

Vanderbilt ultrasoft pseudopotentials

Jürg Hutter
MPI für Festkörperforschung
Stuttgart

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Norm-conserving pseudopotentials

The Schrödinger equation for an atom

$$(T + V_{AE}) |\Psi_l\rangle = \epsilon_l |\Psi_l\rangle$$

is replaced by a valence electron only equation.

$$(T + V_{val}) |\Phi_l\rangle = \hat{\epsilon}_l |\Phi_l\rangle$$

Hamann-Schlüter-Chiang-Recipe (HSC)

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

The pseudopotential should have the following properties

1. Real and pseudo valence eigenvalues agree for a chosen prototype atomic configuration. $\epsilon_l = \hat{\epsilon}_l$
2. Real and pseudo atomic wave functions agree beyond a chosen core radius r_c .

$$\Psi_l(r) = \Phi_l(r) \quad \text{for } r \geq r_c$$

3. The integrals from 0 to R of the real and pseudo charge densities agree for $R \geq r_c$ for each valence state (norm conservation).

$$\langle \Phi_l | \Phi_l \rangle_R = \langle \Psi_l | \Psi_l \rangle_R \quad \text{for } R \geq r_c$$

where

$$\langle \Phi | \Phi \rangle_R = \int_0^R r^2 |\phi(r)|^2 dr$$

4. The logarithmic derivatives of the real and pseudo wave function and their first energy derivatives agree for $r \geq r_c$.

Property 3) and 4) are related through

$$-\frac{1}{2} \left[(r\Phi)^2 \frac{d}{d\epsilon} \frac{d}{dr} \ln \Phi \right]_R = \int_0^R r^2 |\Phi|^2 dr$$

Construction of pseudopotentials

1.

$$V_l^{(1)}(r) = V_{AE}(r) \left[1 - f_1 \left(\frac{r}{r_{cl}} \right) \right]$$

r_{cl} : core radius $\approx 0.4 - 0.6 R_{max}$, where R_{max} is the outermost maximum of the real wave function.

2.

$$V_l^{(2)}(r) = V_l^{(1)}(r) + c_l f_2 \left(\frac{r}{r_{cl}} \right)$$

determine c_l so that $\hat{\epsilon}_l = \epsilon_l$ in

$$(T + V_l^{(2)}(r))w_l^{(2)}(r) = \hat{\epsilon}_l w_l^{(2)}(r)$$

3.

$$\Phi_l(r) = \gamma_l \left[w_l^{(2)}(r) + \delta_l r^{l+1} f_3 \left(\frac{r}{r_{cl}} \right) \right]$$

where γ_l and δ_l are chosen such that

$$\Phi_l(r) \rightarrow \Psi_l(r) \quad \text{for } r \geq r_{cl}$$

and

$$\gamma_l^2 \int |w_l^{(2)}(r) + \delta_l r^{l+1} f_3 \left(\frac{r}{r_{cl}} \right)|^2 dr = 1$$

4. Invert the Schrödinger equation for $\hat{\epsilon}_l$ and $\Phi_l(r)$ to get $V_{val}^l(r)$.5. Unscreen $V_{val}^l(r)$ to get $V_{ps}^l(r)$.

$$V_{ps}^l(r) = V_{val}^l(r) - V_H(\rho_v) - V_{xc}(\rho_v)$$

where $V_H(\rho_v)$ and $V_{xc}(\rho_v)$ are the Hartree and exchange and correlation potentials of the pseudo valence density.

Hamann, Schlüter and Chiang chose $f_1(x) = f_2(x) = f_3(x) = \exp(-x^4)$.

The total pseudopotential in a solid state calculation then takes the form

$$V_{ps}(r) = \sum_L V_{ps}^L(r) \mathcal{P}_L$$

where L is a combined index $\{l, m\}$ and \mathcal{P}_L is the projector on the angular momentum state $\{l, m\}$.

