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

Summer Semester 2013

Lecture

Modeling of Nanostructures and Materials

Jacek A. Majewski

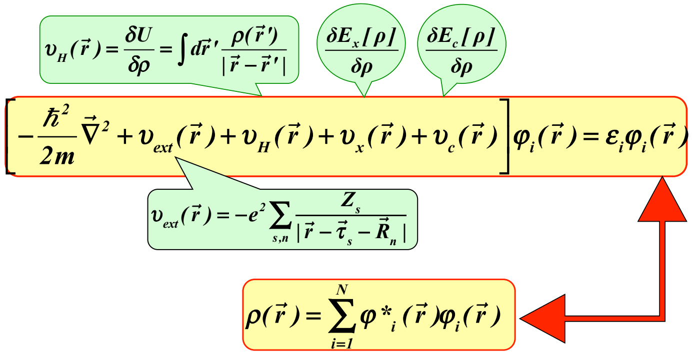
E-mail: Jacek.Majewski@fuw.edu.pl

Lecture 5 – *March 21, 2013*

- Kohn-Sham Method with Plane-waves and pseudopotentials (cnt.)
- Introduction to Molecular Dynamics

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)

Plane-wave formalism

for

Kohn – Sham equations

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

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

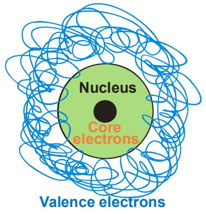
$\{\vec{G}\}$ - reciprocal lattice vectors $\quad \vec{G}_n = n_1\vec{b}_1 + n_2\vec{b}_2 + n_3\vec{b}_3$

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

Kinetic Energy Cutoff

PSEUDOPOTENTIALS - Basic Idea

The basic idea of the pseudopotential theory:

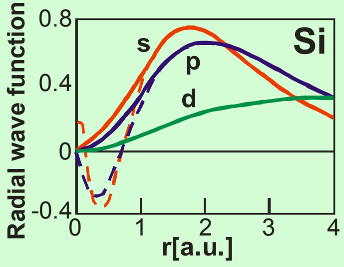


- Core electrons are localized and therefore chemically inactive (inert)
- Valence electrons determine chemical properties of atoms and SOLIDS

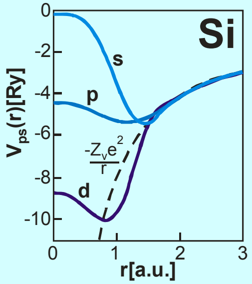
➡ **Describe valence states by smooth wavefunctions**

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



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

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

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

Kleinman-Bylander Separable Pseudopotentials

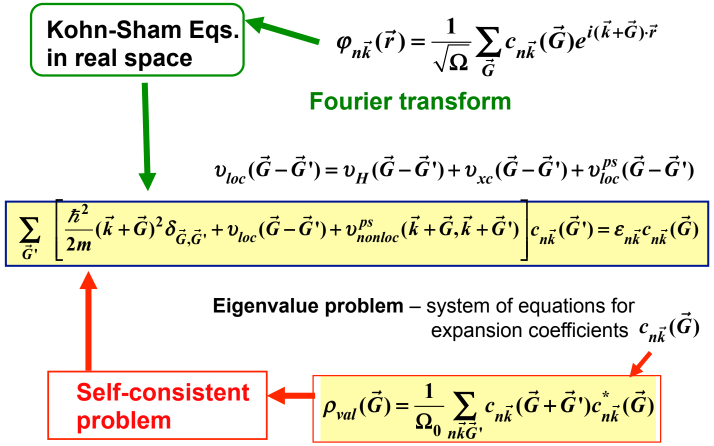
Fully non-local separable PP

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

$$\left(\hat{T}+\hat{V}^{ps}-\varepsilon_i\right)\varphi_i = 0 \qquad \Delta\upsilon_l = \upsilon_l - \upsilon_{loc}$$

- 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

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

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

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

Self-consistent problem

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

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)

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

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

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

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

Pseudopotential plane-wave formalism – practical aspects

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

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

- 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

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

Gradient

We are looking for $\mu \ge N_{occ}$ **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 $\varphi_\mu(\vec{r}_i)$ $\quad c_\mu(G_j) \to \varphi_\mu(\vec{r}_i)$

  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: $\upsilon_H(\vec{G}) \sim \frac{\rho(\vec{G})}{G^2}$

How to deal with other parts of local potential?

