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

Summer Semester 2013

Lecture

Modeling of Nanostructures and Materials

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Modeling of Nanostructures and Materials

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Lecture 4 – *March 14, 2013*

- **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

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

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

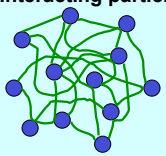
Kinetic energy of nuclei | Kinetic energy of electrons | Nucleus-Nucleus interaction | Electron-Nucleus interaction | Electron-Electron interaction

$$H\Psi = E\Psi$$

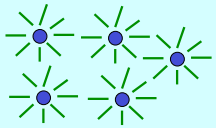
***Ab-initio* (first principles) Method –**
ONLY Atomic Numbers $\{Z_i\}$ as input parameters

Density Functional Theory (DFT) in Kohn-Sham realization

Interacting particles | **Independent particles**



$\Psi(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_{10^{23}})$



$\phi_1(\vec{x}_1)\phi_2(\vec{x}_2)\ldots\phi_3(\vec{x}_{10^{23}})$

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

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

unknown!!!

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

The Kohn- Sham Method – The Kohn-Sham Equations

- Schrödinger-like equations with local potential

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

$$\left[-\frac{\hbar^2}{2m}\vec{\nabla}^2 + v_{ext}(\vec{r}) + v_H(\vec{r}) + v_x(\vec{r}) + v_c(\vec{r})\right]\varphi_i(\vec{r}) = \varepsilon_i\varphi_i(\vec{r})$$

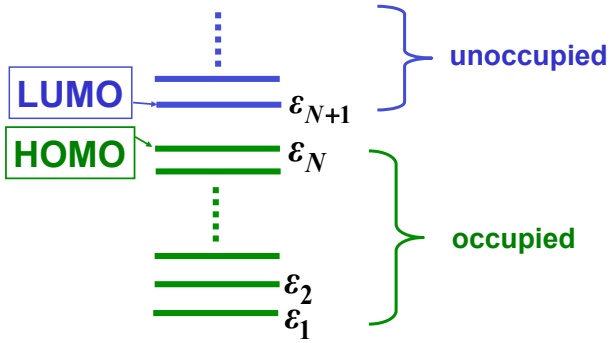
$$v_{ext}(\vec{r}) = -e^2\sum_{s,n}\frac{Z_s}{|\vec{r}-\vec{\tau}_s-\vec{R}_n|}$$

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

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

The Kohn- Sham Method – ‚Aufbau' principle

How to calculate one particle density?



DFT: Implementations of the Kohn-Sham Method

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

- Fully relativistic
- Semi-relativistic
- Non-relativistic

- Beyond LDA
  - GW (quasi-particles)
  - EXX (exact exchange)
  - sX-LDA
  - Time dependent DFT
  - LDA+U
- Generalized Gradient Approximation (GGA)
- Local Density Approximation (LDA)

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

- Non-periodic
- periodic

- Non-spin-polarized
- Spin polarized

- Atomic orbitals (Gaussians(GTO), Slater type (STO), Numerical)
- Plane Waves (Plane waves (FPLAPW), Spherical waves (LMTO, ASW))
- Augmentation
- 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 $\{\chi_{\alpha\vec{k}}(\vec{r})\}$

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

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

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

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

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

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

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

- **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 $\quad \vec{G}_n = n_1\vec{b}_1 + n_2\vec{b}_2 + n_3\vec{b}_3$

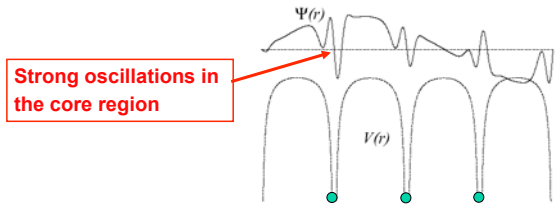
In practical calculations $\{\vec{G} : \frac{1}{2}(\vec{k}+\vec{G})^2 \le E_{cutoff}\}$

Kinetic Energy Cutoff

Concept of pseudopotential

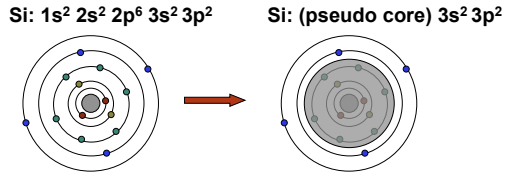
Typical electronic potential and wave function

- 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:



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**

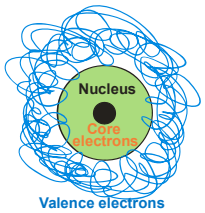


$$V_{ext}(\mathbf{r}) = \frac{-14e^2}{\mathbf{r}} \qquad V_{ext}(\mathbf{r}) = V_{ps}(\mathbf{r})$$

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**

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

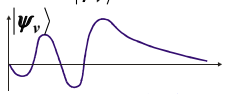
Phillips & Kleinman, Phys. Rev. ***116****, 287 (1959)*

