Chair of Condensed Matter Physics
Institute of Theoretical Physics
Faculty of Physics, Universityof Warsaw

**Summer Semester 2014**

**Lecture**

# Modeling of Nanostructures and Materials

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## Modeling of Nanostructures and Materials

***(Jacek A. Majewski) Nevill Gonzalez Szwacki***

**Lecture 3 –** *March 10, 2014*

- **Kohn-Sham Method with Plane-waves and pseudopotentials**

✓ **Generation of norm conserving pseudopotentials (PPs)**
✓ **Separable (Kleinman-Bylander) PPs**
✓ **Unscreening of PPs (→ ionic PPs)**
✓ **Practical aspects of the calculations**

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## Materials Science: Examples of Schrödinger Equation?

- **Materials are composed of nuclei $\{Z_\alpha, M_\alpha, \vec{R}_\alpha\}$ and electrons $\{\vec{r}_i\}$**

→ **the interactions are known**

$$H=-\sum_{\alpha}\frac{\hbar^2\nabla_\alpha^2}{2M_\alpha}-\sum_{i}\frac{\hbar^2\nabla_i^2}{2m}+\frac{1}{2}\sum_{\alpha,\beta}\frac{Z_\alpha Z_\beta e^2}{|\vec{R}_\alpha-\vec{R}_\beta|}-\sum_{i,\alpha}\frac{Z_\alpha e^2}{|\vec{R}_\alpha-\vec{r}_i|}+\frac{1}{2}\sum_{i,j}\frac{e^2}{|\vec{r}_i-\vec{r}_j|}$$

**Kinetic energy of nuclei**

**Kinetic energy of electrons**

**Nucleus-Nucleus interaction**

**Electron-Nucleus interaction**

**Electron-Electron interaction**

$$\boxed{H\Psi = E\Psi}$$

***Ab-initio*** **(first principles) Method –**
**ONLY Atomic Numbers $\{Z_i\}$ as input parameters**

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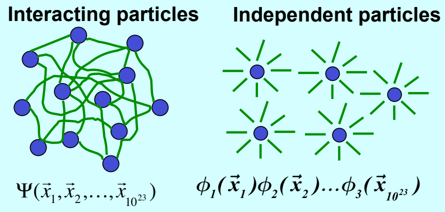
## Density Functional Theory (DFT) in Kohn-Sham realization



Idea: consider electrons as independent particles moving in an effective potential

**This reduction is rigorously possible !**

# DFT- The Kohn- Sham Method

*W. Kohn and L. J. Sham, Phys. Rev.* ***140****, A1133 (1965)*

**System of interacting electrons with density** $\rho(\vec{r})$ ↔ **System of non-interacting electrons with the same density** $\rho(\vec{r})$

"Real" system

$\rho(\vec{r})$ $T[\rho]$

"Fictitious" or Kohn-Sham reference system

$T_S[\rho]$ $\rho_S(\vec{r})=\rho(\vec{r})$

$$E[\rho]=\int d\vec{r}\,\upsilon_{ext}(\vec{r})\rho(\vec{r})+T_S[\rho]+U[\rho]+E_x[\rho]+E_c[\rho]$$

**unknown!!!**

- $\rho(\vec{r})=\sum_{i=1}^{N}\varphi^*_i(\vec{r})\varphi_i(\vec{r})$
- $T_s[\rho]=-\frac{\hbar^2}{2m}\sum_{i=1}^{N}\int d\vec{r}\varphi_i^*(\vec{r})\vec{\nabla}^2\varphi_i(\vec{r})$
- $E_x[\rho]=-\frac{1}{2}\sum_i\iint d\vec{r}d\vec{r}'\varphi_i^*(\vec{r})\left(\sum_j\frac{\varphi_j(\vec{r})\varphi_j^*(\vec{r}')}{|\vec{r}-\vec{r}'|}\right)\varphi_i(\vec{r}')$

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## The Kohn- Sham Method –
## The Kohn-Sham Equations

- **Schrödinger-like equations with local potential**

$$\upsilon_H(\vec{r})=\frac{\delta U}{\delta\rho}=\int d\vec{r}'\frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}\qquad\frac{\delta E_x[\rho]}{\delta\rho}\qquad\frac{\delta E_c[\rho]}{\delta\rho}$$

$$\left[-\frac{\hbar^2}{2m}\vec{\nabla}^2+\upsilon_{ext}(\vec{r})+\upsilon_H(\vec{r})+\upsilon_x(\vec{r})+\upsilon_c(\vec{r})\right]\varphi_i(\vec{r})=\varepsilon_i\varphi_i(\vec{r})$$

$$\upsilon_{ext}(\vec{r})=-e^2\sum_{s,n}\frac{Z_s}{|\vec{r}-\vec{\tau}_s-\vec{R}_n|}$$

$$\rho(\vec{r})=\sum_{i=1}^{N}\varphi^*_i(\vec{r})\varphi_i(\vec{r})$$

- **These equation are nonlinear and must be solved iteratively (self-consistently)**

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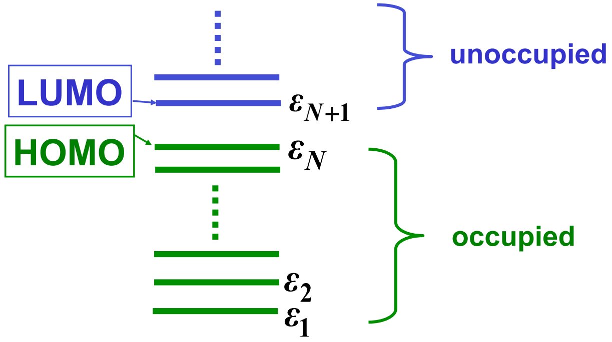
## The Kohn- Sham Method –
## ‚Aufbau' principle

