Electronic Structure: from BlackBoard to Source Code

Stefano de Gironcoli
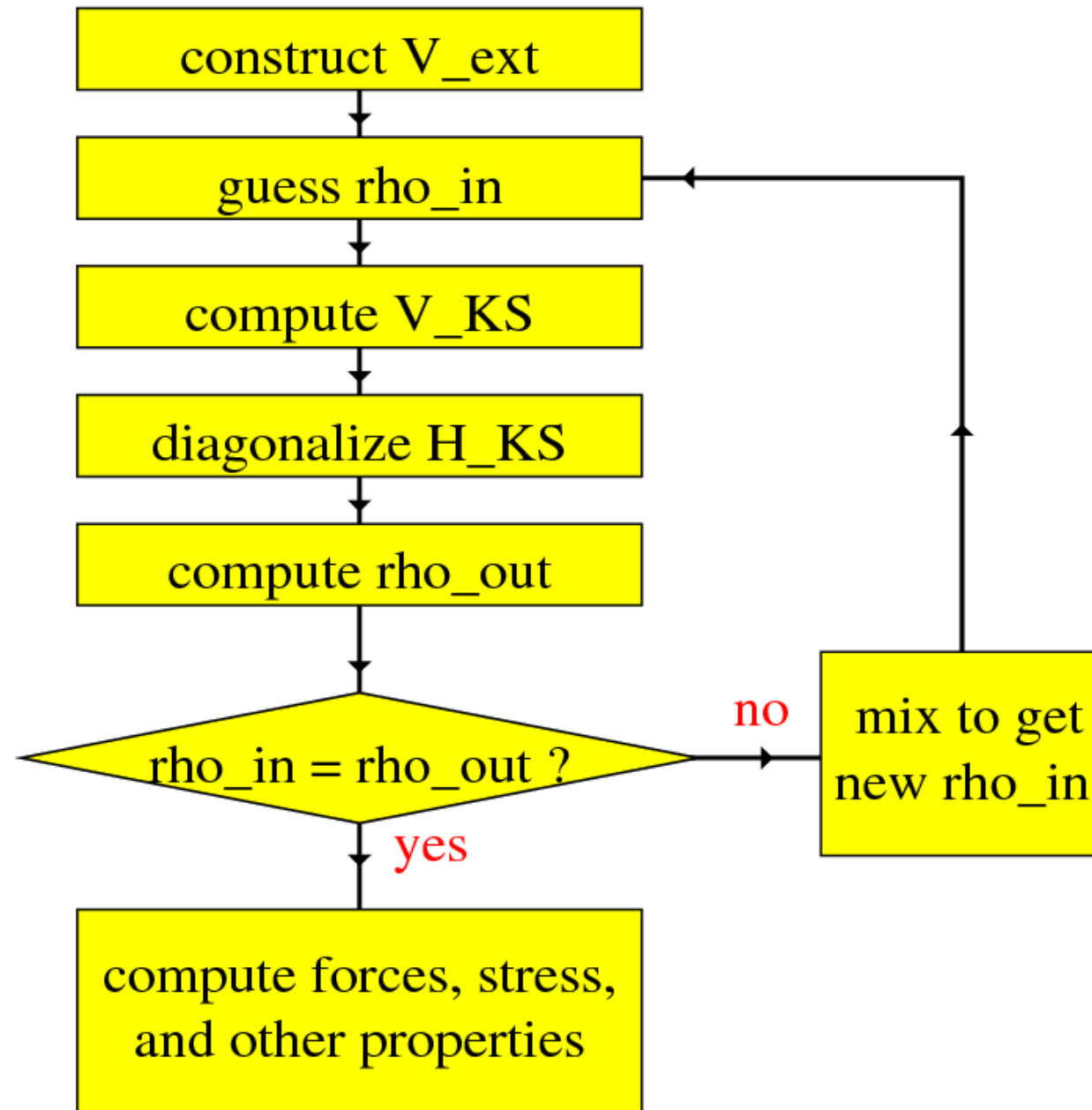
Scuola Internazionale Superiore di Studi Avanzati

Trieste-Italy

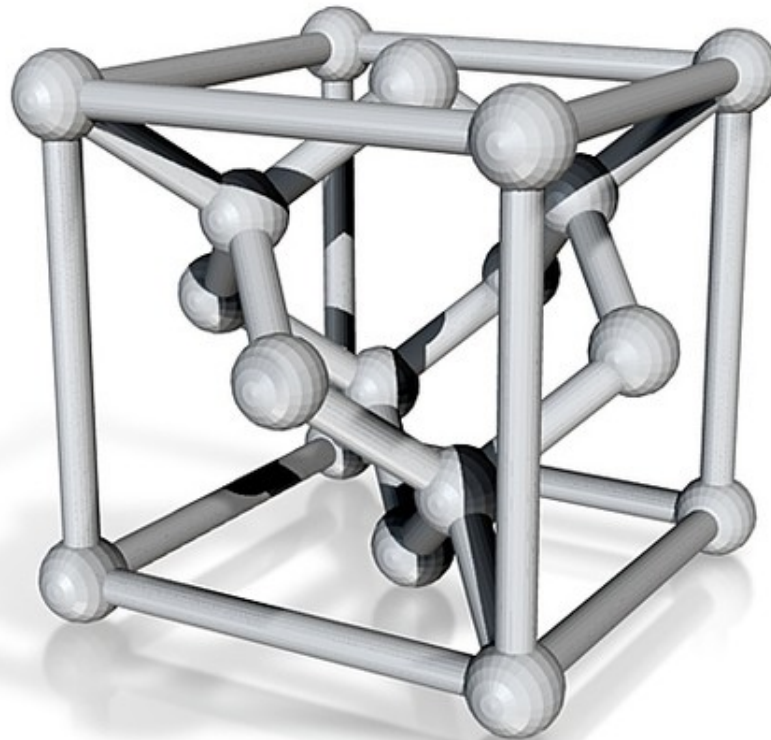# Defining the System
External Potential

PseudoPotentials
NCPP/USPP/PAW

Structure of a self-consistent type code
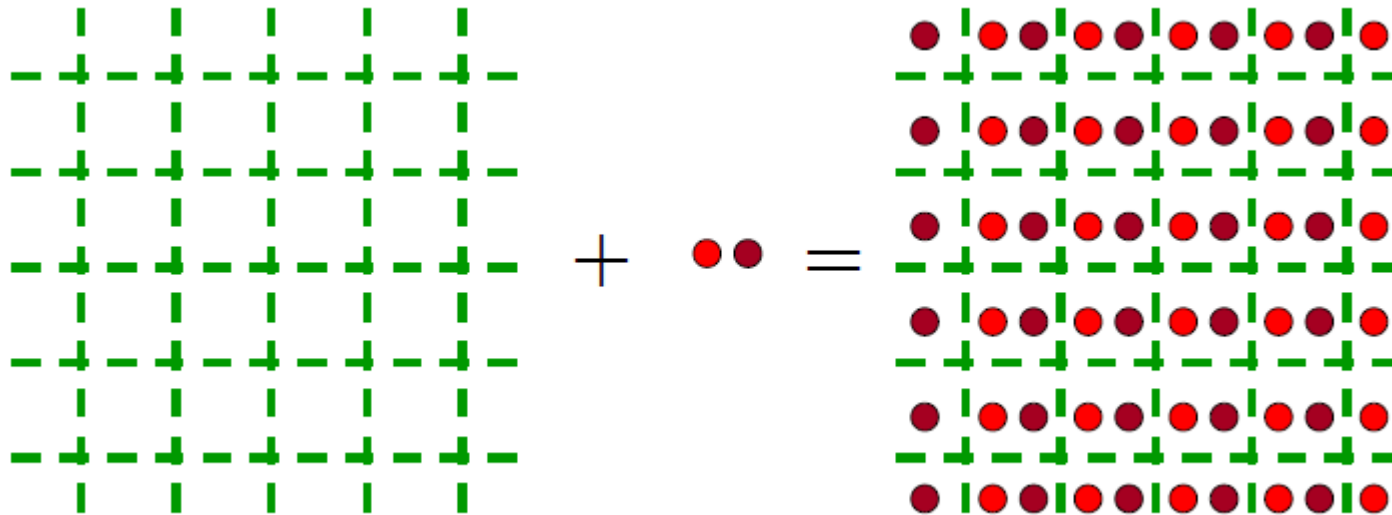
Step 0 : defining your system

QE input: namelist   SYSTEM

Step 0 : defining your system

All periodic systems can be specified by a Bravais Lattice and an atomic basis
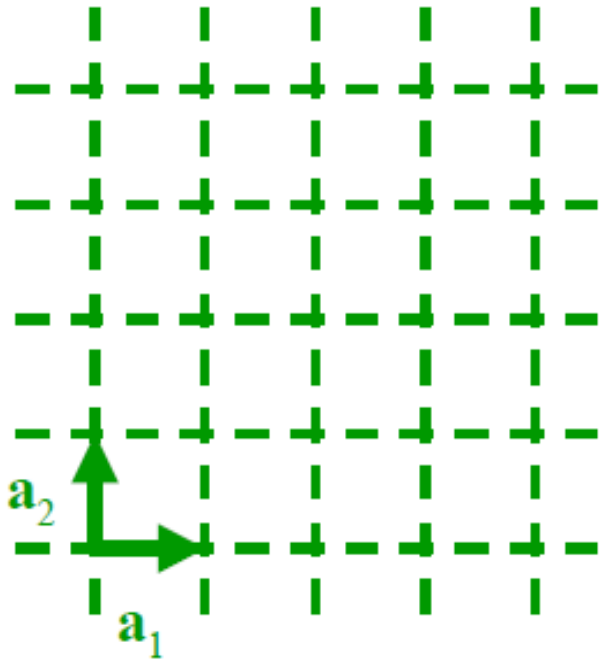
$$\{\tau_s, \ s = 1, 2, ..., N_{at}\}$$

$$\{ \mathbf{R} = n_1\mathbf{a_1} + n_2\mathbf{a_2} + n_3\mathbf{a_3}, \qquad \{ \mathbf{R} + \tau_s \}$$

$$n_1, n_3, n_3 = 0, 1, 2, 3, ..., N \equiv 0, \quad N \to \infty \}$$

Step 0 : defining your system
Bravais Lattice / Unit cell

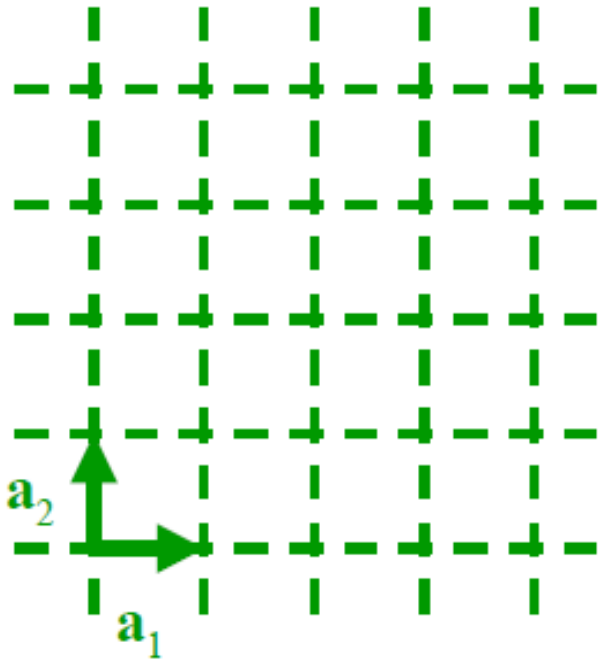$$BL = \{ \mathbf{R} \mid \mathbf{R} = n_1\mathbf{a_1} + n_2\mathbf{a_2} + n_3\mathbf{a_3}\}$$

$$RL = \{ \mathbf{G} \mid \exp(i\mathbf{G}\mathbf{R}) = 1, \ \mathbf{R} \in BL\}$$

$$= \{ \mathbf{G} \mid \mathbf{G} = m_1\mathbf{b_1} + m_2\mathbf{b_2}$$
$$+ m_3\mathbf{b_3}, \ \mathbf{a}_i\mathbf{b}_j = 2\pi\,\delta_{ij}\}$$

there are 14 Bravais Lattice types whose unit cell can be defined by up to 6 cell parameters

