

Integrated Computational Materials Engineering Education

Lecture on Density Functional Theory *An Introduction*

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Acknowledgements

- Portions of these lectures are based on material put together by Daryl Chrzan (UC Berkeley) and Jeff Grossman (MIT) as part of a TMS short course that the three of us taught at the 2010 annual meeting.
- The Division of Materials Research at the National Science Foundation is acknowledged for financial support in the development of the lecture and module

Use of DFT in Materials Research

Table I. Tools Cited by Employers, Categorized and Ranked by the (Normalized) Frequency of Cites, along with Corresponding Results from the Computational Faculty Survey

Category	Example	Employer	Faculty ⁺
Mechanics (mostly FEA)	DEFORM, ABAQUS	80%	14%
Thermodynamics (CALPHAD)	ThermoCalc, Pandat	53%	7%
Density Functional Theory	VASP, ABNIT	47%	21%
Programming Language/Integration	Matlab, Fortran, iSight	40%	43%
Casting	ProCAST, MAGMAsoft	40%	—
Molecular Dynamics/ Monte Carlo	LAMMPS	27%	14%
Fluid Flow/ Heat Transfer	COMSOL, Fluent	20%	7%
Diffusion/ Microstructural Evolution	DICTRA, PrecipiCalc, JMatPro	20%	—
Statistics	Informatics	13%	7%
Materials Modeling Suite	Materials Studio	13%	—
General Visualization	Mathematica, Tecplot	7%	29%
General Data Processing	Spreadsheet	7%	21%
Special Purpose	K-Flow, WARP 3D	7%	—
Materials Selection	CES Materials Selector	—	36%
Crystallography	CaRIne	—	7%

⁺Some of the responses did not provide specific software/categories, and therefore we expect some degree of undercounting in this data.

K. Thornton, S. Nola, R. E. Garcia, MA and G. B. Olson, “*Computational Materials Science and Engineering Education: A Survey of Trends and Needs*,” JOM (2009)

The Role of Electronic Structure Methods in ICME

- A wide variety of relevant properties can be calculated from knowledge of atomic numbers alone
 - Elastic constants
 - Finite-temperature thermodynamic and transport properties
 - Energies of point, line and planar defects
- For many classes of systems accuracy is quite high
 - Can be used to obtain “missing” properties in materials design when experimental data is lacking, hard to obtain, or “controversial”
 - Can be used to discover new stable compounds with target properties
- The starting point for “hierarchical multiscale” modeling
 - Enables development of interatomic potentials for larger-scale classical modeling

Materials Data for Discovery & Design

The screenshot displays the Materials Project website interface. At the top, there is a navigation bar with links for Home, About, Apps, Documentation, API, and Dashboard. The main content area is titled "Explore Materials" and features a search bar with the formula "Fe2O3" entered. Below the search bar is a periodic table where elements are color-coded and numbered. The sidebar on the left, titled "MATERIAL PROPERTIES", contains several filter options: "Material Tags" (with "Imgreite" entered), "Band Gap (eV)" (ranging from 0 to 10), "Energy Above Hull" (ranging from 0 to 27), "Formation Energy" (ranging from -27 to 4), "# unit cell sites" (ranging from 1 to 296), "Density" (ranging from 0.2 to 24.6), "Volume" (ranging from 7 to 7897), "Crystal Systems" (set to "Any"), and a checkbox for "Has bandstructure".

<https://www.materialsproject.org/>

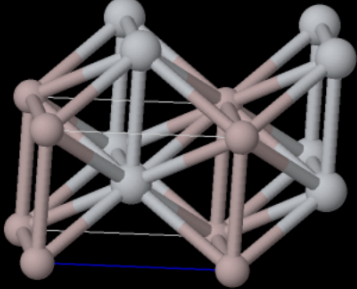
A. Jain, S.P. Ong, G. Hautier, W. Chen, W.D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder, K.A. Persson, *Applied Physics Letters Materials*, 2013, 1(1), 011002.