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 $|\psi_v\rangle$

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

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

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

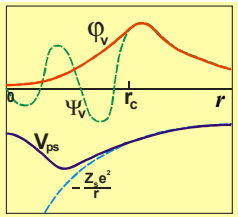
- $\{\hat{H}^{at} - \sum_c (E_c - E_v)|\psi_c\rangle\langle\psi_c|\}|\varphi_v\rangle = E_v|\varphi_v\rangle$
- The pseudo-wave-function fulfills Schrödinger-like equation with Hamiltonian that is dependent on energy and contains additional repulsive, nonlocal potential.
- $\hat{H}_{ps} = \hat{H}^{at}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

PSEUDOPOTENTIALS – Philips-Kleinman Method

$\hat{H}^{at}|\psi_v\rangle = E_v|\psi_v\rangle$ **Atom** — Energies are identical — $\hat{H}_{ps}|\varphi_v\rangle = E_v|\varphi_v\rangle$ **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 φ_v
- **Outside the core region** $r > r_c$

  $\varphi_v = \psi_v$ $\quad V_{ps} = \frac{-Z_s e^2}{r}$
- 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

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} + v^{at}_{l,KS}(r)\right] u_l(r) = \varepsilon_l u_l(r)$$

Atomic units: $\hbar = e = m = 1$

- Effective Kohn-Sham potential contains all electronic interactions

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

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

Atomic density | Core density | Valence density

Construction of Norm Conserving Pseudopotentials

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

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

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. $\int_0^{r_{cl}} |R_l^{ps}(r)|^2 r^2 dr = \int_0^{r_{cl}} |R_l(r)|^2 r^2 dr$ — Pseudo-wavefunctions and atomic wavefunctions lead to identical charge in the core region $r \le r_{cl}$

NORM CONSERVATION

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 ($r < r_{cl}$)

$u_l^{ps}(r) = r^{l+1} \exp[p_l(r^2)]$ p_l - 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.**

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

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

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

- **Unscreening procedure**

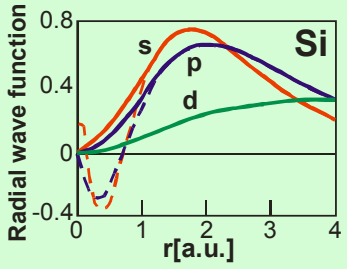
$v^{ps}_{l,atom}(r) \Rightarrow V^{ps}_{l,ion}(r)$ **IONIC PSEUDOPOTENTIAL**

$$V^{ps}_{l,ion}(r) = v^{ps}_{l,atom}(r) - v_H([\rho^{ps}_{val}];r) - v_{xc}([\rho^{ps}_{val}];r)$$

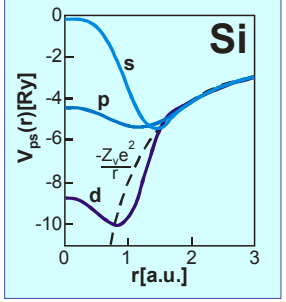
$V^{ps}_{l,ion}(r)$ - For each angular momentum quantum number "l"

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



Norm Conserving Pseudopotentials

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

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

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

Projection operator

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

In Solids:

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

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** $\rho = \rho_c + \rho_v$

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

Equality was assumed, for simplicity, for the unscreening procedure

➡ ***Nonlinear core correction***

Nonlinear Core Correction

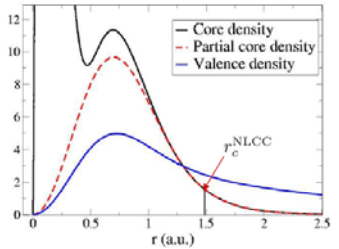
Louie et al.,Phys. Rev. B 26, 1738 (1982)

- Unscreening using smooth function of core density

$$v^{\rm ps}_{\rm ion} = V^{\rm ps}_{\rm eff} - v_{\rm H}[n_v] - v_{\rm xc}\left[n_v + n^{\rm NLCC}_{\rm c}\right]$$

$$n^{\rm NLCC}_{\rm c}(r) = \begin{cases} n_{\rm c}(r) & \text{for } r > r^{\rm NLCC}_{\rm c} \\ \exp\left(\sum_{i=0}^{2} a_i r^{2i}\right) & \text{for } r \le r^{\rm NLCC}_{\rm c} \end{cases}$$

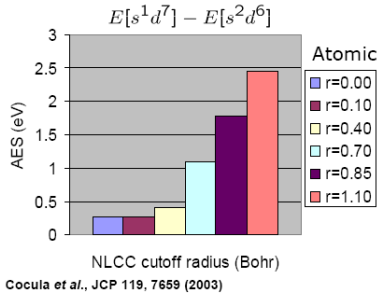
➡



Nonlinear Core Correction – How it works?

Atomic energy splitting for Fe atom

Choice of cutoff radius ?