Bachelet-Hamann-Schlüter (BHS) form

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

These authors proposed an analytic fit to the pseudopotentials generated by the HSC recipe.

$$\begin{aligned}
 V_{ps}(r) &= V_{core}(r) + \sum_L \Delta V_L^{ion}(r) \\
 V_{core}(r) &= -\frac{Z_v}{r} \left[\sum_{i=1}^2 c_i^{core} \operatorname{erf} \left((\alpha_i^{core})^{(1/2)} r \right) \right] \\
 \Delta V_L^{ion}(r) &= \sum_{i=1}^3 \left(A_i + r^2 A_{i+3} \right) \exp(-\alpha_i r^2)
 \end{aligned}$$

Kerker-Recipe

G.P. Kerker, J. Phys. C: Solid State Phys., **13**, L189 (1980)

In this approach pseudopotentials with the HSC properties are constructed. But instead of using cutoff functions (f_1, f_2, f_3) the pseudo wave functions are directly constructed from the all electron wave functions by replacing the all electron wave function inside some cutoff radius by a smooth analytic function that is matched to the all electron wave function at the cutoff radius. The HSC properties then translate into a set of equations for the parameters of the analytic form. After having determined the pseudo wave function the Schrödinger equation is inverted and the resulting potential unscreened.

Some new approaches

Several authors used slightly different approaches from the HSC- and Kerker-recipes. They mainly tried to achieve faster convergence of the Fourier transform of the pseudopotential by changing the form of the cutoff functions.

- D. Vanderbilt, Phys. Rev. B, **32**, 8412 (1985)
- A.M. Rappe, K.M. Rabe, E. Kaxiras, and J.D. Joannopoulos, Phys. Rev. B, **41**, 1227 (1990)

- N. Troullier and J.L. Martins, Phys. Rev. B, **43**, 1993 (1991)
- J.S. Lin, A. Qteish, M.C. Payne, and V. Heine, Phys. Rev. B, **47**, 4174 (1993)

Kleinman-Bylander form

L. Kleinman and D.M. Bylander, Phys. Rev. Lett., **48**, 1425 (1982)
 The HSC form of a pseudopotential is semi local. It is difficult to compute in solid state plane wave calculations. The idea of Kleinman and Bylander was to replace the HSC form by a fully nonlocal but separable form. First we separate a local part from the pseudopotential.

$$V^{PS}(\mathbf{r}) = V_{loc}^{PS}(r) + \sum_L \left(V_L^{PS}(r) - V_{loc}^{PS}(r) \right) \mathcal{P}_L$$

In principle this separation is totally arbitrary, but for plane wave calculations it is most efficient to combine it with the approximation of constant potential for high L values.

$$V_L^{PS}(r) = V_{loc}^{PS}(r) \quad \text{for } L \geq L_{max}$$

Then, we can write the pseudopotential

$$V^{PS}(\mathbf{r}) = V_{L_{max}}^{PS}(r) + \sum_L^{L_{max}-1} \delta V_L(r) \mathcal{P}_L$$

where

$$\delta V_L(r) = V_L^{PS}(r) - V_{L_{max}}^{PS}(r)$$

Replace $\delta V_L(r)$ by $V_{NL}^L(r)$ of the form

$$V_{NL}^L(r) = \frac{|\delta V_L \Phi_L\rangle \langle \Phi_L \delta V_L|}{\langle \Phi_L | \delta V_L | \Phi_L \rangle}$$

We see that

$$V_{NL}^L(r) |\Phi_L\rangle = \frac{|\delta V_L \Phi_L\rangle}{\langle \Phi_L | \delta V_L | \Phi_L \rangle} \langle \Phi_L \delta V_L | \Phi_L \rangle$$

and

$$\sum_{L'} \delta V_{L'} \mathcal{P}_{L'} |\Phi_L\rangle = \delta V_L |\phi_L\rangle |Y_L\rangle = |\delta V_L \Phi_L\rangle$$

with $|\Phi_L\rangle = |\phi_L\rangle|Y_L\rangle$.

$$V_{NL}^L(r)|\Phi_L\rangle = \sum_L^{Lmax-1} \delta V_L(r) \mathcal{P}_L |\Phi_L\rangle$$

The Kleinman-Bylander form is equivalent to the HSC form in atomic calculations but acts differently in a solid state environment where wave functions have contributions of all angular momenta at a given atom.

Generalized norm-conserving pseudopotentials

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

In the HSC recipe the pseudization is done at the bound state energies ϵ_l . To get pseudopotentials for non-bound states, calculations of excited states have to be performed (e.g. to get the d state pseudopotential in silicon). To avoid calculations of excited states Hamann proposed a scheme that allows the construction of pseudopotentials at any given energy.

