Chair of Condensed Matter Physics
Institute of Theoretical Physics
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Wykład

Modelowanie Nanostruktur

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The Kohn- Sham Method –
The Kohn-Sham Equations

- Schrödinger-like equations with local potential

$$\upsilon_H(\vec r) = \frac{\delta U}{\delta\rho} = \int d\vec r\,' \frac{\rho(\vec r\,')}{|\vec r - \vec r\,'|}$$

$$\frac{\delta E_x[\rho]}{\delta\rho}$$

$$\frac{\delta E_c[\rho]}{\delta\rho}$$

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

$$\upsilon_{ext}(\vec r) = -e^2\sum_{s,n}\frac{Z_s}{|\vec r - \vec\tau_s - \vec R_n|}$$

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

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

Modelowanie Nanostruktur, 2011/2012

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Wykład 9 – *6 XII 2011*

Fale płaskie i pseudopotencjały

- Koncepcja pseudopotencjału
- Równania Kohna-Shama w bazie fal płaskich
- Pseudopotencjały zachowujące normę
- Pseudopotencjały empiryczne

The Kohn- Sham Method – The Total Energy

$$E_{el}[\rho] = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\int d\vec r\varphi_i^*(\vec r)\vec\nabla^2\varphi_i(\vec r) + U[\rho] + E_x[\rho] + E_c[\rho] + \int d\vec r\upsilon_{ext}(\vec r)\rho(\vec r)$$

$$E_{el} = \sum_{i=1}^{N}\varepsilon_i \underbrace{-\frac{1}{2}\iint d\vec r d\vec r\,'\frac{\rho(\vec r)\rho(\vec r\,')}{|\vec r - \vec r\,'|} + E_x[\rho] + E_c[\rho] - \int d\vec r(\upsilon_x(\vec r) + \upsilon_c(\vec r))\rho(\vec r)}_{\text{so-called double counting correction}}$$

Total energy of a solid:

$$E_{tot} = E_{el} + E_{ion-ion}$$

$$E_{ion-ion} = \frac{e^2}{2}\sum_{nn'}\sum_{ss'}\frac{Z_s Z_{s'}}{|\vec R_n + \vec\tau_s - \vec R_{n'} - \vec\tau_{s'}|}$$

$$E_{tot}(\{\varphi_i\},\{\vec\tau_s\},\{\vec a_j\}) = E_{el}(\{\varphi_i\},\{\vec\tau_s\},\{\vec a_j\}) + E_{ion-ion}(\{\vec\tau_s\},\{\vec a_j\})$$

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**

Plane-wave formalism

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

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**

Solution of the Kohn-Sham Equations – LCAO & Plane-waves expansion

- **LCAO (Linear Combination of Atomic Orbitals)**

  All electron & pseudopotential

  ➡ **Semiempirical Tight-Binding Method**

- **Plane waves and pseudopotential**

  ➡ **EMP – Empirical Pseudopotential Method**

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

Plane-wave formalism

Fourier coefficients of the electronic (pseudoelectronic) density

$$\rho_{val}(\vec{r}) = \frac{\Omega_0}{(2\pi)^3} \sum_{n}^{occ} \int_{BZ} |\varphi_{n\vec{k}}(\vec{r})|^2 \, d^3\vec{k} = \sum_{n,\vec{k}} \varphi_{n\vec{k}}(\vec{r})|^2$$

Special k-points

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

Methods to solve eigenvalue problem for expansion coefficients

- For small number of expansion coefficients $c_{n\vec{k}}(\vec{G})$ say ~ 2000, standard diagonalization procedure is used.
- For larger number of coefficients, **the modern iterative techniques based on direct minimization of the total energy are used**.

Commercial or open source (GNU-license) codes available
VASP (Univ. Vienna, com.), CASTEP (Accelrys, com.)
ABINIT (Univ. de Louvain, GNU), SPINOR (UCSB, GNU)

Plane-wave formalism

Kohn-Sham equations in momentum space

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

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

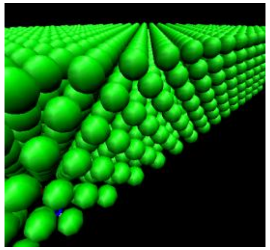
Fourier transformation

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

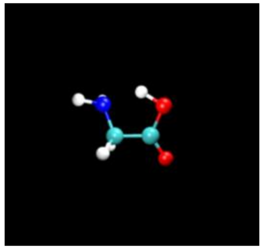
Eigenvalue problem – system of equations
for expansion coefficients $c_{n\vec{k}}(\vec{G})$

Plane-wave formalism for systems with reduced periodicity

How we solve the Kohn-Sham problem when the systems are not periodic: surfaces, interfaces, clusters, molecules… and still take advantage of the plane wave formulation of the problem