Step 0 : defining your system Bravais Lattice / Unit cell

QE input: parameter ibrav
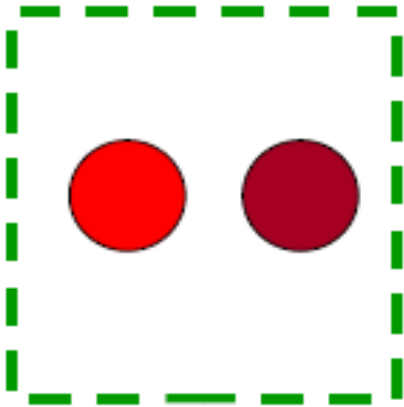
- gives the type of Bravais lattice (SC, FCC, HEX, ...)

QE input: parameters {celldm(i)}

- give the lengths (& directions if needed) of the BL vectors

Note that one can choose a non-primitive unit cell (e.g., 4 atom SC cell for FCC structure).

Step 0 : defining your system
atoms inside the unit cell: How many, where?

QE input: parameter nat
- Number of atoms in the unit cell

QE input: parameter ntyp
- Number of types of atoms

QE input: field ATOMIC_POSITIONS
- Initial positions of atoms (may vary when "relax" done).
- Can choose to give in units of lattice vectors ("crystal") or in Cartesian units ("alat" or "bohr" or "angstrom")

Step 1 : defining V_ext
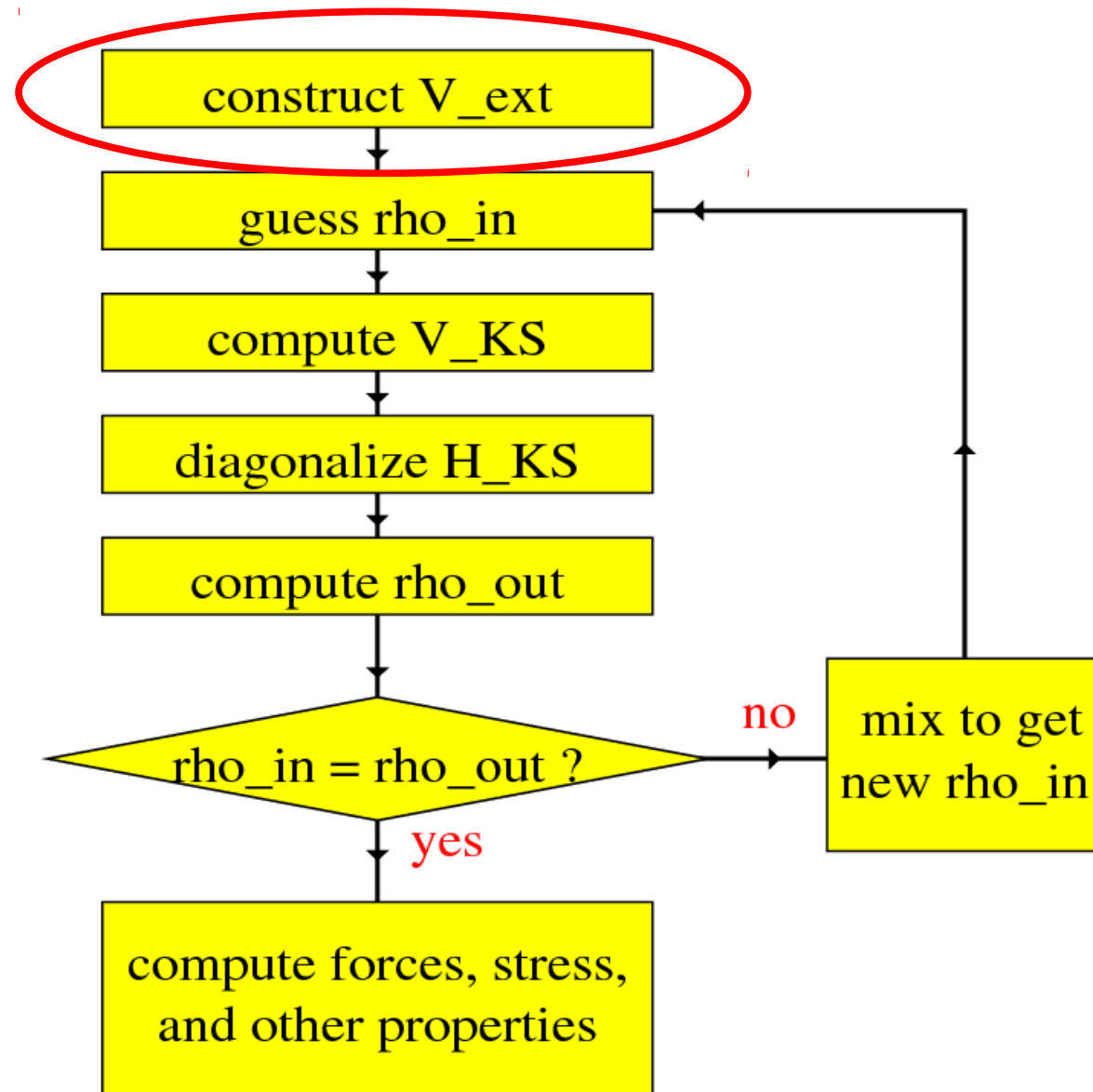
The external potential

Electrons experience a Coulomb potential due to the nuclei.

This has a known simple form.

For a single atom it is

$$V_{nuc}(r) = -\frac{Ze^2}{|r|}$$

Periodic potential

$$V(r) = \sum_s \sum_R V_s(|r - R - \tau_s|)$$

Periodic potential

$$V(r) = \sum_s \sum_R V_s(|r - R - \tau_s|)$$

$$V(G) = \frac{1}{\mathcal{V}} \int_{\mathcal{V}} \sum_s \sum_R V_s(|r - R - \tau_s|) \exp(-iGr) dr$$

Periodic potential

$$V(r) = \sum_s \sum_R V_s(|r - R - \tau_s|)$$

$$V(G) = \frac{1}{\mathcal{V}} \int_{\mathcal{V}} \sum_s \sum_R V_s(|r - R - \tau_s|) \exp(-iGr) dr$$

$$V(G) = \sum_s \int_{\mathcal{V}} V_s(|r|) \exp(-iGr) dr \quad \sum_R \frac{\exp(-iG(R + \tau_s))}{N\Omega}$$

$$\mathcal{V} = N\Omega$$

Periodic potential

$$V(r) = \sum_s \sum_R V_s(|r - R - \tau_s|)$$

$$V(G) = \frac{1}{\mathcal{V}} \int_\mathcal{V} \sum_s \sum_R V_s(|r - R - \tau_s|) \exp(-iGr)dr$$

$$V(G) = \sum_s \int_\mathcal{V} V_s(|r|) \exp(-iGr)dr \ \sum_R \frac{\exp(-iG(R + \tau_s))}{N\Omega}$$

$$V(G) = \sum_s \int_\mathcal{V} V_s(|r|) \exp(-iGr)dr \ \frac{\exp(-iG\tau_s)}{\Omega}$$

Periodic potential

$$V(r) = \sum_s \sum_R V_s(|r - R - \tau_s|)$$

$$V(G) = \frac{1}{\mathcal{V}} \int_{\mathcal{V}} \sum_s \sum_R V_s(|r - R - \tau_s|) \exp(-iGr) dr$$

$$V(G) = \sum_s \int_{\mathcal{V}} V_s(|r|) \exp(-iGr) dr \sum_R \frac{\exp(-iG(R + \tau_s))}{N\Omega}$$

$$V(G) = \sum_s \int_{\mathcal{V}} V_s(|r|) \exp(-iGr) dr \ \frac{\exp(-iG\tau_s)}{\Omega}$$

$$V(G) = \sum_s V_s(|G|) \ S_s(G)$$

Periodic potential

$$V(r) = \sum_s \sum_R V_s(|r - R - \tau_s|)$$

$$V(G) = \frac{1}{\mathcal{V}} \int_{\mathcal{V}} \sum_s \sum_R V_s(|r - R - \tau_s|) \exp(-iGr) dr$$

$$V(G) = \sum_s \int_{\mathcal{V}} V_s(|r|) \exp(-iGr) dr \quad \sum_R \frac{\exp(-iG(R + \tau_s))}{N\Omega}$$

$$V(G) = \sum_s \int_{\mathcal{V}} V_s(|r|) \exp(-iGr) dr \quad \frac{\exp(-iG\tau_s)}{\Omega}$$

$$V(G) = \sum_s V_s(|G|) \; S_s(G)$$

atomic form factor   *crystal structure factor*

nuclear potential

The Coulomb potential due to any single atom is

$$V_{nuc}(|r|) = -\frac{Ze^2}{|r|} \quad \longrightarrow \quad V_{nuc}(|G|) = -Z\frac{4\pi e^2}{|G|^2}$$

The direct use of this potential in a Plane Wave code leads to computational difficulties!
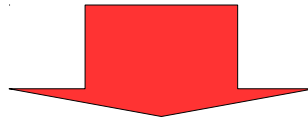
Problems for a Plane-Wave based code

Core wavefunctions:
Sharply peaked close to nuclei due to deep Coulomb potential.

Valence wavefunctions:
Lots of wiggles near nuclei due to orthogonality to core wavefunctions

<u>High Fourier components are present
i.e. large kinetic energy cutoff needed</u>

$$r_{1s} \approx 1/Z \qquad Ecut \approx \left(\frac{2\pi}{r_{1s}}\right)^2 \approx 40Z^2$$

An analogy!

- "Dummy cops" used by many law-enforcement agencies!

- Don't care about internal structure as long as it works right!

- But cheaper!!

