

Pseudopotentials

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Kohn Sham Equation

We want to solve the Kohn Sham equation:

$$\left(\hat{H} - \epsilon_i \right) \psi_i = 0$$

The Kohn Sham Hamiltonian is analogous to the Hamiltonian of the original system:

$$\hat{H} = -\frac{1}{2} \nabla^2 + V_{nuc} + V_H[n] + V_{XC}[n]$$

$$e = \hbar = m_e = 1$$

Solving using a basis set

We chose to limit our wave function to the Hilbert space spanned by a basis set:

$$\psi_i(r) = \sum_{\alpha} c_{i\alpha} e_{\alpha}(r)$$

Now we have a matrix equation:

$$\sum_{\beta} H_{\alpha\beta} c_{i\beta} = \epsilon_i c_{i\alpha}$$

This is a linear problem of finite size (NXN) where N is the size of the basis set

Plane Wave basis set

- PW and CP and all QE are based on plane wave basis sets:
- The reciprocal lattice generates plane wave basis set: $e^{i\mathbf{G}\cdot\mathbf{r}}$
- Given a Bravais lattice and its reciprocal:

$$\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3 \quad \mathbf{b}_i = \frac{2\pi}{\Omega} \sum_{ijk} \epsilon_{ijk} \mathbf{a}_j \wedge \mathbf{a}_k$$

- For any three (Miller) indices we have a wave vector:

$$\mathbf{G} = M_1 \cdot \mathbf{b}_1 + M_2 \cdot \mathbf{b}_2 + M_3 \cdot \mathbf{b}_3$$

Advantages of a Plane Wave basis set:

- **Simple:** Easy to take derivatives, etc => easy for coding
- **Orthonormal:** No overlap integrals
- **Independent of atomic positions:** No “Pulay Forces”
- **Unbiased:** No assumption about charge distribution. (Sometimes this is also a waste -- slabs, molecules, etc
- **FFTS:** basis expansion and decomposition can be performed using Fast Fourier transform algorithms: very efficient
- Very practical to calculate convolutions and solve Poisson’s equation

$$V(r) = \int \frac{n(r')}{|r-r'|} dr' \quad \longrightarrow \quad V(\mathbf{G}) = 4\pi \frac{\tilde{n}(\mathbf{G})}{G^2}$$

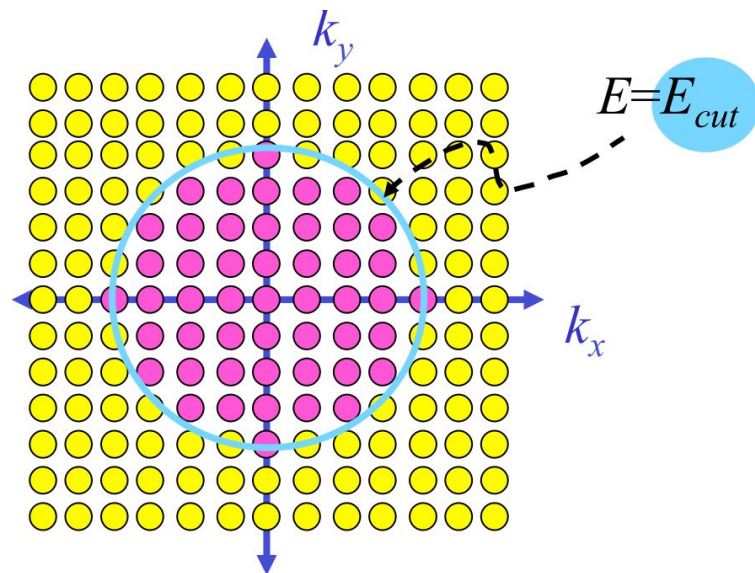
Cons of plane waves

- A huge number of plane waves ($\sim 10^5$ per atom) would be needed (solution introduction of pseudopotentials)
- Periodicity is built in, need a supercell with a lot of vacuum to simulate non periodic systems
- The basis functions have no chemical meaning

