Density-Functional-Theory
Lecture II

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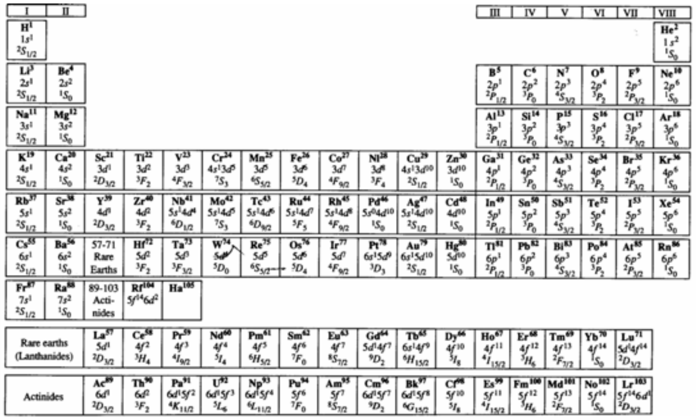
Overview: Tuesday

Review:
- Periodic table.
- Hartree-Fock: Exchange Interaction.
- Density-Functional-Theory (DFT).
- Exchange-correlation energy.

DFT: ins and outs:
- E_{max}, k_{max}.
- Pseudopotentials vs. all-electron calculations.
- Metals and insulators.
- Convergence tests.
- Bulk/surface/molecules.
- Examples.

