Plane Wave Basis Sets

Kohn–Sham method

 $E = \min_{\{\Phi\}} E_{\mathsf{KS}}[\{\Phi_i(\mathbf{r})\}]$

$$\int \Phi_i^{\star}(\mathbf{r}) \Phi_j(\mathbf{r}) d\mathbf{r} = \delta_{ij}$$
$$n(\mathbf{r}) = \sum_{i=1}^N f_i |\Phi_i(\mathbf{r})|^2$$

Kohn-Sham equations

$$\begin{cases} -\frac{1}{2} \nabla^2 + V_{\text{KS}}[n](\mathbf{r}) \\ V_{\text{KS}}[n](\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}) \\ V_{\text{KS}}[n](\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}[n](\mathbf{r}) + V_{\text{xc}}[n](\mathbf{r}) \\ n(\mathbf{r}) = \sum_i f_i |\psi_i(\mathbf{r})|^2 \end{cases}$$

Basis set methods

Arbitrary basis set $\{\varphi_{\alpha}(\mathbf{r})\}_{\alpha=1}^{M}$

Linear expansion of Kohn–Sham orbitals

$$\Phi_i(\mathbf{r}) = \sum_{\alpha=1}^M c_{\alpha i} \varphi_\alpha(\mathbf{r})$$

Atomic orbital basis sets

Philosophy : Molecules are assemblies of slightly distorted atoms

 $\varphi_{\alpha}(\mathbf{r}) = \varphi_{\alpha}(r) Y_{lm}(\Theta, \phi)$

$$\varphi_{\alpha}(r) = \begin{cases} \exp[-\alpha r^2] & \text{Gaussian} \\ \exp[-\alpha r] & \text{Slater} \end{cases}$$

 $\varphi_{\alpha}(\mathbf{r}; \mathbf{R}_{I})$: basis functions are attached to nuclear positions

Advantages/disadvantages of AO basis sets

- + according to chemical insight
- + small basis sets give already good results
- non-orthogonal
- depend on atomic position
- basis set superposition errors (BSSE)

Plane waves

Philosophy : Assemblies of atoms are slight distortions to free electrons

$$\varphi_{\alpha}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \exp[iG_{\alpha} \cdot \mathbf{r}]$$

+ orthonormal

+ independent of atomic positions

+ no BSSE

- \pm naturally periodic
- many functions needed
- localised functions difficult to represent

Computational box

In plane wave calculations one *always* has to define a computational box, even for isolated, molecular systems

In real space



- Box matrix: $\mathbf{h} = [\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3]$
- Box volume: $\Omega = \det h$

Lattice vectors

- Direct lattice $h = [a_1, a_2, a_3]$
- Direct lattice vectors : $\mathbf{L} = i \cdot \mathbf{a}_1 + j \cdot \mathbf{a}_2 + k \cdot \mathbf{a}_3$
- Reciprocal lattice $2\pi(\mathbf{h}^t)^{-1} = [\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3]$

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi \delta_{ij}$$

• Reciprocal lattice vectors : $\mathbf{G} = i \cdot \mathbf{b}_1 + j \cdot \mathbf{b}_2 + k \cdot \mathbf{b}_3$

Properties of plane waves

$$\varphi_{\mathbf{G}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \exp[i\mathbf{G} \cdot \mathbf{r}]$$

- \bullet Plane waves are periodic wrt. box h
- Plane waves are orthonormal

$$\langle \varphi_{\mathbf{G}'} | \varphi_{\mathbf{G}} \rangle = \delta_{\mathbf{G}',\mathbf{G}}$$

• Plane waves are complete

$$\psi(\mathbf{r}) = \psi(\mathbf{r} + \mathbf{L}) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} \psi(\mathbf{G}) \exp[i\mathbf{G} \cdot \mathbf{r}]$$

Local (radial) functions

A function depending on the angles only via spherical harmonics

$$\phi(\mathbf{r}) = \phi(r)Y_{lm}(\Theta, \Phi)$$

= $\sum_{\mathbf{G}} \phi(G) \exp[iGr] Y_{lm}(\tilde{\Theta}, \tilde{\Phi})$

 $\tilde{\Theta}, \tilde{\Phi}$ angles of G

Bessel transform

$$\phi(G) = 4\pi (-i)^l \int_0^\infty dr \ r^2 \phi(r) \ j_l(Gr)$$

 j_l : Spherical Bessel functions of the first kind

Position dependence

Translation

$$\phi(\mathbf{r}) \longrightarrow \phi(\mathbf{r} - \mathbf{R}_{I})$$

$$\phi(\mathbf{r} - \mathbf{R}_{I}) = \sum_{\mathbf{G}} \phi(\mathbf{G}) \exp[i\mathbf{G} \cdot (\mathbf{r} - \mathbf{R}_{I})]$$

$$= \sum_{\mathbf{G}} \phi(\mathbf{G}) \exp[i\mathbf{G} \cdot \mathbf{r}] \exp[-i\mathbf{G} \cdot \mathbf{R}_{I}]$$