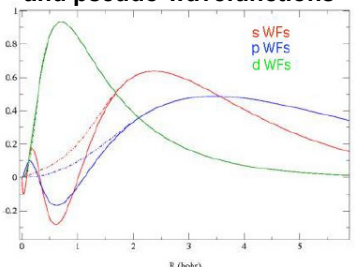
Cocula *et al.*, JCP 119, 7659 (2003)

- 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***

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

Fourier transformation

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

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

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

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

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

Kohn-Sham equations in pseudopotential formalism

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

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

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

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

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

Local and nonlocal parts of pseudopotential

Pseudopotential for atomic species α

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

Pseudopotential for a collection of atoms

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

local part

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

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

non-local part

Kleinman-Bylander Separable Pseudopotentials

Fully non-local separable PP

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

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

- 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

$$v_{loc}(\vec{G}-\vec{G}') = v_H(\vec{G}-\vec{G}') + v_{xc}(\vec{G}-\vec{G}') + v^{ps}_{loc}(\vec{G}-\vec{G}')$$

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

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? $v_{loc}(\vec{G}-\vec{G}')$

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

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

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

Pseudopotential plane-wave formalism – practical aspects

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

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

- 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

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

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 $c_\mu^{(n+1)} = c_\mu^{(n)} + \eta g^{(\mu)}(n)$

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 $\varphi_\mu(\vec{r}_i)$ $\quad c_\mu(G_j) \to \varphi_\mu(\vec{r}_i)$

  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 $\rho(\vec{G})$ $\quad \rho(\vec{r}_i) \to \rho(\vec{G}_j)$

Total cost ~$NlogN$

Pseudopotential plane-wave formalism – practical aspects: local potential

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

How to deal with other parts of local potential?

- Separate local pseudopotential into long-range and short range part

$$v_{loc}^{ps,\alpha}(r) = -\frac{Z_v e^2}{r} + \underbrace{(v_{loc}^{ps,\alpha}(r) + \frac{Z_v e^2}{r})}_{v_{loc,SR}^{ps,\alpha}(r)}$$

- Calculate Fourier coefficient of Coulomb potential analytically and of the short range one numerically
- Calculate $v_{loc}^{ps}(\vec{G}_j)$
- Use FFT to obtain local pseudopotential plus Hartree on mesh $\{\vec{r}_i\}$ $\quad v_{loc}^{ps}(\vec{G}_j) + v_H(\vec{G}_j) \to v(\vec{r}_i)$

Pseudopotential plane-wave formalism – practical aspects: local potential

- Calculate exchange-correlation potential on the mesh $\{\vec{r}_i\}$ $v_{xc}(\vec{r}_i)$ using values of $\rho(\vec{r}_i)$ (LDA, GGA approximation)
- Compute $g_{loc}^{(\mu)}(\vec{r}_i) := [v_{xc}(\vec{r}_i) + v_{loc}^{ps}(\vec{r}_i)] \varphi_\mu(\vec{r}_i)$
- FFT $g_{loc}^{(\mu)}(\vec{r}_i)$ to get $g_{loc}(\vec{G}_j)$

$$g_{loc}^{(\mu)}(\vec{G}) = \sum_{\vec{G}'} v_{loc}(\vec{G}-\vec{G}') c_\mu(\vec{G}')$$

- Very simple calculation of

$$g_{kin}^{(\mu)}(\vec{G}) = \sum_{\vec{G}'} \left[\frac{\hbar^2}{2m} (\vec{k}+\vec{G})^2 \delta_{\vec{G},\vec{G}'} \right] c_{n\vec{k}}(\vec{G}')$$

No problem!

Pseudopotential plane-wave formalism – practical aspects: nonlocal potential

Calculation of gradient corresponding to nonlocal semilocal pseudopotential is very costly

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

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

➡ Therefore, separable nonlocal pseudopotential of the Bylander-Kleinman form

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

Local part maybe identical in K-B and semilocal PP

Pseudopotential plane-wave formalism – practical aspects: nonlocal potential

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

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

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

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.

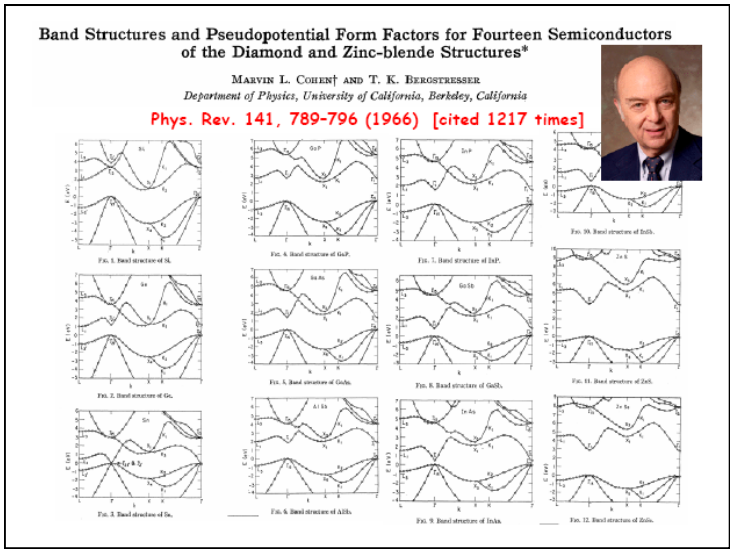
Particularly simple model

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

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!