Pseudopotentials for interacting atoms

Extended capabilities of pseudopotential approach based on all-electron pseudopotentials

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What is pseudopotential:

operator simulating the effect (within LDA):
of [NUCLEUS + CORE ELECTRONS]
on electronic states
in the energy range of interest, e.g. valence states,
unoccupied states (LDA!) (i.e. not on any state !!!)
in the real-space region significant for chemical bonds

Requirements, expected properties:

- “sufficient” accuracy in wide energy range (transferability)
- real merit to computational efficiency and/or accuracy
  - by reducing the basis set size (compared to AE)
  - by eliminating large energies of core states

Standard pseudopotentials - history

- *Empirical pseudopotentials*
  parameters tuned so that PSP give “good results” for some particular structure; then PSP is assumed to be transferable to another structure
- *Ab-initio pseudopotentials*
  1. free atom calculation; for the atomic state of interest
  2. construct pseudowavefunction for a given l and E

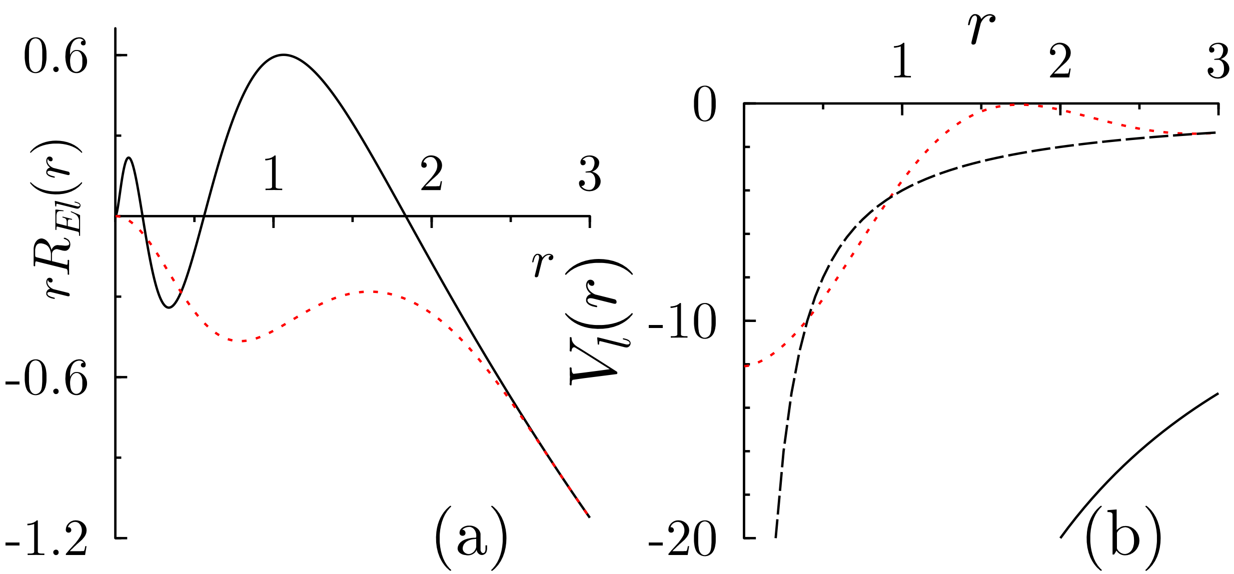
$$\psi_{l,E}^{\mathrm{PS}}(r) \equiv \psi_{l,E}^{\mathrm{AE}}(r), \quad r > R_C$$

  3. obtain pseudopotentials by inverted Schrödinger (Dirac) equation
  4. “unscreen”: $V_l^{\mathrm{ion}}(r) = V_l^{\mathrm{scr}}(r) - V_{\mathrm{H,XC}}\left[\rho^{\mathrm{ps}}\right](r)$.

