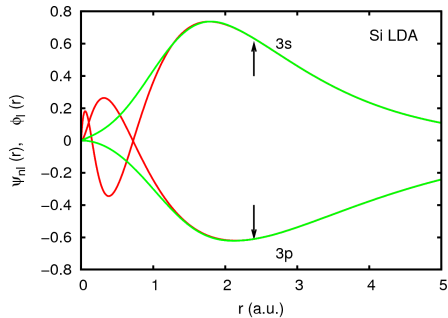
$$\Delta V_{ps,\ell}(r) = \frac{1}{\phi_\ell(r)} \left[\epsilon_\ell + \frac{1}{2} \frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{2r^2} - V_{eff}(r) \right] \phi_\ell(r).$$

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:

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

An example: Si

An example: the wavefunctions of Si.



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:

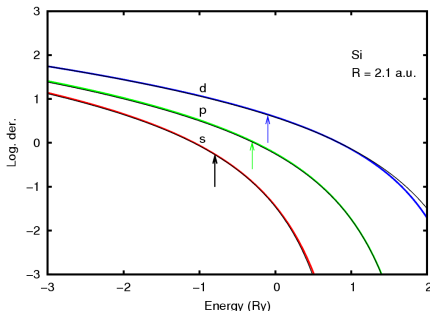
$$[T_\ell + V_{KS}(r)] \psi_\epsilon(r) = \epsilon \psi_\epsilon(r),$$

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

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

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) :



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 ℓ , we use projectors into subspaces of well defined ℓ :

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

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 ℓ_{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:

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

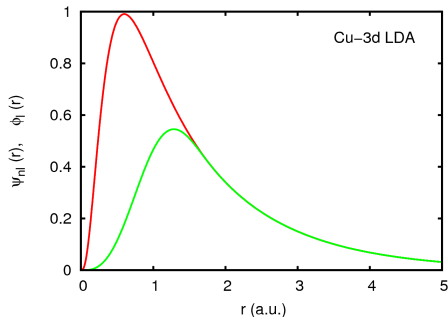
As a consequence, the equation

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

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

Ultrasoft pseudopotentials - I

What about fitting the pseudopotential at more than one energy for each ℓ ? This is possible and one can also relax the norm-conserving condition:



But the orbitals obey a generalized orthogonality constraint:

$$\langle \tilde{\psi}_i | \mathbf{S} | \tilde{\psi}_j \rangle = \delta_{ij}$$

Ultrasoft pseudopotentials - II

The resulting Hamiltonian is the following:

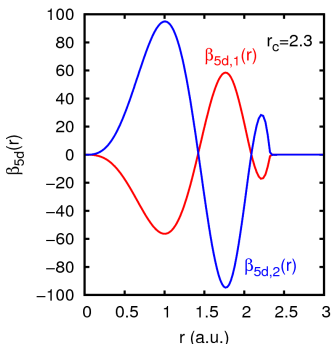
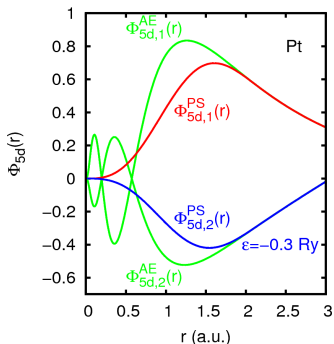
$$H = -\frac{1}{2}\nabla^2 + \tilde{V}_{eff}(\mathbf{r}) + \sum_{l,mn} \left(\int d^3r \tilde{V}_{eff}(\mathbf{r}) Q'_{mn}(\mathbf{r}) + D_{l,mn}^{(0)} \right) |\beta'_m\rangle \langle \beta'_n|,$$

and one solves a generalized eigenvalue equation:

$H|\tilde{\psi}_i\rangle = \varepsilon_i \mathbf{S}|\tilde{\psi}_i\rangle$. The functions $Q'_{mn}(\mathbf{r})$ are used to recover the correct charge density:

$$\rho(\mathbf{r}) = \sum_i |\tilde{\psi}_i(\mathbf{r})|^2 + \sum_{l,mn} Q'_{mn}(\mathbf{r}) \langle \tilde{\psi}_i | \beta'_m \rangle \langle \beta'_n | \tilde{\psi}_i \rangle$$

PAW mapping: from pseudo-wave-functions to all-electron wave-functions



$$\langle \beta_m^I | \Phi_n^{I,PS} \rangle = \delta_{mn}$$

$$\sum_n |\beta_n^I\rangle \langle \Phi_n^{I,PS} | = \mathbf{1}$$

$$|\Psi_i\rangle = |\tilde{\Psi}_i\rangle + \sum_{l,m} \left[|\Phi_m^{l,AE}\rangle - |\Phi_m^{l,PS}\rangle \right] \langle \beta_m^l | \tilde{\Psi}_i \rangle.$$

PAW Hamiltonian

In the PAW scheme one still solves a generalized eigenvalue equation $(H - \epsilon_j \mathbf{S})|\tilde{\psi}_j\rangle = 0$, with the Hamiltonian

$$H = -\frac{1}{2}\nabla^2 + \tilde{V}_{\text{eff}} + \sum_{l,mn} \left(\int d^3r \tilde{V}_{\text{eff}}(\mathbf{r}) Q'_{mn}(\mathbf{r}) + D'_{l,mn} - \tilde{D}'_{l,mn} \right) |\beta'_m\rangle \langle \beta'_n|,$$

where

$$D'_{l,mn} = \langle \phi_m^{l,AE} | \frac{\mathbf{p}^2}{2} + V'_{\text{eff}} | \phi_n^{l,AE} \rangle,$$

$$\tilde{D}'_{l,mn} = \langle \phi_m^{l,PS} | \frac{\mathbf{p}^2}{2} + \tilde{V}'_{\text{eff}} | \phi_n^{l,PS} \rangle + \int_{\Omega_l} d^3r \hat{Q}'_{mn}(\mathbf{r}) \tilde{V}'_{\text{eff}}(\mathbf{r}).$$

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