- Obviously it can't reproduce all the functions of a real cop, but should be convincing enough to produce desired results....

Shobhana Narasimhan, JNCASR
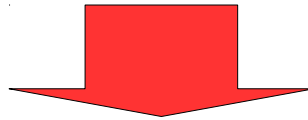
Solutions for a Plane-Wave based code

Core wavefunctions:
Sharply peaked close to nuclei due to deep Coulomb potential.

Valence wavefunctions:
Lots of wiggles near nuclei due to orthogonality to core wavefunctions

Don't solve for core wavefunction

Remove wiggles from valence wavefunctions

<u>Replace hard Coulomb potential by smooth PseudoPotentials</u>
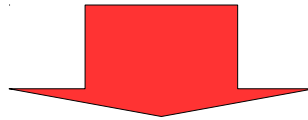
Solutions for a Plane-Wave based code

Core wavefunctions:
Sharply peaked close to nuclei due to deep Coulomb potential.

Valence wavefunctions:
Lots of wiggles near nuclei due to orthogonality to core wavefunctions

Don't solve for core wavefunction

Remove wiggles from valence wavefunctions

Replace hard Coulomb potential
by smooth PseudoPotentials

This can be done on an empirical basis by fitting experimental band structure data ..

Empirical PseudoPotentials

$$V(G) = \sum_s V_s(|G|) \ S_s(G)$$

	$V_3{}^S$	$V_8{}^S$	$V_{11}{}^S$
Si	−0.21	+0.04	+0.08
Ge	−0.23	+0.01	+0.06
Sn	−0.20	0.00	+0.04

Cohen & Bergstresser,
  PRB 141, 789 (1966)
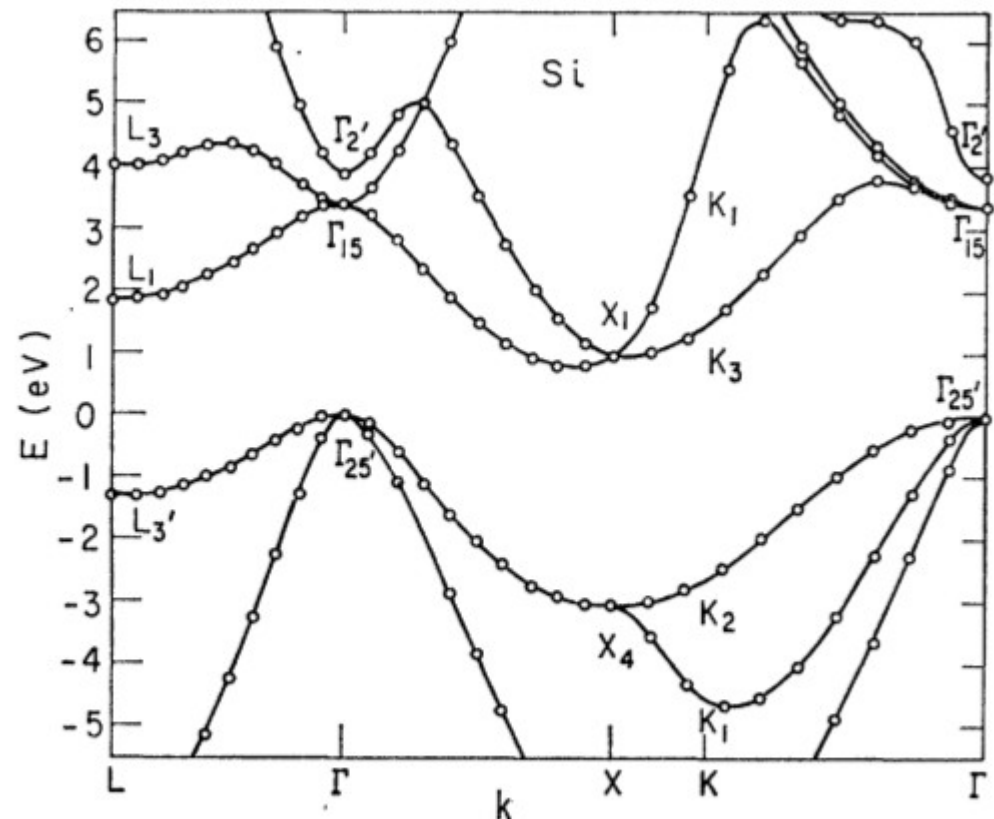
FIG. 1. Band structure of Si.

Empirical PseudoPotentials

$$V(G) = \sum_s V_s(|G|) \; S_s(G)$$

	V_3^S	V_8^S	V_{11}^S
Si	−0.21	+0.04	+0.08
Ge	−0.23	+0.01	+0.06
Sn	−0.20	0.00	+0.04

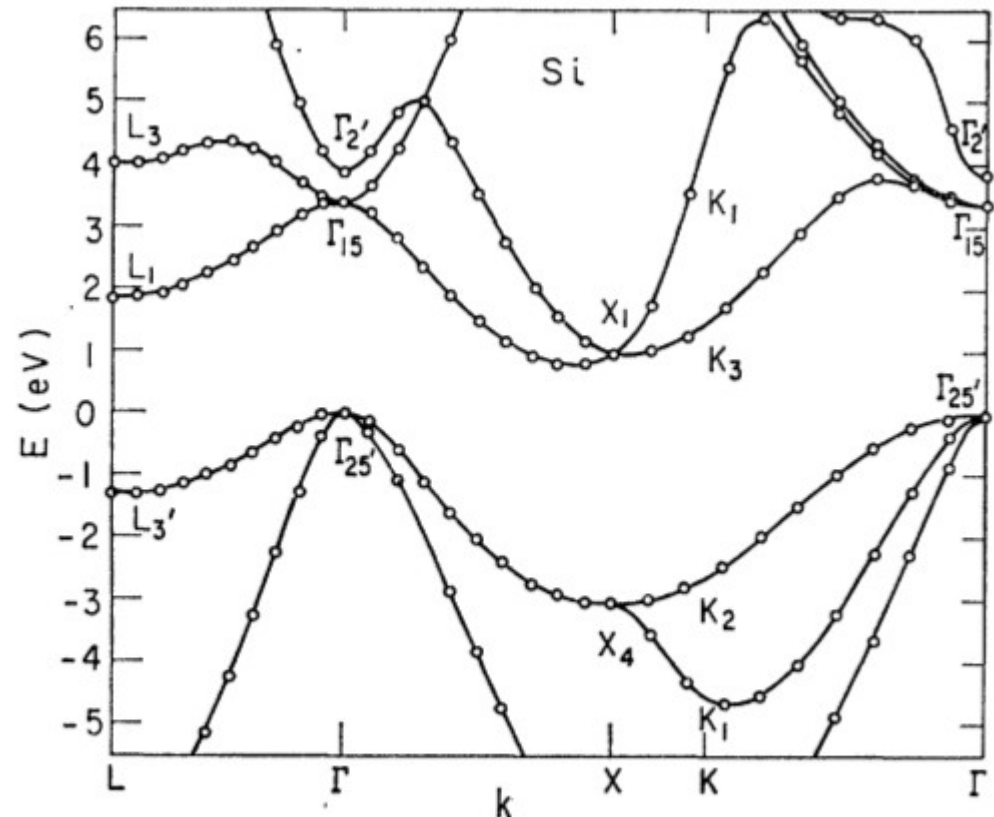Cohen & Bergstresser,
  PRB 141, 789 (1966)

FIG. 1. Band structure of Si.

transferability to other systems is problematic

ab initio Norm Conserving PseudoPotentials

Let's consider an atomic problem ...

$$\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{|r|} + e^2 \int \frac{\rho(r')}{|r-r'|} d^3r' + v_{xc}[\rho(r)] \right] \varphi_i(r) = \varepsilon_i \, \varphi_i(r)$$

... in the frozen core approximation: $\rho(r) = \rho_v(r) + \rho_c(r)$

ab initio Norm Conserving PseudoPotentials

Let's consider an atomic problem ...

$$\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{|r|} + e^2 \int \frac{\rho(r')}{|r-r'|}d^3r' + v_{xc}[\rho(r)] \right] \varphi_i(r) = \varepsilon_i \, \varphi_i(r)$$

... in the frozen core approximation: $\rho(r) = \rho_v(r) + \rho_c(r)$

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + e^2 \left(-\frac{Z}{|r|} + \int \frac{\rho_c(r')}{|r-r'|}d^3r' \right) + e^2 \int \frac{\rho_v(r')}{|r-r'|}d^3r' \right.$$

$$\left. + v_{xc}[\rho_v(r) + \rho_c(r)] \right] \varphi_i(r) = \varepsilon_i \, \varphi_i(r)$$

ab initio Norm Conserving PseudoPotentials

Let's consider an atomic problem ...

$$\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{|r|} + e^2 \int \frac{\rho(r')}{|r-r'|}d^3r' + v_{xc}[\rho(r)] \right] \varphi_i(r) = \varepsilon_i \, \varphi_i(r)$$

... in the frozen core approximation: $\rho(r) = \rho_v(r) + \rho_c(r)$

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + e^2 \left(-\frac{Z}{|r|} + \int \frac{\rho_c(r')}{|r-r'|}d^3r' \right) + e^2 \int \frac{\rho_v(r')}{|r-r'|}d^3r' \right.$$

$$\left. + v_{xc}[\rho_v(r) + \rho_c(r)] \right] \varphi_i(r) = \varepsilon_i \, \varphi_i(r)$$

if $\rho_v(r)$ and $\rho_c(r)$ do not overlap significantly:

$$v_{xc}[\rho_v(r) + \rho_c(r)] \approx v_{xc}[\rho_v(r)] + v_{xc}[\rho_c(r)]$$

ab initio Norm Conserving PseudoPotentials

... hence

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{Z_v}^{PS}(|r|) + e^2 \int \frac{\rho(r')}{|r-r'|}d^3r' + v_{xc}[\rho_v(r)] \right] \varphi_i(r) = ...$$

with
$$V_{Z_v}^{PS}(|r|) = e^2 \left(-\frac{Z}{|r|} + \int \frac{\rho_c(r')}{|r-r'|}d^3r' \right) + v_{xc}[\rho_c(r)]$$

ab initio Norm Conserving PseudoPotentials

... hence

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{Z_v}^{PS}(|r|) + e^2 \int \frac{\rho(r')}{|r-r'|}d^3r' + v_{xc}[\rho_v(r)] \right]\varphi_i(r) = \ldots$$

with $\quad V_{Z_v}^{PS}(|r|) = e^2\left(-\frac{Z}{|r|} + \int \frac{\rho_c(r')}{|r-r'|}d^3r' \right) + v_{xc}[\rho_c(r)]$

with a Coulomb tail corresponding to $Z_v = Z - N_{core}^{el}$

ab initio Norm Conserving PseudoPotentials

... hence

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{Z_v}^{PS}(|r|) + e^2 \int \frac{\rho(r')}{|r-r'|}d^3r' + v_{xc}[\rho_v(r)] \right] \varphi_i(r) = ...$$

with $\quad V_{Z_v}^{PS}(|r|) = e^2 \left(-\frac{Z}{|r|} + \int \frac{\rho_c(r')}{|r-r'|}d^3r' \right) + v_{xc}[\rho_c(r)]$

with a Coulomb tail corresponding to $Z_v = Z - N_{core}^{el}$

or in case of overlap we have (***non-linear core correction***)

