

# EVALUATION OF $n^{GS}(\vec{r})$ WITH THE KS FUNCTIONAL

$$\left\{ \begin{aligned} E^{GS} &= \min_{\Psi_i^{KS}} \left\{ T_0[\{\Psi_i^{KS}\}] + E_{KS}^{LDA, GGA}[n(\vec{r})] \right\} \\ n(\vec{r}) &= 2 \sum_{i=1}^{N/2} \langle \Psi_i^{KS} | \delta(\vec{r}) | \Psi_i^{KS} \rangle \end{aligned} \right.$$

IN A PRACTICAL CALCULATION WE USE A VARIATIONAL APPROACH AND WE EXPAND  $\Psi_i^{KS}$  ON A FINITE BASIS (HILBERT SPACE)

E.G. ● WITH ATOMIC ORBITALS:

$$|\Psi_i^{KS}\rangle = \sum_I \sum_m C_{Im}^i |\Phi_{I,m}\rangle$$

SUM OVER ATOMS      SUM OVER ATOMIC QUANTUM NUMBERS

THIS IS THE MOST COMMON APPROACH USED IN QUANTUM CHEMISTRY

# ATOMIC ORBITAL BASIS SETS

**ADVANTAGES :** → IT IS AN ALL-ELECTRON METHOD

→ SMART BASIS ⇒ SMALL SIZE

→ PROPERTIES ARE DESCRIBED IN TERMS OF ATOMIC ORBITALS (STANDARD VIEW OF BONDING)

→ NOTE THAT IT IS A TIGHT-BINDING APPROACH

**DISADVANTAGES :** → THE BASIS DEPENDS ON THE ATOM POSITION (PROBLEM IN WEAK BONDING)

→ THERE IS NOT A SYSTEMATIC WAY TO INCREASE THE BASIS (CRITICAL FOR SOME PROPERTIES)

→ THE STATES DELOCALIZED IN A REGION WITHOUT ATOMS ARE DIFFICULT TO BE DESCRIBED (E.G. ELECTRONS IN A CRYSTAL VACANCY)

● WITH PLANE-WAVE BASIS SETS  
(IN A PERIODIC SYSTEM)

$$|\Psi_{i, \vec{q}}^{KS}\rangle = e^{i\vec{q} \cdot \vec{r}} \sum_{\vec{G}} C_{\vec{G}}^{i, \vec{q}} |\vec{G}\rangle$$

quasi-momentum  
(OF THE BLOCH  
WAVE FUNCTION)

SUM OVER THE RECIPROCAL  
LATTICE VECTORS

$$\langle \vec{r} | \vec{G} \rangle = \frac{1}{\sqrt{\Omega}} e^{i\vec{G} \cdot \vec{r}}$$

$\Omega$ : UNIT CELL VOLUME

IN THE  $\sum_{\vec{G}}$  ALL  $\vec{G}$  VECTORS UP TO A  
KINETIC ENERGY CUTOFF ARE TAKEN:

$$\forall \vec{G} : \frac{1}{2m} (\vec{q} + \vec{G})^2 \leq E_{\text{CUT}}$$

THE NUMBER OF PW IS TYPICALLY  $\sim 150 - 300$  PER ATOM  
IN CONDENSED SYSTEMS (WITH NO VACUUM)



# PLANE WAVE BASIS SETS :

- ADVANTAGES :**
- THE BASIS COVERS ALL THE SPACE UNIFORMLY (THE ELECTRON<sup>n</sup> STATE ARE WELL DESCRIBED EVEN IN THE CASES WHERE ELECTRONS STAY NOT WHERE WE EXPECT TO BE)
  - THE BASIS DOES NOT DEPEND ON ATOM POSITION (GOOD IN WEAK BONDS)
  - THE PW ARE SIMPLE ⇒ EVALUATION IN PW ARE SIMPLE AND FAST E.G. KINETIC ENERGY OPERATOR IS DIAGONAL

$$T = \frac{1}{2m} (\vec{q} + \vec{G})^2$$

POISSON EQUATION FOR COULOMB POTENTIAL

$$V_H(\vec{r}) = \int d^3r' \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} \quad \text{IS DIAGONAL IN } \vec{G} \text{ SPACE}$$