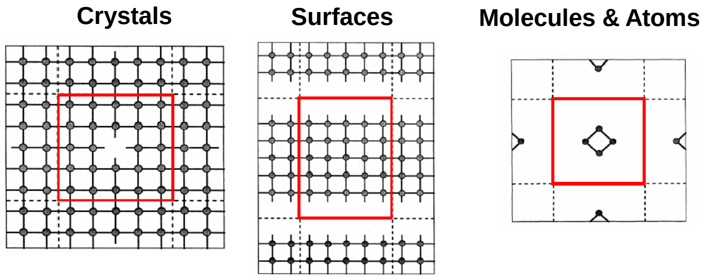


Surface



Molecule

Plane-wave formalism – Supercell method



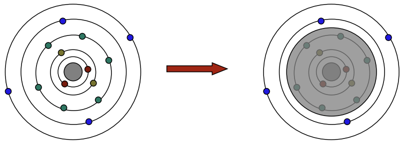
- Impose periodic boundary conditions to describe extended, translationally ordered (periodic) bulk crystals, surfaces, and interfaces. Can also use same formalism to describe molecules or atoms.

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

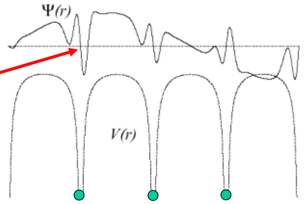
$$V_{ext}(\mathbf{r}) = \frac{-14e}{\mathbf{r}}$$

4 (valence) electrons

$$V_{ext}(\mathbf{r}) = V_{ps}(\mathbf{r})$$

Typical electronic potential and wave function

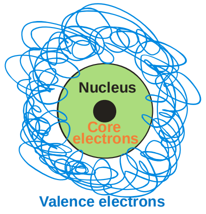
- When solving the K-S equations for the full system of nuclei and electrons we find that:
  - Close to the nuclei, the potential is dominated by strong Coulomb interactions
  - In interstitial regions the potential is much weaker and reflects the symmetry of the crystal
- A typical wavefunction would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



Strong oscillations in the core region

PSEUDOPOTENTIALS - Basic Idea

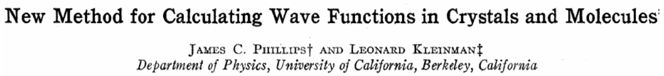
The basic idea of the pseudopotential theory:



- 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

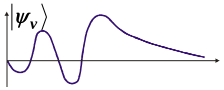
Phillips & Kleinman, Phys. Rev. ***116****, 287 (1959)*

Construction of pseudopotentials from atomic wavefunctions

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

$$\hat{H}^{at}|\psi_v\rangle = E_v|\psi_v\rangle \qquad |\psi_c\rangle \text{ -core states} \qquad |\psi_v\rangle \text{ - valence states}$$

- 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

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

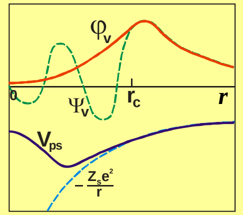
Atom

Energies are identical

Pseudoatom

Effective potential acting on the pseudo-valence electrons

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



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** $r > r_c$

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

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.
- $\boxed{\hat{H}_{ps} = \hat{H}^{at} + \sum_c (E - E_c)|\psi_c\rangle\langle\psi_c|}$

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

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

- Effective Kohn-Sham potential contains all electronic interactions

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

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

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

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

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.**

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

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

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

- ● ● ● **Unscreening procedure**

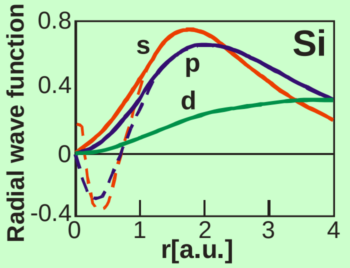
$\upsilon_{l,atom}^{ps}(r)\Rightarrow V_{l,ion}^{ps}(r)$ IONIC PSEUDOPOTENTIAL

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

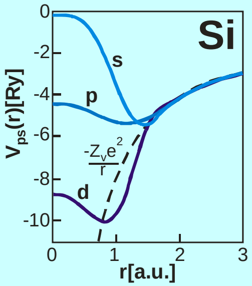
$V_{l,ion}^{ps}(r)$ - For each angular momentum quantum number "l"

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



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

Pseudopotential in Kohn-Sham Method

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

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

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

non-local pseudopotential !!