**How to calculate one particle density?**



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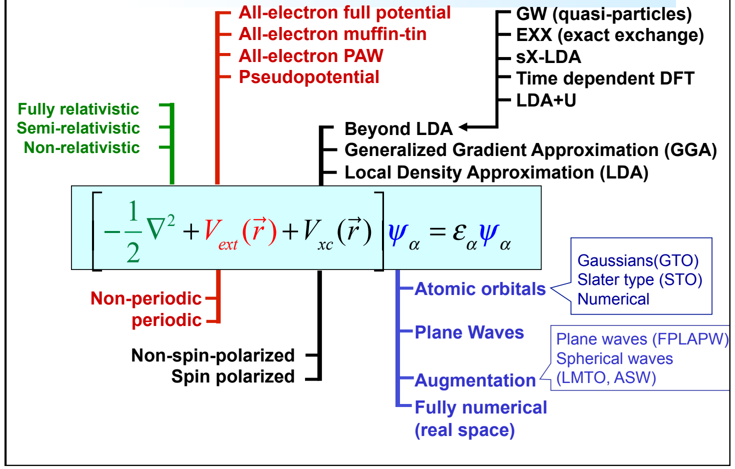
## DFT: Implementations of the Kohn-Sham Method



$$\left[-\frac{1}{2}\nabla^2+V_{ext}(\vec{r})+V_{xc}(\vec{r})\right]\psi_\alpha=\varepsilon_\alpha\psi_\alpha$$

**Fully relativistic**
**Semi-relativistic**
**Non-relativistic**

**All-electron full potential**
**All-electron muffin-tin**
**All-electron PAW**
**Pseudopotential**

**Beyond LDA** ←
- **GW (quasi-particles)**
- **EXX (exact exchange)**
- **sX-LDA**
- **Time dependent DFT**
- **LDA+U**

**Generalized Gradient Approximation (GGA)**
**Local Density Approximation (LDA)**

**Non-periodic**
**periodic**

**Non-spin-polarized**
**Spin polarized**

**Atomic orbitals**
- Gaussians(GTO)
- Slater type (STO)
- Numerical

**Plane Waves**

**Augmentation**
- Plane waves (FPLAPW)
- Spherical waves (LMTO, ASW)

**Fully numerical (real space)**

## Solution of the Kohn-Sham Equations

- Direct methods on a mesh in $r$-space
- Expansion of the Kohn-Sham orbitals in a basis $\{\chi_{\alpha\vec{k}}(\vec{r})\}$

$$\varphi_{n\vec{k}}(\vec{r}) = \mathbb{N}\sum_{\alpha} c_{\alpha}(n,\vec{k})\chi_{\alpha\vec{k}}(\vec{r})$$

$$\left[\sum_{\alpha'} \left\langle \chi_{\alpha\vec{k}} \,|\, -\frac{\hbar^2}{2m}\vec{\nabla}^2 + \upsilon_{KS}(\vec{r}) \,|\, \chi_{\alpha'\vec{k}} \right\rangle - \varepsilon_n(\vec{k})\left\langle \chi_{\alpha\vec{k}} \,|\, \chi_{\alpha'\vec{k}} \right\rangle\right] c_{\alpha'}(n,\vec{k}) = 0$$

Hamiltonian matrix elements

Overlap integrals

$$[H_{\alpha\alpha'}(\vec{k}) - \varepsilon_n(\vec{k})S_{\alpha\alpha'}(\vec{k})]c_{\alpha'}(n,\vec{k}) = 0$$

**Eigenvalueproblem** $\det[H_{\alpha\alpha'}(\vec{k}) - \varepsilon_n(\vec{k})S_{\alpha\alpha'}(\vec{k})] = 0$

➡ $\varepsilon_n(\vec{k})$ **Bandstructure**

## Kohn-Sham

## plane-waves formalism

## Plane-wave formalism

$$\phi_n^{K-S}(\vec{r}) = \sum_{\vec{P}} C_{\vec{p}n}\chi_{\vec{p}}(\vec{r})$$

Plane-waves

$$\chi_{\vec{p}}(\vec{r}) = \frac{1}{\sqrt{V}}exp(i\vec{p}\cdot\vec{r})$$

Plane-waves constitute orthonormal system

$$\left\langle \chi_{\vec{p}} \,|\, \chi_{\vec{p}'} \right\rangle = \delta_{\vec{p}\vec{p}'}$$

**Problem:**

- $\vec{p}$ **continuous variable**

➡ **For periodic systems, one can introduce discrete values**

## Plane-wave formalism

**Periodic systems**

$\{\vec{a}_i\}$ primitive translations characterizing periodicity

$\{\vec{G}\}$ - reciprocal lattice vectors $\vec{G}_n = n_1\vec{b}_1 + n_2\vec{b}_2 + n_3\vec{b}_3$

$\vec{k} \in BZ$ Wave vectors characterize Bloch States

$\vec{p} = \vec{k} + \vec{G}$

$$\boxed{\chi_{\vec{G}}(\vec{r}) = \frac{1}{\sqrt{V}}exp(i\vec{G}\cdot\vec{r})} \qquad \left\langle \chi_{\vec{G}} \,|\, \chi_{\vec{G}'} \right\rangle = \delta_{\vec{G}\vec{G}'}$$

- **Discrete, orthonormal set of basis functions**

## Plane-wave formalism

$$\varphi_{n\vec{k}}(\vec{r}) = \frac{1}{\sqrt{\Omega}} e^{i\vec{k}\cdot\vec{r}} u_{n\vec{k}}(\vec{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\vec{G}} c_{n\vec{k}}(\vec{G}) e^{i(\vec{k}+\vec{G})\cdot\vec{r}}$$

Expansion coefficients

**Basis – plane waves**

$$\chi_{\vec{k}}^{\vec{G}}(\vec{r}) = e^{i(\vec{k}+\vec{G})\cdot\vec{r}}$$

$\{\vec{G}\}$ - reciprocal lattice vectors $\vec{G}_n = n_1\vec{b}_1 + n_2\vec{b}_2 + n_3\vec{b}_3$

**In practical calculations** $\{\vec{G} : \frac{1}{2}(\vec{k}+\vec{G})^2 \le E_{cutoff}\}$

**Kinetic Energy Cutoff**

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# Concept of pseudopotential