Structure Factor

$$S_I(\mathbf{G}) = \exp[-i\mathbf{G}\cdot\mathbf{R}_I]$$

Derivatives

$$\frac{\partial \phi(\mathbf{r}; \mathbf{R}_I)}{\partial \mathbf{R}_{I,s}} = -i \sum_{\mathbf{G}} \mathbf{G}_s \phi(\mathbf{G}) \exp[i \mathbf{G} \cdot \mathbf{r}] S_I(\mathbf{G})$$

Example of operators

Kinetic energy operator is diagonal in the plane wave basis

$$-\frac{1}{2}\nabla^2\varphi_{\mathbf{G}}(\mathbf{r}) = -\frac{1}{2}(iG)^2\frac{1}{\sqrt{\Omega}}\exp[i\mathbf{G}\cdot\mathbf{r}] = \frac{1}{2}G^2\varphi_{\mathbf{G}}(\mathbf{r})$$

$$E_{\mathsf{kin}}(\mathbf{G}) = \frac{1}{2} G^2$$

Cutoff: Finite basis set



Basis set size depends on volume of box and cutoff only !

Real space grid Sampling Theorem

- Sampling interval $\Delta = \frac{L}{N}$ (L = length, N number of points)
- Nyquist critical frequency $f_c = \frac{1}{2\Delta}$

For a given plane wave cutoff (frequency) there is a minimum number of equidistant real space grid points needed for the same accuracy: $N = \frac{L}{\pi} E_{\text{cut}}^{1/2}$

Real space grid:
$$\mathbf{R}_i = (i-1)\Delta$$

Fast Fourier Transform (FFT)

 $\psi(\mathbf{G}) \longleftrightarrow \psi(\mathbf{R})$

The information contained in $\psi(G)$ and $\psi(R)$ are equivalent

Transform from $\psi(\mathbf{G})$ to $\psi(\mathbf{R})$ and back is done using Fourier methods. If the number of grid points can be decomposed into small prime numbers fast Fourier transform techniques can be used

Fourier transform N^2 operationsfast Fourier transform $N \log[N]$ operations

Integrals

$$I = \int_{\Omega} A^{*}(\mathbf{r})B(\mathbf{r})d\mathbf{r}$$

= $\sum_{\mathbf{GG}'} A^{*}(\mathbf{G})B(\mathbf{G}) \int \exp[-i\mathbf{G} \cdot \mathbf{r}] \exp[i\mathbf{G}' \cdot \mathbf{r}]d\mathbf{r}$
= $\sum_{\mathbf{GG}'} A^{*}(\mathbf{G})B(\mathbf{G}) \Omega \,\delta_{\mathbf{GG}'}$
= $\Omega \sum_{\mathbf{G}} A^{*}(\mathbf{G})B(\mathbf{G})$

Parseval's theorem

$$\Omega \sum_{\mathbf{G}} A^{\star}(\mathbf{G}) B(\mathbf{G}) = \frac{\Omega}{N} \sum_{i} A^{\star}(\mathbf{R}_{i}) B(\mathbf{R}_{i})$$

Electron density

$$n(\mathbf{r}) = \sum_{i} f_{i} |\Phi_{i}(\mathbf{r})|^{2} = \frac{1}{\Omega} \sum_{i} f_{i} \sum_{\mathbf{G},\mathbf{G}'} c_{i}^{\star}(\mathbf{G}) c_{i}(\mathbf{G}') \exp[i(\mathbf{G} - \mathbf{G}') \cdot \mathbf{r}]$$

$$n(\mathbf{r}) = \sum_{\mathbf{G}=-2G_{\text{max}}}^{2G_{\text{max}}} n(\mathbf{G}) \exp[i\mathbf{G} \cdot \mathbf{r}]$$

The electron density can be expanded *exactly* in a plane wave basis with a cutoff four times the basis set cutoff :

$$N_{\mathsf{PW}}(4E_{\mathsf{cut}}) = 8N_{\mathsf{PW}}(E_{\mathsf{cut}})$$

Comparison to AO Basis Set

Plane Waves :

$$\frac{1}{2}G^2 < E_{\text{cut}}$$
$$\frac{1}{2}G'^2 < E_{\text{cut}}$$
$$\frac{1}{2}(G+G')^2 < \left(\sqrt{E_{\text{cut}}} + \sqrt{E_{\text{cut}}}\right)^2 = 4E_{\text{cut}}$$

Atomic orbitals : every product results in a new function

$$\varphi_{\alpha}(\mathbf{r}-\mathbf{A})\varphi_{\beta}(\mathbf{r}-\mathbf{B})=\varphi_{\gamma}(\mathbf{r}-\mathbf{C})$$

Linear dependence for plane waves vs. quadratic dependence for AO basis sets.