Periodic Table



I	II											III	IV	V	VI	VII	VIII
H^{1} $1s^{1}$ $^{2}S_{1/2}$																	He^{2} $1s^{2}$ $^{1}S_{0}$
Li^{3} $2s^{1}$ $^{2}S_{1/2}$	Be^{4} $2s^{2}$ $^{1}S_{0}$											B^{5} $2p^{1}$ $^{2}P_{1/2}$	C^{6} $2p^{2}$ $^{3}P_{0}$	N^{7} $2p^{3}$ $^{4}S_{3/2}$	O^{8} $2p^{4}$ $^{3}P_{2}$	F^{9} $2p^{5}$ $^{2}P_{3/2}$	Ne^{10} $2p^{6}$ $^{1}S_{0}$
Na^{11} $3s^{1}$ $^{2}S_{1/2}$	Mg^{12} $3s^{2}$ $^{1}S_{0}$											Al^{13} $3p^{1}$ $^{2}P_{1/2}$	Si^{14} $3p^{2}$ $^{3}P_{0}$	P^{15} $3p^{3}$ $^{4}S_{3/2}$	S^{16} $3p^{4}$ $^{3}P_{2}$	Cl^{17} $3p^{5}$ $^{2}P_{3/2}$	Ar^{18} $3p^{6}$ $^{1}S_{0}$
K^{19} $4s^{1}$ $^{2}S_{1/2}$	Ca^{20} $4s^{2}$ $^{1}S_{0}$	Sc^{21} $3d^{1}$ $^{2}D_{3/2}$	Ti^{22} $3d^{2}$ $^{3}F_{2}$	V^{23} $3d^{3}$ $^{4}F_{3/2}$	Cr^{24} $4s^{1}3d^{5}$ $^{7}S_{3}$	Mn^{25} $3d^{5}$ $^{6}S_{5/2}$	Fe^{26} $3d^{6}$ $^{5}D_{4}$	Co^{27} $3d^{7}$ $^{4}F_{9/2}$	Ni^{28} $3d^{8}$ $^{3}F_{4}$	Cu^{29} $4s^{1}3d^{10}$ $^{2}S_{1/2}$	Zn^{30} $3d^{10}$ $^{1}S_{0}$	Ga^{31} $4p^{1}$ $^{2}P_{1/2}$	Ge^{32} $4p^{2}$ $^{3}P_{0}$	As^{33} $4p^{3}$ $^{4}S_{3/2}$	Se^{34} $4p^{4}$ $^{3}P_{2}$	Br^{35} $4p^{5}$ $^{2}P_{3/2}$	Kr^{36} $4p^{6}$ $^{1}S_{0}$
Rb^{37} $5s^{1}$ $^{2}S_{1/2}$	Sr^{38} $5s^{2}$ $^{1}S_{0}$	Y^{39} $4d^{1}$ $^{2}D_{3/2}$	Zr^{40} $4d^{2}$ $^{3}F_{2}$	Nb^{41} $5s^{1}4d^{4}$ $^{6}D_{1/2}$	Mo^{42} $5s^{1}4d^{5}$ $^{7}S_{3}$	Tc^{43} $5s^{1}4d^{6}$ $^{6}D_{9/2}$	Ru^{44} $5s^{1}4d^{7}$ $^{5}F_{5}$	Rh^{45} $5s^{1}4d^{8}$ $^{4}F_{9/2}$	Pd^{46} $5s^{0}4d^{10}$ $^{1}S_{0}$	Ag^{47} $5s^{1}4d^{10}$ $^{2}S_{1/2}$	Cd^{48} $4d^{10}$ $^{1}S_{0}$	In^{49} $5p^{1}$ $^{2}P_{1/2}$	Sn^{50} $5p^{2}$ $^{3}P_{0}$	Sb^{51} $5p^{3}$ $^{4}S_{3/2}$	Te^{52} $5p^{4}$ $^{3}P_{2}$	I^{53} $5p^{5}$ $^{2}P_{3/2}$	Xe^{54} $5p^{6}$ $^{1}S_{0}$
Cs^{55} $6s^{1}$ $^{2}S_{1/2}$	Ba^{56} $6s^{2}$ $^{1}S_{0}$	57-71 Rare Earths	Hf^{72} $5d^{2}$ $^{3}F_{2}$	Ta^{73} $5d^{3}$ $^{3}F_{3/2}$	W^{74} $5d^{4}$ $^{5}D_{0}$	Re^{75} $5d^{5}$ $^{6}S_{5/2}$	Os^{76} $5d^{6}$ $^{5}D_{4}$	Ir^{77} $5d^{7}$ $^{4}F_{9/2}$	Pt^{78} $6s^{1}5d^{9}$ $^{3}D_{3}$	Au^{79} $6s^{1}5d^{10}$ $^{2}S_{1/2}$	Hg^{80} $5d^{10}$ $^{1}S_{0}$	Tl^{81} $6p^{1}$ $^{2}P_{1/2}$	Pb^{82} $6p^{2}$ $^{3}P_{0}$	Bi^{83} $6p^{3}$ $^{4}S_{3/2}$	Po^{84} $6p^{4}$ $^{3}P_{2}$	At^{85} $6p^{5}$ $^{2}P_{3/2}$	Rn^{86} $6p^{6}$ $^{1}S_{0}$
Fr^{87} $7s^{1}$ $^{2}S_{1/2}$	Ra^{88} $7s^{2}$ $^{1}S_{0}$	89-103 Acti-nides	Rf^{104} $5f^{14}6d^{2}$	Ha^{105}													
Rare earths (Lanthanides)		La^{57} $5d^{1}$ $^{2}D_{3/2}$	Ce^{58} $4f^{2}$ $^{3}H_{4}$	Pr^{59} $4f^{3}$ $^{4}I_{9/2}$	Nd^{60} $4f^{4}$ $^{5}I_{4}$	Pm^{61} $4f^{5}$ $^{6}H_{5/2}$	Sm^{62} $4f^{6}$ $^{7}F_{0}$	Eu^{63} $4f^{7}$ $^{8}S_{7/2}$	Gd^{64} $5d^{1}4f^{7}$ $^{9}D_{2}$	Tb^{65} $6s^{1}4f^{9}$ $^{6}H_{15/2}$	Dy^{66} $4f^{10}$ $^{5}I_{8}$	Ho^{67} $4f^{11}$ $^{4}I_{15/2}$	Er^{68} $4f^{12}$ $^{3}H_{6}$	Tm^{69} $4f^{13}$ $^{2}F_{7/2}$	Yb^{70} $4f^{14}$ $^{1}S_{0}$	Lu^{71} $5d^{1}4f^{14}$ $^{2}D_{3/2}$	
Actinides		Ac^{89} $6d^{1}$ $^{2}D_{3/2}$	Th^{90} $6d^{2}$ $^{3}F_{2}$	Pa^{91} $6d^{1}5f^{2}$ $^{4}K_{11/2}$	U^{92} $6d^{1}5f^{3}$ $^{5}L_{6}$	Np^{93} $6d^{1}5f^{4}$ $^{6}L_{11/2}$	Pu^{94} $5f^{6}$ $^{7}F_{0}$	Am^{95} $5f^{7}$ $^{8}S_{7/2}$	Cm^{96} $6d^{1}5f^{7}$ $^{9}D_{2}$	Bk^{97} $6d^{1}5f^{8}$ $^{6}G_{15/2}$	Cf^{98} $5f^{10}$ $^{5}I_{8}$	Es^{99} $5f^{11}$ $^{4}I_{15/2}$	Fm^{100} $5f^{12}$ $^{3}H_{6}$	Md^{101} $5f^{13}$ $^{2}F_{7/2}$	No^{102} $5f^{14}$ $^{1}S_{0}$	Lr^{103} $5f^{14}6d^{1}$ $^{2}D_{3/2}$	

Adiabatic Decoupling

Decouple electronic and nuclear degrees of freedom:
➔ Nuclei: classic treatment.
➔ Electrons: quantum mechanics.

If T=0 K ➔ Kinetic energy of the nuclei is zero.
Note: Nuclei are ***not*** eliminated from the problem, $U_{nuc\text{-}nuc}$ and $U_{nuc\text{-}el}$.
Static problem.
If T>0 K ➔ Nuclei are no longer fixed. Lattice vibrations; thermodynamics.

Kohn and Sham Equations

Kohn and Sham (1965)

$$\left[-\frac{\hbar^2}{2m_{el}}\nabla_r^2 + V_{eff}\left(r, n(r)\right)\right]\phi_i(r) = \varepsilon_i \phi_i(r)$$

$V_{eff}\left(r, n(r)\right) = V(r)$ External potential.

$+e^2 \int \frac{n(r')}{|r-r'|} dr'$ Coulomb interaction.

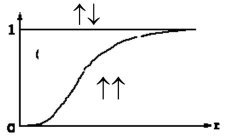
$+\frac{\delta E_{XC}\left(n(r)\right)}{\delta n(r)}$ Exchange-correlation.