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

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 $g_{loc}^{(\mu)}(\vec{r}_i) := [\upsilon_{xc}(\vec{r}_i) + \upsilon_{loc}^{ps}(\vec{r}_i)]\varphi_\mu(\vec{r}_i)$
- FFT $g_{loc}^{(\mu)}(\vec{r}_i)$ to get $g_{loc}(\vec{G}_j)$

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

- 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

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

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

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

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

Local part maybe identical in K-B and semilocal PP

Pseudopotential plane-wave formalism – practical aspects: nonlocal potential

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

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

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…*

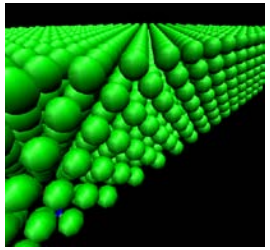
Very accurate
•Comparable accuracy to AE in most cases
•Simpler formalism

Low computational cost
•Perform calculations on 'real-life' materials

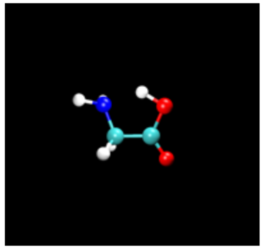
Allows full advantage of plane-wave basis sets
•Systematic convergence
•Easy to perform dynamics

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

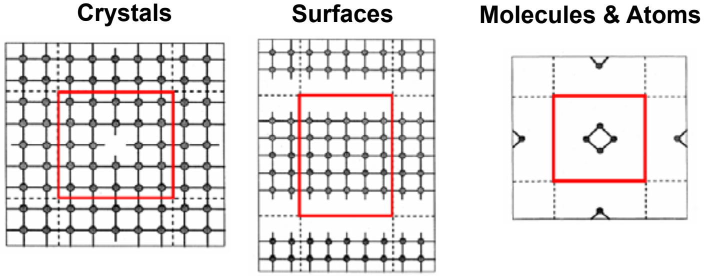


Surface



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.

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.

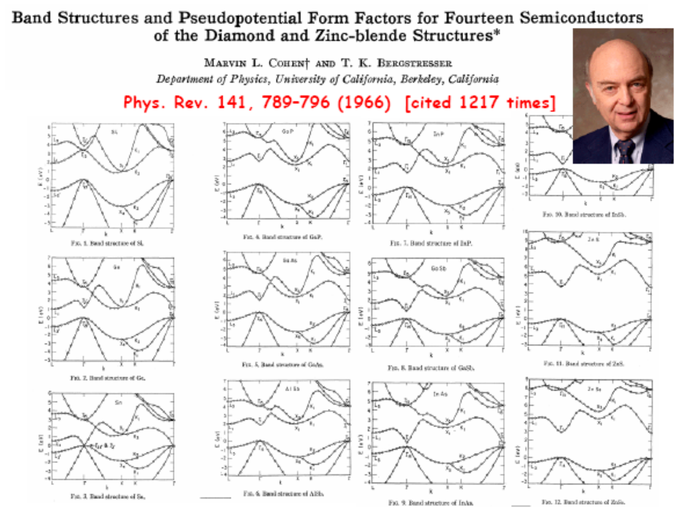
Particularly simple model

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

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]

Properties of Materials From static K-S DFT calculations

The Kohn-Sham Method –Total Energy & Forces

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

total electronic energy in the field of ions

Energy of ions

$$E_{ion}=\frac{1}{2}\sum_{\alpha,\beta}\frac{Z_\alpha Z_\beta}{|\vec{R}_\alpha-\vec{R}_\beta|}$$