Operators

Matrix representation of operators in Kohn–Sham theory:

 $O(G,G') = \langle G | \mathcal{O} | G' \rangle$

Example: Kinetic energy operator

$$\mathbf{T}_{\mathbf{G},\mathbf{G}'} = \langle \mathbf{G} | -\frac{1}{2} \nabla^2 | \mathbf{G}' \rangle = \frac{1}{2} G^2 \delta_{\mathbf{G},\mathbf{G}'}$$

Local operators

$$\begin{aligned} \langle \mathbf{G}' | \mathcal{O}(\mathbf{r}) | \mathbf{G}'' \rangle &= \frac{1}{\Omega} \sum_{\mathbf{G}} \mathbf{O}(\mathbf{G}) \int e^{[-i\mathbf{G}' \cdot \mathbf{r}]} e^{[i\mathbf{G} \cdot \mathbf{r}]} e^{[i\mathbf{G}'' \cdot \mathbf{r}]} d\mathbf{r} \\ &= \frac{1}{\Omega} \sum_{\mathbf{G}} \mathbf{O}(\mathbf{G}) \int e^{[i(\mathbf{G} - \mathbf{G}' + \mathbf{G}'') \cdot \mathbf{r}]} d\mathbf{r} \\ &= \frac{1}{\Omega} \mathbf{O}(\mathbf{G}' - \mathbf{G}'') \end{aligned}$$

Local operators can be expanded in plane waves with a cutoff four times the basis set cutoff.

Applying operators In reciprocal space

$$B(\mathbf{G}) = \sum_{\mathbf{G}'} \mathbf{O}(\mathbf{G}, \mathbf{G}') A(\mathbf{G}')$$

Local Operators: Convolution

$$B(\mathbf{G}) = \sum_{\mathbf{G}'} \frac{1}{\Omega} \mathbf{O}(\mathbf{G} - \mathbf{G}') A(\mathbf{G}') = (\mathbf{O} * A)(\mathbf{G})$$

Convolution in frequency space transforms to product in real space

$$B(\mathbf{R}_i) = \mathbf{O}(\mathbf{R}_i)A(\mathbf{R}_i)$$

Thus local operators — e.g. $V_{\text{KS}}(\mathbf{r})$ — are better applied in real space

Kohn–Sham orbitals

• KS-orbitals (for periodic system) Bloch theorem

$$\Phi_i(\mathbf{r}, \mathbf{k}) = \exp[i\mathbf{k} \cdot \mathbf{r}] u_i(\mathbf{r}, \mathbf{k})$$

$$u_i(\mathbf{r}, \mathbf{k}) = u_i(\mathbf{r} + \mathbf{L}, \mathbf{k})$$

- Γ point approximation: $\mathbf{k} = \mathbf{0}$ only point considered in the Brillouin zone.
- Γ point KS-orbitals

$$\Phi_{i}(\mathbf{r}) = u_{i}(\mathbf{r})$$

= $\frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} c_{i}(\mathbf{G}) \exp[i\mathbf{G} \cdot \mathbf{r}]$

Valid approximation in large or disordered systems

Kohn–Sham energy

$$E_{\rm KS} = E_{\rm kin} + E_{\rm PP} + E_{\rm ES} + E_{\rm XC}$$

 E_{kin} Kinetic energy

 E_{PP} Pseudopotential energy

 E_{ES} Electrostatic energy (sum of electron-electron interaction + nuclear core-electron interaction + ion-ion interaction)