Ab-initio pseudopotential

- *Norm-conserving pseudopotentials*
  Top and Hopfield [1973], Hamann et al[1979]

$$\left.\frac{\partial}{\partial \epsilon}\frac{\partial}{\partial r}\ln \psi_{\epsilon,l}(r)\right|_{\epsilon=E,r=R_C} = \frac{-2}{R_C^2\psi_{E,l}^2(R_C)}\int_0^{R_C}\left|\psi_{E,l}(r)\right|^2 r^2 dr$$



norm-conserving PSP - continued

$$\int_0^{R_C} \left|\psi^{\mathrm{P}S}_{E,l}\right|^2 r^2 dr = \int_0^{R_C} \left|\psi^{\mathrm{A}E}_{E,l}\right|^2 r^2 dr$$

$$\Downarrow$$

$$\frac{\partial}{\partial\epsilon}\frac{\partial \ln \psi^{\mathrm{P}S}_{\epsilon,l}(r)}{\partial r}\bigg|_{\epsilon=E,r=R_C} = \frac{\partial}{\partial\epsilon}\frac{\partial \ln \psi^{\mathrm{A}E}_{\epsilon,l}(r)}{\partial r}\bigg|_{\epsilon=E,r=R_C}$$

Equal amount of charge of $\psi^{\mathrm{A}E}$ and $\psi^{\mathrm{P}S}$ implies *equal logarithmic derivative, i.e. equal phase shift and equal scattering properties in the neighbourhood of $E_{\mathrm{re}f}$ to the 1-st order*

Ab-initio pseudopotentials - continued

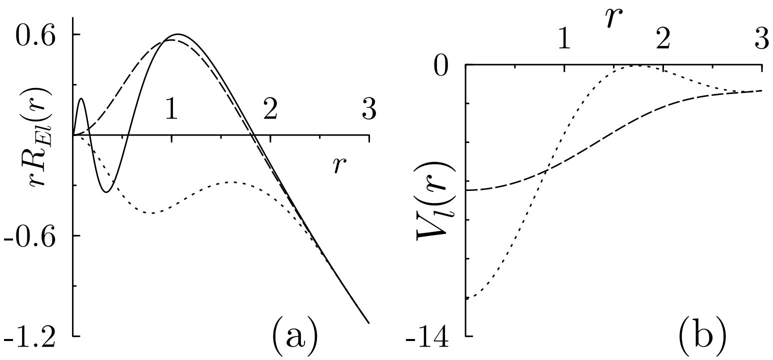
- *... several various types of norm-conserving PSP*
  Generalized ... [Hamann 1989], [RRKJ 1990],
  Extended ... [Shirley et al 1990]
- *Ultrasoft pseudopotentials*
  Vanderbilt [1990]; relaxing norm-conserving condition
  $\Rightarrow$ softer PSP, smaller R_C
- *PAW (Projector Augmented Wave) method*
  Blöchl [1995]; (-)partial waves in the basis set, (-)still frozen core, (+)unambiguous assignment between AE and PS quantities

Desirable PSP properties ... and problems

1. “softness”

– means the size of basis (as small as possible) set that we need to achieve required accuracy in a given application;
is there any independent criterion ?
not discoverd so far, but we have some “indicators”:

- Visual softness, curvature at $r = 0$



- Fourier image of PS-potential in reciprocal space
- Fourier image of PS-wave function in reciprocal space

2. “transferability”

intuitive meaning: the ability to work properly in different environments (solids, compounds, molecules),
e.g. Na in metal Na and NaCl

two main components:

- (a) the precision of reproducing the scattering properties of AE potential (log. derivative) as a function of ϵ in some neighborhood of E_{ref}
  (energy transferability)
- (b) the precision of reproducing the AE eignevalues under varying the external environmental conditions (i.e. charge density within DFT)

transferability ... - continued

(a) and (b) related via the *higher momenta* of the charge density [Shirley et al 1989] (related to higher energy derivatives of the phase-shift):

norm-conserving PSP

$\Rightarrow$ correct 1-st energy derivative of scattering properties

$\Rightarrow$ correct PSP behavior with respect to
making *first order* changes to external charge density