Total energy

$$E_{tot}(\{\vec{R}_\alpha\})=E_{el}(\{\vec{R}_\alpha\})+E_{ion}(\{\vec{R}_\alpha\})$$

Forces on ions $\vec{F}_\alpha=-\frac{\partial E_{tot}}{\partial\vec{R}_\alpha}=-\nabla_{\vec{R}_\alpha}E_{tot}$

Equilibrium: $\forall_\alpha \vec{F}_\alpha=0$ **Dynamics:** $M_\alpha\ddot{\vec{R}}_\alpha=\vec{F}_\alpha$

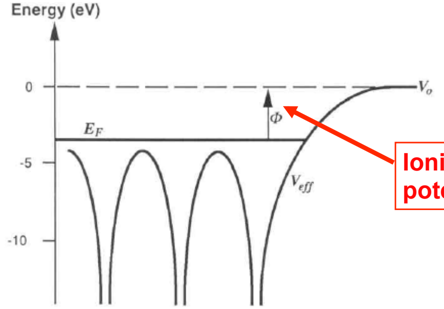
Materials Properties from Calculations

Structural Properties

- Geometries of molecules
- Crystal structures (packing)
- Density
- Defect structures
- Crystal morphology
- Surface structures
- Adsorption
- Interface structures

Calculation of Surface Properties-Surface Potential

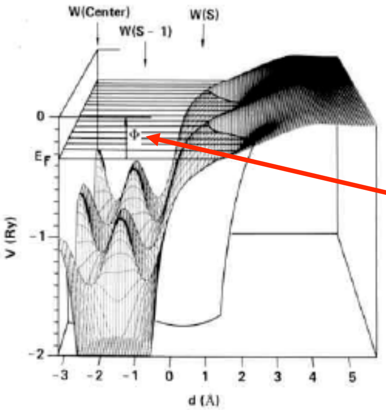
Schematics of surface potential



Ionization potential

Calculation of Surface Properties-Surface Potential of W (001)

W – wolframium = tungsten

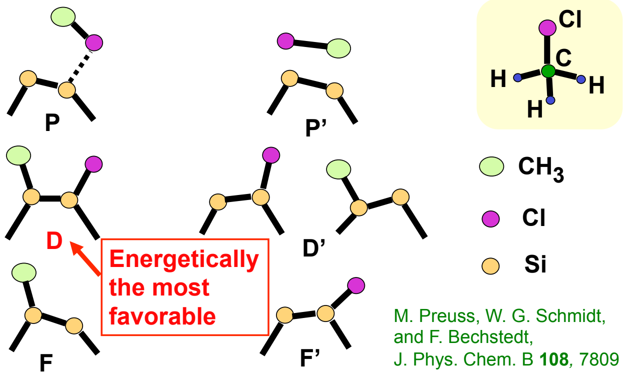


Ionization potential

E. Wimmer, A. J. Freeman,
J. R. Hiskes and A. J. Karo,
Phys. Rev. B **28**, 3074 (1983)

Methyl Chloride Adsorption on Si(001): *Ab initio* calculations

Sketches of the six adsorption geometries
(only relevant Si surface atoms are indicated)

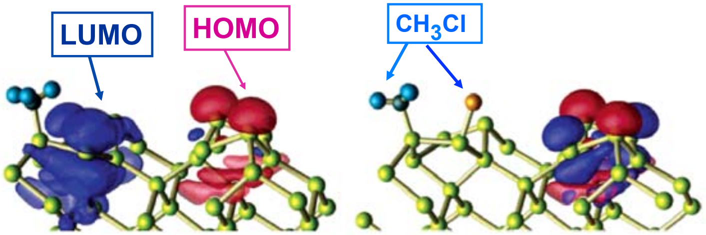


Energetically the most favorable

M. Preuss, W. G. Schmidt,
and F. Bechstedt,
J. Phys. Chem. B **108**, 7809 (2004)

Methyl Chloride Adsorption on Si(001): *Ab initio* calculations

Distribution of charge for the HOMO and LUMO orbitals



Configuration F **Configuration D**

M. Preuss, W. G. Schmidt, and F. Bechstedt, J. Phys. Chem. B **108**, 7809 (2004)

Materials Properties from Calculations (2)