Can be generalized to include magnetism:

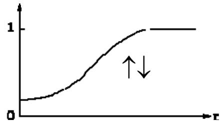
$$n = n_\uparrow + n_\downarrow$$

What is the Exchange-Correlation Potential, E_{XC}?

Thermodynamics: ground state == lowest energy state



Pauli exclusion principle
➔ Exchange energy.



Repulsion of opposite spins
➔ Correlation energy.

Exchange Correlation Functionals

Active research field to develop better E_{XC} functionals:

- LDA : $E_{XC} = E_{XC}(\rho)$
  Ceperley and Alder (1981)…
- GGA : $E_{XC} = E_{XC}(\rho, \nabla\rho)$
  PW91 (1991), PBE (1996),
  revPBE (1996), rPBE (1999)…

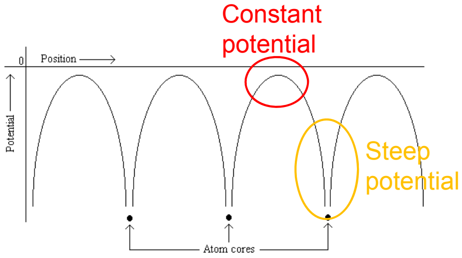
Exchange Correlation Functionals: Which one to choose?

Depends on system and variable of interest:

Iron: *LDA* gives *incorrect* ground state (hcp rather than bcc); *GGA correct* ground state.

SiO_2: LDA gives better agreement with experiment at high pressures then GGA.

Suitable Electronic Wave Functions



Solutions to Schrödinger equation with constant potential:

Planewaves: ψ~exp(i k r)

Works best for “flat” potentials.

http://gauss.sdsmt.edu/~bhemmelm/quantu1.gif

Brillouin zones

Crystal: Periodic Structure in 3-d space

Planewaves: ψ~exp(ikr)

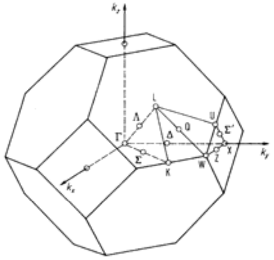
➔ Fourier transform.

1st Brillouin zone: range of independent values.

Definition:

$$\vec{k}_i = \frac{n_i}{N_i}\vec{b}_i;\quad \vec{b}_1 = 2\pi\frac{\vec{a}_2\times\vec{a}_3}{V_{cell}}$$

1,2,3 cyclic



Face-centered cubic

Same as in xrd.

Energy Cutoff

Planewaves: ψ~exp(ikr)

Energy:

$$E(\vec{k}) = \frac{\hbar^2}{2\cdot m_e}\vec{k}^2$$

Define cutoff energy: E_{max}

$$E_{\max} = \frac{\hbar^2}{2\cdot m_e}\vec{k}_{\max}^2$$

Note:

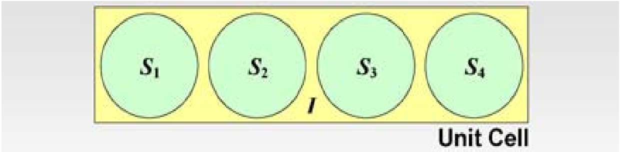
$$k = \frac{2\pi}{\lambda} \Rightarrow E_{\max}\uparrow\rightarrow k_{\max}\uparrow\rightarrow \lambda_{\min}\downarrow$$

Increase E_{max} to resolve finer details of the charge density.

Pseudopotentials

“Problem”: Steep potential close to nuclei

➔ plane waves are not well suited.



Idea: Most material/chemical properties rely on valence electrons.

Eliminate core electrons

Pseudopotential.

Generation of Pseudopotentials

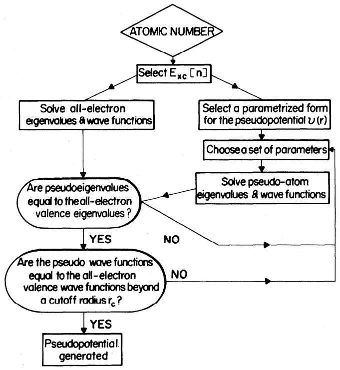
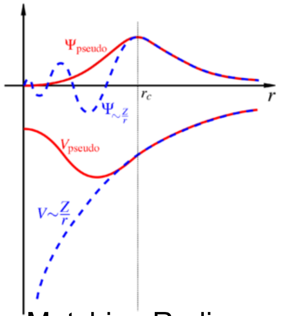


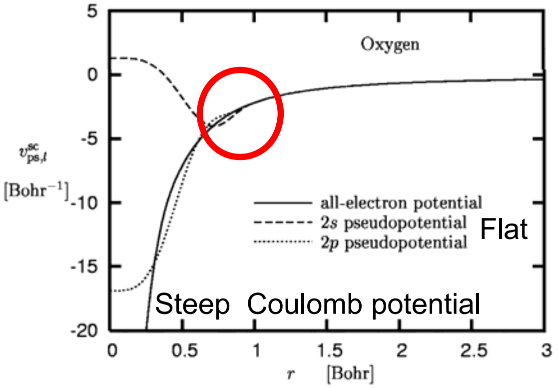
FIG. 6. Flow chart describing the construction of an ionic pseudopotential for an atom.



