

#### **DFT METHODS**

Why are there so many DFT codes and why should I consider FLEUR for my research?

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Wikipedia lists >90 DFT codes

#### Pseudopotentials LCAO method

Wavelets

Planewaves

Finite differences

Gaussian orbitals

Local basis sets

All-electron codes

LMTO method

Numerical atomic orbitals

PAW method

Green functions



#### Basis sets e.g.: MANY ASPECTS ... Plane waves • Numerical/Analytical Localized basis sets (L)APWs Local density approximation (LDA), GGA LDA+U Real space grids Hybrid Functionals Green functions **GW-Approximation** $\left(-\frac{1}{2}\nabla^2 + V_{eff}\right)\psi = \epsilon\psi$ All-electron Finite difference approx. Pseudo-potential Non-relativistic equation Shape approximations Scalar-relativistic approx. Full potential Spin-orbit coupling Spin-polarized calculations Dirac equation



## **TWO MAIN CRITERIAS OF CLASSIFICATION**





#### **BIG CHALLENGE: THE 1/R SINGULARITY**

The nuclei potential: 
$$V \sim -rac{Z}{r}$$

- For large Z many low energy wavefunctions exist that are localized close to the nucleus → Core states
- Core states can be treated as completely localized
- These states do not contribute to the chemical binding
- Other states: Valence states
- These are rather delocalized and determine chemical binding



#### **THE 1/R SINGULARITY**









### **CORE STATES VERSUS VALENCE STATES**

Core states localized
 Valence states delocalized

 $\psi_c(r > r_{cut}) = 0$  in general:  $\psi_v(\vec{r}) \neq 0$ 

- Two different parts of function space with different numerics
- Core states can be calculated separately from valence states and vice versa

 $\rightarrow$  valence states see the ion



# ALL-ELECTRON $\leftarrow \rightarrow$ PSEUDO-POTENTIAL METHODS

#### Two consequence of the 1/r singularity:

- 1. Core states
- 2. Strong oscillations of valence states
- All electron methods: treat the 1/r singularity seriously
- Alternative: modify the potential to make it easier to treat

 $\rightarrow$  pseudo-potential methods





## **IDEA BEHIND A PSEUDO-POTENTIAL**





## TRANSFERABILITY

- Pseudo-potential has been constructed from atomic calculation:
- → It reproduces the correct wavefunction far away from the single atom
- $\rightarrow$  scattering theory
- $\rightarrow$  Strictly speaking this works only for a single energy!
- Is the pseudo-potential also good for other situations?
  - → Transferability



# Leur ALL-ELECTRON CODE

- We keep the 1/r singularity in the potential
- All electrons incl. core-states are treated in the self-consistency cycle
- No pseudo-potentials are used



# HOW TO SOLVE A PDE?

DFT: We have to solve a differential equation

• Kohn-Sham equation:

$$\left(-\frac{1}{2}\nabla^2 + V_{eff}(\vec{r})\right)\psi(\vec{r}) = \epsilon\psi(\vec{r})$$

- For a general effective potential this can be only done numerically
- Different schemes have been used, here we discuss:
  - 1. Basis set → Linear algebra problem
  - 2. Real space grid



## **CRITERIA FOR BASIS SETS**

How to choose a basis set

- Efficiency, i.e. how many basis functions are needed?
- How easy is the calculation of the Hamiltonian?
- Is there a specific structure of the eigenvalue problem one can exploit?
- Is the basis set systematic?
- Does the basis set incorporate the correct boundary condifitions?



## **SYSTEMATIC CONVERGENCE**

• Example for wavefunction:

$$\psi^{N_b}(\vec{r}) = \sum_i^{N_b} c_i \phi_i(\vec{r})$$
  
 $|\psi(\vec{r}) - \psi^{N_b}(\vec{r})|$ 

- Residual should be small:
- True wavefunction unkown, so one tests for two different basis set sizes  $N_b$  and  $N'_b$

$$|\psi^{N_b'}(\vec{r}) - \psi^{N_b}(\vec{r})|$$

• This requires, that the basis set can be improved systematically by increasing the basis set size



### **STRUCTURE OF EIGENVALUE PROBLEM**

Generalized/Standard form

$$[H_{ij}]\vec{c}=\epsilon[S_{ij}]\vec{c}$$

- Real/Complex matrices?
  - Complex due to boundary condition/basis functions!
- How many eigenvalues does one need?
  - Iterative diagonalization (large matrix, few vectors)
  - Direct solvers (>5% of eigenvectors?)
- Special structure of the matrix?
  - Sparse matrix

Mitglied der Helmholtz-Gemeinschaft



V

Η



#### **Examples:**

#### Plane wave basis set

$$\phi_{\vec{g}}(\vec{r}) = \frac{1}{N} e^{i\vec{g}\vec{r}}$$

- ✓ Orthonormal basis set
- ✓ Single convergence parameter: #(PW)
- $\checkmark$  PWs are momentum eigenfunctions
- X V(r) must be Fourier transformable
  - $\rightarrow$  need to use pseudo-potentials
  - $\rightarrow$  usually large basis set sizes
- X Dense potential matrix

#### Local basis set

$$\phi(\vec{r}) = \frac{1}{N} e^{-\alpha(\vec{r}-\vec{R})^2}$$

- $\checkmark$  Can be very efficient efficient
- ✓ Sparse matrix
- X Numerical local orbitals can be difficult to calculate
- X Atoms moving  $\rightarrow$  basis is changing
- X Unsystematic convergence
- X Density must be in different basis





# **FLAPW CODE**

- Full-potential linearized augmented plane wave code
- Combines PW and localized basis set
- Complex but highly versatile method



# **FLEUR IS SPECIALIZED**

#### Periodic systems

- ✓ 3d bulk systems (periodic in all directions)
- ✓ Surface via special ,film' mode
- X Not so well suited for molecules

#### High accuracy

- ✓ Reference results
- ✓ Simulation of complex materials
- Investigation of small energy differences

All electron method
All elements can be treated
Systematic convergence
Computational expensive, many convergence parameters

#### Fields of applicability

- ✓ Magnetism, spin-orbit physics
- ✓ Heavy elements, complex electronic structure
- X Molecular dynamics