Mechanical Properties

- Compressibility
- Elastic moduli
- Thermal expansion coefficients
- Vibrational properties
- Hardness
- Fracture toughness

Thermodynamic Properties

- Binding energies
- Pressure induced phase transitions

Materials Properties from Calculations (3)

Electronic, optical, and magnetic properties

- Electron density distribution - electrical moments
- Polarizabilities
- Ionization energies and electron affinities
- Electrostatic potential, work function
- Energy band structure - metal, semiconductor, insulator, superconductor
- Band offsets at hetero-junctions
- Optical spectra
- Spin density distribution, magnetic moments, crystalline magnetic anisotropy
- Magneto-optical properties (Kerr rotation)
- NMR chemical shifts
- Dielectric response
- Luminescence

Materials Properties from Calculations ?

Thermodynamic Properties

- Temperature induced phase transitions
- Phase diagrams
  (liquid-gas, liquid-liquid, liquid-solid, solid-solid)

Transport Properties

- Thermal conductivity
- Viscosity
- Diffusion constants

Require dynamic treatment of ion movement

➡ **Molecular Dynamics**

Chemical Properties – Molecular Dynamics needed

Chemical and other properties

- Chemical reaction rates (catalytic properties, corrosion, electrochemistry)
- Reactivity with surfaces
- Photochemical properties

Molecular Dynamics

- ✓ **Classical vs. *ab initio***
- ✓ **Ehrenfest vs. Born Oppenheimer**
- ✓ **Car-Parrinello MD**

Molecular Dynamics – What is it ?

- **Classical dynamics (given by Newton equations) of atoms in the system**

$$\boxed{\begin{aligned} M_I \ddot{\vec{R}}_I &= \vec{F}_I \\ \vec{F}_I &= -\nabla_I V_{eff}(\{\vec{R}_I\}) \end{aligned}}$$

- Goal **– to determine classical trajectories of all atoms in the system** $\{R_I(t)\}$
- At the very heart of any molecular dynamics scheme is the question of how to describe - that is in practice how to approximate - the ***interatomic interactions***.
- **Where to get forces on atoms from ?**

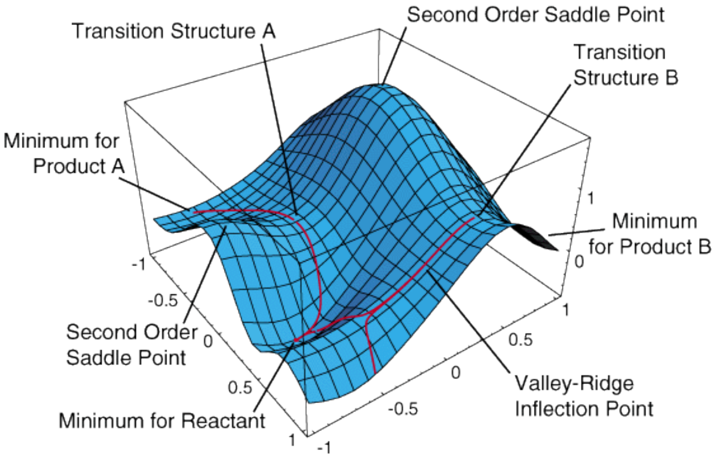
Classical vs. *Ab initio* Molecular Dynamics

$$\boxed{M_I \ddot{\vec{R}}_I = -\nabla_I V_{eff}(\{\vec{R}_I(t)\})}$$

Potential energy surface

- ***Classical*** – based on **predefined potentials**
  - either obtained from empirical data, or
  - obtained from independent electronic structure calculations
- ***Ab initio*** – based on fully **quantum mechanical calculations**