 E_{xc} Exchange–correlation energy

Kinetic energy

$$E_{kin} = \sum_{i} f_{i} \langle \Phi_{i} | -\frac{1}{2} \nabla^{2} | \Phi_{i} \rangle$$

$$= \sum_{i} \sum_{GG'} c_{i}^{*}(G) c_{i}(G') \langle G | -\frac{1}{2} \nabla^{2} | G' \rangle$$

$$= \sum_{i} \sum_{GG'} c_{i}^{*}(G) c_{i}(G') \Omega \frac{1}{2} G^{2} \delta_{G,G'}$$

$$= \frac{\Omega}{2} \sum_{i} \sum_{G} G^{2} | c_{i}(G) |^{2}$$

Electrostatic energy

$$E_{\mathsf{ES}} = \frac{1}{2} \iint d\mathbf{r} \, d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \sum_{I} \int d\mathbf{r} \, V_{\mathsf{core}}^{I}(\mathbf{r})n(\mathbf{r}) + \frac{1}{2} \sum_{I \neq J} \frac{Z_{I} Z_{J}}{|\mathbf{R}_{I} - \mathbf{R}_{J}|}$$

Problem: Divergencies in individual terms

Gaussian charge distributions

$$n_{\rm C}^{I}(\mathbf{r}) = -\frac{Z_{I}}{\left(\mathsf{R}_{I}^{\rm C}\right)^{3}} \pi^{-3/2} \exp\left[-\left(\frac{\mathbf{r}-\mathbf{R}_{I}}{\mathsf{R}_{I}^{\rm C}}\right)^{2}\right]$$

Electrostatic potential of $n_{\rm C}^I$

$$V_{\text{core}}^{I}(\mathbf{r}) = \int d\mathbf{r}' \frac{n_{\text{C}}^{I}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} = -\frac{Z_{I}}{|\mathbf{r} - \mathbf{R}_{I}|} \text{erf}\left[\frac{|\mathbf{r} - \mathbf{R}_{I}|}{\mathsf{R}_{I}^{\mathsf{C}}}\right]$$

Electrostatic energy

$$E_{\text{ES}} = \frac{1}{2} \iint d\mathbf{r} \, d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{1}{2} \iint d\mathbf{r} \, d\mathbf{r}' \frac{n_{\text{C}}(\mathbf{r})n_{\text{C}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \iint d\mathbf{r} \, d\mathbf{r}' \frac{n_{\text{C}}(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} - \frac{1}{2} \iint d\mathbf{r} \, d\mathbf{r}' \frac{n_{\text{C}}(\mathbf{r})n_{\text{C}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} ,$$

where $n_{\rm C}({\bf r}) = \sum_I n_{\rm C}^I({\bf r})$

The first three terms can be combined to the electrostatic energy of a total charge distribution

$$n_{\text{tot}}(\mathbf{r}) = n(\mathbf{r}) + n_{\text{C}}(\mathbf{r})$$

and the other two terms calculated analytically

Electrostatic energy

$$E_{\text{ES}} = \frac{1}{2} \iint d\mathbf{r} \, d\mathbf{r}' \frac{n_{\text{tot}}(\mathbf{r}) n_{\text{tot}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \text{erfc} \left[\frac{|\mathbf{R}_I - \mathbf{R}_J|}{\sqrt{\mathbf{R}_I^{c2} + \mathbf{R}_J^{c2}}} \right] - \sum_I \frac{1}{\sqrt{2\pi}} \frac{Z_I^2}{R_I^c}$$

- 1. Term: Long-ranged forces (reciprocal space)
- 2. Term: Short-ranged two-center terms (direct space)
- 3. Term: One-center term

Periodic systems

Plane wave expansion of n_{tot}

$$n_{\text{tot}}(\mathbf{G}) = n(\mathbf{G}) + \sum_{I} n_{\mathsf{C}}^{I}(\mathbf{G}) S_{I}(\mathbf{G})$$
$$= n(\mathbf{G}) - \frac{1}{\Omega} \sum_{I} \frac{Z_{I}}{\sqrt{4\pi}} \exp\left[-\frac{1}{2}G^{2}R_{I}^{\mathsf{C}^{2}}\right] S_{I}(\mathbf{G})$$

Criteria for parameter $R_I^{\rm C}$: PW expansion of $n_{\rm C}^I$ has to be converged with density cutoff

- The smaller the R_I^{C} , the higher the cutoff
- The larger the $R_I^{\rm C}$, the heavier the terms in direct space

Poisson's equation Periodic systems

 $\nabla^2 V_{\mathsf{H}}(\mathbf{r}) = -4\pi n_{\mathsf{tot}}(\mathbf{r})$

For periodic boundary conditions

$$V_{\mathsf{H}}(\mathbf{G}) = 4\pi \frac{n_{\mathsf{tot}}(\mathbf{G})}{G^2}$$

 $V_{\mathsf{H}}(\mathbf{G})$ is a local operator with same cutoff as n_{tot}

The solution in plane waves is *very* much easier than *e. g.* in local basis set, offering a *huge* advantage