Matching Radius: r_c

http://upload.wikimedia.org/wikipedia/en/thumb/7/7e/SketchPseudopotenials.png/300px-SketchPseudopotenials.png

Oxygen: an example

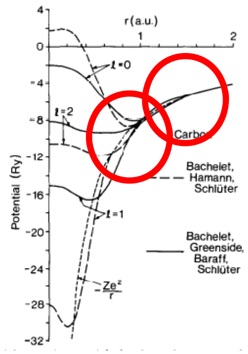


Flat

Steep Coulomb potential

http://th.physik.uni-frankfurt.de/~engel/ncpp/fig4.jpg

Carbon



Smaller r_c:

➔ Better transferability.

➔ higher energy cutoff.

Pickett, 1989

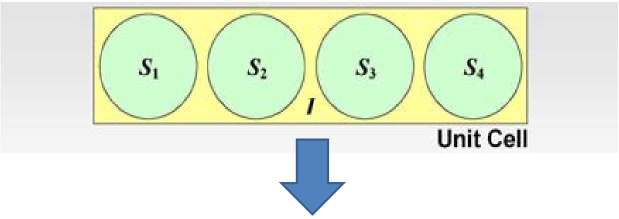
Alternative

Separate space in different regions:

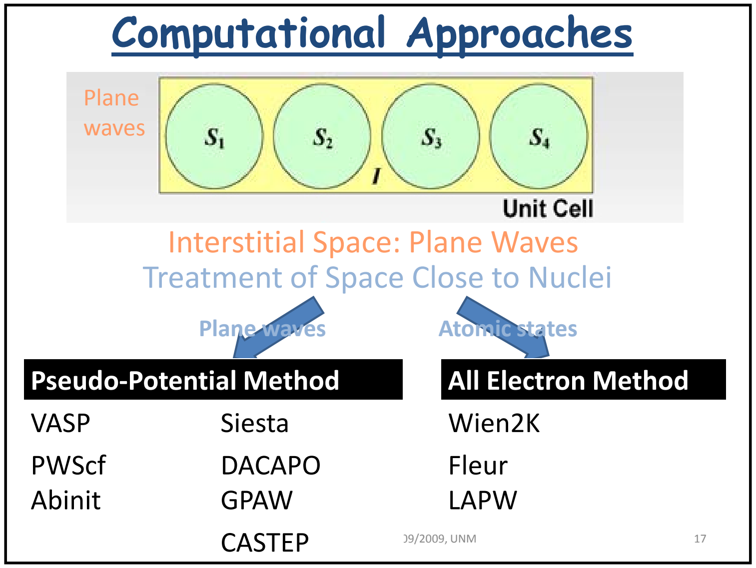
Interstitial regions ➔ plane waves as before.

Regions around the nucleus:

use atomic-like states.



All-electron methods.
(structural optimization difficult to implement, i.e. WIEN2k)

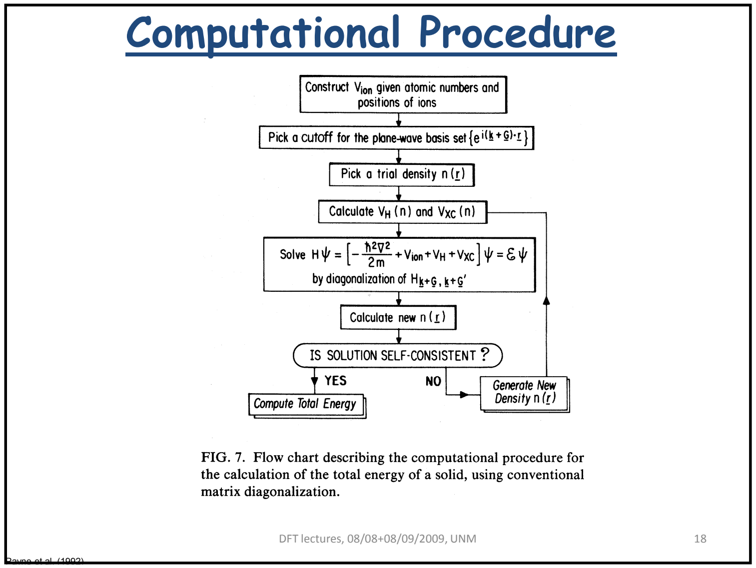


Computational Approaches

Interstitial Space: Plane Waves

Treatment of Space Close to Nuclei

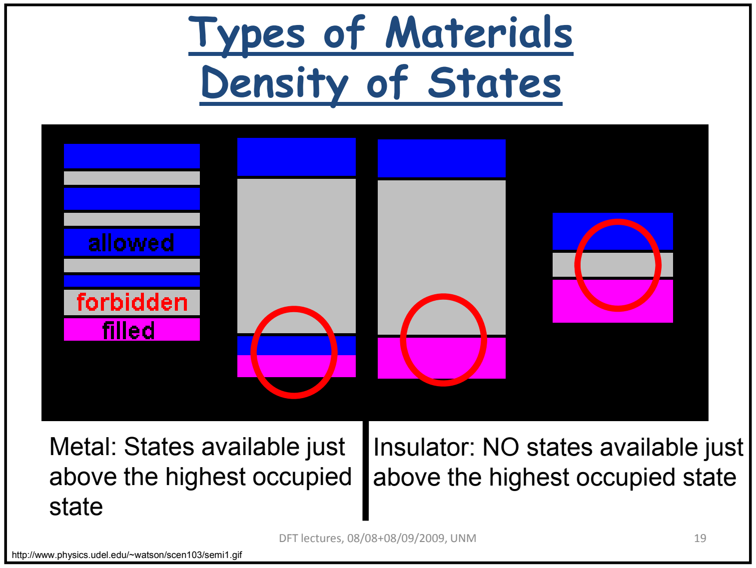
Pseudo-Potential Method		**All Electron Method**
VASP	Siesta	Wien2K
PWScf	DACAPO	Fleur
Abinit	GPAW	LAPW
	CASTEP	