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{Z_v}^{PS}(|r|) + e^2 \int \frac{\rho(r')}{|r-r'|}d^3r' + v_{xc}[\rho_v(r) + \rho_c(r)] \right] \varphi_i$$

with $\quad V_{Z_v}^{PS}(|r|) = e^2 \left(-\frac{Z}{|r|} + \int \frac{\rho_c(r')}{|r-r'|}d^3r' \right)$

ab initio Norm Conserving PseudoPotentials

$V_{Z_v}^{PS}(|r|)$ is further modified in the core region so that the reference valence wavefunctions are *nodeless and smooth* and properly normalized (*norm conservation*) so that the valence charge density (outside the core) is simply:

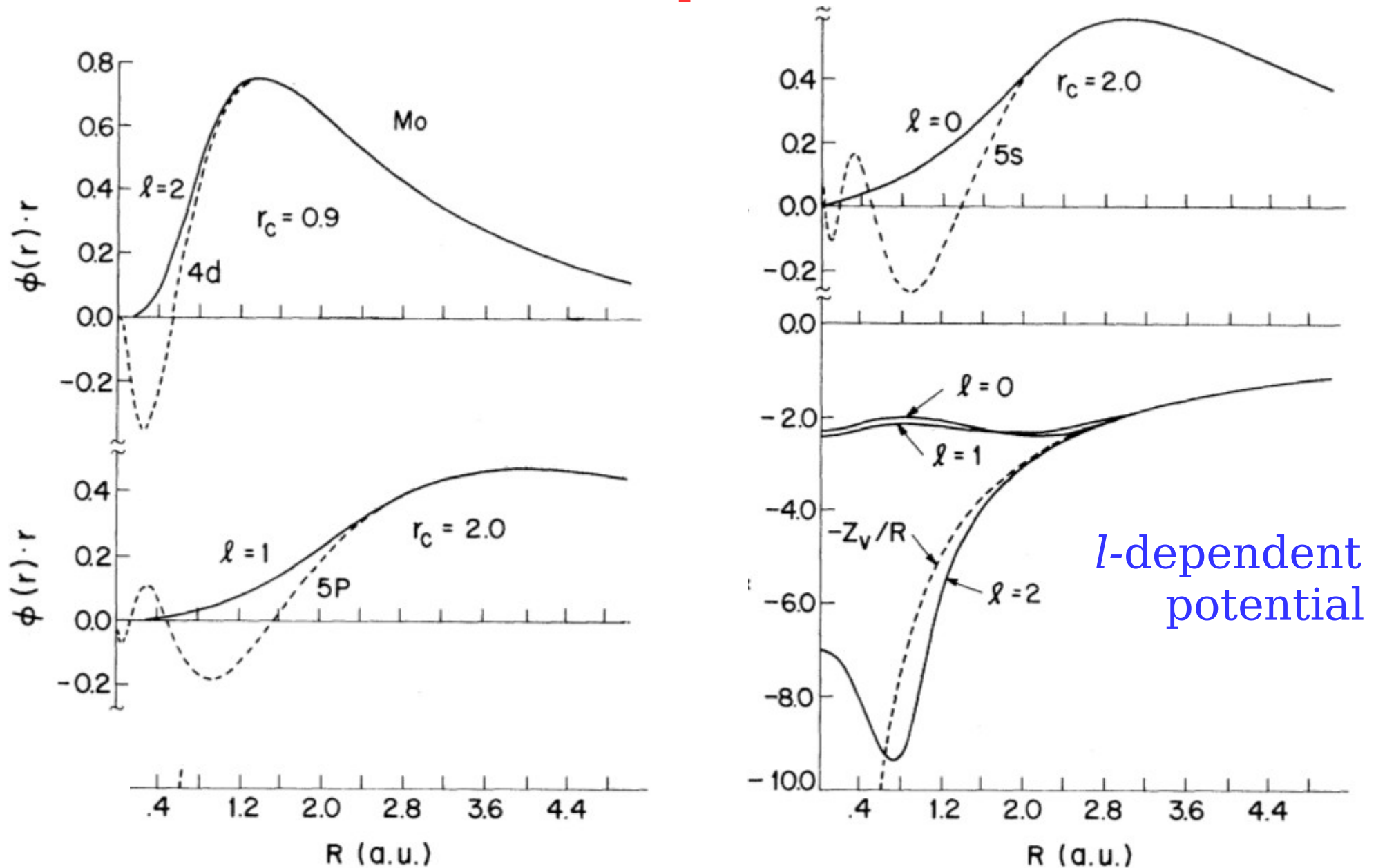$$\rho_v(r) = \sum_v |\varphi_v(r)|^2$$

The norm-conservation condition ensures correct electrostatics outside the core region and that atomic scattering properties are reproduced correctly

$$4\pi \int_0^R |\varphi(r)|^2 r^2 dr = 2\pi \left[r^2 |\varphi(r)|^2 \frac{d}{d\varepsilon} \frac{d}{dr} \ln \varphi(r) \right]_{r=R}$$

this determines *transferability*

An example:　Mo

l-dependent potential

Hamann, schlueter & Chiang, *PRL* **43**, 1494 (1979)
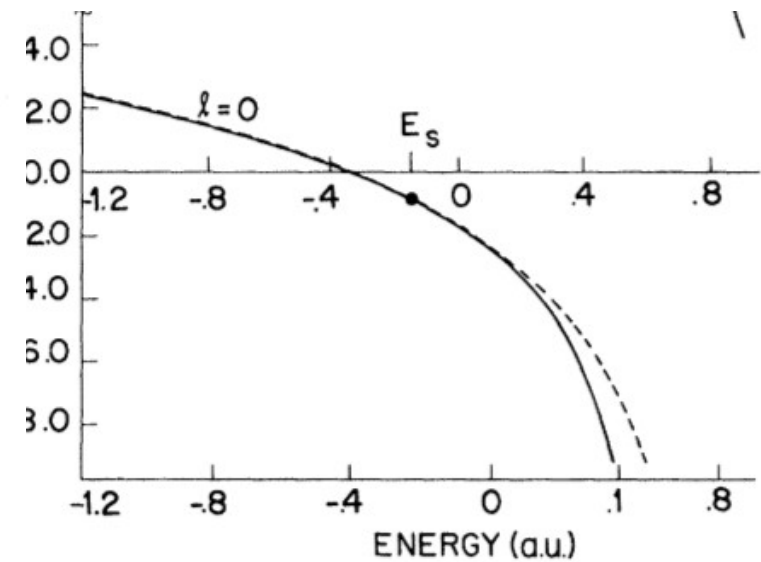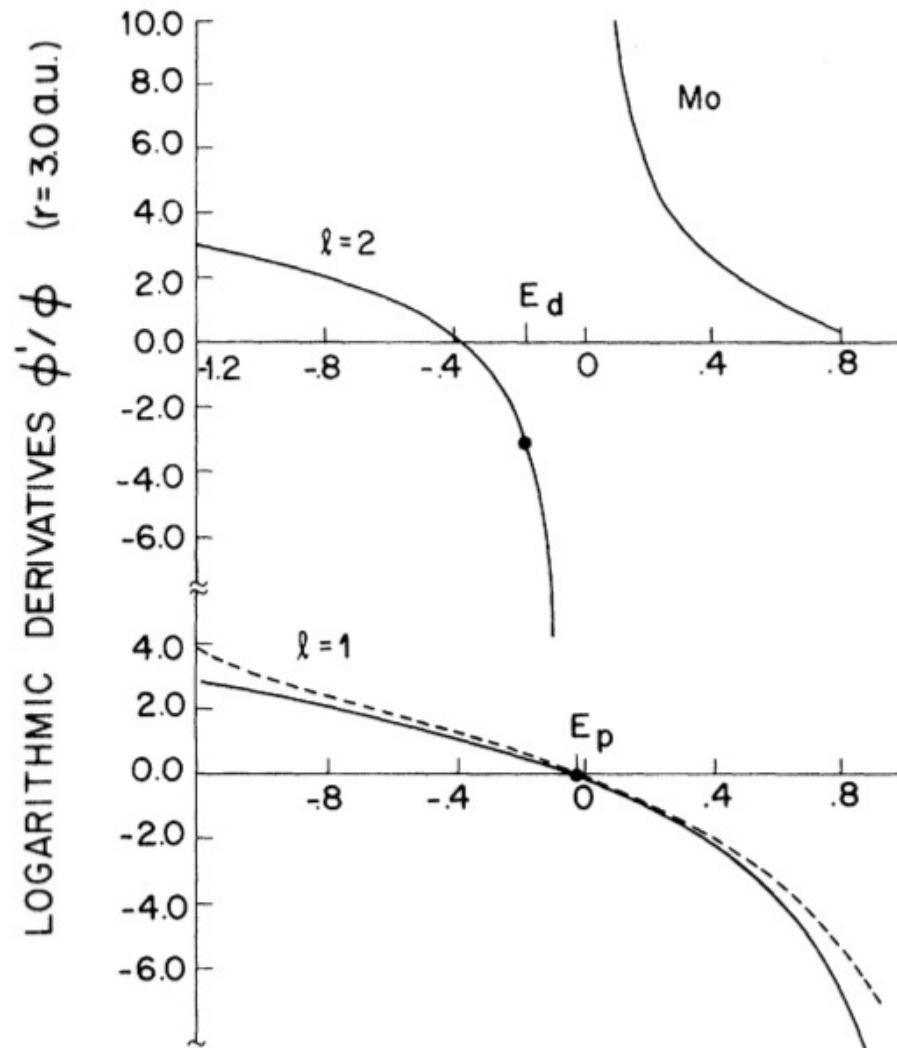
An example: Mo

FIG. 2. Energy dependence of logarithmic derivatives at $r = 3.0$ a.u. for Mo *ab initio* full-core atomic wave functions (broken lines) and pseudo wave functions (solid lines) as shown in Fig. 1.