1. calculate the all electron wave function Ψ_l for a given ϵ_l . If ϵ_l is not an eigenvalue of the atomic Schrödinger equation Ψ_l is unbound. In this case pick r_{cl} and $R_l \approx 2.5r_{cl}$ and normalize

$$\langle \Psi_l | \Psi_l \rangle_{R_l} = 1$$

- 2.

$$V_l^{(2)}(r) = \left[\left(1 - f_1 \left(\frac{r}{r_{cl}} \right) \right) V_{AE}(r) + c_l f_2 \left(\frac{r}{r_{cl}} \right) \right]$$

determine c_l from

$$\frac{\dot{\Psi}_l}{\Psi_l} \Big|_{R_l} = \frac{\dot{w}_l^{(2)}}{w_l^{(2)}} \Big|_{R_l}$$

3. equivalent to HSC
4. equivalent to HSC
5. equivalent to HSC

Kleinman-Bylander form of GNCCP's

Problem: Is $\langle \Phi_l \delta V_l \Phi_l \rangle$ defined even if Φ_l is unbound?

Yes, if $\delta V_l(r)$ goes faster to zero for $r \rightarrow \infty$ than $|\Phi_l|^2$. This is the case for our choice of V_{loc} .

Generalized separable potentials

- P.E. Blöchl, Phys. Rev. B, **41**, 5414 (1990)
- D. Vanderbilt, Phys. Rev. B, **41**, 7892 (1990)

We expand the potential δV in a set of functions $|\chi_i\rangle$

$$V_{NL} = \sum_{ij} |\chi_i\rangle (B^{-1})_{ij} \langle \chi_j|$$

$$|\chi_i\rangle = |\delta V \Phi_i\rangle$$

with

$$\sum_k B_{ik} \langle \Phi_k | \delta V \Phi_j \rangle = \delta_{ij}$$

If we take only one term in the expansion, then $B = 1/\langle \Phi | \delta V \Phi \rangle$ and we recover the original Kleinman-Bylander form.

It is not necessary to first construct a HSC type pseudopotential but it is possible to directly generate a nonlocal pseudopotential.

1. Choose a set of pseudo wave functions $|\Phi_i\rangle$ which match the all electron wave function at a set of energies ϵ_i outside a radius r_c . Enforce the norm-conservation property.

$$\langle \Phi_i | \Phi_j \rangle_R = \langle \Psi_i | \Psi_j \rangle_R$$

2. Choose a smooth local potential that matches the true atomic potential outside r_c .
3. Construct the inside r_c localized function

$$|\chi_i\rangle = [\epsilon_i - T - V_{loc}] |\Phi_i\rangle$$

4. Calculate B from

$$\sum_k B_{ik} \langle \Phi_i | \chi_j \rangle = \delta_{ij}$$

and

$$V_{NL} = \sum_{ij} (B^{-1})_{ij} |\chi_i\rangle \langle \chi_j|$$

or with $|\beta_i\rangle = \sum_j (B^{-1})_{ji} |\chi_j\rangle$

$$V_{NL} = \sum_{ij} B_{ij} |\beta_i\rangle \langle \beta_j|$$

Vanderbilt's ultrasoft pseudopotentials

- D. Vanderbilt, Phys. Rev. B, **41**, 7892 (1990)

If we don't enforce the norm-conserving property $q_{ij} = 0$, where

$$q_{ij} = \langle \Psi_i | \Psi_j \rangle_R - \langle \Phi_i | \Phi_j \rangle_R$$

then we can define a nonlocal overlap operator

$$\hat{S} = 1 + \sum_{ij} q_{ij} |\beta_i\rangle \langle \beta_j|$$

and we get

$$\begin{aligned} \langle \Phi_i | \hat{S} | \Phi_j \rangle_R &= \langle \Phi_i | \Phi_j \rangle_R + \sum_{kl} kl \langle \Phi_i | \beta_k \rangle \langle \beta_l | \Phi_j \rangle_R \\ &= \langle \Phi_i | \Phi_j \rangle_R + \sum_{kl} kl q_{kl} \delta_{ik} \delta_{jl} \\ &= \langle \Phi_i | \Phi_j \rangle_R + q_{ij} \\ &= \langle \Psi_i | \Psi_j \rangle_R \end{aligned}$$

where we have used that $|\beta_i\rangle$ are duals to $|\Phi_i\rangle$.