Computational Procedure

FIG. 7. Flow chart describing the computational procedure for the calculation of the total energy of a solid, using conventional matrix diagonalization.

Payne et al. (1992)

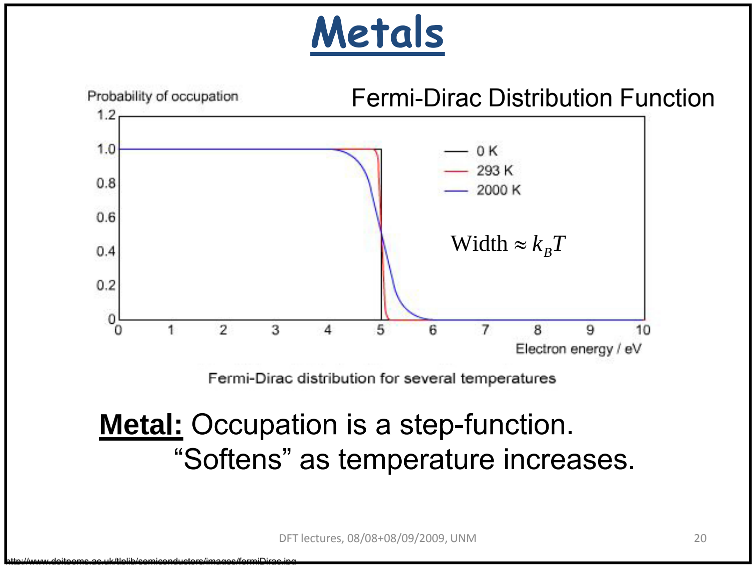


Types of Materials
Density of States

Metal: States available just above the highest occupied state

Insulator: NO states available just above the highest occupied state

http://www.physics.udel.edu/~watson/scen103/semi1.gif



Metals

Fermi-Dirac distribution for several temperatures

Metal: Occupation is a step-function.
“Softens” as temperature increases.

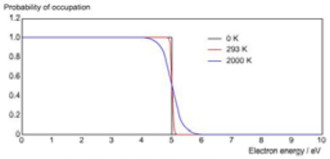
http://www.doitpoms.ac.uk/tlplib/semiconductors/images/fermiDirac.jpg

Metals: Consequences - I

Problem:

At T=0 K (low temperatures)

Rapid change of occupation from 1 to zero.



Fermi-Dirac distribution for several temperatures

During optimization: unoccupied wave functions become occupied and vice versa

➔ Oscillations and instabilities.

Metals: Consequences-II

Need to know charge density (wave functions) in the (1^{st}) Brillouin zone very well

➔ Expectation that we need a dense k-point mesh.

Convergence Test

Carefully check variation of

$E=E(E_{max}, \text{k-point mesh})$

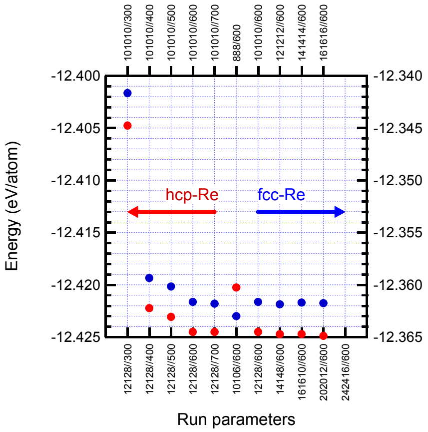
Two steps:

1) Fix E_{max} and increase k-point mesh size.
2) Fix k-point mesh size and vary E_{max}.

Changes between subsequent calculations should be less than 1 meV/atom.

(criterion may vary for specific applications)

Convergence Test: Rhenium



Rhenium (Re):

- Convergence:
hcp-Re: 600 eV; 12x12x8.
fcc-Re: 600 eV; 10x10x10.
- E(hcp) < E(fcc)
➔hcp-Re more stable, as observed experimentally.
(Not shown: Pt: 600 eV; 14x14x14).

Insulators

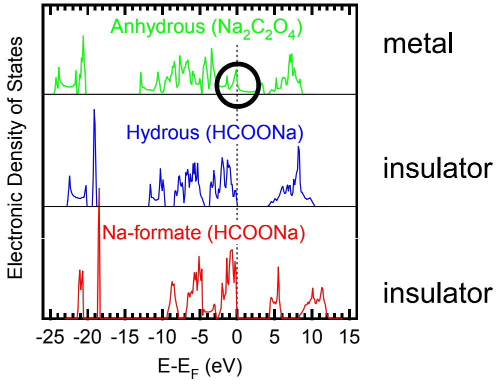
Occupied and unoccupied states are separated by an energy gap of finite width.