To be finite we need cut the plane wave basis set

- In practice the contribution of large ($\mathbf{k}+\mathbf{G}$) components becomes negligible
- It is traditional to express this cut-off in energy units.
- Beware wave functions and density have different cutoffs $ecutrho = 4Xecutwfc$ (at least)

$$\frac{\hbar^2 |\mathbf{k}+\mathbf{G}|^2}{2m_e} \leq E_{cut}$$



Kohn Sham equations in plane wave basis

- Eigenvalue equation is now: $\sum_{\mathbf{G}'} H_{\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}'} = c_{i,\mathbf{k}+\mathbf{G}}$
- Matrix elements are:

$$\frac{1}{2}|\mathbf{k} + \mathbf{G}|^2 \delta_{\mathbf{G},\mathbf{G}'} + V_{ion}(\mathbf{k} + \mathbf{G}, \mathbf{k} + \mathbf{G}') + V_{H+XC}(\mathbf{G} - \mathbf{G}')$$

- Nuclear (\rightarrow ionic) potential giveb by (structure factor):

$$V_{ion}(\mathbf{G}) = \sum_{\alpha} S_{\alpha}(\mathbf{G}) v_{\alpha}(\mathbf{G})$$

$$S_{\alpha}(\mathbf{G}) = \sum_I e^{i\mathbf{G} \cdot \mathbf{R}_I}$$

A feasible $v_a(G)$ pseudopotentials:

- Electrons in atoms are arranged in **shells**
- Quantum numbers:
 - n (principal), l (angular), m_l (magnetic), m_s (spin)
- Rare gas have complete shells + complete d or f subshells:
 - He: $1s^2$; Ne [He], $2s^2$, $2p^6$; Ar [Ne], $3s^2$, $3p^6$; Kr: [Ar] $3d^{10}$, $4s^2$, $4p^6$
.... Rn: [Xe], $4f^{14}$, $5d^{10}$, $6s^2$, $6p^6$
- Can divide electrons in any atom into “**core**” and “**valence**”
- Lot of exceptions but usually **core = [rare gas configuration] + [filled d or f subshells]**

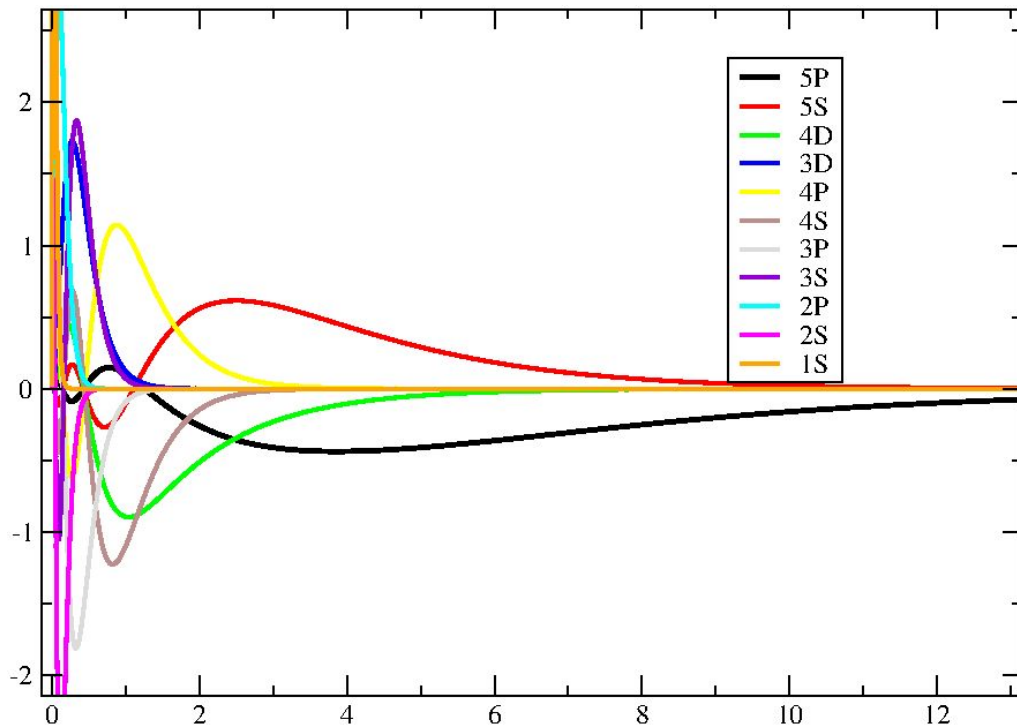
Atomic wave functions

$$\psi_{lm}(\mathbf{r}) = \psi_l(r)Y_{lm}(\theta, \phi) = r^{-1}\phi_l(r)Y_{lm}(\theta, \phi)$$