Periodic systems

$$E_{\text{ES}} = 2\pi \Omega \sum_{\mathbf{G} \neq 0} \frac{|n_{\text{tot}}(\mathbf{G})|^2}{G^2} + E_{\text{ovrl}} - E_{\text{self}}$$

where

$$E_{\text{ovrl}} = \sum_{I,J}' \sum_{\mathbf{L}} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J - \mathbf{L}|} \operatorname{erfc} \left[\frac{|\mathbf{R}_I - \mathbf{R}_J - \mathbf{L}|}{\sqrt{\mathbf{R}_I^{c2} + \mathbf{R}_J^{c2}}} \right]$$

and

$$E_{\mathrm{self}} = \sum_{I} \frac{1}{\sqrt{2\pi}} \frac{Z_{I}^{2}}{R_{I}^{\mathrm{c}}}$$

Sums expand over all atoms in the simulation cell, all direct lattice vectors L, and the prime in the first sum indicates that I < J is imposed for L = 0

Exchange and correlation energy

$$E_{\mathsf{XC}} = \int d\mathbf{r} \, \varepsilon_{\mathsf{XC}}(\mathbf{r}) \, n(\mathbf{r}) = \Omega \sum_{\mathbf{G}} \varepsilon_{\mathsf{XC}}(\mathbf{G}) n^{\star}(\mathbf{G})$$

 $\varepsilon_{xc}(G)$ is not local in G space. Calculation in real space requires very accurate integration scheme

New definition of $E_{\rm XC}$

$$E_{\mathsf{XC}} = \frac{\Omega}{N_{\mathsf{X}}N_{\mathsf{Y}}N_{\mathsf{Z}}} \sum_{\mathbf{R}} \varepsilon_{\mathsf{XC}}(\mathbf{R})n(\mathbf{R}) = \Omega \sum_{\mathbf{G}} \tilde{\varepsilon}_{\mathsf{XC}}(\mathbf{G})n(\mathbf{G})$$

where $\tilde{\varepsilon}_{xc}(G)$ is the finite Fourier transform of $\varepsilon_{xc}(R)$

Only translations by a multiple of the grid spacing do not change the total energy. This introduces a small modulation of the energy hyper surface, known as "ripples"

Energy and force of helium atom



The energy should be a constant, the force zero

Energy of oxygen atom

Oxygen atom



PW'91: 40 / 3.2 Ry • PW'91: 70 / 4.0 Ry + PW'91: 50 / 3.85 Ry × PBE: 50 / 3.85 °

Plane waves: Summary

- Plane waves are delocalised, periodic basis functions
- Plenty of them are needed, however the operations are simple
- The quality of basis set adjusted using a *single* parametre, the cut-off energy
- Fast Fourier-transform used to efficiently switch between real and reciprocal space
- The size of basis set is independent of number of atoms (for a given volume), $N_{\rm G}\propto\Omega$, $N_{\rm G}\propto E_{\rm cut}^{3/2}$

Pseudo potentials

Why use pseudo potentials?

- Reduction of basis set size effective speedup of calculation
- Reduction of number of electrons reduces the number of degrees of freedom For example in Pt: 10 instead of 78

• Unnecessary

"Why bother? They are inert anyway..."

• Inclusion of relativistic effects

relativistic effects can be included "partially" into effective potentials

Why use pseudo potentials? Estimate for number of plane waves

plane wave cutoff ↓ most localized function

1s Slater type function $\approx exp[-Zr]$ Z: effective nuclear charge



	Cutoff	Plane waves
Η	1	1
Li	4	8
C	9	27
Si	27	140
Ge	76	663



- Replacement of the all-electron, -Z/r problem with a Hamiltonian containing an effective potential
- It should reproduce the necessary physical properties of the full problem in the reference state
- The potential should be transferable, *i. e.* also be accurate in different environments

The construction consists of two steps of approximations

- Frozen core approximation
- Pseudisation

Frozen core approximation

- Core electrons are chemically inert
- Core/valence separation is often not clear in plane wave calculations: core = all filled shells
- Core wavefunctions are transferred from atomic reference calculation
- Core electrons of different atoms do not overlap

Remaining problems

- Valence wavefunctions have to be orthogonalized to core states \rightarrow nodal structures \rightarrow high plane wave cutoff
- Pseudo potential should produce node-less functions and include Pauli repulsion
- Pseudo potential replaces Hartree and XC potential due to the core electrons
- XC functionals are not linear: approximation

$$E_{\mathsf{XC}}(n_{\mathsf{C}} + n_{\mathsf{V}}) = E_{\mathsf{XC}}(n_{\mathsf{C}}) + E_{\mathsf{XC}}(n_{\mathsf{V}})$$

This assumes that core and valence electrons do not overlap. This restriction can be overcome with the "non–linear core correction" (NLCC) discussed later.