➔ We do not expect instabilities and oscillations due to changing occupation numbers.

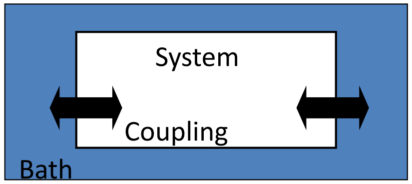
➔Less dense k-point meshes than for metals.

Even though not shown here experience shows that this expectation is supported.

Example: Computed Density of States



Temperature: Extended System Approach (Anderson, 1980)



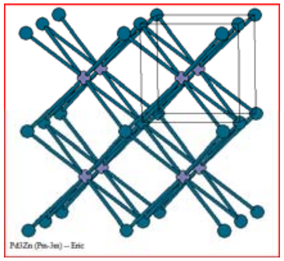
Idea: 0^{th} law of thermodynamics: Bring system in contact with heat bath.

Thermostat: <T> = constant.
➔Choose coupling such that the proper ensemble is modeled (Nose, 1984a, 1984b).

But other options exist: Lattice-dynamics.

Lattice Dynamics

Bulk-Structures-I

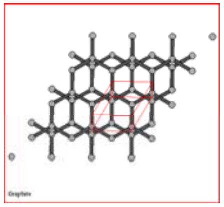


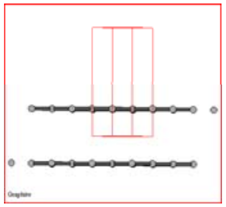
Hypothetical:
Cubic-Pd_8Zn_8
Cubic-$Pd_{50}Zn_{50}$

Bulk-calculations:

- Periodic ➔ good match with plane waves.
- Solid solutions (alloying): Vary composition. Pd_8Zn_8 ➔ Pd_9Zn_7 …
- Disorder: fixed composition. Exchange Pd ⇔ Zn.

Bulk-Structures-II





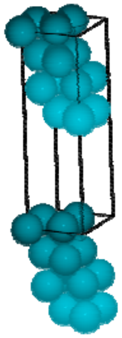
Graphite:

- sp^2 – hybridization.
- intra-plane sigma bonds.
- inter-plane van der Waals. Origin: fluctuating dipoles.

But:

- theory here: time independent ➔ van der Waals compounds not necessarily well described. (New functionals).

Surfaces-I



fcc-Pd(111)-slab.

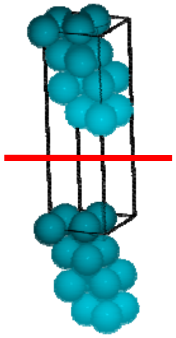
- 2-d periodic.
- Symmetry broken in 3rd dimension.
- Vacuum layer (10-20 A).
- No electrons in vacuum.

But: we use planewaves…

➔Need higher energy cutoff to make charge density zero in vacuum.

Alternative: do not use planewaves. But more localized functions: wavelets, finite-elements…

Surfaces-II



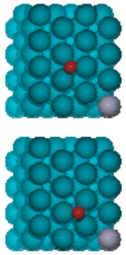
fcc-Pd(111)-slab.

- slab thick enough such that surface relaxation can be accounted for. 4 layers sufficient, relax top two layers (test convergence).
- asymmetric slab: *Artificial* induced (electrical) dipole moment. Long ranged

➔two options:

1) make vacuum thick enough, 15 – 20 A.
2) Compensate by additional dipole. (VASP: middle of the cell).

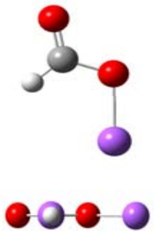
Surfaces-III



fcc-Pd(111)-slab.
(top-view)

- adsorption.
  Example: CO, MeOH, EtOH,…
  ➔ Many molecules are polar
  (Δ EN ≠ 0)
- Same problem as with the asymmetric slab, same options to solve the problem.

Molecules



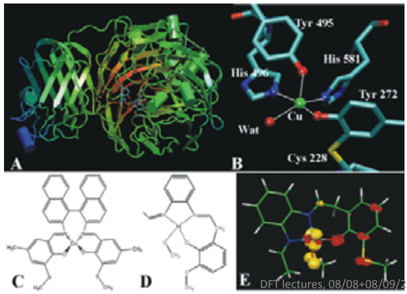
- Electrons are localized.
- Same difficulty as for surfaces.

Note: Adsorption energies are energy differences
➔At least partial compensation.

Alternatives to plane waves are: Wavelets and finite elements.

Quantum Mechanics + Molecular Mechanics/dynamics

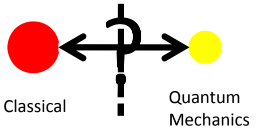
Hybrid methods: QM//MM/MD
- "Local" ➔ quantum mechanics.
- "Non-local" ➔ classical mechanics/ molecular dynamics.



http://bio.phys.uniroma1.it/goase.gif

Advantage:
- Focus on active portion.
- Large scale: details are "less" important.

Disadvantage:
- Boundary: QM + MM?
- "Cutting" through bonds.



Some Applications of DFT

Earth's and Planetary Sciences:
- Electrons in planetary interiors.
- Melts at high pressure.