Potential Energy Surface



Classical Molecular Dynamics

- Typically, the full ***interaction potential*** is broken up into two-body, three-body and many-body contributions, long-range and short-range terms etc., which have to be represented by suitable functional forms.

$$V_{\mathrm{e}}^{\mathrm{E}} \approx V_{\mathrm{e}}^{\mathrm{approx}}(\{\mathbf{R}_I\}) = \sum_{I=1}^{N} v_1(\mathbf{R}_I) + \sum_{I<J}^{N} v_2(\mathbf{R}_I, \mathbf{R}_J) + \sum_{I<J<K}^{N} v_3(\mathbf{R}_I, \mathbf{R}_J, \mathbf{R}_K) + \cdots$$

- The electronic degrees of freedom are replaced by interaction potentials v_1 , v_2 **,** etc. and are not featured as explicit degrees of freedom in the equations of motion.

Classical Molecular Dynamics

- Very often, the interactions can faithfully be described by additive two-body terms

$$V_{\mathrm{e}}^{\mathrm{approx}}(\{\mathbf{R}_I\}) \approx \sum_{I<J}^{N} v_2(|\mathbf{R}_I - \mathbf{R}_J|)$$

For example, Argon in liquid phase

E. Ermakova, J. Solca, H. Huber, and D. Marx, Chem. Phys. Lett. **246**, 204 (1995).

- Well established tool to investigate many-body condensed matter systems
- A lot of monographs, e.g.,
  - M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Clarendon Press, Oxford, 1987; reprinted 1990).
  - D. Frenkel and B. Smit, *Understanding Molecular Simulation - From Algorithms to Applications* (Academic Press, San Diego, 1996).

Classical Molecular Dynamics - Drawbacks

☺ Moderate computation time and possibility to deal with large systems.

world's record – about 19 billion atoms

☹ **Limitations in applicable phenomena**

☹ **Restricted predictive power,**
specifically in ***simulating bond breaking and forming***

☹ Very difficult fitting procedure of *ab initio* results to a suitable functional form of interaction potential.
- It can be done only for extremely small systems.
- It is difficult to design a well-behaved fitting function.

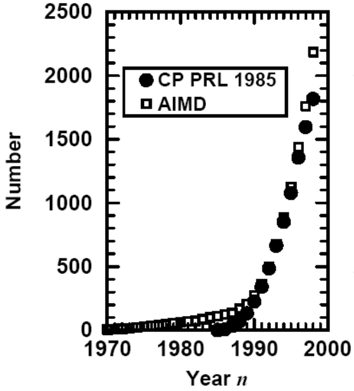
➡ ***Ab initio* Molecular Dynamics**

Ab initio Molecular Dynamics (AIMD)

- The fitting step can be bypassed and the dynamics performed directly by **calculating the inter-atomic forces** (obtained from the electronic structure calculated *on-the-fly*) **at each time-step of an MD simulation**
- The methods are widely applicable and possess potential to predict new phenomena and novel materials.

  ➡ **New Area in Materials Science – Materials Design**
- The methods may cost huge computation time, however
  - Progress in Computational Techniques (new solvers, new optimization techniques, etc.)
  - Progress in high-performance computers

Ab initio Molecular Dynamics (AIMD)



Squares: number of publications which appeared up to the year *n* that contain the keyword “ab initio molecular dynamics" (or synonyms such as “first principles MD", “Car-Parrinello simulations" etc.) in title, abstract or keyword list.