Materials Data for Discovery & Design

MATERIAL ID: mp-1953 DOI: 10.17188/1194736 [Show Help Guides](#)

[Electronic Structure](#) [X-Ray Diffraction](#) [X-Ray Absorption](#) [Substrates](#) [Elasticity](#) [Similar Structures](#) [Calculation Summary](#) [Provenance/Citation](#)

HM: P 1
a=2.824 Å
b=2.824 Å
c=4.065 Å
α=90.000°
β=90.000°
γ=90.000°



Structure Type: Conventional Standard Primitive Refined [CIF](#)

Space Filling Polyhedra

Zoom in/out: Shift + Drag cursor
Rotate along the center axis: Option + Drag cursor

Material Details

Final Magnetic Moment: 0.000 μ_B

Magnetic Ordering: Unknown

Formation Energy / Atom: -0.403 eV

Energy Above Hull / Atom: 0.000 eV

Density: 3.83 g/cm³

Decomposes To: Stable

Band Gap: 0.000 eV

Space Group

Hermann Mauguin: P4/mmm [123]

Lattice Parameters

computed	ICSD
a: 2.824 Å	a: 2.829 Å
b: 2.824 Å	b: 2.829 Å
c: 4.065 Å	c: 4.071 Å
Volume: 32.418 Å ³	Volume: 32.581 Å ³

Final Structure

Fractional Coordinates

Al		
a	b	c
0	0	0

Ti		
a	b	c
0.5	0.5	0.5


Materials Data for Discovery & Design


MATERIAL
TiAl

ID:
mp-1953

DOI:
10.17188/1194736 

Elasticity

Reference for tensor and properties: 

 [Visualize with ELATE](#)

Stiffness Tensor C_{ij} (GPa)

200	62	84	0	0	0
62	200	84	0	0	0
84	84	174	0	0	0
0	0	0	112	0	0
0	0	0	0	112	0
0	0	0	0	0	41

[Compliance Tensor \$S_{ij}\$](#)

Shear Modulus G_V

76 GPa

Bulk Modulus K_V

115 GPa

Shear Modulus G_R

63 GPa

Bulk Modulus K_R

115 GPa

Shear Modulus G_{VRH}

70 GPa

Bulk Modulus K_{VRH}

115 GPa

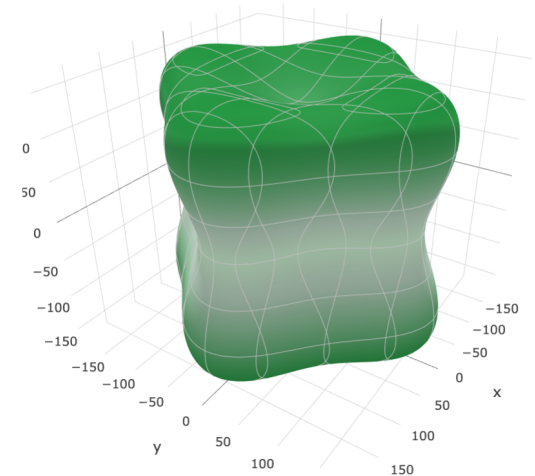
Elastic Anisotropy

0.98

Poisson's Ratio

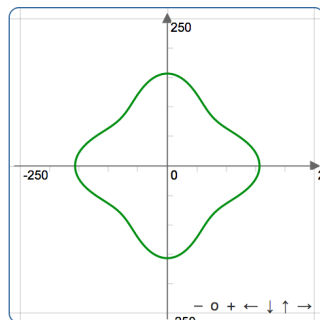
0.25

Young's modulus

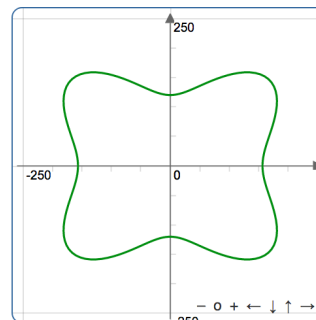


Spatial dependence of Young's modulus

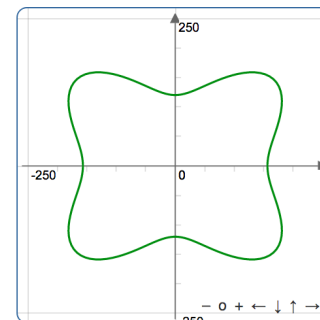
[Visualize in 3D](#)