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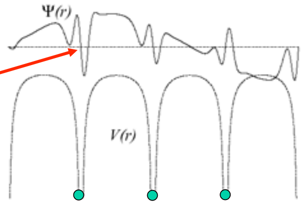
## Typical electronic potential and wave function

- When solving the K-S equations for the full system of nuclei and electrons we find that:
  - Close to the nuclei, the potential is dominated by strong Coulomb interactions
  - In interstitial regions the potential is much weaker and reflects the symmetry of the crystal
- A typical wavefunction would look like:



**Strong oscillations in the core region**

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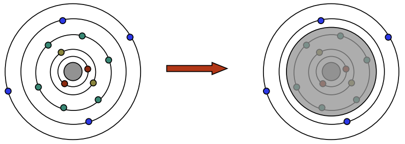
## The Pseudopotential Concept

- ***IDEA***: group all the electrons around the nuclear core into an effective ionic core, where all the strong oscillations close to the nuclei are damped, and leave out only the valence electrons that contribute to the bonding of the solid. **Core electrons are left basically unchanged going from the atom to the solid**

**Si: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$** **Si: (pseudo core) $3s^2\ 3p^2$**

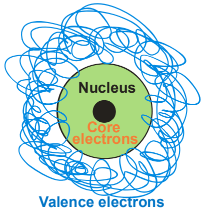


**14 electrons** **4 (valence) electrons**

$$V_{ext}(\mathbf{r}) = \frac{-14e^2}{\mathbf{r}} \qquad V_{ext}(\mathbf{r}) = V_{ps}(\mathbf{r})$$

# PSEUDOPOTENTIALS - Basic Idea

**The basic idea of the pseudopotential theory**:



- Core electrons are localized and therefore chemically inactive (inert)
- Valence electrons determine chemical properties of atoms and SOLIDS

➡ **Describe valence states by smooth wavefunctions**

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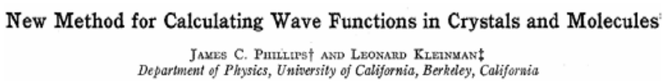
# PSEUDOPOTENTIALS – Philips-Kleinman Method



**New Method for Calculating Wave Functions in Crystals and Molecules**

JAMES C. PHILLIPS† AND LEONARD KLEINMAN‡
*Department of Physics, University of California, Berkeley, California*

*Phillips & Kleinman, Phys. Rev.* ***116****, 287 (1959)*

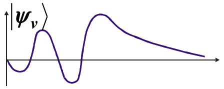
**Construction of pseudopotentials from atomic wavefunctions**

$$\hat{H}^{at}|\psi_c\rangle = E_c|\psi_c\rangle$$

$$\hat{H}^{at}|\psi_v\rangle = E_v|\psi_v\rangle$$

$|\psi_c\rangle$ -core states $|\psi_v\rangle$ - valence states

- Orthogonality condition $\langle\psi_v|\psi_c\rangle = 0$ leads to oscillations in $|\psi_v\rangle$



- ***How to get smooth pseudo-valence- wavefunctions*** $|\varphi_v\rangle$ ***from atomic valence wavefunctions ?***
- **IDEA**: Project out oscillations from $|\psi_v\rangle$

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# PSEUDOPOTENTIALS – Philips-Kleinman Method

- First, we define pseudo-wave-function for valence electrons $|\varphi_v\rangle = |\psi_v\rangle + \sum_c |\psi_c\rangle \underbrace{\langle\psi_c|\varphi_v\rangle}_{\alpha_{cv}}$
- Second, we act with atomic Hamiltonian on the pseudo-wavefunction

$$\hat{H}^{at}|\varphi_v\rangle = E_v|\psi_v\rangle + \sum_c E_c|\psi_c\rangle\alpha_{cv} =$$

$$= E_v|\varphi_v\rangle - E_v\sum_c|\psi_c\rangle\alpha_{cv} + \sum_c E_c|\psi_c\rangle\alpha_{cv} =$$

$$= E_v|\varphi_v\rangle + \sum_c (E_c - E_v)|\psi_c\rangle\alpha_{cv}$$

$$\hat{H}^{at}|\varphi_v\rangle - \sum_c (E_c - E_v)|\psi_c\rangle\langle\psi_c|\varphi_v\rangle = E_v|\varphi_v\rangle$$

- $\{\hat{H}^{at} - \sum_c (E_c - E_v)|\psi_c\rangle\langle\psi_c|\}|\varphi_v\rangle = E_v|\varphi_v\rangle$
- The pseudo-wave-function fulfills Schrödinger-like equation with Hamiltonian that is dependent on energy and contains additional repulsive, nonlocal potential.
- $\boxed{\hat{H}_{ps} = \hat{H}^{at} + \sum_c (E - E_c)|\psi_c\rangle\langle\psi_c|}$

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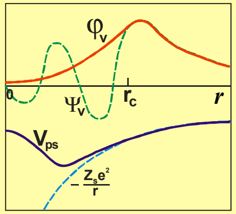
# PSEUDOPOTENTIALS – Philips-Kleinman Method

$\boxed{\hat{H}^{at}|\psi_v\rangle = E_v|\psi_v\rangle}$ $\boxed{\hat{H}_{ps}|\varphi_v\rangle = E_v|\varphi_v\rangle}$

**Atom** Energies are identical **Pseudoatom**

Effective potential acting on the pseudo-valence electrons

$\hat{V}_{ps} = \hat{V}^{core} + \sum_c (E - E_c)|\psi_c\rangle\langle\psi_c|$ $\hat{V}_{ps}$ is weaker than $\hat{V}^{core}$



$Z_S$ – No. of valence electrons in neutral atom

- **Within the core region** $(0 \le r \le r_c)$

  The potential $V^{core}(r) = \frac{-Z_s e^2}{r}$

  and atomic valence wavefunctions are substituted by pseudopotential $V_{ps}$ and knot free pseudowavefunction $\varphi_v$
- **Outside the core region** $r > r_c$

  $\varphi_v = \psi_v$ $V_{ps} = \frac{-Z_s e^2}{r}$
- Construction procedure keeps the energies of atomic and pseudoatomic states unchanged.