$$\begin{aligned} \langle \beta_l | \Phi_j \rangle_R &= \sum_k (B^{-1})_{kl} \langle \chi_k | \Phi_j \rangle_R \\ &= \sum_k (B^{-1})_{kl} B_{jk} \\ &= \delta_{lj} \end{aligned}$$

Within this new metric, the $|\Phi_i\rangle$ have to be solutions to the generalized eigenvalue equation

$$(T + V_{loc} + V_{NL} - \epsilon_i \hat{S})|\Phi_i\rangle = 0$$

Making an ansatz in the usual form for the nonlocal potential

$$V_{NL} = \sum_{ij} D_{ij} |\beta_i\rangle \langle \beta_j|$$

we get

$$(T + V_{loc} + \sum_{nm} D_{nm} |\beta_n\rangle \langle \beta_m|)|\Phi_i\rangle = \epsilon_i (1 + \sum_{nm} q_{nm} |\beta_n\rangle \langle \beta_m|)|\Phi_i\rangle$$

Making use of the definition of $|\chi_i\rangle$

$$(-T - V_{loc} + \epsilon_i)|\Phi_i\rangle = |\chi_i\rangle$$

and the dual property of $|\beta_i\rangle$ and $|\Phi_i\rangle$ we get

$$\begin{aligned} \sum_n (D_{ni} - \epsilon_i q_{ni}) |\beta_n\rangle &= |\chi_i\rangle \\ \sum_{nk} (D_{ni} - \epsilon_i q_{ni}) (B^{-1})_{kn} |\chi_k\rangle &= |\chi_i\rangle \end{aligned}$$

The last equation can be fulfilled by choosing

$$D_{nm} = B_{nm} + \epsilon_m q_{nm}.$$

The valence electron density is defined by

$$\begin{aligned} n_v(r) &= \sum_i |\Phi_i(r)|^2 + \sum_{kl} \rho_{kl} Q_{kl}(r) \\ \rho_{kl} &= \sum_i \langle \beta_k | \Phi_i \rangle \langle \Phi_i | \beta_l \rangle \\ Q_{ij}(r) &= \Psi_i^*(r) \Psi_j(r) - \Phi_i^*(r) \Phi_j(r) \end{aligned}$$

Unscreening the pseudopotentials leads to

$$\begin{aligned} V_{loc}^{ion} &= V_{loc} - V_H(n_v) - V_{xc}(n_v) \\ D_{ij}^{ion} &= D_{ij} - \int V_{loc} n_v dr \end{aligned}$$

Construction of the pseudo electron charge density

In a plane wave calculation with norm-conserving pseudopotentials the relation

$$E_c^{dens} = 4E_c^{wf}$$

is strictly fulfilled. In the ultrasoft scheme this is only true for the charge coming from the pseudo wave functions. The augmentation charge density might not be converged within a cutoff of $4 E_c^{wf}$. To avoid the complication of having yet another cutoff for this part of the calculation one tries to pseudize the functions $Q_{nm}(r)$.

This is achieved by decomposing the Q_{nm} according to angular momentum L

$$Q_{nm}(r) = \sum_{LM} c_{LM}^{nm} Y_{LM} Q_{nm}^{rad}(r)$$

where c_{LM}^{nm} are Clebsch-Gordan coefficients. In a next step the L-independent functions Q_{nm}^{rad} are replaced by L-dependent functions and these functions are pseudized below a certain cutoff r_{in} .

Ultrasoft pseudopotentials are fully determined by the quantities $V_{loc}^{ion}(r)$, D_{nm}^{ion} , $Q_{nm}(r)$, and $\beta_n(r)$. The generation of these quantities is characterized by the three cutoff radii

r_{loc} : cutoff radius for local pseudopotential

r_{cut} : cutoff radius for nonlocal pseudopotential

r_{in} : pseudization radius for augmentation charge

Ultrasoft pseudopotentials in CPMD

We assume that we can describe the augmentation charges with the same cutoff as the soft part of the density. The Fourier transform of $|\beta\rangle$ and $Q_{nm}^L(r)$ are calculated in a initialization phase. Whenever needed the functions $Q_{nm}(G)$ are calculated from

$$Q_{nm}(G) = \sum_{LM} c_{LM}^{nm} Y_{LM}(\hat{\Theta}, \hat{\phi}) Q_{nm}^L(G)$$

The augmentation part of the charge is calculated in G-space, transformed to real space and added to the total charge.