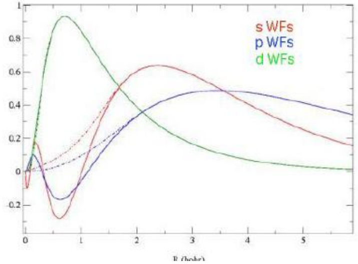
- **External potential (pseudopotential) is non-local !**
- **Is it compatible with derivation of Kohn-Sham equations?**

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

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

Kohn-Sham equations in pseudopotential formalism

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

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

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

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

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

Local and nonlocal parts of pseudopotential

Pseudopotential for atomic species α

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

Pseudopotential for a collection of atoms

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

local part

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

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

non-local part

Pseudopotential plane-wave formalism – practical aspects

Number of plane waves in the wavefunction expansion N

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

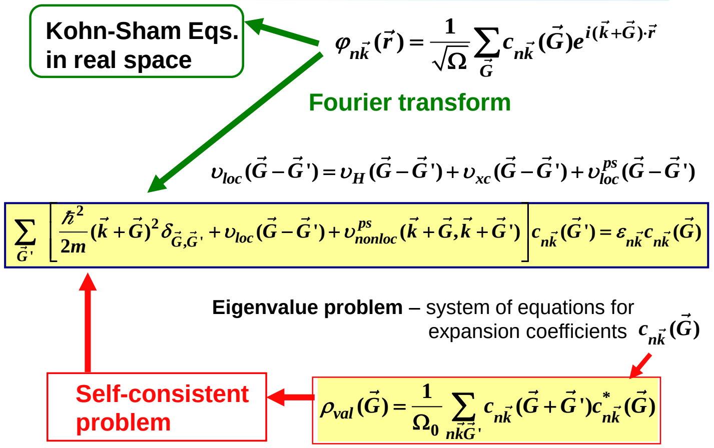
Number of needed Fourier coefficients of the local potential? $\upsilon_{loc}(\vec{G}-\vec{G}\,')$

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

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

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

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

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

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

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

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

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

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

- 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

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

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

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

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 $\varphi_\mu(\vec{r}_i)$ $\quad c_\mu(\vec{G}_j) \rightarrow \varphi_\mu(\vec{r}_i)$

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

Total cost ~$NlogN$

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

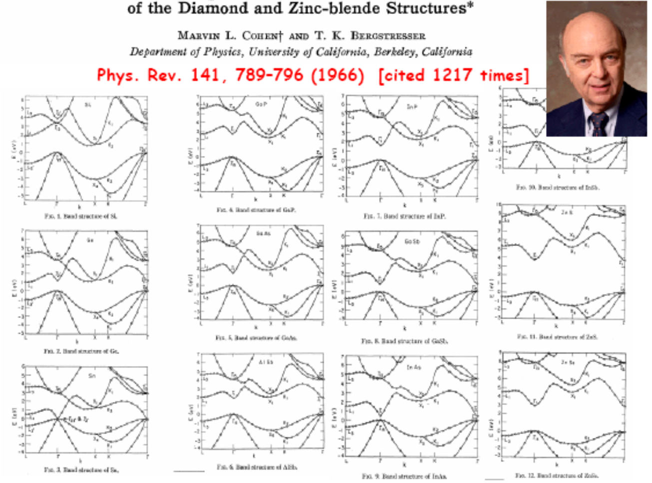
J. Chelikovsky & M. Cohen, "Electronic Structure and Optical Properties of Semiconductors", (Springer, Heidelberg, 1988)

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

Marvin L. Cohen† and T. K. Bergstresser

Department of Physics, University of California, Berkeley, California

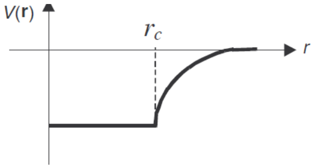
Phys. Rev. 141, 789-796 (1966) [cited 1217 times]



Model Pseudopotentials

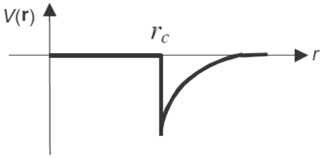
Constant effective potential in the core region:

$$V(r) = \begin{cases} \dfrac{-Ze^2}{4\pi\varepsilon_0 r}; & r > r_C \\ \dfrac{-Ze^2}{4\pi\varepsilon_0 r_C}; & r \le r_C \end{cases}$$



Empty core model:

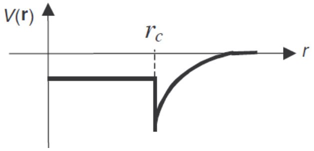
$$V(r) = \begin{cases} \dfrac{-Ze^2}{4\pi\varepsilon_0 r}; & r > r_C \\ 0; & r \le r_C \end{cases}$$



Model Pseudopotentials (2)

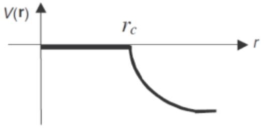
Model potential due to Heine and Abarenkov:

$$V(r) = \begin{cases} \dfrac{-Ze^2}{4\pi\varepsilon_0 r}; & r > r_C \\ A; & r \le r_C \end{cases}$$