Young's modulus in (xy) plane



Young's modulus in (xz) plane



Young's modulus in (yz) plane

Materials Data for Discovery & Design

MATERIAL ID: **SiO₂** mp-7000

DOI: [10.17188/1272685](https://doi.org/10.17188/1272685)

[Show Help Guides](#)

[Electronic Structure](#) [Phonon Dispersion](#) [X-Ray Diffraction](#) [X-Ray Absorption](#) [Substrates](#) [Elasticity](#) [Piezoelectricity](#) [Similar Structures](#) [Calculation Summary](#)

[Provenance/Citation](#)

Material Details

Final Magnetic Moment
0.000 μ_B

Magnetic Ordering
Unknown

Formation Energy / Atom
-3.274 eV

Energy Above Hull / Atom
0.011 eV

Density
2.49 g/cm³

Decomposes To
[SiO₂](#)

Band Gap
5.719 eV

Space Group
Hermann Mauguin
P3₁21 [152]

Lattice Parameters

computed **ICSD**

a	5.022 Å	α	90.000°
b	5.022 Å	β	90.000°
c	5.511 Å	γ	120.000°
Volume		120.336 Å ³	

Final Structure [CIF](#)

Fractional Coordinates

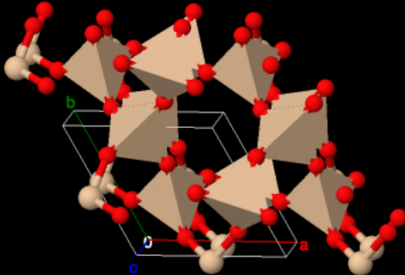
O		
a	b	c
0.1588	0.7439	0.4612
0.2561	0.4149	0.7945
0.4149	0.2561	0.2055
0.5851	0.8412	0.1279
0.7439	0.1588	0.5388

Si

computed **ICSD**

a	4.914 Å	α	90.000°
b	4.914 Å	β	90.000°
c	5.407 Å	γ	120.000°
Volume		113.081 Å ³	

HM: P 1
a=5.022 Å
b=5.022 Å
c=5.511 Å
 $\alpha=90.000^\circ$
 $\beta=90.000^\circ$
 $\gamma=120.000^\circ$



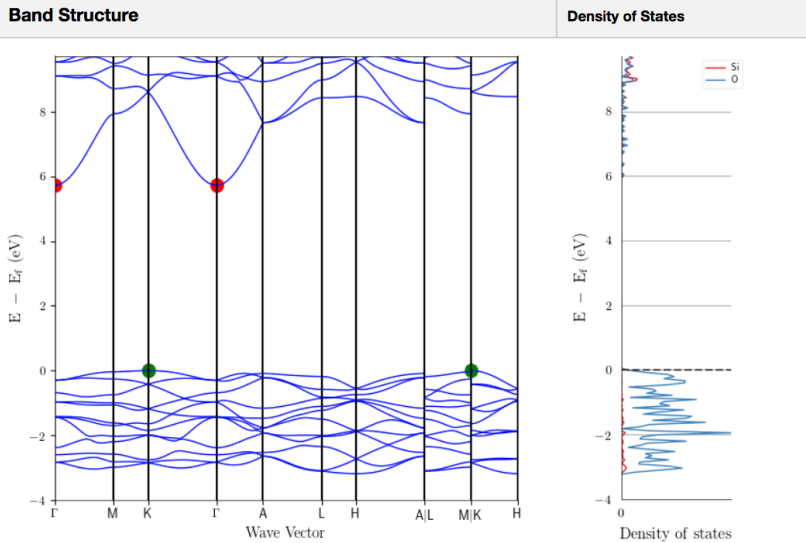
Structure Type: Conventional Standard Primitive Refined [CIF](#)

Space Filling Polyhedra

Zoom in/out: Shift + Drag cursor
Rotate along the center axis: Option + Drag cursor

Materials Data for Discovery & Design

MATERIAL ID: DOI:
SiO₂ **mp-7000** **10.17188/1272685**



Warning! Semi-local DFT tends to severely underestimate bandgaps. Please see the wiki for more info.