- Radial part depend on r , angular on angles
- They are orthonormal.
 - Functions with same n have equal radial part and orthogonal angular part
 - Functions with same l have orthogonal radial parts
 - 1s, 2p, 3d, 4f radial functions are nodeless
 - 2s, 3p, 4d, 5f radial functions have one node
 - ... and so on

Example Ag [Kr], $4d^{10}$, $5s^1$, $5p^0$

- Core orbitals strongly localized
- Valence functions outet peak far from the radius, strongly oscillating close to the nucleus
- 4d has an outer peak more or less close to the valence orbitals: is it valence or core ?



Electrons in molecules and solids

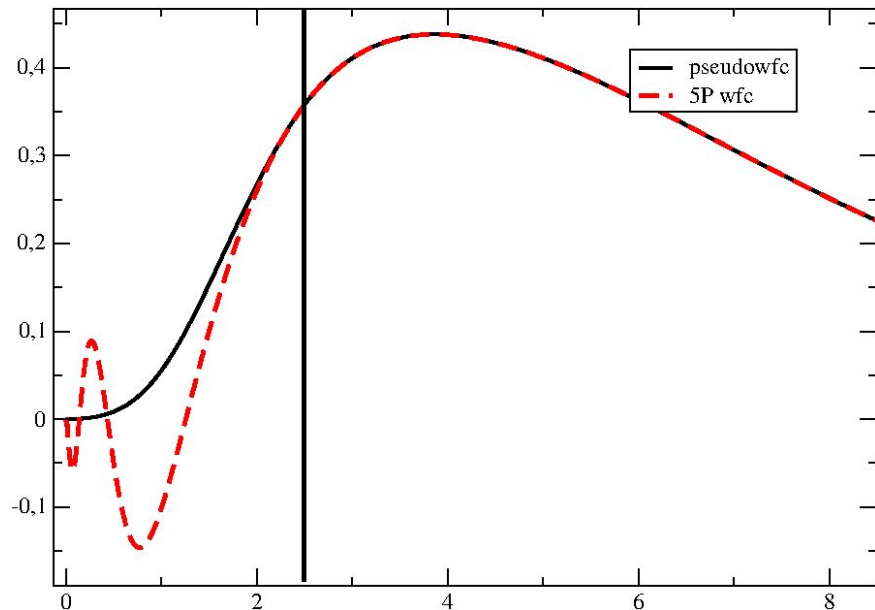
- Chemistry is done by the transfer and sharing of electrons
- Only valence electrons orbitals participate in bonding, their shape may change significantly once bonds are formed
- When bonding with other elements the 5p orbital may start being filled
- Core orbitals change only slightly when bonds are formed

The pseudopotential approximation

- **Frozen Core.** The core orbitals are not made to vary, the core density is considered fixed.
- **The screening action** of the frozen core density is **reproduced**, valence electrons see a weaker potential than the full Coulomb one.
- Modify this nucleus + core density potential in order to reproduce the scattering properties outside an outer radius and eliminate wiggles in the inner region

Building a pseudopotential

- Select an cutoff radius just before the outer peak of Ag 5P wave function
- generate a pseudo wave function which connect smoothly with the all electron wave function outside the cutoff radius
- Invert the radial equation to obtain the pseudopotential V_l
- Unscreen the pseudopotential



$$V_l^{PS}(r) = V_l^{scr}(r) - V_H[n_l^{val}(r)] - V_{XC}[n_{val}^l(r)]$$

Generating the pseudopotential

- Different schemes for generation the pseudo wave functions (Hamann, Troullier-Martins, RRKJ)
- The pseudowave function is generated imposing that:

$$\int_0^{rc} \phi^{*AE}(r) \phi^{AE}(r) dr = \int_0^{rc} \phi^{*PS}(r) \phi^{PS}(r) dr$$