After paper of Philips & Kleinman, various models of pseudopotentials have been developed. Main weakness: many parameters involved

## Parameter Free (*Ab-initio*) Pseudopotentials – Norm Conserving Pseudopotentials

- **Density Functional Theory for Atoms** – Kohn-Sham equations for atoms
- Spherical symmetry of atoms is assumed

$$\psi^{at}(\vec{r}) = \sum_{lm} R_l(r) Y_{lm}(\hat{\Omega}) = \sum_{lm} \frac{u_l(r)}{r} Y_{lm}(\hat{\Omega})$$

- For each "*l*", one-dimensional Kohn-Sham equation

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} + \upsilon_{l,KS}^{at}(r)\right] u_l(r) = \varepsilon_l u_l(r) \qquad \text{Atomic units: } \hbar = e = m = 1$$

- Effective Kohn-Sham potential contains all electronic interactions

$$\upsilon_{l,KS}^{at}(r) = -\frac{Z_s}{r} + \frac{l(l+1)}{2r^2} + \upsilon_H([\rho_c + \rho_v]) + \upsilon_{xc}([\rho_c + \rho_v])$$

$$\boxed{\rho^{at} = \rho_c + \rho_v}$$

Atomic density

Core density

Valence density

## Construction of Norm Conserving Pseudopotentials

- **Construction of pseudo-wavefunctions $u_l^{ps}(r)$ from atomic solutions** $u_l(r)$

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} + \upsilon_l^{ps}(r)\right] u_l^{ps}(r) = \varepsilon_l u_l^{ps}(r)$$

The pseudo-wavefunctions $u_l^{ps}(r)$ have to fulfill certain conditions

① $u_l^{ps}(r) = u_l(r)$ for $r > r_{cl}$

② $\int_0^{r_{cl}} |R_l^{ps}(r)|^2 r^2 dr = \int_0^{r_{cl}} |R_l(r)|^2 r^2 dr$

***NORM CONSERVATION***

Pseudo-wavefunctions and atomic wavefunctions lead to identical charge in the core region $r \le r_{cl}$

③ $\varepsilon_l^{ps} = \varepsilon_l$

④ $\left.\frac{\frac{d}{dr}R_l^{ps}(r)}{R_l^{ps}(r)}\right|_{r=r_{cl}} = \left.\frac{\frac{d}{dr}R_l(r)}{R_l(r)}\right|_{r=r_{cl}}$

Identical logarithmic derivatives at cutoff radii

These conditions do not determine the pseudo-wavefunctions uniquely

⇒ Different types of ab-initio pseudopotentials

## Construction of Norm Concerving Pseudopotentials

**Older pseudopotentials**

BHS pseudopotential *G.B. **B**achelet, D.R. **H**aman, and M. **S**chlüter, Phys. Rev. B **26**, 4199 (1982)*

Kerker pseudopotential *G.P.Kerker, J. Phys. C **13**, L189 (1980)*

**Troullier-Martins-Pseudopotentials** *N. Troullier & J. L. Martins, Phys. Rev. B **43**, 8861 (1991)*

The pseudo-wavefunction in the core region ($r < r_{cl}$)

$$u_l^{ps}(r) = r^{l+1} \exp[p_l(r^2)] \qquad p_l \text{ - polynomial of 6th order}$$

Coefficients of the polynomial are determined from:

a) Conditions 1-4

b) Continuity of the first, second, third, and fourth derivative of $u_l^{ps}$ in $r_{cl}$

c) Second derivative of ionic pseudopotential should vanish in $r = 0$

**Very good convergence properties !**

When pseudo-wavefunctions $u_l^{ps}$ are established, then proceed to the next step of pseudopotential construction.

## Construction of Norm Conserving Pseudopotentials

● ● **Inversion of the Kohn-Sham equations ⇒ Atomic pseudopot.**

$$\upsilon_{l,atom}^{ps}(r) = \varepsilon_l - \frac{l(l+1)}{2r^2} + \frac{1}{2}\frac{\frac{d^2}{dr^2}u_l^{ps}(r)}{u_l^{ps}(r)}$$

Note, $u_l^{ps}(r)$ are knot free

Atomic pseudopotential contains interaction between valence electrons. This interaction should be subtracted.

● ● ● **Unscreening procedure**

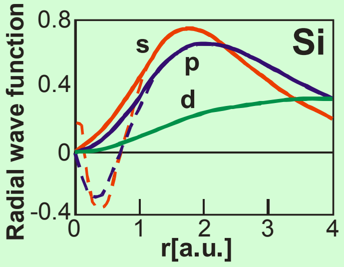
$\upsilon_{l,atom}^{ps}(r) \Rightarrow V_{l,ion}^{ps}(r)$ **IONIC PSEUDOPOTENTIAL**

$$\boxed{V_{l,ion}^{ps}(r) = \upsilon_{l,atom}^{ps}(r) - \upsilon_H([\rho_{val}^{ps}];r) - \upsilon_{xc}([\rho_{val}^{ps}];r)}$$

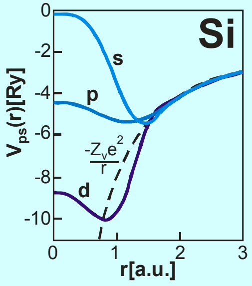
$V_{l,ion}^{ps}(r)$ - For each angular momentum quantum number "*l*"

# Norm Conserving Pseudopotentials

Comparison of the **pseudo-wavefunction** (solid lines) and the corresponding all-electron wavefunctions (dashed lines)



Components of the ionic pseudo-potential for angular momentum $l$ = 0,1,2



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# Norm Conserving Pseudopotentials

$V^{ps}_{l,ion}(r)$ - different component for each " $l$ "

➡ **Non-local pseudopotential** $\left\langle \vec{r}\,|\,\hat{V}^{ps}_{ion}\,|\,\vec{r}\,'\right\rangle = V^{ps}_{ion}(\vec{r},\vec{r}\,')$

$$\hat{V}^{ps}_{ion} = \sum_l V^{ps}_{l,ion}(r)\hat{P}_l = \sum_l V^{ps}_{l,ion}(r)\left|l\right\rangle\left\langle l\right|$$