Atomic pseudo potentials

$$n(\mathbf{r}) = n_{\mathsf{C}}(\mathbf{r}) + n_{\mathsf{V}}(\mathbf{r})$$

Valence Kohn–Sham Equations

$$\left(T + V(\mathbf{r}, \mathbf{r}') + V_{\mathsf{H}}(n_{\mathsf{V}}) + V_{\mathsf{XC}}(n_{\mathsf{V}})\right) \Phi_{i}^{\mathsf{V}}(\mathbf{r}) = \epsilon_{i} \Phi_{i}^{\mathsf{V}}(\mathbf{r})$$

Pseudo potential $V(\mathbf{r}, \mathbf{r}')$ has to be chosen such that the main properties of the atom (*reference state*) are reproduced. Several values of I (angular quantum number) have to be used for good accuracy

Pseudisation of valence wave functions



General recipe

- 1. Atomic all–electron calculation (reference state) $\Rightarrow \Phi_i^{\sf V}(\mathbf{r})$ and ϵ_i
- 2. Pseudise $\Phi_i^{\mathsf{V}} \Rightarrow \Phi_i^{\mathsf{PS}}$ (node-less!)
- 3. Calculate potential from

$$(T + V_i(\mathbf{r})) \Phi_i^{\mathsf{PS}}(\mathbf{r}) = \epsilon_i \Phi_i^{\mathsf{PS}}(\mathbf{r})$$

4. Calculate pseudo potential by unscreening of $V_i(\mathbf{r})$

$$V_i^{\mathsf{PS}}(\mathbf{r}) = V_i(\mathbf{r}) - V_{\mathsf{H}}(n_{\mathsf{PS}}) - V_{\mathsf{XC}}(n_{\mathsf{PS}})$$

 V_i^{PS} is state dependent!

Hamann-Schlüter-Chiang-recipe (HSC) DR Hamann, M Schlüter and C Chiang, Phys. Rev. Lett. **43**, 1494 (1979)

- 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 :

$$\Psi_l(r) = \Phi_l(r)$$
 for $r \ge r_c$

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*):

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

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 $r \ge r_c$.

Property 3) and 4) are related through

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

Recipes to construct norm-conserving pseudo potentials

• Bachelet-Hamann-Schüter (BHS) Form

G.B. Bachelet et al., Phys. Rev. B, **26**, 4199 (1982) Recipe and analytic form of V_l^{PS}

- Kerker Recipe G.P. Kerker, J. Phys. C 13, L189 (1980) analytic pseudisation function
- D. Vanderbilt, Phys. Rev. B, **32**, 8412 (1985)
- Kinetic energy optimized pseudo potentials
 A.M. Rappe et al., Phys. Rev. B, 41, 1227 (1990)
 J.S. Lin et al., Phys. Rev. B, 47, 4174 (1993)
- Troullier–Martins recipe

Troullier–Martins recipe

N Troullier and JL Martins, Phys. Rev. B, 43, 1993 (1991)

$$\Phi_l^{\mathsf{PS}}(\mathbf{r}) = r^{l+1} e^{p(r)} \quad r \le r_c$$

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

Determine c_n from

- norm-conservation
- smoothness at r_c (for m = 0...4) $\frac{d^m \Phi}{dr^m}\Big|_{r=r_c-} = \frac{d^m \Phi}{dr^m}\Big|_{r=r_c+}$

•
$$\left. \frac{d\Phi}{dr} \right|_{r=0} = 0$$

Optimised for smoothness *i. e.* small basis set

Separation of local and nonlocal parts

$$V^{\mathsf{PS}}(\mathbf{r},\mathbf{r}') = \sum_{L=0}^{\infty} V_L^{\mathsf{PS}}(r) |Y_L\rangle \langle Y_L| \quad , \ L = \{l,m\}$$

$$V^{\mathsf{PS}}(\mathbf{r}, \mathbf{r}') = \sum_{L=0}^{\infty} V_L^{\mathsf{PS}}(r) |Y_L\rangle \langle Y_L| - \sum_{L=0}^{\infty} V_{\mathsf{loc}}^{\mathsf{PS}}(r) |Y_L\rangle \langle Y_L| + V_{\mathsf{loc}}^{\mathsf{PS}}(r)$$
$$= \sum_{L=0}^{\infty} \left(V_L^{\mathsf{PS}}(r) - V_{\mathsf{loc}}^{\mathsf{PS}}(r) \right) |Y_L\rangle \langle Y_L| + V_{\mathsf{loc}}^{\mathsf{PS}}(r)$$