- In the original scheme there was a pseudopotential for each angular quantum number l and the total pseudopotential was expressed as

$$V_{ps}(r) = V_{loc}(r) + \sum_l \sum_{l=-m}^{l=m} Y_{lm} \delta V_l(r) Y_{lm}^*$$

Building the pseudopotential

- The pseudopotential may be rewritten in the Kleinmann-Bylander form:

$$V_{ps} = V_{loc} + \sum_{lm} \frac{|\delta V_l \chi_{lm}\rangle \langle \chi_{lm} \delta V_l|}{\langle \chi_{lm} | \delta V_l | \chi_{lm} \rangle}$$

- This form is very convenient computationally but the pseudopotential may present ghost states.

Vanderbilt Formalism

- Possibility to have more projectors per angular momentum: improved transferability
- Gives way to USPP
- For each energy reference we generate as before a pseudo wave function and its pseudopotential V_{loc} which is equal to V_{AE} outside a cutoff radius. Then we define:

$$|\chi_i\rangle = (\epsilon_i - T - V_{ps})|\phi_i\rangle$$

- This functions should be localized within the cutoff radius the right hand side vanishes outside r_c

Vanderbilt formalism

- We define the coefficients

$$B_{ij} = \langle \phi_i | \phi_j \rangle$$

- and the beta projectors

$$|\beta_i\rangle = \sum_j B_{ji}^{-1} |\chi_i\rangle$$

- The non local part of the pseudopotential now can be written as:

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

Dropping norm conservation

- In this formalism the norm conservation is:

$$Q_{ij} = \langle \phi_i^{AE} | \psi_j^{AE} \rangle_{R_C} - \langle \phi_i^{PS} | \phi_j^{PS} \rangle_{R_C} = 0$$

- It is possible to drop this condition and allow Q_{ij} to be different from 0. This allows much more soft pseudopotentials. This complicates somewhat the formalism

USPP

- In this case the non local part of the pseudopotential includes an augmentation part

$$V_{NL} = \sum_{ij} D_{ij} |\beta_i\rangle \langle \beta_j| \quad D_{ij} = B_{ij} + \epsilon_j Q_{ij}$$

- The scalar product between wave function becomes:

$$\langle \psi_a | \psi_b \rangle + \sum_{ij} \langle \psi_a | \beta_i \rangle \langle \beta_j | \psi_b \rangle$$

- The expression for the total density is:

$$n_v(\mathbf{r}) = \sum_{n,\mathbf{k}} \phi_{n,\mathbf{k}}^* \phi_{n,\mathbf{k}} + \sum_{ij} \rho_{ij} Q_{ij}(\mathbf{r}) \quad \rho_{ij} = \sum_{n,\mathbf{k}} \langle \phi_{n,\mathbf{k}} | \beta_i \rangle \langle \beta_j | \phi_{n,\mathbf{k}} \rangle$$

USPP

- The total energy and the electronic density now include augmentation terms which depend on the functions $Q_{ij}(r)$.
- These functions may be defined in a FFT grid that is more dense than the one of the wave functions. The cutoff for the electronic density may be significantly larger than 4 times the cutoff for the wave functions.

Where to find pseudopotentials

- Quantum Espresso: <http://www.quantum-espresso.org/pseudopotentials>
- PSLibrary <http://pslibrary.quantum-espresso.org> provides also many alternative inputs to generate pseudopotentials
- <http://www.pseudo-dojo.org/> provides a full set of ONCV pseudopotentials
- <https://www.physics.rutgers.edu/gbrv/> provides a full set of well tested USPP pseudopotentials
- Pseudopotentials on materials cloud
<https://www.materialscloud.org/discover/sssp/table/efficiency>, provide suggested pseudopotentials, cutoff and a wide set of tests.