Circles: number of publications which appeared up to the year *n* that cite the 1985 paper by Car and Parrinello

---

Ab initio Molecular Dynamics (AIMD) - Theory

$$\frac{d\mathbf{P}_I}{dt} = -\nabla_I \int d\mathbf{r}\; \Psi^\star \mathcal{H}_e \Psi \qquad \text{or}$$

■
$$\boxed{\begin{aligned} M_I \ddot{\mathbf{R}}_I(t) &= -\nabla_I \int d\mathbf{r}\; \Psi^\star \mathcal{H}_e \Psi \\ &= -\nabla_I V_e^{E}(\{\mathbf{R}_I(t)\}) \end{aligned}}$$

- Thus, the nuclei move according to classical mechanics in an effective potential V_e^E due to the electrons.
- This potential is a function of only the nuclear positions at time t as a result of averaging H_e over the electronic degrees of freedom, i.e. computing its quantum expectation value $<\psi|\hat{H}_e|\psi>$, while keeping the nuclear positions fixed at their instantaneous values $\{\vec{R}_I(t)\}$.

Ab initio Molecular Dynamics (AIMD) - Theory

Time-dependent wave equation for the electrons

■■
$$\boxed{\begin{aligned} i\hbar\frac{\partial\Psi}{\partial t} &= -\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2\Psi + V_{n-e}(\{\mathbf{r}_i\},\{\mathbf{R}_I(t)\})\Psi \\ &= \mathcal{H}_e(\{\mathbf{r}_i\},\{\mathbf{R}_I(t)\})\;\; \Psi(\{\mathbf{r}_i\},\{\mathbf{R}_I\};t) \end{aligned}}$$

- Hamiltonian and wave-function are parametrically dependent on the classical nuclear positions $\{\vec{R}_I(t)\}$
- Procedure of solving simultaneously Eqs. ■ and ■■ is very often called ***“Ehrenfest molecular dynamics*** “.
- It was never in widespread use for systems with many active degrees of freedom typical for condensed matter problems

Ehrenfest molecular dynamics

In practical calculations only ground state considered

$$\boxed{\begin{aligned} M_I \ddot{\mathbf{R}}_I(t) &= -\nabla_I \langle \Psi_0 | \mathcal{H}_e | \Psi_0 \rangle \\ i\hbar \frac{\partial \Psi_0}{\partial t} &= \mathcal{H}_e \Psi_0 \end{aligned}}$$

- Electronic Hamiltonian is time-dependent via the nuclear coordinates
- The propagation of the wavefunction is unitary, i.e. the wavefunction preserves its norm and the set of orbitals used to build up the wavefunction will stay orthonormal

---

Born-Oppenheimer AIMD

An alternative approach to include the electronic structure in molecular dynamics simulations

- Straightforwardly solve the static electronic structure problem in each molecular dynamics step given the set of fixed nuclear positions at that instance of time.
- $\boxed{E_0(\{\vec{R}_I\}) = min < \Psi_0 | \hat{H}_e(\{\vec{R}_I\}) | \Psi_0 >}$
- $\boxed{M_I \ddot{\vec{R}}_I = -\nabla_I E_0(\{\vec{R}_I\})}$ $\quad \hat{H}_e(\{\vec{R}_I\})\Psi_0 = E_0(\{\vec{R}_I\})\Psi_0$
- $E_0(\{\vec{R}_I\})$ -- ***ground state energy*** of electrons for instantaneous ionic positions $\{\vec{R}_I(t)\}$ **may be calculated using DFT (Kohn –Sham)** [or Hartree-Fock method]

Density Functional Theory (DFT)

- **One particle density determines the ground state energy of the system for arbitrary external potential**

$$E[\rho] = \int d^3\vec{r}\rho(\vec{r})v_{ext}(\vec{r}) + F[\rho]$$

$$\boxed{E[\rho_0] = E_0}$$

ground state energy

ground state density

Total energy functional

Kinetic energy

Exchange energy

Correlation energy

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

External energy

Classic Coulomb energy

unknown!!!

Born-Oppenheimer AIMD (cnt.)