Approximation: all potentials with $L > L_{\text{max}}$ are equal to $V_{\text{loc}}^{\text{PS}}$ (or $\langle Y_L | \psi \rangle$ becomes negligible)

$$V^{\mathsf{PS}}(\mathbf{r},\mathbf{r}') = \sum_{L=0}^{L_{\max}} \left[V_L^{\mathsf{PS}}(r) - V_{\mathsf{loc}}^{\mathsf{PS}}(r) \right] |Y_L\rangle \langle Y_L| + V_{\mathsf{loc}}^{\mathsf{PS}}(r)$$

Final *semi-local* form

$$V^{\mathsf{PS}}(\mathbf{r},\mathbf{r}') = V_{\mathsf{loc}}^{\mathsf{PS}}(r) + \sum_{L=0}^{L_{\mathsf{max}}} \Delta V_L^{\mathsf{PS}}(r) |Y_L\rangle \langle Y_L|$$

- Local pseudo potential $V_{\text{loc}}^{\text{PS}}$
- Radially local pseudo potential $\Delta V_L^{\mathsf{PS}}(r)$; vanishes beyond core radii
- Any L quantum number can have a non-local part



Silicon: Radial wave functions

Silicon: Pseudo vs all-electron wave functions



Silicon: Radial densities

Silicon: lonic pseudo potentials



Non-local PP in PW calculations

$$E_{\mathsf{PS}} = \sum_{L} \sum_{i} f_{i} \int_{r} \langle \Phi_{i} | Y_{L} \rangle_{r} \Delta V_{L}^{\mathsf{PS}}(r) \langle Y_{L} | \Phi_{i} \rangle_{r} dr$$

$$\langle \Phi_i | Y_L \rangle_r = \int \Phi_i(\mathbf{r}) Y_L(\hat{\mathbf{r}}) d\hat{\mathbf{r}}$$

Integral depends on r

Gauss–Hermite Integration

$$E_{\mathsf{PS}}^{\mathsf{nl}} = \sum_{L} \sum_{i} f_{i} \sum_{k} w_{k} \Delta V_{L}^{\mathsf{PS}}(r_{k}) \left[\langle \Phi_{i} \mid Y_{L} \rangle_{r} (r_{k}) \right]^{2}$$

Accurate integration requires \approx 15 - 25 points.

For an atom with s and p non-local potential this requires the calculation of 60 - 100 times number of states integrals $\langle \Phi_i | Y_L \rangle_r$.

Basis set expansion

Resolution of identity $1 = \sum_{n} |\varphi_n\rangle \langle \varphi_n|$ for a complete orthonormal basis set $\{\varphi_n\}$:

$$E_{\mathsf{PS}} = \sum_{L} \sum_{i} f_{i} \sum_{nm} \langle \Phi_{i} | \varphi_{n} \rangle \int \langle \varphi_{n} | Y_{L} \rangle_{r} V_{L}^{\mathsf{PS}}(r) \langle Y_{L} | \varphi_{m} \rangle_{r} dr \langle \varphi_{m} | \Phi_{i} \rangle$$

Using $\langle \varphi_n \mid Y_L \rangle_r = \varphi_n(r)$ we can calculate the basis set expansion of the pseudo potential

$$V_{L,nm}^{\mathsf{PS}} = \int \varphi_n(r) V_L^{\mathsf{PS}}(r) \varphi_m(r) dr$$

and get

$$E_{\mathsf{PS}} = \sum_{L} \sum_{i} f_{i} \sum_{nm} \langle \Phi_{i} \mid \varphi_{n} \rangle V_{L,nm}^{\mathsf{PS}} \langle \varphi_{m} \mid \Phi_{i} \rangle$$

Typical basis set expansions contain only a few functions.

Kleinman–Bylander form

Basis set expansion with the following approximation for the identity:

$$1 = \sum_{L} \frac{|\varphi_L\rangle \langle \Delta V_L \varphi_L|}{\langle \varphi_L \Delta V_L \varphi_L \rangle}$$

where φ_L is the pseudo–atomic wavefunction from the reference calculation.

 $|\Delta V_L \varphi_L\rangle$ is localized within r_c .