⇓

$$V_H(\vec{G}) = \frac{4\pi}{G^2} \rho(\vec{G})$$

- FOR EVALUATION PURPOSE WE CAN USE  $\vec{r}$  SPACE OR  $\vec{G}$  SPACE USING THE FAST FOURIER TRANSFORM (FFT) WHICH SCALE AS  $N_G \ln N_G$

→ THE COMPLETENESS (ACCURACY) OF THE BASIS IS FIXED BY A SINGLE PARAMETER  $E_{\text{CUT}}$  FOR  $E_{\text{CUT}} \rightarrow \infty$  WE OBTAIN A COMPLETE HILBERT SPACE

**DISADVANTAGES :** → THE BASIS SET COVERS ALL THE SPACE (ALSO REGIONS OF VACUUM)

→ TO HAVE A CONVERGED RESULT WITH A REASONABLE SMALL  $E_{\text{CUT}}$  WE DESCRIBE ONLY VALENCE ELECTRONS AND WE USE PSEUDO POTENTIALS INSTEAD OF THE REAL POTENTIALS (NOT A ALL ELECTRON METHOD)

## REFERENCIES ON PSEUDOPOTENTIALS :

[HAMANN, SCHLÜTER, CHIANG PRL 43, 1494 (1979)  
BACHELET, HAMMAN, SCHLÜTER PRB 26, 4199 (1982)]

TROULLIER MARTINS, PRB 43, 1993 (1991)

KLEINMAN-BYLANDER PRL 48, 1425 (1982)

BLÖCHL, PRB 50, 17953 (1994)

# AB-INITIO (NORM-CONSERVING)

## PSEUDOPOTENTIALS

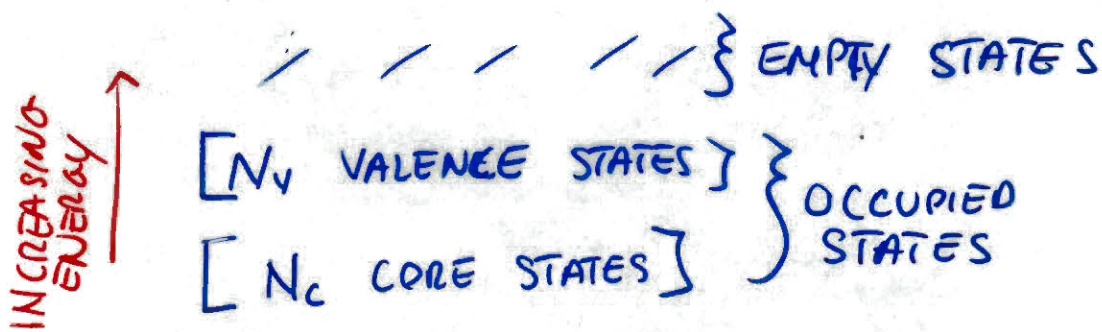
JUST THE OUTER SHELL ELECTRONS PARTICIPATE IN THE CHEMICAL BONDING



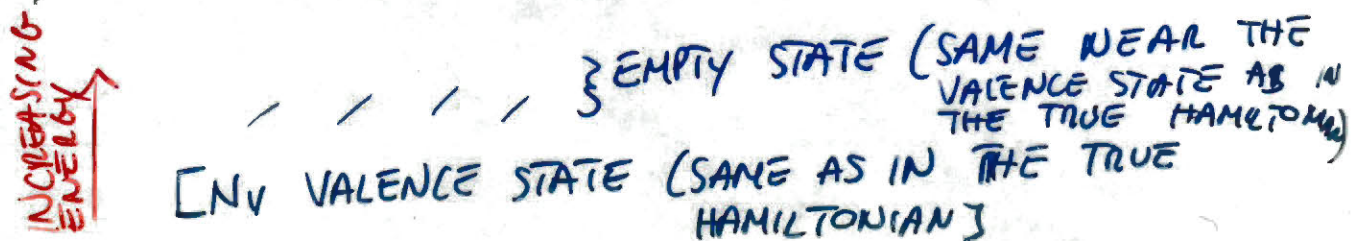
TO REPRODUCE THE CHEMICAL PROPERTIES WE CAN PARTITION THE ELECTRON STATES

IN  $\rightarrow N_c$  CORE STATES  
 $\rightarrow N_v$  VALENCE STATES

THE TRUE (K.S) HAMILTONIAN HAS THE FOLLOWING SPECTRUM



WE CONSTRUCT A PSEUDO HAMILTONIAN  $H^{ps}$  WHOSE SPECTRUM DOES NOT CONTAIN CORE STATES:





WITH  $H^{ps}$  WE CAN JUST TREAT THE  $V$   
ELECTRONS AND STILL USE THE  
VARIATIONAL PRINCIPLE

BUT:

THE VALENCE WAVE FUNCTIONS ARE ORTHONORMAL  
TO THE CORE STATE  $\Rightarrow$  OSCILLATE NEAR THE  
CORE

THESE OSCILLATIONS REQUIRES MANY PLANE WAVES

IF WE ARE NOT INTERESTED IN THE CORE  
REGION (THE CHEMICAL BONDING OCCURS IN THE  
BONDING REGION AND NOT IN THE CORE REGION)

WE MODIFY THE IN SUCH A WAY THAT:

$\rightarrow$  OUTSIDE THE CORE REGION THE  
PSEUDO WAVEFUNCTIONS OF VALENCE STATES  
AND OF THE CONDUCTION STATE NEAR (IN ENERGY)  
TO THE  $V$  STATES COINCIDE WITH THE  
TRUE WAVEFUNCTION (SAME SCATTERING PROPERTIES  
IN AN ENERGY WINDOW)

$\rightarrow$  INSIDE THE CORE REGION THE PSEUDO WAVEFUNCTIONS  
ARE SMOOTH (CAN BE DESCRIBED WITH FEW PW)





THE TRUE KS AND EXTERNAL POTENTIALS ARE LOCAL

$$\langle \vec{r} | V_{KS}^{TRUE} | \psi \rangle = V_{KS}^{TRUE}(\vec{r}) \langle \vec{r} | \psi \rangle$$

THE PSEUDO POTENTIAL IS A NON LOCAL OPERATOR  
ITS STANDARD FORM IS

$$\langle \vec{r} | V_{PS}^{KS} | \psi \rangle = \underbrace{V_{KS}^{LOC}(\vec{r})}_{\text{LOCAL PART}} \langle \vec{r} | \psi \rangle +$$

(SELF CONSISTENT:  
IT DEPENDS ON  
THE DENSITY)

$$+ \langle \vec{r} | \left[ \sum_I \sum_m |\beta_{Im}\rangle \langle \beta_{Im}| \right] | \psi \rangle$$

NON LOCAL PART  
(NON SELF-CONSISTENT)

SUM OVER ATOMS

SUM OVER "SOME QUANTUM NUMBER"  
(TYPICALLY  $l, m$ )