Hamann, schlueter & Chiang, *PRL **43**, 1494 (1979)*

ab initio Norm Conserving PseudoPotentials

semilocal form

$$V_{Z_v}^{PS}(r, r') = V^{loc}(|r|)\delta(r - r') + \sum_{l=0}^{l_{max}} \Delta V_l(|r|)\delta(|r| - |r'|)P_l(r, r')$$

where $P_l(r, r') = \sum_m Y_{lm}(r)Y_{lm}^*(r')$ projects over $L^2 = l(l+1)$

ab initio Norm Conserving PseudoPotentials

semilocal form

$$V_{Z_v}^{PS}(r,r') = V^{loc}(|r|)\delta(r-r') + \sum_{l=0}^{l_{max}} \Delta V_l(|r|)\delta(|r|-|r'|)P_l(r,r')$$

where $P_l(r,r') = \sum_m Y_{lm}(r)Y_{lm}^*(r')$ projects over $L^2 = l(l+1)$

$V^{loc}(|r|)$ is local with a Coulomb tail $Z_v = Z - N_{core}^{el}$

$\Delta V_l(|r|)$ is local in the radial coordinate, short ranged and l-dependent

ab initio Norm Conserving PseudoPotentials

semilocal form

$$V_{Z_v}^{PS}(r, r') = V^{loc}(|r|)\delta(r - r') + \sum_{l=0}^{l_{max}} \Delta V_l(|r|)\delta(|r| - |r'|)P_l(r, r')$$

where $P_l(r, r') = \sum_m Y_{lm}(r)Y_{lm}^*(r')$ projects over $L^2 = l(l+1)$

$V^{loc}(|r|)$ is local with a Coulomb tail $Z_v = Z - N_{core}^{el}$

$\Delta V_l(|r|)$ is local in the radial coordinate, short ranged and l-dependent

$$\langle q|V_{Z_v}^{PS}|q'\rangle = V^{loc}(q - q') + \sum_{l=0}^{l_{max}} \Delta V_l(|q|, |q'|)P_l(q, q')$$

is a full matrix !   NO use of dual-space approach

ab initio Norm Conserving PseudoPotentials

from semilocal form ...

$$V_{Z_v}^{PS}(r, r') = V^{loc}(|r|)\delta(r - r') + \sum_{l=0}^{l_{max}} \Delta V_l(|r|)\delta(|r| - |r'|)P_l(r, r')$$

... to Kleinman-Bylander fully non-local form

$$\tilde{V}_{Z_v}^{PS}(r, r') = V^{loc}(|r|)\delta(r - r') + \sum_{l=0}^{l_{max}} \sum_{m=-l}^{l} \langle r|\beta_{lm}\rangle \, D_l \, \langle \beta_{lm}|r'\rangle$$

ab initio Norm Conserving PseudoPotentials

from semilocal form ...

$$V_{Z_v}^{PS}(r,r') = V^{loc}(|r|)\delta(r-r') + \sum_{l=0}^{l_{max}} \Delta V_l(|r|)\delta(|r|-|r'|)P_l(r,r')$$

... to Kleinman-Bylander fully non-local form

$$\tilde{V}_{Z_v}^{PS}(r,r') = V^{loc}(|r|)\delta(r-r') + \sum_{l=0}^{l_{max}} \sum_{m=-l}^{l} \langle r|\beta_{lm}\rangle \, D_l \, \langle\beta_{lm}|r'\rangle$$

$V^{loc}(|r|)$ is local with a Coulomb tail $Z_v = Z - N_{core}^{el}$

$\langle r|\beta_{lm}\rangle = \Delta V_l(r)\phi_l(r)Y_{lm}(r)$ are localized radial functions such that the transformed pseudo acts in the same way as the original form on the reference config.

One has $D_l = \langle\phi_l|\Delta V_l|\phi_l\rangle^{-1}$

ab initio Norm Conserving PseudoPotentials

Kleinman-Bylander fully non-local form

$$\tilde{V}_{Z_v}^{PS} = V^{loc}(|r|)\delta(r - r') + \sum_{l=0}^{l_{max}} \sum_{m=-l}^{l} \langle r|\beta_{lm}\rangle \, D_l \, \langle\beta_{lm}|r'\rangle$$

$V^{loc}(|r|)$ is local with a Coulomb tail $Z_v = Z - N_{core}^{el}$

$\langle r|\beta_{lm}\rangle = \Delta V_l(r)\phi_l(r)Y_{lm}(r)$ are localized radial functions such that the transformed pseudo acts in the same way as the original form on the reference config.

One has $D_l = \langle\phi_l|\Delta V_l|\phi_l\rangle^{-1}$

The pseudopotential reduces to a sum of dot products

$$\tilde{V}_{Z_v}^{PS}|\psi\rangle = V^{loc}(|r|)\langle r|\psi\rangle + \sum_{l=0}^{l_{max}} \sum_{m=-l}^{l} \langle r|\beta_{lm}\rangle \, D_l \, \langle\beta_{lm}|\psi\rangle$$

ab initio Norm Conserving PseudoPotentials

Kleinman-Bylander fully non-local form

$$\tilde{V}_{Z_v}^{PS} = V^{loc}(|r|)\delta(r - r') + \sum_{l=0}^{l_{max}} \sum_{m=-l}^{l} \langle r|\beta_{lm}\rangle D_l \langle\beta_{lm}|r'\rangle$$

The KB form is more efficiently computed than the original semi-local form.

ab initio Norm Conserving PseudoPotentials

Kleinman-Bylander fully non-local form

$$\tilde{V}_{Z_v}^{PS} = V^{loc}(|r|)\delta(r - r') + \sum_{l=0}^{l_{max}} \sum_{m=-l}^{l} \langle r|\beta_{lm}\rangle \, D_l \, \langle \beta_{lm}|r'\rangle$$

The KB form is more efficiently computed than the original semi-local form.

By construction it behaves as the original form on the reference configuration ... but ... there is no guarantee that the reference configuration is the GS of the modified potential.

ab initio Norm Conserving PseudoPotentials

Kleinman-Bylander fully non-local form

$$\tilde{V}_{Z_v}^{PS} = V^{loc}(|r|)\delta(r - r') + \sum_{l=0}^{l_{max}} \sum_{m=-l}^{l} \langle r|\beta_{lm}\rangle \, D_l \, \langle\beta_{lm}|r'\rangle$$

The KB form is more efficiently computed than the original semi-local form.

By construction it behaves as the original form on the reference configuration ... but ... there is no guarantee that the reference configuration is the GS of the modified potential.

When this happens the pseudopotential has GHOST states and should not be used.

ab initio Norm Conserving PseudoPotentials

Desired properties of a pseudopotential are

- *Transferability* (norm-conservation, small core radii, non-linear core correction, multi projectors)

- *Softness* (various optimization/smoothing strategies, large core radii)

For some elements it's easy to obtain "soft" Norm-Conserving PseudoPotentials.

For some elements it's instead very difficult!

Expecially for <u>first row elements</u> (very localized 2p orbitals) and <u>1st row transition metals</u> (very localized 3d orbitals)

Norm-Conserving PseudoPotentials
basic literature

<1970 empirical PP. es: Cohen & Bergstresser, *PRB **141**, 789 (1966)*

1979 Hamann, Schlueter & Chang, *PRL **43**, 1494 (1979), ab initio NCPP*
1982 Bachelet, Hamann, Schlueter, *PRB **26**, 4199 (1982), BHS PP table*
1982 Louie, Froyen & Cohen, *PRB **26**, 1738 (1982), non-linear core corr.*
1982 Kleinman & Bylander*, PRL **48**, 1425 (1982), KB fully non local PP*

1985 Vanderbilt*, PRB **32**, 8412 (1985), optimally smooth PP*
1990 Rappe,Rabe,Kaxiras,Joannopoulos*, PRB **41**, 1227 (1990), optm. PP*
1990 Bloechl*, PRB **41**, 5414 (1990), generalized separable PP*
1991 Troullier & Martins, *PRB **43**, 1993 (1991), efficient PP*
....

1990 Gonze, Kackell, Scheffler, *PRB **41**, 12264 (1990), Ghost states*

1991 King-Smith, Payne, Lin, *PRB **44**, 13063 (1991), PP in real space*

Ultra Soft PseudoPotentials

In spite of the devoted effort NCPP's are still "hard"and require a large plane-wave basis sets (Ecut > 70Ry) for first-row elements (in particular N, O, F) and for transition metals, in particular the 3d row: Cr, Mn, Fe, Co, Ni, ...
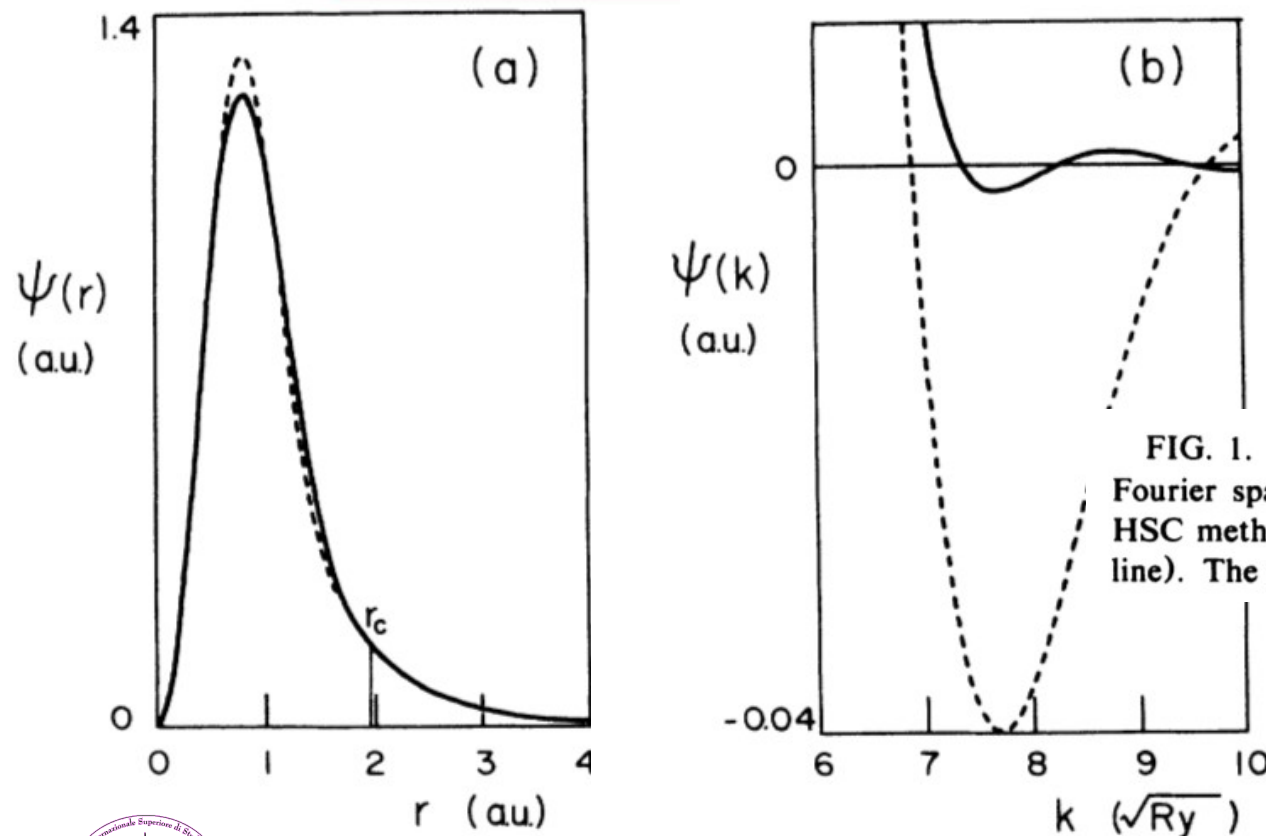
Copper 3d orbital
nodeless

FIG. 1. Pseudo wave functions (a) in real space and (b) in Fourier space, for the copper 3d eigenstate, generated by the HSC method (dashed line) and by the present approach (solid line). The pseudo wave functions are normalized to unity.