Kleinman–Bylander form

$$E_{\mathsf{PS}} = \sum_{L} \sum_{i} f_i \langle \Phi_i \mid \Delta V_L \varphi_L \rangle \omega_L \langle \Delta V_L \varphi_L \mid \Phi_i \rangle$$

where

$$\omega_L = \langle \varphi_L \mid \Delta V_L \mid \varphi_L \rangle$$

For an atom with s and p non-local potential this requires the calculation of 4 times number of states integrals $\langle \Delta V_L \varphi_L | \Phi_i \rangle$ Generalization of the Kleinman–Bylander form to more than 1 reference function by Blöchl (1990) and Vanderbilt (1990).

Ghost States

Problem: in Kleinman–Bylander form, the node-less wfn is no longer the solution with the lowest energy **Solution**: carefully tune the local part of the pseudo potential until the ghost states disappear

How to find host states: Look for following properties

- Deviations of the logarithmic derivatives of the energy of the KB-pseudo potential from those of the respective semi-local pseudo potential or all-electron potential.
- Comparison of the atomic bound state spectra for the semi-local and KB-pseudo potentials.
- Ghost states below the valence states are identified by a rigorous criteria by Gonze et al.

Dual Space Pseudo potentials

- S. Goedecker et al., Phys. Rev. B, 54 1703 (1996)
- C. Hartwigsen et al., Phys. Rev. B, 58 3641 (1998)
 - Functional form of pseudo potential: local part + fully separable non-local part
 - All functions are expanded in Gaussians
 - All free parameters are globally optimized

Ultra-soft Pseudo potentials and PAW method

- Many elements require high cutoff for plane wave calculations
 - First row elements: O, F
 - Transition metals: Cu, Zn
 - f elements: Ce
- Relax norm-conservation condition

$$\int n^{\mathsf{PS}}(\mathbf{r})d\mathbf{r} + \int Q(\mathbf{r})d\mathbf{r} = \mathbf{1}$$

- Augmentation functions $Q(\mathbf{r})$ depend on environment
- No full un-screening possible, $Q(\mathbf{r})$ has to be recalculated for each atom and atomic position
- Complicated orthogonalization and force calculations
- Allows for larger r_c , reduces cutoff for all elements to about 20...30 Rydberg

Non-Linear Core Correction (NLCC)

For many atoms (e.g. alkali atoms, transition metals) core states overlap with valence states. Linearization assumption for XC energy breaks down.

- Add additional states to valence
 - adds more electrons
 - needs higher cutoff
- Add core charge to valence charge in XC energy ⇒ non-linear core correction (NLCC)
 S.G. Louie et al., Phys. Rev. B, 26 1738 (1982)

Non-Linear Core Correction (NLCC)



Non-Linear Core Correction (NLCC)

The total core charge of the system depends on the atomic positions.

$$\tilde{n}_{core}(\mathbf{G}) = \sum_{I} \tilde{n}_{core}^{I}(\mathbf{G}) S_{I}(\mathbf{G})$$

This leads to additional terms in the derivatives wrt to nuclear positions and the box matrix (for the pressure).

$$\frac{\partial E_{\mathsf{XC}}}{\partial \mathbf{R}_{I,s}} = -\Omega \sum_{\mathbf{G}} i \mathbf{G}_s V_{\mathsf{XC}}^{\star}(\mathbf{G}) \tilde{n}_{\mathsf{core}}^{I}(\mathbf{G}) S_{I}(\mathbf{G})$$

Specification of Pseudo potentials

- The pseudo potential recipe used and for each I value r_c and the atomic reference state
- The definition of the local potential and which angular momentum state have a non-local part
- For Gauss–Hermit integration: the number of integration points
- Was the Kleinman–Bylander scheme used ?
- NLCC: definition of smooth core charge and r_{loc}

Testing of Pseudo potentials

- calculation of other atomic states
- calculation of transferability functions, logarithmic derivatives, hardness
- calculation of small molecules, compare to all electron calculations (geometry, harmonic frequencies, dipole moments)
- check of basis set convergence (cutoff requirements)
- calculation of test systems

Example : Oxygen dimer



Pseudo potentials: Summary

- Pseudo potential are necessary when using plane wave basis sets in order to keep the number of the basis function manageable
- Pseudo potentials are generated at the reference state; transferability is the quantity describing the accuracy of the properties at other conditions
- The mostly used scheme in plane wave calculations is the Troullier-Martins pseudo potentials in the fully non-local, Kleinman-Bylander form
- Non-linear core correction is need if the core and valence electron densities overlap excessively
- Once created, a pseudo potential must be tested, tested, tested!!!