Projection operator

$$\left\langle \vec{r}\,|\,l\right\rangle = Y_{lm}(\hat{\vec{r}})$$

*In Solids*: $$\boxed{\hat{V}^{ps}_{ion} = \sum_{n,s}\sum_l V^{ps,(s)}_{l,ion}(|\vec{r}-\vec{R}_n-\vec{\tau}_s|)\hat{P}_l}$$

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# Norm Conserving Pseudopotentials

## Extensions

- **Relativistic effects are extremely important for core electrons**
  - Dirac equation for atoms
  - Schrödinger-like equation for pseudo-valence wavefunctions
  - "$l$" component of the ionic pseudopotential is obtained through the averaging over "$j$ +" and "$j$ -" components

- **Exchange-correlation functional is nonlinear in** $\rho = \rho_c + \rho_v$

$$\upsilon_{xc}[\rho_c+\rho_v] \neq \upsilon_{xc}[\rho_c] + \upsilon_{xc}[\rho_v]$$

**Equality was assumed, for simplicity, for the unscreening procedure**

➡ ***Nonlinear core correction***

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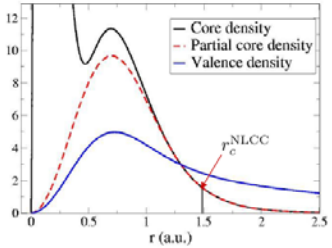
# Nonlinear Core Correction

Louie et al.,Phys. Rev. B 26, 1738 (1982)

- Unscreening using smooth function of core density

$$\left.\begin{array}{l} v^{\rm ps}_{\rm ion} = V^{\rm ps}_{\rm eff} - v_{\rm H}[n_v] - v_{\rm xc}\left[n_v + n_c^{\rm NLCC}\right] \\ n_{\rm c}^{\rm NLCC}(r) = \begin{cases} n_{\rm c}(r) & \text{for } r > r_{\rm c}^{\rm NLCC} \\ \exp\left(\sum_{i=0}^{2} a_i r^{2i}\right) & \text{for } r \le r_{\rm c}^{\rm NLCC} \end{cases} \end{array}\right\}$$

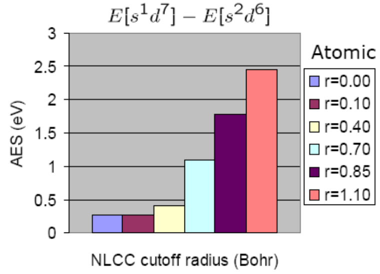
➡



## Nonlinear Core Correction – How it works?

**Atomic energy splitting for Fe atom**

*Choice of cutoff radius ?*



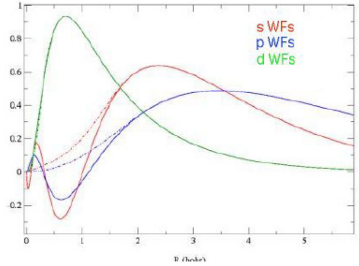
Cocula *et al.*, JCP 119, 7659 (2003)

- High sensitivity to cutoff
- Use of full-core improves accuracy but usually costs are too high

## Pseudopotential Smoothness & Accuracy

***Pseudopotential quality*** is measured by its ***transferability,*** i.e., ability of the PP to match AE values when put in different chemical environments

**Iron wavefunctions and pseudo-wavefunctions**



- Move outward cutoff radius to get smoother pseudo-wavefunctions
  - Acceptable basis size
  - Penalty:
    decreased transferability
- Small cutoff =
  - sharp function
  - expensive to expand in PWs

## Plane-wave formalism

## Plane-wave formalism

**Kohn-Sham equations in momentum space**

- **Expansion with respect to basis = Fourier series**
- **External potential substituted by** ***Pseudopotential***

$$\left[-\frac{\hbar^2}{2m}\vec{\nabla}^2 + \upsilon_H(\vec{r}) + \upsilon_{xc}(\vec{r}) + \hat{V}_{ion}^{ps}\right]\varphi_{n\vec{k}}(\vec{r}) = \varepsilon_{n\vec{k}}\varphi_{n\vec{k}}(\vec{r}) \quad \text{(KS-Eq.)}$$

⇩ **Fourier transformation**

$$\sum_{\vec{G}'}\left[\frac{\hbar^2}{2m}(\vec{k}+\vec{G})^2\delta_{\vec{G},\vec{G}'} + \upsilon_H(\vec{G}-\vec{G}') + \upsilon_{xc}(\vec{G}-\vec{G}') + V^{ps}(\vec{k}+\vec{G},\vec{k}+\vec{G}')\right]c_{n\vec{k}}(\vec{G}) = \varepsilon_{n\vec{k}}c_{n\vec{k}}(\vec{G})$$

**Eigenvalue problem** – system of equations for expansion coefficients $c_{n\vec{k}}(\vec{G})$

## Pseudopotential in Kohn-Sham Method

- External potential substituted by ***Pseudopotential***

$$\left[-\frac{\hbar^2}{2m}\vec{\nabla}^2+\upsilon_H(\vec{r})+\upsilon_{xc}(\vec{r})+\hat{V}^{ps}_{nonloc}(\vec{r},\vec{r}\,')\right]\varphi_{n\vec{k}}(\vec{r})=\varepsilon_{n\vec{k}}\varphi_{n\vec{k}}(\vec{r})$$

(KS-Eq.)

$$\left\langle\vec{r}\,|\hat{V}^{ps}_{ion}|\,\vec{r}\,'\right\rangle=V^{ps}_{ion}(\vec{r},\vec{r}\,')$$

non-local pseudopotential !!