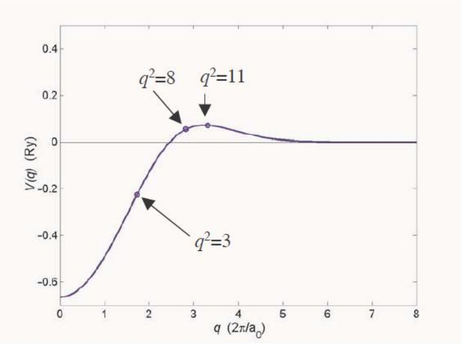


Lin and Kleinman model potentials:

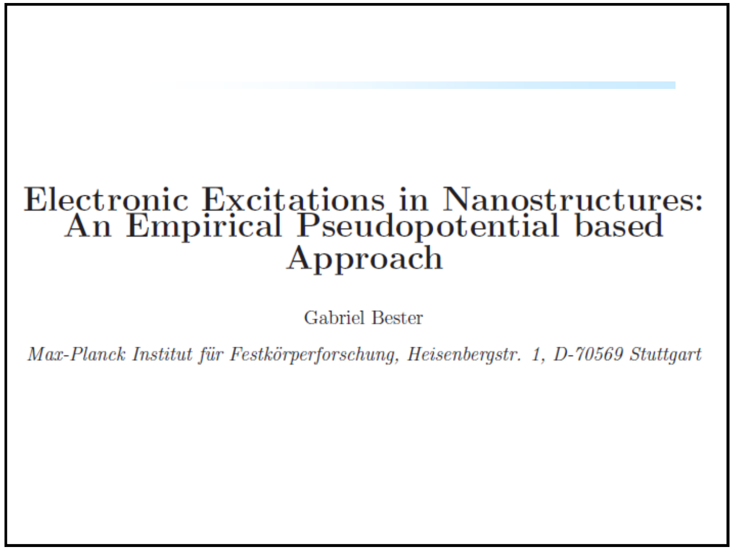
$$V(r) = \begin{cases} 2\dfrac{-Ze^2}{4\pi\varepsilon_0 r}\{1-\exp[-\beta(r-r_C)]\}; & r > r_C \\ 0; & r \le r_C \end{cases}$$



A Typical Empirical Pseudopotential



Fourier transform of the pseudopotential. (Note that $q = |\mathbf{G}-\mathbf{G}'|$)



Electronic Excitations in Nanostructures: An Empirical Pseudopotential based Approach

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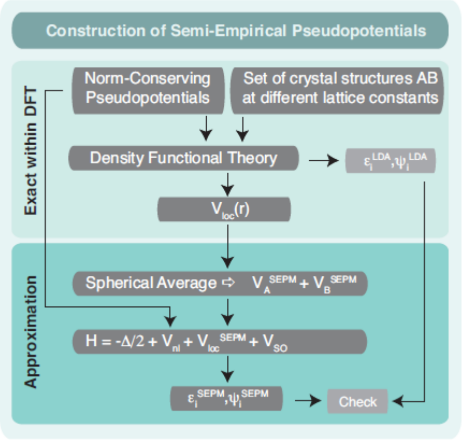
Semi-empirical PPs from *ab initio* calculations



Construction of Semi-Empirical Pseudopotentials

Exact within DFT

Norm-Conserving Pseudopotentials

Set of crystal structures AB at different lattice constants

Density Functional Theory → $\varepsilon_i^{LDA},\psi_i^{LDA}$

$V_{loc}(r)$

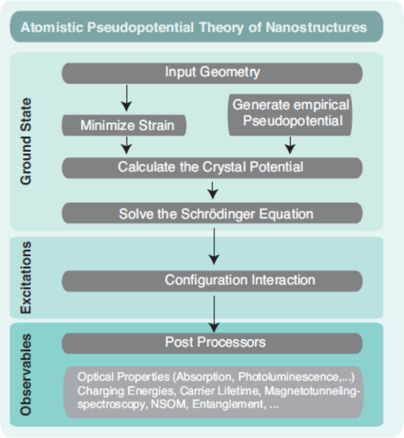
Approximation

Spherical Average ⇨ $V_A^{SEPM} + V_B^{SEPM}$

$H = -\Delta/2 + V_{nl} + V_{loc}^{SEPM} + V_{SO}$

$\varepsilon_i^{SEPM},\psi_i^{SEPM}$ → Check

Atomistic PP Theory of Nanostructures



Atomistic Pseudopotential Theory of Nanostructures

Ground State

Input Geometry

Minimize Strain

Generate empirical Pseudopotential

Calculate the Crystal Potential

Solve the Schrödinger Equation

Excitations

Configuration Interaction

Observables

Post Processors

Optical Properties (Absorption, Photoluminescence,...)
Charging Energies, Carrier Lifetime, Magnetotunneling-spectroscopy, NSOM, Entanglement, ...

Semi-empirical Pseudopotential