RRKJ, *PRB* **41**,1227 (1990)

Ultra Soft PseudoPotentials

Even if just one atom is "hard", a high cutoff is required.

UltraSoft (Vanderbilt) PseudoPotentials (USPP) are devised to overcome such a problem.
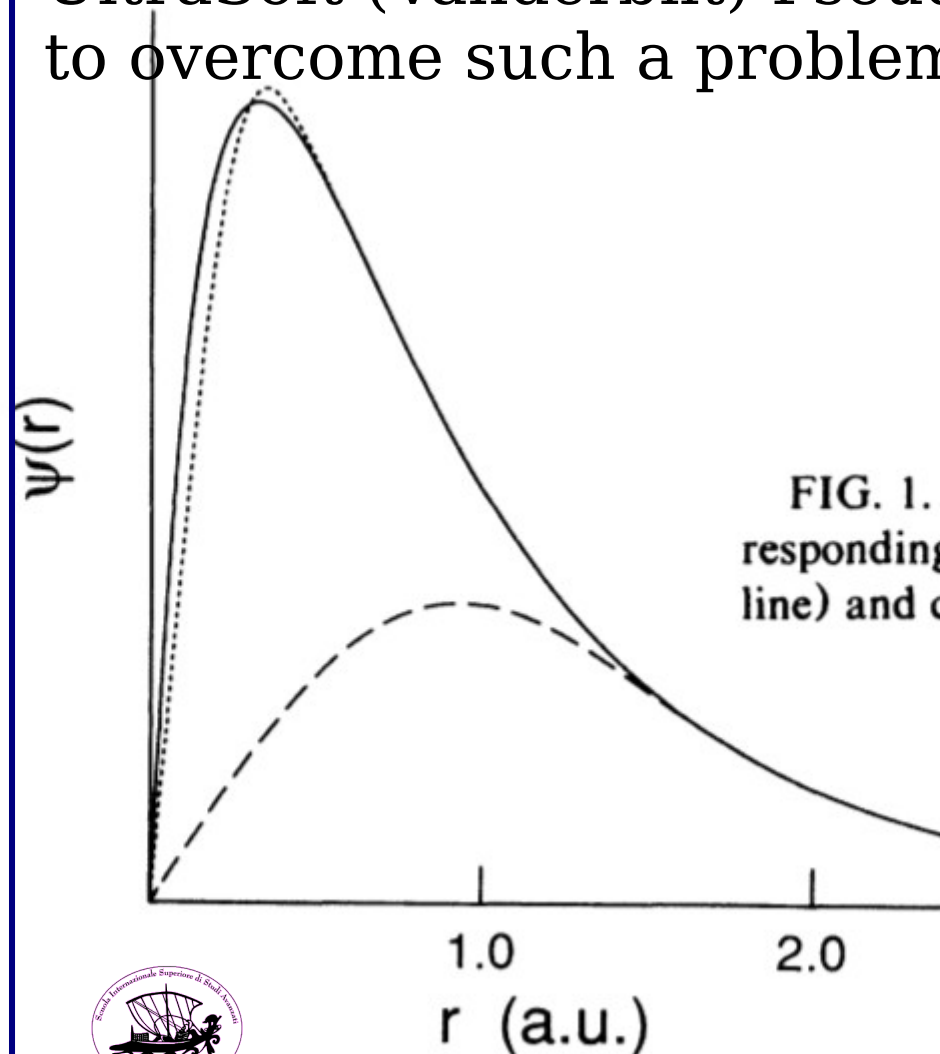
Oxygen 2p orbital
<u>nodeless</u>

FIG. 1. Oxygen 2p radial wave function (solid line), and corresponding pseudo-wave-functions generated using HSC (dotted line) and current (dashed line) methods.

Vanderbilt, *PRB* **41**, *7892 (1991)*

Ultra Soft PseudoPotentials
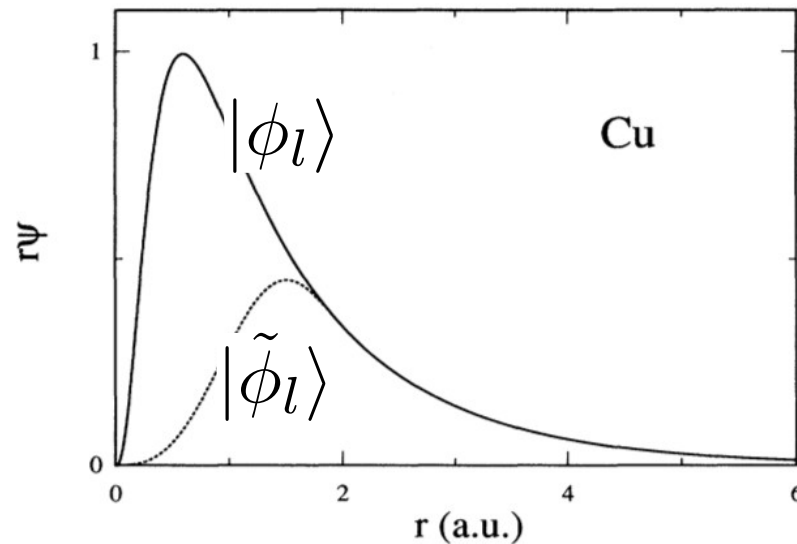
$$\rho(r) = \sum_i |\psi_i(r)|^2 + \sum_i \sum_{lm} \langle \psi_i | \beta_l \rangle Q_{lm}(r) \langle \beta_m | \psi_i \rangle$$

where the "augmentation charges" are

$$Q_{lm}(r) = \phi_l^*(r)\phi_m(r) - \tilde{\phi}_l^*(r)\tilde{\phi}_m(r)$$

$|\beta_l\rangle$ are projectors

$|\phi_l\rangle$ are atomic states (not necessarily bound)

$|\tilde{\phi}_l\rangle$ are pseudo-waves (coinciding with $|\phi_l\rangle$ beyond some *core radius*)

Ultra Soft PseudoPotentials

$$\hat{V}^{USPP} = V_{loc}(r) + \sum_{lm} |\beta_l\rangle D^0_{lm} \langle\beta_m|$$

Orthogonality with USPP:

$$\langle\psi_i|S|\psi_j\rangle = \langle\psi_i|\psi_j\rangle + \sum_{lm} \langle\psi_i|\beta_l\rangle q_{lm} \langle\beta_m|\psi_j\rangle = \delta_{ij}$$

where $\quad q_{lm} = \int Q_{lm}(r)dr$

leading to a generalized eigenvalue problem

$$[H_{KS} - \varepsilon_i S] \, |\psi_i\rangle = 0$$

Ultra Soft PseudoPotentials

There are additional terms in the density, in the energy, in the hamiltonian in the forces, ...

$$E = \sum_i \langle \psi_i | \hat{T}_s + \hat{V}^{USPP} | \psi_i \rangle + E_{Hxc}[\rho] - \sum_{ij} \lambda_{ij}(\langle \psi_i | S | \psi_j \rangle - \delta_{ij})$$

where

$$\rho(r) = \sum_i |\psi_i(r)|^2 + \sum_i \sum_{lm} \langle \psi_i | \beta_l \rangle Q_{lm}(r) \langle \beta_m | \psi_i \rangle$$

$$\frac{\delta E}{\delta \psi_i^*} = 0 \longrightarrow [H_{KS} - \varepsilon_i S] \, |\psi_i\rangle = 0$$

$$H_{KS} = -\frac{\hbar^2}{2m}\nabla^2 + V_{loc}(r) + V_{Hxc}(r) + \sum_{lm} |\beta_l\rangle D_{lm} \langle \beta_m|$$

$$D_{lm} = D_{lm}^0 + \int V_{Hxc}(r) Q_{lm}(r) dr$$

Ultra Soft PseudoPotentials

There are additional terms in the density, in the energy, in the hamiltonian in the forces, ...

Electronic states are orthonormal with a (configuration dependent) overlap matrix

The "augmentation charges" typically require a larger cutoff for the charge density:

QE Input parameter: ecutrho (SYSTEM namelist)

Default value is ecutrho = 4 × ecutwfc (OK for NC PP)

For USPP a larger value ecutrho is often needed.

Projector Augmented Waves

an all-electron method !

It is always possible to express the AE wfc via augmentation of a smooth (pseudo) wfc using atomic reference states

$$|\psi\rangle = |\tilde{\psi}\rangle + \sum_l \left(|\phi_l\rangle - |\tilde{\phi}_l\rangle \right) \langle \beta_l | \tilde{\psi} \rangle = (1 + T)|\tilde{\psi}\rangle$$

where...

Projector Augmented Waves

an all-electron method !

It is always possible to express the AE wfc via augmentation of a smooth (pseudo) wfc using atomic reference states

$$|\psi\rangle = |\tilde{\psi}\rangle + \sum_l \left(|\phi_l\rangle - |\tilde{\phi}_l\rangle \right) \langle \beta_l | \tilde{\psi} \rangle = (1 + T)|\tilde{\psi}\rangle$$

where

$|\psi\rangle$ all-electron wave function

$|\tilde{\psi}\rangle$ pseudo wave function

$\{ \, |\phi_l\rangle, l = 1, ..., N_{proj} \}$ all-electron atomic partial waves

$\{ \, |\tilde{\phi}_l\rangle, l = 1, ..., N_{proj} \}$ pseudo atomic partial waves

$\{ \, |\beta_l\rangle, l = 1, ..., N_{proj} \}$ localized projectors on the atomic partial waves such that $\langle \beta_l | \tilde{\phi}_m \rangle = \delta_{lm}$

Projector Augmented Waves

an all-electron method !

It is always possible to express the AE wfc via augmentation of a smooth (pseudo) wfc using atomic reference states

$$|\psi\rangle = |\tilde{\psi}\rangle + \sum_l \left(|\phi_l\rangle - |\tilde{\phi}_l\rangle \right) \langle \beta_l | \tilde{\psi}\rangle = (1 + T)|\tilde{\psi}\rangle$$

pictorially
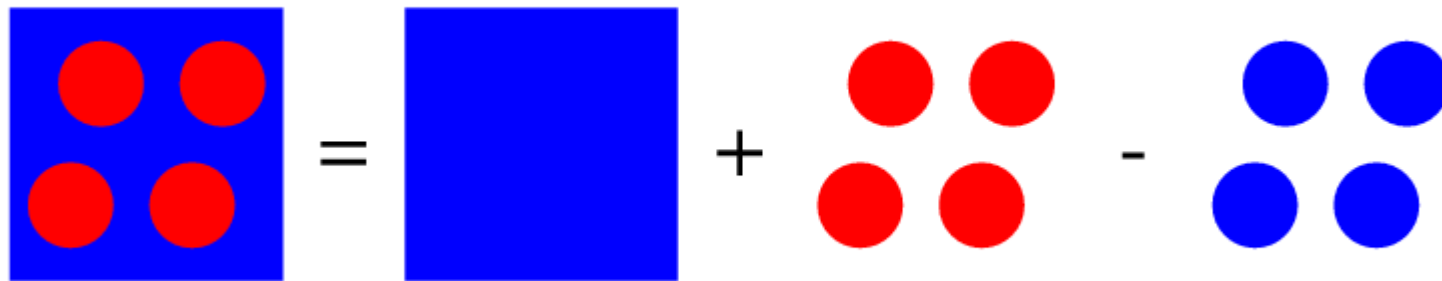
T is a localized operator !