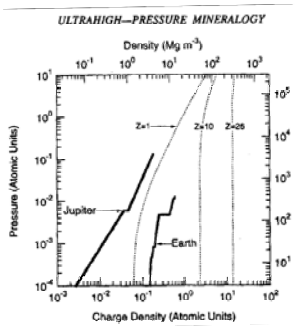
Environmental Geosciences:
- Structure of $(H_3O)^+Fe(SO_4)_2$

Student presentations

• Andrew:	$Pt_{1-x}Re_x$ solid solutions.
• Eric:	Pd on gamma-Al_2O_3.
• Levi:	Pd on alpha-Al_2O_3.
• Sam:	non-Pt based catalysts.

Planetary Interiors

(Stixrude et al.,1998)



Plasma model

$$P = 0.176\, r_s^5 \cdot \left[1 - \left(0.407 \cdot Z^{2/3} + 0.207\right) \cdot r_s\right]$$

$$r_s = \left(\frac{3}{4\pi\rho}\right)^{1/3}$$

Gellman and Brueckner (1949)
Hubbard (1984)

Observations:
Charge density too high.

Explanation:
➔Coulomb attraction important.
➔Electrons are not a plasma.
➔Predicted density is too HIGH.
➔Electronic screening.

Melts at High Pressure

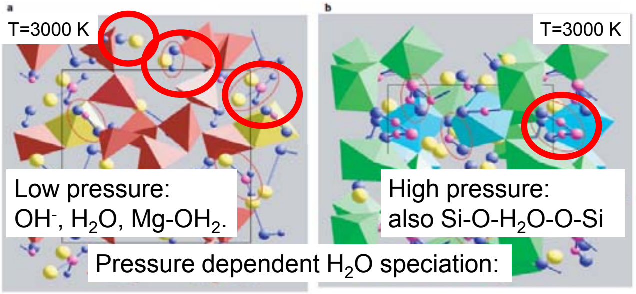
(Mookherjee et al., 2008)

Background:

1 GPa ~ 10^4 atm

- Constitution of the Earth's interior.
- Abundance and distribution of hydrogen.
- Hydrogen affects: density, viscosity, elasticity, electrical conductivity, …

12 * $MgSiO_3$ + 8 * H_2O = 84 atoms. 0 – 120 GPa, 3000 – 6000 K.



Low pressure:
OH^-, H_2O, $Mg\text{-}OH_2$.

High pressure:
also $Si\text{-}O\text{-}H_2O\text{-}O\text{-}Si$

Pressure dependent H_2O speciation:

Implications

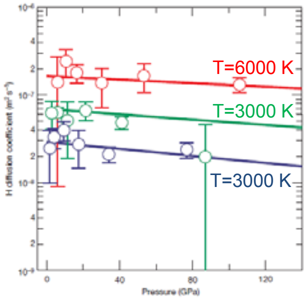
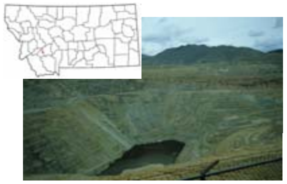


Figure 3 | Self-diffusion coefficient of hydrogen. Results at 3,000 K (blue), 4,000 K (green) and 6,000 K (red) from our simulations (symbols) and an Arrhenius fit to the simulation results (lines) (equation (1) with $D_0 = 9.2 \times 10^{-7}\ m^2 s^{-1}$, $E^* = 86$ kJ mol^{-1} and $V^* = 0.11\ cm^3 mol^{-1}$). The value of the activation energy is similar to that found in hydrous basaltic melts at low pressure[29] (126 ± 32 kJ mol^{-1}), and the value of the diffusivity agrees well with that extrapolated to 3,000 K from lower temperature, low-pressure experiments[29] ($2.4 \times 10^{-8}\ m^2 s^{-1}$), indicating that proton diffusion does not depend strongly on melt composition. Error bars represent one-s.d. uncertainties.

- Neutrally buoyant?
  Hydrous melt lenses.
  Seismic observations
  (Song et al., 2004).
- Conduction dominated by
  hydrogen diffusion.
- P=14 GPa, T=1800 K:
  σ~18 S/m.
- Conduction should be high
  enough to be detectable,
  through electromagnetic
  sounding.

Environment Geochemistry



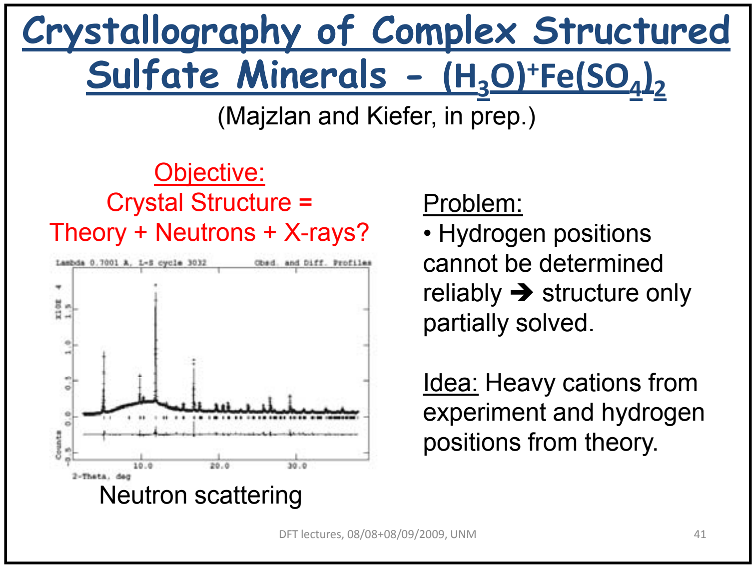
Berkeley Pit; Butte,
Montana
Mining operation: 1955 - .
Copper, silver, gold.