- **External potential (pseudopotential) is non-local !**
- **Is it compatible with derivation of Kohn-Sham equations?**

➡ **Not really, but generalization of the formalism possible**

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## Semilocal Pseudopotentials

**Norm conserving pseudopotential – semilocal PP**

$$V^{ps,\alpha}_{ion}(\vec{r},\vec{r}\,')=\sum_{lm}\upsilon^{ps,\alpha}_{l,ion}(r)Y^*_{lm}(\vec{r})Y_{lm}(\vec{r}\,')$$

$$V^{ps,\alpha}_{ion}(\vec{r},\vec{r}\,')=\upsilon^{ps,\alpha}_{l_0,ion}(r)+\sum_{lm}[\underbrace{\upsilon^{ps,\alpha}_{l,ion}(r)-\upsilon^{ps,\alpha}_{l_0,ion}(r)}_{\Delta\upsilon_l}]Y^*_{lm}(\vec{r})Y_{lm}(\vec{r}\,')$$

local in $r$, nonlocal in angles
$\Delta\upsilon_l$ is short range

$$\hat{\upsilon}^{ps}=\upsilon_{loc}(r)+\sum_{lm}\upsilon_l(r)\left|lm\right\rangle\left\langle lm\right|$$

- **Expensive calculations of** $\upsilon^{ps}(\vec{k}+\vec{G},\vec{k}+\vec{G}')$

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## Kohn-Sham equations in pseudopotential formalism

$$V^{ps}(\vec{r},\vec{r}\,')=\upsilon^{ps}_{loc}(\vec{r})+\upsilon^{ps}_{nonloc}(\vec{r},\vec{r}\,')$$

$$\left[-\frac{\hbar^2}{2m}\vec{\nabla}^2+\underbrace{\upsilon_H(\vec{r})+\upsilon_{xc}(\vec{r})+\upsilon^{ps}_{loc}(\vec{r})}+\upsilon^{ps}_{nonloc}(\vec{r},\vec{r}\,')\right]\varphi_{n\vec{k}}(\vec{r})=\varepsilon_{n\vec{k}}\varphi_{n\vec{k}}(\vec{r})$$

$$\upsilon_{loc}(\vec{r})=\upsilon_H(\vec{r})+\upsilon_{xc}(\vec{r})+\upsilon^{ps}_{loc}(\vec{r})$$

$$\boxed{\left[-\frac{\hbar^2}{2m}\vec{\nabla}^2+\upsilon_{loc}(\vec{r})+\upsilon^{ps}_{nonloc}(\vec{r},\vec{r}\,')\right]\varphi_{n\vec{k}}(\vec{r})=\varepsilon_{n\vec{k}}\varphi_{n\vec{k}}(\vec{r})}$$

$$\boxed{\rho(\vec{r})=\sum_{i=1}^{N}\varphi^*_i(\vec{r})\varphi_i(\vec{r})}$$

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## Local and nonlocal parts of pseudopotential

**Pseudopotential for atomic species $\alpha$**

$$V^{ps,\alpha}_{ion}(\vec{r},\vec{r}\,')=\underbrace{\upsilon^{ps,\alpha}_{loc}(r)}_{\text{Local}}+\underbrace{\sum_{lm}\upsilon^{\alpha}_{l}(r)Y^*_{lm}(\vec{r})Y_{lm}(\vec{r}\,')}_{\text{Non-local}}$$

Pseudopotential for a collection of atoms

$$\boxed{V^{ps}(\vec{r},\vec{r}\,')=\sum_{\alpha}V^{ps,\alpha}_{ion}(\vec{r}-\vec{X}_\alpha,\vec{r}\,'-\vec{X}_\alpha)}$$

*local part*

$$V^{ps}(\vec{r},\vec{r}\,')=\sum_{\alpha}\upsilon^{ps,\alpha}_{loc}(|r-\vec{X}_\alpha|)+$$

$$+\sum_{\alpha}\sum_{lm}\upsilon^{\alpha}_{l}(|\vec{r}-\vec{X}_\alpha|)Y^*_{lm}(\vec{r}-\vec{X}_\alpha)Y_{lm}(\vec{r}\,'-\vec{X}_\alpha)$$

*non-local part*

## Kleinman-Bylander Separable Pseudopotentials

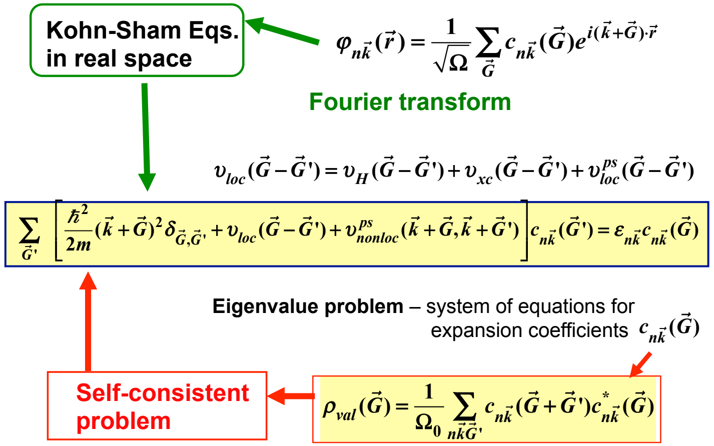
**Fully non-local separable PP**

$$\hat{V}^{ps}_{K-B} = \upsilon_{loc}(r) + \sum_{lm} \frac{|\Delta\upsilon_l \varphi_{lm}\rangle\langle\Delta\upsilon_l \varphi_{lm}|}{\langle\varphi_{lm}|\upsilon_l|\varphi_{lm}\rangle}$$

$$\left(\hat{T} + \hat{V}^{ps} - \varepsilon_i\right)\varphi_i = 0$$

- Exact for the reference atomic energies
- Approximate for all other energies
- **Much easier calculations** ( in comparison to semi-local PP) **of Fourier components**

## Kohn-Sham equations in pseudopotential plane-wave formalism



**Kohn-Sham Eqs. in real space**

$$\varphi_{n\vec{k}}(\vec{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\vec{G}} c_{n\vec{k}}(\vec{G}) e^{i(\vec{k}+\vec{G})\cdot\vec{r}}$$