$$n^{aug}(G) = \sum_{Inm} \left(\sum_i f_i \langle \Phi_i | \beta_i^I \rangle \langle \beta_m^I | \Phi_i \rangle \right) Q_{nm}(G) \exp(-iGR_I)$$

The screened functions D_{nm}^I are calculated in every iteration from

$$D_{nm}^I = D_{nm}^{ion} + \Omega \sum_G (V_{eff}(G) Q_{nm}^*(G) \exp(-iGR_I))$$

where

$$V_{eff}(r) = V_{loc}^{ion}(r) + V_H(r) + V_{xc}(r)$$

Total energy

$$\begin{aligned} E_{tot} &= \sum_i \langle \Phi_i | -\nabla^2 + V_{NL} | \Phi_i \rangle \\ &+ \frac{1}{2} \int V_H(r) n(r) dr + E_{xc}(n) + \int V_{loc}^{ion}(r) n(r) dr + U(R_I) \end{aligned}$$

Wave function forces

The ground state orbitals are those which minimize the total energy under the generalized orthonormality constraint.

$$\frac{\delta E_{tot}}{\delta \Phi_i^*(r)} = \epsilon_i \hat{S} \Phi_i(r)$$

This equation reduces to the form

$$\begin{aligned} H | \Phi_i \rangle &= \epsilon_i \hat{S} \Phi_i(r) \\ H &= -\nabla^2 + V_{eff} + \sum_{Inm} D_{nm}^I | \beta_n^I \rangle \langle \beta_m^I | \end{aligned}$$

Where the local parts of the functional derivatives are collected in V_{eff} and the nonlocal parts add up to D_{nm}^I .

$$\begin{aligned} \frac{\delta E_{xc}(n)}{\delta \Phi_i^*(r)} &= \int dr' \frac{\delta E_{xc}(n)}{\delta n(r')} \frac{\delta n(r')}{\delta \Phi_i^*(r)} \\ &= \mu_{xc}(r) \Phi_i(r) + \sum_{Inm} \beta_n^I(r) \langle \beta_m^I | \Phi_i \rangle \int dr' \mu_{xc}(r') Q_{nm}^I(r') \\ \frac{\delta E_H(n)}{\delta \Phi_i^*(r)} &= V_H(r) \Phi_i(r) + \sum_{Inm} \beta_n^I(r) \langle \beta_m^I | \Phi_i \rangle \int dr' V_H(r') Q_{nm}^I(r') \\ \frac{\delta E_{loc}(n)}{\delta \Phi_i^*(r)} &= V_{loc}^{ion}(r) \Phi_i(r) + \sum_{Inm} \beta_n^I(r) \langle \beta_m^I | \Phi_i \rangle \int dr' V_{loc}^{ion}(r') Q_{nm}^I(r') \end{aligned}$$

Ionic forces

Derivative of the overlap matrix.

$$\begin{aligned} \langle \Phi_i | \frac{\partial \hat{S}}{\partial R_I} | \Phi_j \rangle &= \sum_{Inm} q_{nm}^I \frac{\partial}{\partial R_I} \left(\langle \Phi_i | \beta_n^I \rangle \langle \beta_m^I | \Phi_i \rangle \right) \\ &= \sum_{nm} q_{nm}^I \left(\langle \Phi_i | \frac{\partial \beta_n^I}{\partial R_I} \rangle \langle \beta_m^I | \Phi_i \rangle + \langle \Phi_i | \beta_n^I \rangle \langle \frac{\partial \beta_m^I}{\partial R_I} | \Phi_i \rangle \right) \end{aligned}$$

The new terms in the force are

$$F_I^{VDB} = - \int dr V_{eff} \sum_{nm} \frac{\partial Q_{nm}^I}{\partial R_I} - \sum_{nm} D_{nm}^I \frac{\partial \rho_{nm}^I}{\partial R_I}$$

where

$$\begin{aligned} \rho_{nm}^I &= \sum_i \langle \Phi_i | \beta_n^I \rangle \langle \beta_m^I | \Phi_i \rangle \\ \frac{\partial \rho_{nm}^I}{\partial R_I} &= \sum_i \left[\langle \Phi_i | \frac{\partial \beta_n^I}{\partial R_I} \rangle \langle \beta_m^I | \Phi_i \rangle + \langle \Phi_i | \beta_n^I \rangle \langle \frac{\partial \beta_m^I}{\partial R_I} | \Phi_i \rangle \right] \end{aligned}$$