- The electronic structure part is reduced to solving a ***time-independent quantum problem***
- The time-dependence of the electronic structure is a consequence of nuclear motion, and not intrinsic as in Ehrenfest molecular dynamics.

Ehrenfest vs. Born-Oppenheimer MD

- In **Ehrenfest dynamics** the ***time scale is dictated by the intrinsic dynamics of the electrons***.
- Since electronic motion is much faster than nuclear motion, the largest possible time step is that which allows to integrate the electronic equations of motion.
- There is no electron dynamics whatsoever involved in solving the **Born-Oppenheimer dynamics**, i.e. they can be integrated on the ***time scale given by nuclear motion***.
- However, this means that the electronic structure problem has to be solved self-consistently at each molecular dynamics step.

Car- Parrinello Method - Motivation

R. Car and M. Parrinello, Phys. Rev. Lett 55, 2471 (1985)

- A non-obvious approach to cut down the computational expenses of molecular dynamics
- It can be seen as an attempt to combine the advantages of both Ehrenfest and Born-Oppenheimer molecular dynamics.
- From an algorithmic point of view the main task achieved in ground-state Ehrenfest dynamics is simply to keep the wavefunction automatically minimized as the nuclei are propagated.
- This, however, might be achieved -- in principle – by another sort of deterministic dynamics than first-order Schrödinger dynamics.

Car- Parrinello Method - Motivation

The “Best of all Worlds Method" should

(i) integrate the equations of motion on the (long) time scale set by the nuclear motion but nevertheless

(ii) take intrinsically advantage of the smooth time-evolution of the dynamically evolving electronic subsystem as much as possible.

The second point allows to circumvent explicit diagonalization or minimization to solve the electronic structure problem for the next molecular dynamics step.

- ***Car-Parrinello molecular dynamics*** is an efficient method to satisfy requirement (ii) in a numerically stable fashion and makes an acceptable compromise concerning the length of the time step (i).

Car- Parrinello Method – Lagrangian

Lagrangian

Kohn-Sham Energy Functional

Ionic positions

$$L = \sum_i \mu \int_\Omega d^3r \, |\dot{\psi}_i|^2 + \sum_I \frac{1}{2} M_I \dot{R}_I^2 - E[\{\psi_i\},\{R_I\}] + \sum_{i,j} \Lambda_{ij} \left(\int_\Omega d^3r \, \psi_i^*(\vec{r}) \psi_j(\vec{r}) - \delta_{ij} \right)$$

Ficticious ‘masses’ of the wavefunctions

Ionic masses

One particle orbitals

Lagrange multipliers to ensure the orthonormality of the orbitals

The corresponding Newtonian equations of motion are obtained from the associated Euler-Lagrange equations

$$\frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \dot{\mathbf{R}}_I} = \frac{\partial \mathcal{L}}{\partial \mathbf{R}_I}$$

$$\frac{d}{dt}\frac{\delta \mathcal{L}}{\delta \dot{\psi}_i^\star} = \frac{\delta \mathcal{L}}{\delta \psi_i^\star}$$

Car- Parrinello Method – Equations of Motion

Equations of motion

$$\mu\ddot{\psi}(\vec{r}) = -\frac{\delta E}{\delta\psi_i^*(\vec{r},t)} + \sum_j \Lambda_{ij}\psi_j(\vec{r},t)$$

$$M_I\ddot{R}_I = -\nabla_{\vec{R}_I} E$$

(+) **Coupling to some external reservoir in order to maintain the ionic temperature, the so-called ‘Nose’s thermostat’**

- **Born-Oppenheimer surface** $\Phi(\{\vec{R}_I\}) = \min_{\{\psi_i\}} E[\{\psi_i\},\{\vec{R}_I\}]$