**Fourier transform**

$$\upsilon_{loc}(\vec{G}-\vec{G}') = \upsilon_H(\vec{G}-\vec{G}') + \upsilon_{xc}(\vec{G}-\vec{G}') + \upsilon^{ps}_{loc}(\vec{G}-\vec{G}')$$

$$\sum_{\vec{G}'} \left[\frac{\hbar^2}{2m}(\vec{k}+\vec{G})^2 \delta_{\vec{G},\vec{G}'} + \upsilon_{loc}(\vec{G}-\vec{G}') + \upsilon^{ps}_{nonloc}(\vec{k}+\vec{G},\vec{k}+\vec{G}')\right] c_{n\vec{k}}(\vec{G}') = \varepsilon_{n\vec{k}} c_{n\vec{k}}(\vec{G})$$

**Eigenvalue problem** – system of equations for expansion coefficients $c_{n\vec{k}}(\vec{G})$

**Self-consistent problem**

$$\rho_{val}(\vec{G}) = \frac{1}{\Omega_0} \sum_{n\vec{k}\vec{G}'} c_{n\vec{k}}(\vec{G}+\vec{G}') c^*_{n\vec{k}}(\vec{G})$$

## Pseudopotential plane-wave formalism – practical aspects

**Number of plane waves in the wavefunction expansion** $N$

$$\{\vec{G} : \frac{1}{2}(\vec{k}+\vec{G})^2 \le E_{cutoff}\}$$

**Number of needed Fourier coefficients of the local potential?** $\upsilon_{loc}(\vec{G}-\vec{G}')$

$$8N \Longleftrightarrow \vec{G}_{\max} : \frac{1}{2}(\vec{k}+\vec{G}_{\max})^2 = E_{cutoff}$$

$$max|\vec{G}-\vec{G}'| = 2\vec{G}_{max}$$

$\rho(\vec{G})$ **-- $8N$ Fourier coefficients required**

## Pseudopotential plane-wave formalism – practical aspects

$$\mu \equiv (n\vec{k})$$

$$\sum_{\vec{G}'} \left[\frac{\hbar^2}{2m}(\vec{k}+\vec{G})^2 \delta_{\vec{G},\vec{G}'} + \upsilon_{loc}(\vec{G}-\vec{G}') + \upsilon^{ps}_{nonloc}(\vec{k}+\vec{G},\vec{k}+\vec{G}')\right] c_\mu(\vec{G}') = \varepsilon_\mu c_\mu(\vec{G})$$

- Solution of eigenvalue problem gives N eigenvalues and eigenfunctions
- For self-consistent solution of the problem, it is necessary to known **only occupied states**

**Number of occupied states << N**

- **Traditional methods** (based on the solution of eigenvalue problem) only practicable for moderate N (say N~2000)
- **For N > 2000 (large supercells), reformulation of the problem is required**

## Pseudopotential plane-wave formalism – practical aspects – Iterative methods

$\mu \equiv (n\vec{k})$ $$g^{(\mu)}(\vec{G}) = \sum_{\vec{G}'} (H(\vec{G},\vec{G}') - \varepsilon_\mu \delta_{\vec{G},\vec{G}'}) c_\mu(\vec{G}')$$

Gradient

**We are looking for $\mu \geq N_{occ}$ wavefunctions**

- **mutually orthogonal** $\langle \mu | \mu' \rangle = \sum_{\vec{G}} c^*_\mu(\vec{G}) c_{\mu'}(\vec{G}) = \delta_{\mu\mu'}$
- **such that the gradients vanish** $g^{(\mu)}(\vec{G}) = 0$

**Searching procedure ?**

**e.g. steepest descent** $c^{(n+1)}_\mu = c^{(n)}_\mu + \eta g^{(\mu)}(n)$

**conjugate gradient**

**Davidson method**

**Required: effective method to calculate gradient**

## Pseudopotential plane-wave formalism – practical aspects

**Calculation of $\rho(\vec{G})$ from the formula**

$$\rho_{val}(\vec{G}) = \frac{1}{\Omega_0} \sum_{n\vec{k}\vec{G}'} c_{n\vec{k}}(\vec{G}+\vec{G}') c^*_{n\vec{k}}(\vec{G})$$

**requires ~$N^2$ operations**

**Inefficient !!**

**Better solution**

- Introduce mesh in r-space with 8N points $\{\vec{r}_i\}$
- Fourier transform wavefunction in $G$-space into wave function in real space $\varphi_\mu(\vec{r}_i)$ $c_\mu(\vec{G}_j) \rightarrow \varphi_\mu(\vec{r}_i)$

  Use **Fast Fourier Transform –** it costs **~$NlogN$** operations
- Calculate $\rho(\vec{r}_i) = \sum_\mu^{occ} \varphi^*_\mu(\vec{r}_i) \varphi_\mu(\vec{r}_i)$
- Use inverse FFT to obtain $\rho(\vec{G})$ $\rho(\vec{r}_i) \rightarrow \rho(\vec{G}_j)$

**Total cost ~$NlogN$**

## Pseudopotential plane-wave formalism – practical aspects: local potential

- Calculation of Hartree potential is very cheap: $\upsilon_H(\vec{G}) \sim \frac{\rho(\vec{G})}{G^2}$

**How to deal with other parts of local potential?**

- Separate local pseudopotential into long-range and short range part $$\upsilon^{ps,\alpha}_{loc}(r) = -\frac{Z_v e^2}{r} + \underbrace{(\upsilon^{ps,\alpha}_{loc}(r) + \frac{Z_v e^2}{r})}_{\upsilon^{ps,\alpha}_{loc,SR}(r)}$$
- Calculate Fourier coefficient of Coulomb potential analytically and of the short range one numerically
- Calculate $\upsilon^{ps}_{loc}(\vec{G}_j)$
- Use FFT to obtain local pseudopotential plus Hartree on mesh $\{\vec{r}_i\}$ $$\upsilon^{ps}_{loc}(\vec{G}_j) + \upsilon_H(\vec{G}_j) \rightarrow \upsilon(\vec{r}_i)$$