$\equiv$ *causing constant potential shift*

Sources of errors in pseudopotential method

- linearized method ⇒ higher order errors:
  - energy bands in a solid doesn’t coincide with atomic eignevalues
  - external charge density (caused by neighboring atoms) is not a *first order* change (doesn’t cause constant potential shift)
  ⇒ attempts to mimick the chemical bond by choosing *suitable* atomic configuration for generating pseudopotential
- next step in psedopotential construction: subtracting the XC-potential of valence charge density: can cause **even first order error** since the XC-term is not linear; reduced by NLCC (non-linear core correction)

All electron pseudopotential (AEPP)

– selfconsistent pseudopotential-generating scheme that takes into account the solid state environment:

1. all-electron atom recontruction using the crystal boundary conditions
2. constructing screened PSP: by minimizing a functional assembled from conditions to be satisfied
3. unscreening the PSP by *real solid-state valence charge density*

AEPP - 1.atomic reconstruction

1. crystal charge density forms a *boundary condition*

$$\frac{d}{dr}\ln\left(r^2\left|\psi^{\rm at}_{E_{{\rm val},l},l}(r)\right|^2\right)\Bigg|_{r=R_C} = \frac{d}{dr}\ln\left(r^2\rho^{\rm sps}_l(r)\right)\Bigg|_{r=R_C},$$

where partial charge density in a solid $\rho^{\rm sps}_l(r)$ is evaluated by summing over all occupied states,

$$\begin{aligned}\rho^{\rm sps}_l(r) &= \sum_{\vec{k},n}\sum_{m=-l}^{l}\frac{1}{4\pi r^2}\int_{SPH}d\Omega d\Omega' \\ &\qquad \psi^*_{\vec{k},n}(r\hat{\mathbf{n}})Y_{lm}(\hat{\mathbf{n}})\,Y^*_{lm}(\hat{\mathbf{n}}')\psi_{\vec{k},n}(r\hat{\mathbf{n}}')\end{aligned}$$

The boundary condition (above) replaces the standard condition for the wavefunctions to be normalizable ($\psi_{E,l}(r)\to 0$ for $r\to\infty$) and determines the eigenvalue E_l.

AEPP - 1. atomic reconstruction - continued

The normalization condition for the valence atomic-like radial wavefunctions is

$$\int_0^{R_C} \left|\psi^{\mathrm{at}}_{E_{\mathrm{val},l},l}(r)\right|^2 r^2 dr = \int_0^{R_C} \rho_l^{\mathrm{sps}}(r) r^2 dr$$

(reversed norm-conserving condition)

The core states are recalculated selfconsistently with the valence (augmented to the crystal charge density) states.

AEPP - 2. screened PSP

2. each component $V_l^{\mathrm{scr}}(r)$ satisfies

(i) At $r = R_C$ the potential $V_l^{\mathrm{scr}}(r)$ matches the all-electron potential $V^{\mathrm{at}}(r)$ up to the second derivative,
(ii) At $r = R_C$ the radial pseudo-wavefunctions $R^{\mathrm{ps}}_{E_{n,l},l}(r)$ match the corresponding atomic-like radial functions by their values and first derivatives (for each energy window), and
(iii) the correct energy derivative of the pseudo-wavefunction is ensured by the norm-conserving condition (for main -valence- energy window; relaxed for semicore state)

AEPP - continued

differences with respect to conservative methods:

<table>
<tr><th>standard methods</th><th>AEPP</th></tr>
<tr><td colspan="2">• *boundary conditions* for initial atomic calculation:</td></tr>
<tr><td>free, isolated atom</td><td>derived from partial $l-$projected charge density in a solid</td></tr>
<tr><td colspan="2">• *chemical bond* is taken into account in PSP</td></tr>
<tr><td>by intuitive, ad-hoc choice of atomic occupation numbers</td><td>in natural way via the boundary condition</td></tr>
<tr><td colspan="2">• *transferability ranges* are located</td></tr>
<tr><td>around the atomic eigenvalues</td><td>around centers of $l-$projected DOS (bands) in a solid</td></tr>
</table>

- *core states*

atomic, frozen-core approximation	self-consistent with the charge density in a solid

- *screening — XC potential term*

atomic valence charge density, NLCC	self-consistent charge density in a solid