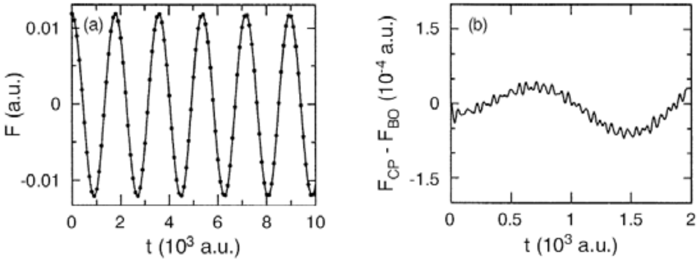
*R. Car & M. Parrinello, PRL **55**, 2471 (1985)*

Car- Parrinello Method – Two temperatures

- According to the Car-Parrinello equations of motion, the nuclei evolve in time at a certain (instantaneous) physical temperature $\propto \sum_I M_I \dot{\vec{R}}_I^2$
- A ‘fictitious temperature’ associated to the electronic degrees of freedom $\propto \sum_i \mu_i < \dot{\psi}_i | \dot{\psi}_i >$
- “***Low electronic temperature***" or “***cold electrons***" means that the electronic subsystem is close to its instantaneous minimum energy $min_{\{\psi_i\}} < \Psi_0 | \widehat{H}_e(\{\vec{R}_I\}) | \Psi_0 >$

  i.e. close to the exact Born-Oppenheimer surface.
- **It must be achieved during the simulation process**

Car- Parrinello Method vs. Born-Oppenheimer MD



Comparison of the x-component of the force acting on one atom of a model system obtained from Car-Parrinello (solid line) and well-converged Born-Oppenheimer (dots) molecular dynamics.

Ab initio Molecula Dynamics: Applications – From Materials Science to Biochemistry

- **Solids, Polymers, and Materials**
  - Thermal expansion of solids
- **Surfaces, Interfaces, and Adsorbates**
- **Liquids and Solutions**
  - Liquid phases of solids
  - Phase transitions liquid → solid
- **Glasses and Amorphous Systems**
- **Matter at Extreme Conditions**
- **Clusters, Fullerenes, and Nanotubes**
- **Chemical Reactions and Transformations**
- **Biophysics and Biochemistry**

CPMD
consortium
page

http://www.cpmd.org

Welcome to the CPMD consortium page

The CPMD code is a parallelized plane wave/pseudopotential implementation of Density Functional Theory, particularly designed for ab-initio molecular dynamics.

NEW!!! NEW!!! CPMD Version 3.11 (what is new) NEW!!! NEW!!!

Include IBM BlueGene version that has recently been demonstrated to run at 110.4 TFlops !!!

CPMD is copyrighted jointly by IBM Corp and by Max Planck Institute, Stuttgart, and is distributed free of charge to non-profit organizations. It is used world wide by more than 6000 users.

CPMD consortium - http://www.cpmd.org - Last Modified Thu, 27 Mai 2004

John von Neumann Institute for Computing

NIC

Ab initio molecular dynamics: Theory and Implementation

Dominik Marx and Jürg Hutter

published in

Modern Methods and Algorithms of Quantum Chemistry,
J. Grotendorst (Ed.), John von Neumann Institute for Computing,
Jülich, NIC Series, Vol. 1, ISBN 3-00-005618-1, pp. 301-449, 2000.

http://www.fz-juelich.de/nic-series/

(150 pages, 708 references)

AIMD – computer codes

CPMD Version 3.3:
developed by J. Hutter, A. Alavi, T. Deutsch, M. Bernasconi, St. Goedecker, D. Marx, M. Tuckerman, and M. Parrinello, Max-Planck-Institut für Festkörperforschung and IBM Zurich Research Laboratory (1995-1999).

CASTEP	Accelrys
CP-PAW	P. E. Blöchl
fhi98md	Fritz-Haber-Institut, Berlin
NWChem	developed and distributed by Pacic Northwest National Laboratory, USA.
VASP	University of Vienna

Extensive review (708 references): D. Marx and Jürg Hutter
http://www.fz-juelich.de/nic-series/

Thank you!