2007: 1249 Superfund-sites in
the USA

Toxic metals and
formation of SO_4^{2-}.

Objectives:

- Restoration of mining areas.
- Environmental hazards.
- Superfund sites.
- Water management.
- Ecology.



Crystallography of Complex Structured Sulfate Minerals – $(H_3O)^+Fe(SO_4)_2$

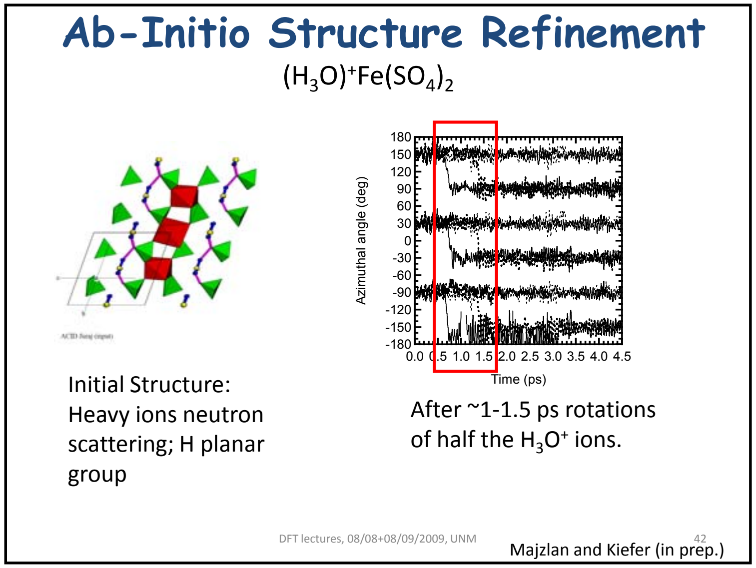
(Majzlan and Kiefer, in prep.)

Objective:
Crystal Structure =
Theory + Neutrons + X-rays?

Neutron scattering

Problem:
- Hydrogen positions cannot be determined reliably ➔ structure only partially solved.

Idea: Heavy cations from experiment and hydrogen positions from theory.



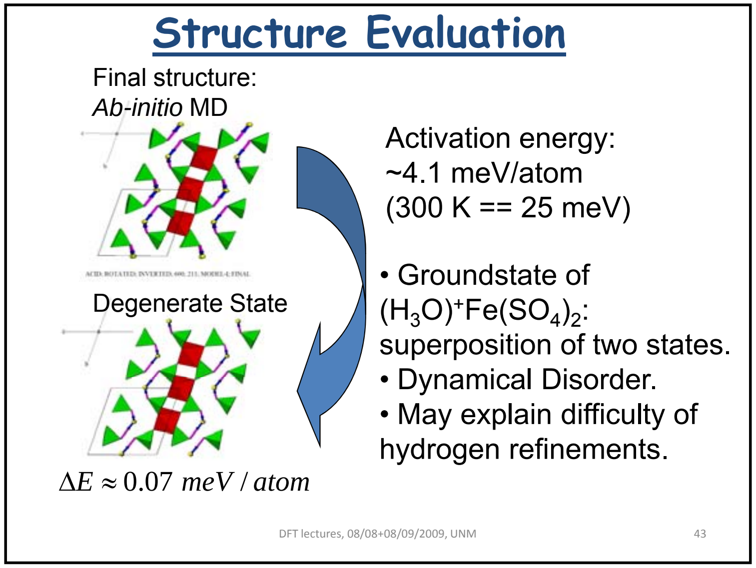
Ab-Initio Structure Refinement

$(H_3O)^+Fe(SO_4)_2$

Initial Structure:
Heavy ions neutron scattering; H planar group

After ~1-1.5 ps rotations of half the H_3O^+ ions.

Majzlan and Kiefer (in prep.)



Structure Evaluation

Final structure:
Ab-initio MD

Degenerate State

$\Delta E \approx 0.07\ meV/atom$

Activation energy:
~4.1 meV/atom
(300 K == 25 meV)

- Groundstate of $(H_3O)^+Fe(SO_4)_2$: superposition of two states.
- Dynamical Disorder.
- May explain difficulty of hydrogen refinements.

Summary

- Classical Potentials: Pro's and Con's.
- Density-Functional-Theory (DFT):
  - ➔ Universal, E_{XC}.
  - ➔ Pseudopotentials.
  - ➔ Planewaves.
  - ➔ Predictive power.
  - ➔ Complementary to experiment.
- Finite temperature *ab-initio* Molecular Dynamics.

Theory addresses different classes of problems:
- Determination of significant fact.
- Matching of facts with theory.
- Articulation of theory.

(Categorization after: T. Kuhn, 1962)

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Other Links

Units and fundamental constants:
http://physics.nist.gov/cuu/Constants/Table/allascii.txt