Interactive plots

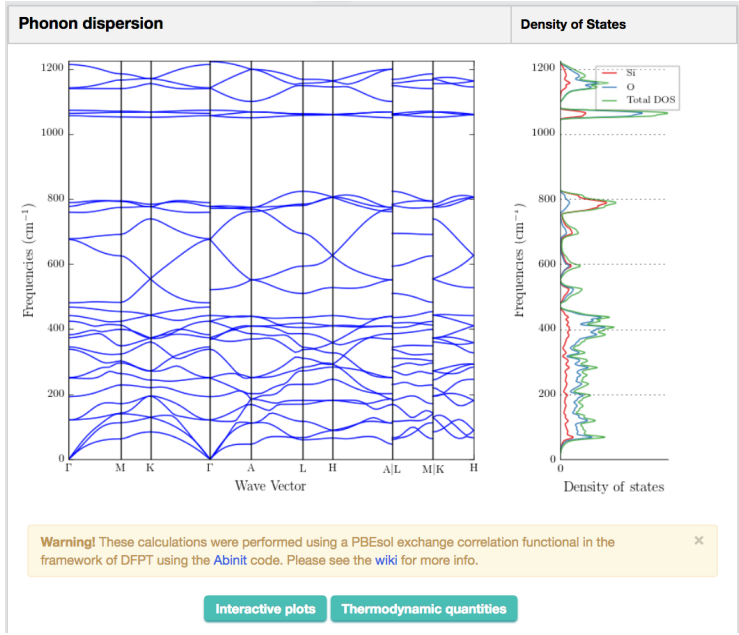
Piezoelectricity

Reference for tensor and properties: [Methodology](#)

Piezoelectric Tensor e_{ij} (C/m ²)					
-0.13685	0.13685	0.00000	-0.00972	0.00000	0.00000
0.00000	0.00000	0.00000	0.00000	0.00972	0.13685
0.00000	0.00000	0.00000	0.00000	0.00000	0.00000

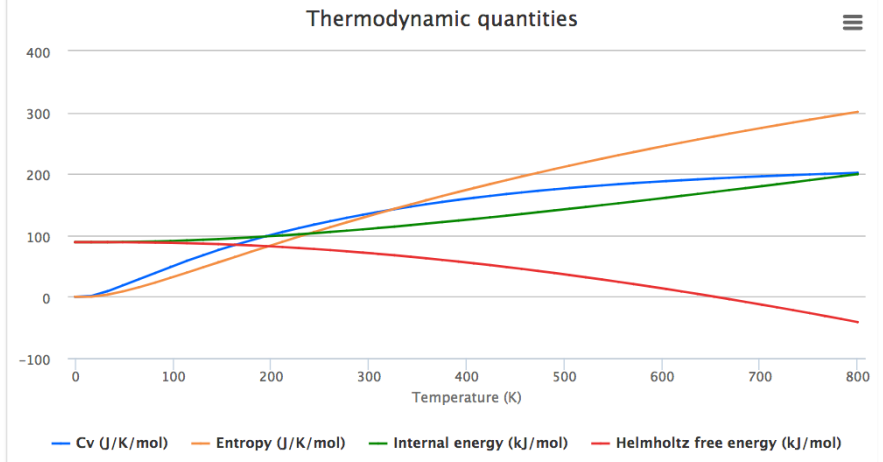
Piezoelectric Modulus $|le_{ij}|_{max}$: 0.13685 C/m²

Crystallographic Direction v_{max}
1.00000
0.00000
0.00000



Warning! These calculations were performed using a PBEsol exchange correlation functional in the framework of DFPT using the Abinit code. Please see the wiki for more info.