$|\phi_l\rangle$'s and $|\tilde{\phi}_l\rangle$'s coincide outside the core region

and we can truncate them

The $|\beta_l\rangle$'s projectors are localized in the core region...

Projector Augmented Waves
an all-electron method !

AE matrix elements of any operator can then be computed as

$$\langle \psi | A | \psi \rangle \ = \ \langle \tilde{\psi} | (1 + T^{\dagger}) A (1 + T) | \tilde{\psi} \rangle \ = \ \langle \tilde{\psi} | \tilde{A} | \tilde{\psi} \rangle$$

if the $|\beta_l\rangle$ expansion is complete $\qquad \sum_l |\tilde{\phi}_l\rangle \langle \beta_l| \ \approx I_{\Omega_{core}}$

for local operators (kinetic energy, potential,...) one can show

$$\tilde{A} \ = \ A + \sum_{lm} |\beta_l\rangle \left(\langle \phi_l | A | \phi_m \rangle - \langle \tilde{\phi}_l | A | \tilde{\phi}_m \rangle \right) \langle \beta_m|$$
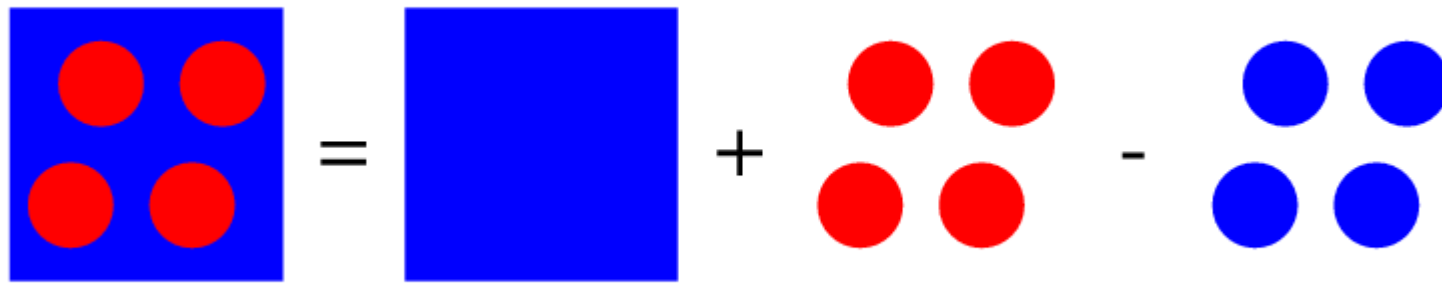
Projector Augmented Waves

an all-electron method !

AE matrix elements of any operator can then be computed as

$$\langle\psi|A|\psi\rangle = \langle\tilde{\psi}|(1+T^\dagger)A(1+T)|\tilde{\psi}\rangle = \langle\tilde{\psi}|\tilde{A}|\tilde{\psi}\rangle$$

if the $|\beta_l\rangle$ expansion is complete $\qquad \sum_l |\tilde{\phi}_l\rangle\langle\beta_l| \approx I_{\Omega_{core}}$

for local operators (kinetic energy, potential,...) one can show

$$\tilde{A} = A + \sum_{lm} |\beta_l\rangle \left(\langle\phi_l|A|\phi_m\rangle - \langle\tilde{\phi}_l|A|\tilde{\phi}_m\rangle \right) \langle\beta_m|$$

and normalization of wfc is computed with

$$\tilde{1} = 1 + \sum_{lm} |\beta_l\rangle \left(\langle\phi_l|\phi_m\rangle - \langle\tilde{\phi}_l|\tilde{\phi}_m\rangle \right) \langle\beta_m|$$

Projector Augmented Waves

an all-electron method !

AE results can be computed from the PS matrix elements augmented by KB-like contributions that can be computed from atomic AE and PS reference calculations.

$$\langle\psi|A|\psi\rangle = \langle\tilde\psi|A|\tilde\psi\rangle + \sum_{lm}\langle\tilde\psi|\beta_l\rangle\left(\langle\phi_l|A|\phi_m\rangle - \langle\tilde\phi_l|A|\tilde\phi_m\rangle\right)\langle\beta_m|\tilde\psi\rangle$$
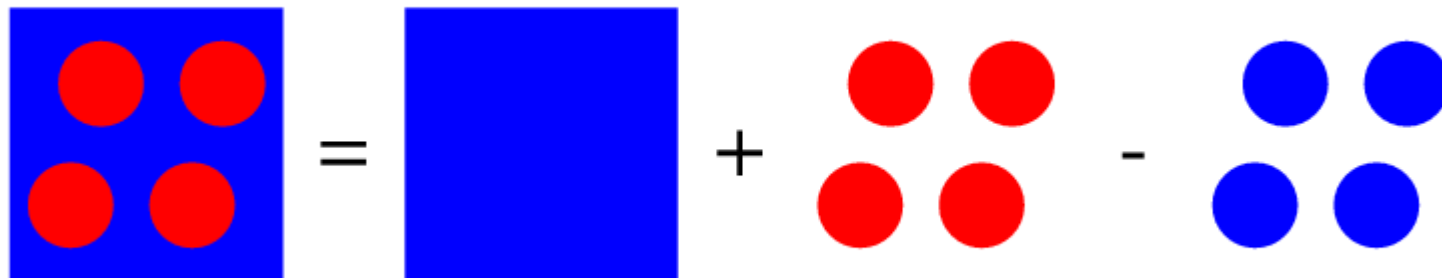
$$\langle A\rangle = \langle\tilde A\rangle + \sum\left(\langle A\rangle^{at} - \langle\tilde A\rangle^{at}\right)$$

Projector Augmented Waves

an all-electron method !

The charge density is therefore

$$|\psi_i(r)|^2 = |\tilde{\psi}_i(r)|^2 + \sum_{lm} \langle \tilde{\psi}_i | \beta_l \rangle \left(\phi_l(r)\phi_m(r) - \tilde{\phi}_l(r)\tilde{\phi}_m(r) \right) \langle \beta_m | \tilde{\psi}_i \rangle$$

$$\rho(r) \quad = \quad \tilde{\rho}(r) \; + \sum \left(\rho^{at}(r) - \tilde{\rho}^{at}(r) \right)$$

Projector Augmented Waves

an all-electron method !

The charge density is therefore

$$|\psi_i(r)|^2 = |\tilde{\psi}_i(r)|^2 + \sum_{lm}\langle\tilde{\psi}_i|\beta_l\rangle\left(\phi_l(r)\phi_m(r) - \tilde{\phi}_l(r)\tilde{\phi}_m(r)\right)\langle\beta_m|\tilde{\psi}_i\rangle$$

but it is convenient to add/subtract a compensating charge so that the AE and PS atomic references have the same Multipole expansion
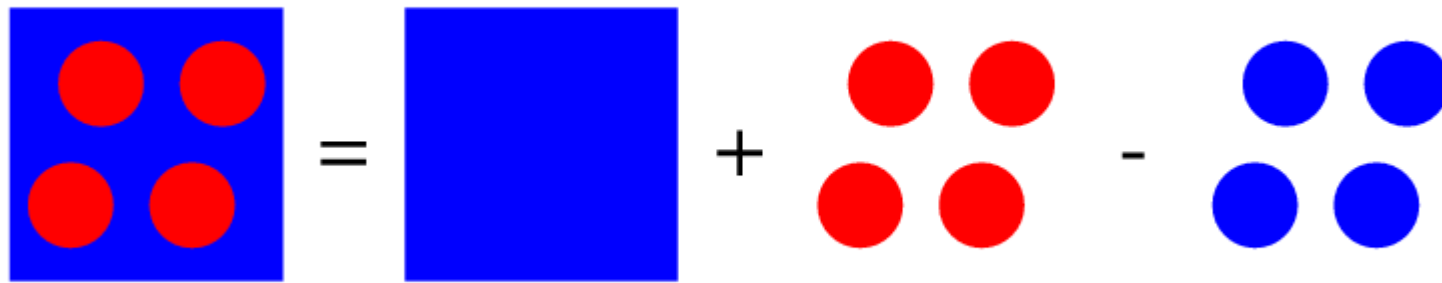
$$\rho(r) \quad = \quad \tilde{\rho}(r) + \sum\left(\rho^{at}(r) - \tilde{\rho}^{at}(r)\right)$$

Projector Augmented Waves

an all-electron method !

The charge density is therefore

$$|\psi_i(r)|^2 = |\tilde{\psi}_i(r)|^2 + \sum_{lm} \langle \tilde{\psi}_i | \beta_l \rangle Q_{lm}(r) \langle \beta_m | \tilde{\psi}_i \rangle$$

$$+ \sum_{lm} \langle \tilde{\psi}_i | \beta_l \rangle \, \phi_l(r) \phi_m(r) \, \langle \beta_m | \tilde{\psi}_i \rangle$$

$$- \sum_{lm} \langle \tilde{\psi}_i | \beta_l \rangle \left(\tilde{\phi}_l(r) \tilde{\phi}_m(r) + Q_{lm}(r) \right) \langle \beta_m | \tilde{\psi}_i \rangle$$
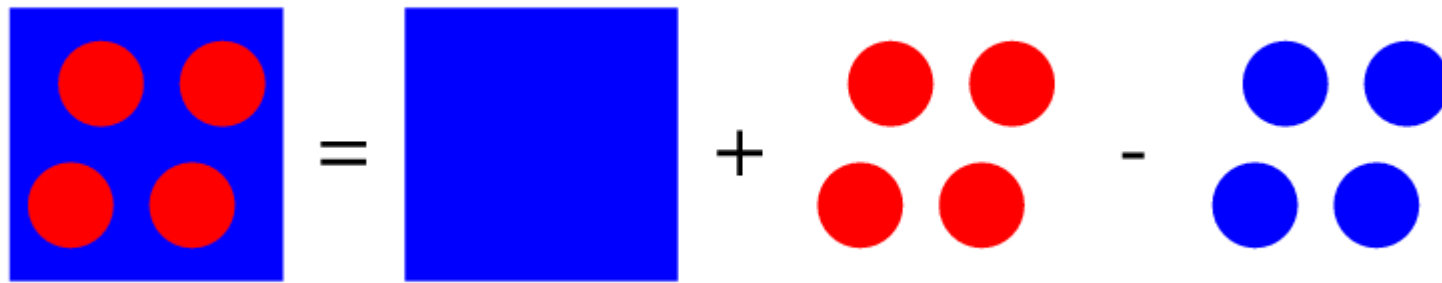
$$\rho(r) \quad = \quad \tilde{\rho}(r) \; + \sum \left(\rho^{at}(r) - \tilde{\rho}^{at}(r) \right)$$

Projector Augmented Waves

an all-electron method !