● THE  $|\beta_{Im}\rangle$  FUNCTIONS OF ATOM I ARE ZERO OUTSIDE THE CORE REGION

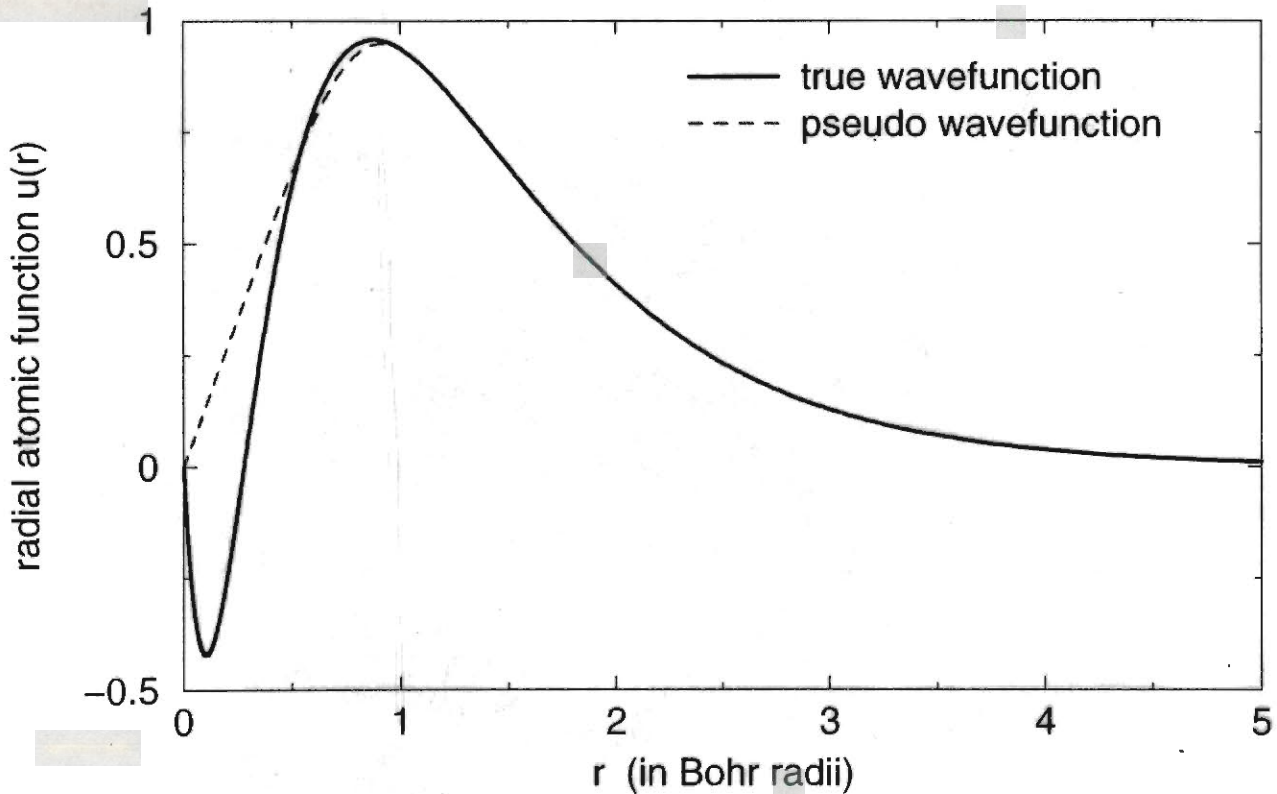
●  $V_{KS}^{LOC}(\vec{r}) = V_{KS}^{TRUE}(\vec{r})$  OUTSIDE THE CORE REGION

IN AN ATOM

$$\vec{\psi}_{n,\ell,m}(\vec{r}) = Y_{\ell m}(\frac{\vec{r}}{r}) \frac{u(r)}{r}$$

Oxygen atom

2s wavefunction



# PSEUDOPOTENTIAL CONSTRUCTION

STEP (1) FOR EACH ATOM TYPE, WE CONSTRUCT THE TRUE VALENCE WAVEFUNCTION  $|\psi_{AT,m}^{TRUE}\rangle$  FOR THE ANGULAR MOMENTUM CHANNEL RELEVANT FOR THE PROBLEM WE WANT TO TREAT (TYPICALLY S P D)

STEP (2) FOR EACH ATOMS TYPE WE CONSTRUCT THE PSEUDOWAVEFUNCTIONS  $|\psi_{AT,m}^{PS}\rangle$  WHICH COINCIDE OUTSIDE THE CORE RADII WITH  $|\psi_{AT,m}^{TRUE}\rangle$

STEP (3) WE CONSTRUCT THE  $|\beta_{l,m}\rangle$  FUNCTIONS AND  $V_{KS}^{PS}(\vec{r})$

NOTE THAT THE CONSTRUCTION IS DONE ON THE ATOMS BUT IT IS TRANSFERABLE TO MOLECULES AND SOLIDS (IF THE CORE RADII ARE SMALL ENOUGH)



# MINIMISATION OF THE KS FUNCTIONAL

(1) WITH MIXING:

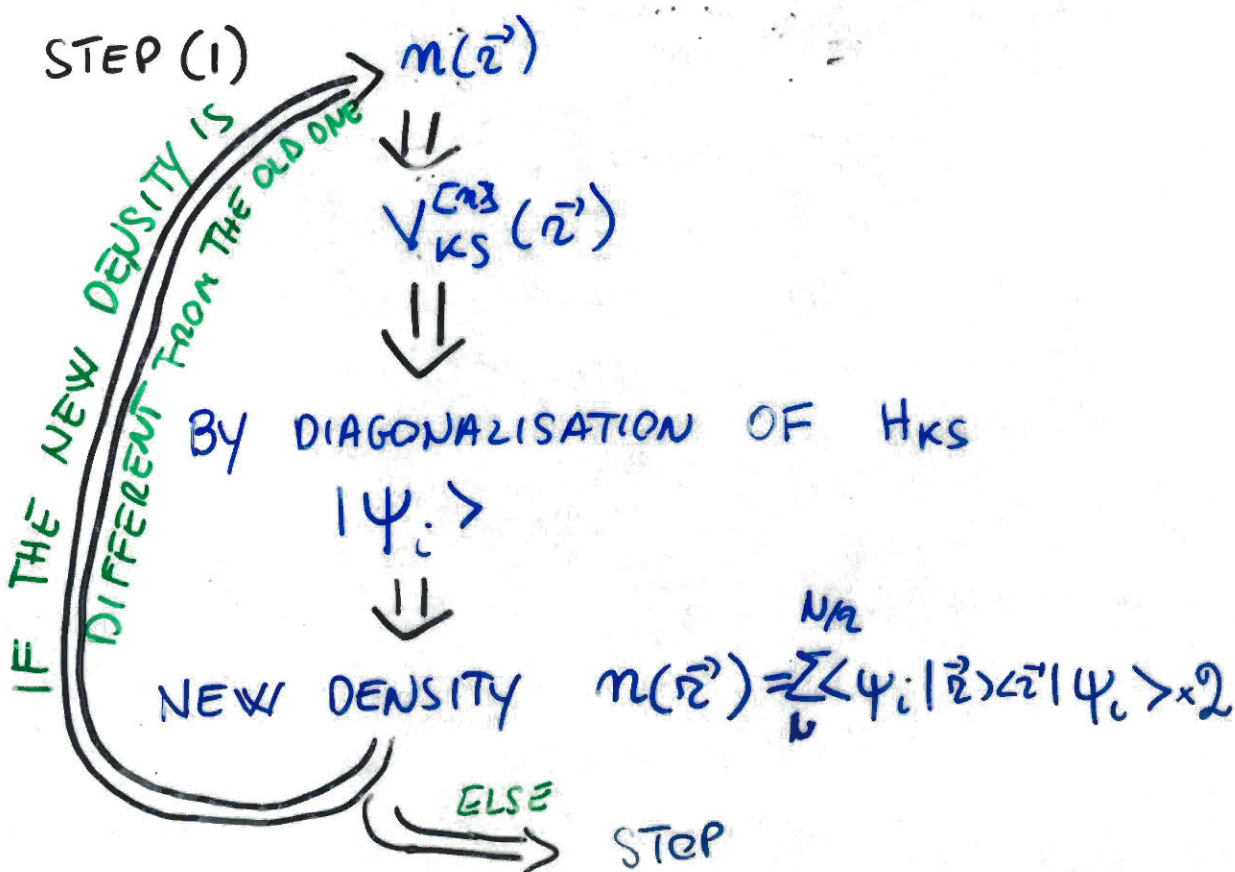
AT THE MINIMUM:

$$\left\{ \begin{array}{l} \underline{|\psi_i^{GS}\rangle} \text{ ARE EIGENVECTORS OF } H_{KS}[\underline{m^{GS}}] \\ \text{WHERE } \underline{m^{GS}(\vec{r})} = \sum_{i=1}^{N/2} \underline{\langle \psi_i^{GS} | \vec{r} \rangle \langle \vec{r} | \psi_i^{GS} \rangle} \end{array} \right.$$

SELF CONSISTENT HAMILTONIAN:

SOLUTION CAN BE OBTAINED BY ITERATIONS:

STEP (0)  $n(\vec{r}) = n_{ST}(\vec{r}) \leftarrow$  STARTING DENSITY



(1) BY DIRECT MINIMISATION (MUCH MORE EFFICIENT IN NON METALLIC SYSTEMS)

WE CAN SEE THE PROBLEM AS A STANDARD OPTIMISATION PROBLEM AND USE STANDARD MINIMISATION ALGORITHMS (USUALLY THE LDA-GGA FUNCTIONAL HAS ONE MINIMUM)  
 TYPICALLY A CONJUGATE GRADIENT ALGORITHM (CG)

IN A CG WE NEED TO EVALUATE THE GRADIENT OF THE FUNCTION WITH RESPECT THE DEGREES OF FREEDOM

$$\frac{\partial}{\partial \langle \psi_k |} \left[ T_0[\{\psi\}] + E_{KS}[n] + 2 \sum_{ij}^{N/2} \lambda_{ij} (\delta_{ij} - \langle \psi_i | \psi_j \rangle) \right] =$$

LAGRANGIAN MULTIPLIER

$$= 2 \left( H_{KS}^{[n]} | \psi_k \rangle - \sum_{j=1}^{N/2} \lambda_{kj} | \psi_j \rangle \right)$$

$$\text{WHERE } n(\vec{r}) = 2 \sum_{i=1}^{N/2} \langle \psi_i | \vec{r} \rangle \langle \vec{r} | \psi_i \rangle$$

NOTE THAT TO COMPUTE  $E[\{\psi\}]$  AND ITS GRADIENT WE DO NOT NEED TO EVALUATE THE HAMILTONIAN ON A FULL HILBERT SPACE BUT JUST TO APPLY  $H_{KS}$  TO THE OCCUPIED WAVE FUNCTIONS  $\Rightarrow$  BIG TIME SAVING WITH PW BASIS SETS AND MEMORY (SINCE NOW  $\gg$  SELECT)



# EXAMPLE OF THE OPERATIONS

$$\langle \vec{G} | \Psi_i \rangle \rightarrow \langle \vec{G} | H_{KS}^{[m]} | \Psi_i \rangle$$

IN THE CODE  $|\Psi_i\rangle$  ARE STORED IN  $\vec{G}$  SPACE

- (1)  $\langle \vec{G} | \Psi_i \rangle \xrightarrow{\text{FFT}} \langle \vec{r} | \Psi_i \rangle$
- (2)  $\langle \vec{r} | \Psi_i \rangle \rightarrow n(\vec{r}) = 2 \sum_c^{N/2} \langle \Psi_i | \vec{r} \rangle \langle \vec{r} | \Psi_i \rangle$
- (3)  $n(\vec{r}) \xrightarrow{\text{FFT}} n(\vec{G})$
- (4)  $V_H(\vec{G}) = \frac{4\pi}{G^2} n(\vec{G})$
- (5)  $V_H(\vec{G}) \xrightarrow{\text{FFT}} V_H(\vec{r})$
- (6)  $V_{xc}(\vec{r}) = f(n(\vec{r}), |\nabla n(\vec{r})|)$   
LDA, GGA
- (7)  $V_{loc}^{KS}(\vec{r}) = V_{loc}^{PS}(\vec{r}) + V_H(\vec{r}) + V_{xc}(\vec{r})$
- (8)  $\langle \vec{r} | \Phi_i \rangle = V_{loc}^{KS}(\vec{r}) \langle \vec{r} | \Psi_i \rangle$
- (9)  $\langle \vec{r} | \Phi_i \rangle \xrightarrow{\text{FFT}} \langle \vec{G} | \Phi_i \rangle$
- (10)  $\langle \vec{G} | \Phi_i \rangle = \sum_{\Gamma} \sum_n \langle \vec{G} | \beta_{\Gamma, n} \rangle \langle \beta_{\Gamma, n} | \Psi_i \rangle$
- (11)  $\langle \vec{G} | H_{KS} | \Psi_i \rangle = \langle \vec{G} | \Phi_i \rangle + \langle \vec{G} | \Phi_i \rangle + \frac{\hbar^2 G^2}{2m} \langle \vec{G} | \Psi_i \rangle$