## Pseudopotential plane-wave formalism – practical aspects: local potential

- Calculate exchange-correlation potential on the mesh $\{\vec{r}_i\}$ $\upsilon_{xc}(\vec{r}_i)$ using values of $\rho(\vec{r}_i)$ (LDA, GGA approximation)
- Compute $g^{(\mu)}_{loc}(\vec{r}_i) := [\upsilon_{xc}(\vec{r}_i) + \upsilon^{ps}_{loc}(\vec{r}_i)] \varphi_\mu(\vec{r}_i)$
- FFT $g^{(\mu)}_{loc}(\vec{r}_i)$ to get $g_{loc}(\vec{G}_j)$ $$g^{(\mu)}_{loc}(\vec{G}) = \sum_{\vec{G}'} \upsilon_{loc}(\vec{G}-\vec{G}') c_\mu(\vec{G}')$$
- Very simple calculation of $$g^{(\mu)}_{kin}(\vec{G}) = \sum_{\vec{G}'} \left[ \frac{\hbar^2}{2m} (\vec{k}+\vec{G})^2 \delta_{\vec{G},\vec{G}'} \right] c_{n\vec{k}}(\vec{G}')$$

**No problem!**

## Pseudopotential plane-wave formalism – practical aspects: nonlocal potential

**Calculation of gradient corresponding to nonlocal semilocal pseudopotential is very costly**

$$g^{(\mu)}_{nonloc}(\vec{G}) = \sum_{\vec{G}'} \upsilon^{ps}_{nonloc}(\vec{k}+\vec{G},\vec{k}+\vec{G}')c_{n\vec{k}}(\vec{G}')$$

**Calculation of Fourier coefficients always of the order of N$^2$**

→ **Therefore, separable nonlocal pseudopotential of the Bylander-Kleinman form**

$$\upsilon^{K-B}_{nonloc}(\vec{r},\vec{r}') = \sum_{\alpha}\sum_{lm} f^{*}_{lm,\alpha}(\vec{r}-\vec{X}_{\alpha})f_{lm,\alpha}(\vec{r}'-\vec{X}_{\alpha})$$

**Local part maybe identical in K-B and semilocal PP**

## Pseudopotential plane-wave formalism – practical aspects: nonlocal potential

$$\boxed{\upsilon^{K-B}_{nonloc}(\vec{r},\vec{r}') = \sum_{\alpha}\sum_{lm} f^{*}_{lm,\alpha}(\vec{r}-\vec{X}_{\alpha})f_{lm,\alpha}(\vec{r}'-\vec{X}_{\alpha})}$$

**The knowledge of $f_{lm,\alpha}(\vec{G})$ is sufficient to calculate**

$$g^{(\alpha)}_{nonloc}(\vec{G})$$

**Computational cost proportional to N, but with rather large prefactor**

## Pseudopotential plane-wave formalism – practical aspects norm conserving PPs

- **Computational schemes with norm conserving PPs**
- **Computational burden ~$N \log N$**
- **Good transferability of the PPs**
- **Atoms from the first row of Periodic Table require kinetic energy cutoff of ~60-70 Ry**
- **Too many plane-waves required in many applications**
  atoms from the first row of Periodic Table
  semicore d-states
  Even one atom of this type requires large cutoff

→ *Ultra soft pseudoptentials*

## Features of the Pseudopotential Method

- *Pseudopotential is approximation to all-electron case, but…*

**Very accurate**
•Comparable accuracy to AE in most cases
•Simpler formalism

**Low computational cost**
•Perform calculations on ‘real-life’ materials

**Allows full advantage of plane-wave basis sets**
•Systematic convergence
•Easy to perform dynamics

## Empirical Pseudopotential Method

$$\sum_{\vec{G}'}\left[\frac{\hbar^2}{2m}(\vec{k}+\vec{G})^2\delta_{\vec{G},\vec{G}'}+V_{EMP}^{ps}(\vec{k}+\vec{G},\vec{k}+\vec{G}')\right]c_{n\vec{k}}(\vec{G})=\varepsilon_n(\vec{k})c_{n\vec{k}}(\vec{G})$$

**Non-local empirical pseudopotential**

**Fourier components are treated as empirical parameters**

Very accurate band structure description of elemental (diamond), zinc-blende, wurtzite, and chalcopyrite structure semiconductors.

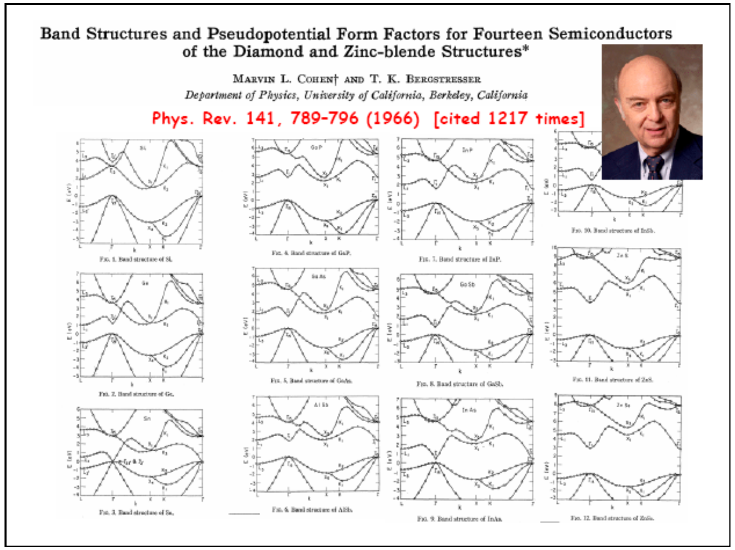
Particularly simple model

$$\sum_{\vec{G}'}\left[\frac{\hbar^2}{2m}(\vec{k}+\vec{G})^2\delta_{\vec{G},\vec{G}'}+V_{EMP,loc}^{ps}(\vec{G}-\vec{G}')\right]c_{n\vec{k}}(\vec{G})=\varepsilon_n(\vec{k})c_{n\vec{k}}(\vec{G})$$

Local empirical pseudopotentials

Ten parameters give very reasonable description of the band structure

*J. Chelikovsky & M. Cohen, "Electronic Structure and Optical Properties of Semiconductors", (Springer, Heidelberg, 1988)*



Band Structures and Pseudopotential Form Factors for Fourteen Semiconductors of the Diamond and Zinc-blende Structures*

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Phys. Rev. 141, 789-796 (1966) [cited 1217 times]

## Thank you!