The different energy contributions so become

$$E_H[\rho] = E_H[\tilde{\rho} + \sum(\rho^{at} - \tilde{\rho}^{at})] = E_H[\tilde{\rho}] + \sum(E_H^{at}[\rho^{at}] - E_H^{at}[\tilde{\rho}^{at}])$$

$$E_{xc}[\rho] = E_{xc}[\tilde{\rho} + \sum(\rho^{at} - \tilde{\rho}^{at})] = E_{xc}[\tilde{\rho}] + \sum(E_{xc}^{at}[\rho^{at}] - E_{xc}^{at}[\tilde{\rho}^{at}])$$

$$T_s[\rho] = T_s[\tilde{\rho} + \sum(\rho^{at} - \tilde{\rho}^{at})] = T_s[\tilde{\rho}] + \sum(T_s^{at}[\rho^{at}] - T_s^{at}[\tilde{\rho}^{at}])$$

...
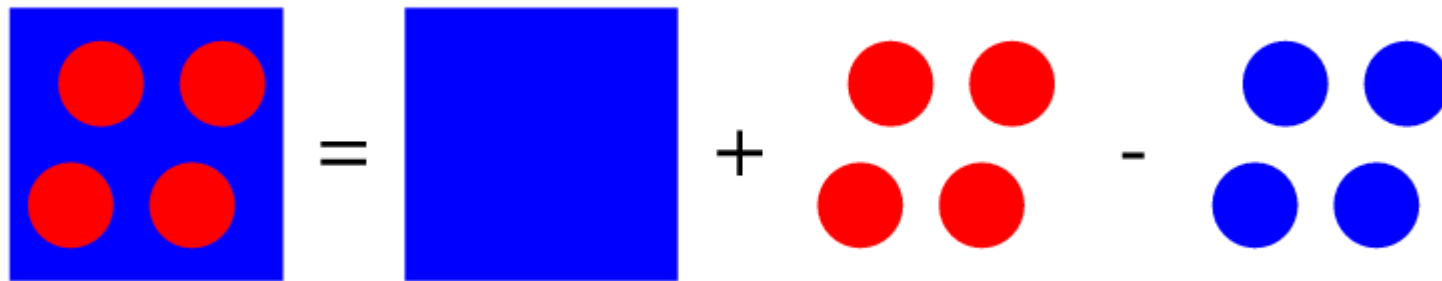
$$E_{tot} = \tilde{E}_{tot} + \sum\left(E_{tot}^{at} - \tilde{E}_{tot}^{at}\right)$$

Projector Augmented Waves

an all-electron method !

Finally the KS eigenvalue problem is as for USPP

$$[H_{KS} - \varepsilon_i S] \; |\psi_i\rangle = 0$$

with

$$S \; = \; 1 + \sum_{lm} |\beta_l\rangle \, q_{lm} \, \langle\beta_m|$$

where

$$H_{KS} = -\frac{\hbar^2}{2m}\nabla^2 + \tilde{V}_{eff}(r) + \sum_{lm} |\beta_l\rangle D_{lm}\langle\beta_m|$$

$$q_{lm} = \langle\phi_l|\phi_m\rangle - \langle\tilde{\phi}_l|\tilde{\phi}_m\rangle = \int Q_{lm}(r)dr$$

$$D_{lm} = D_{lm}^{at} - \tilde{D}_{lm}^{at} + \int \tilde{V}_{eff}(r)Q_{lm}(r)dr$$

$$D_{lm}^{at} = \langle\phi_l|T_s + V_{eff}|\phi_m\rangle$$

$$\tilde{D}_{lm}^{at} = \langle\tilde{\phi}_l|T_s + \tilde{V}_{eff}|\tilde{\phi}_m\rangle + \int \tilde{V}_{eff}(r)Q_{lm}(r)dr$$

Step 2 : initial guess for rho_in
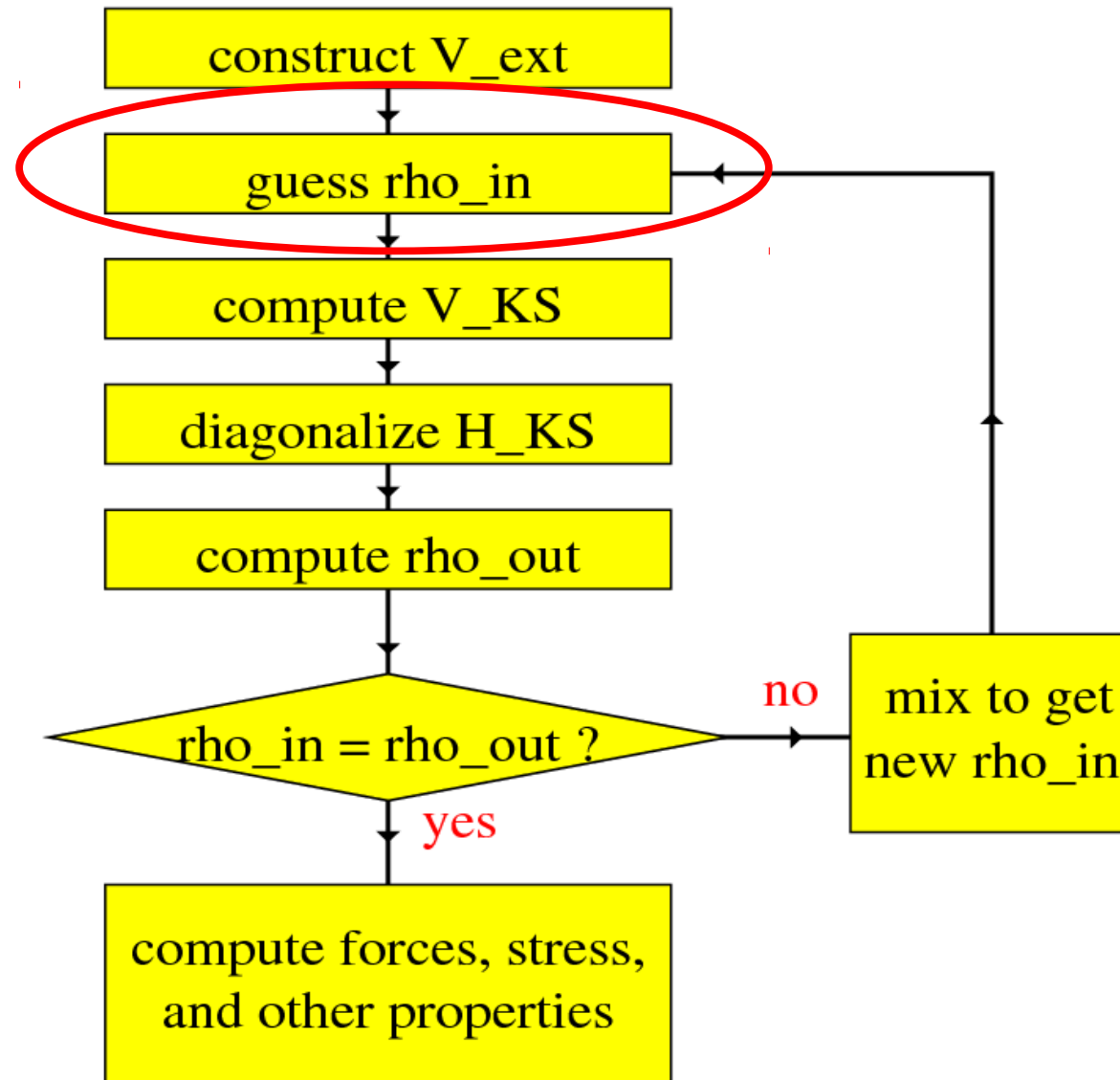
Initial choice of rho_in

Various possible choices, e.g.,:

- Superpositions of atomic densities.
- Converged n(r) from a closely related calculation (e.g., one where ionic positions slightly different).
- Approximate n(r) , e.g., from solving problem in a smaller/different basis.
- Random numbers.

Initial choice of rho_in

Various possible choices, e.g.,:

- Superpositions of atomic densities.
- Converged n(r) from a closely related calculation (e.g., one where ionic positions slightly different).
- Approximate n(r) , e.g., from solving problem in a smaller/different basis.
- Random numbers.

Initial guess of wfc

QE input parameter startingwfc

'atomic' | *'atomic+random'* | *'random'* | *'file'*

Pseudopotentials in Quantum ESPRESSO

Go to http://www.quantum-espresso.org/

Pseudopotentials for Quantum ESPRESSO

Click on the element for which the PP is desired

Pseudopotentials for Quantum ESPRESSO

Name: **Oxygen**
Symbol: **O**
Atomic number: **8**
Atomic configuration: **[He] 2s2 2p4**
Atomic mass: **15.9994 (3)**

Available pseudopotentials:

O.pbe-van_ak.UPF   (details)

  Perdew-Burke-Ernzerhof (PBE) exch-corr
  Vanderbilt ultrasoft
   author: ak

O.pbe-rrkjus.UPF   (details)

  Perdew-Burke-Ernzerhof (PBE) exch-corr
  Rabe Rappe Kaxiras Joannopoulos (ultrasoft)

O.pbe-kjpaw.UPF   (details)

  Perdew-Burke-Ernzerhof (PBE) e
  Projector Augmented Waves (Kre

O.rel-pz-rrkjus.UPF   (details)

  rel => full-relativistic
  Perdew-Zunger (LDA) exch-corr
  Rabe Rappe Kaxiras Joannopoulos (ultrasoft)

O.pz-rrkjus.UPF   (details)

  Perdew-Zunger (LDA) exch-corr
  Rabe Rappe Kaxiras Joannopoulos (ultrasoft)

Pseudopotential's name gives
Information about

-exchange correlation functional

-type of pseudopotential

O.pbe-rrkjus.UPF   (details)

  Perdew-Burke-Ernzerhof (PBE) exch-corr
  Rabe Rappe Kaxiras Joannopoulos (ultrasoft)

Atomic and V_ion info for QE

QE input card ATOMIC_SPECIES example:

ATOMIC_SPECIES
Ba 137.327 Ba.pbe-nsp-van.UPF
Ti 47.867 Ti.pbe-sp-van_ak.UPF
O 15.999 O.pbe-van_ak.UPF

NOTE
should use the same XC functional for all pseudopentials.
ecutwfc, ecutrho depend on type of pseudopotentials used
(should test for system & property of interest).