Interactive plots Thermodynamic quantities



Outline

- Formalism
 - Hydrogen Atom
 - Density Functional Theory
 - Exchange-Correlation Potentials
 - Pseudopotentials and Related Approaches
 - Some Commercial and Open Source Codes
- Practical Issues
 - Implementation
 - Periodic boundary conditions
 - k-Points
 - Plane-wave basis sets
 - Parameters controlling numerical precision
- Example Exercise

Introduction

The Hydrogen Atom

Proton with mass M_1 , coordinate \mathbf{R}_1

Electron with mass m_1 , coordinate \mathbf{r}_1

$$\left(-\frac{\hbar^2}{2M_1} \nabla_1^2 - \frac{\hbar^2}{2m_2} \nabla_2^2 - \frac{e^2}{r} \right) \Psi(R_1, r_2) = E \Psi(R_1, r_2)$$

$$r = r_1 - r_2, \quad R = \frac{M_1 R_1 + m_2 r_2}{M_1 + m_2}, \quad m = \frac{M_1 m_2}{M_1 + m_2}, \quad M = M_1 + m_2$$

$$\left(-\frac{\hbar^2}{2M} \nabla_R^2 - \frac{\hbar^2}{2m} \nabla_r^2 - \frac{e^2}{r} \right) \Psi(R, r) = E \Psi(R, r)$$

$$\Psi(R, r) = \psi_{cm}(R) \psi_r(r)$$

$$\left(-\frac{\hbar^2}{2M} \nabla_R^2 \right) \psi_{cm}(R) = E_{cm} \psi_{cm}(R)$$

$$\left(-\frac{\hbar^2}{2m} \nabla_r^2 - \frac{e^2}{r} \right) \psi_r(r) = E_r \psi_r(r)$$

Hydrogen Atom

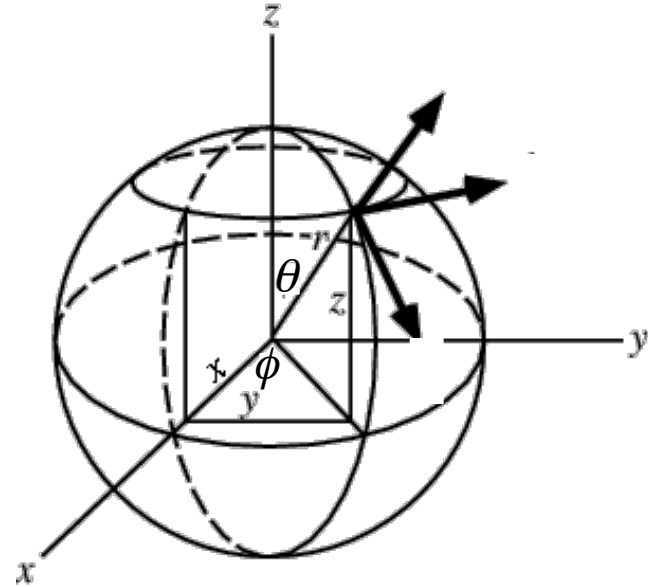
Switch to Spherical Coordinates

$$-\frac{\hbar^2}{2m} \left(\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} \right) - \frac{e^2}{r} \psi = E \psi$$

$$\psi(r, \theta, \phi) = R_{nl}(r) Y_l^m(\theta, \phi)$$

$$-\frac{\hbar^2}{2m} \left(\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) - \frac{l(l+1)}{r^2} - \frac{e^2}{r} \right) R_{nl}(r) = E_n R_{nl}(r)$$

$$E_n = -\frac{me^4}{2\hbar^2} \frac{1}{n^2} = -\frac{13.6}{n^2} \text{ eV}$$

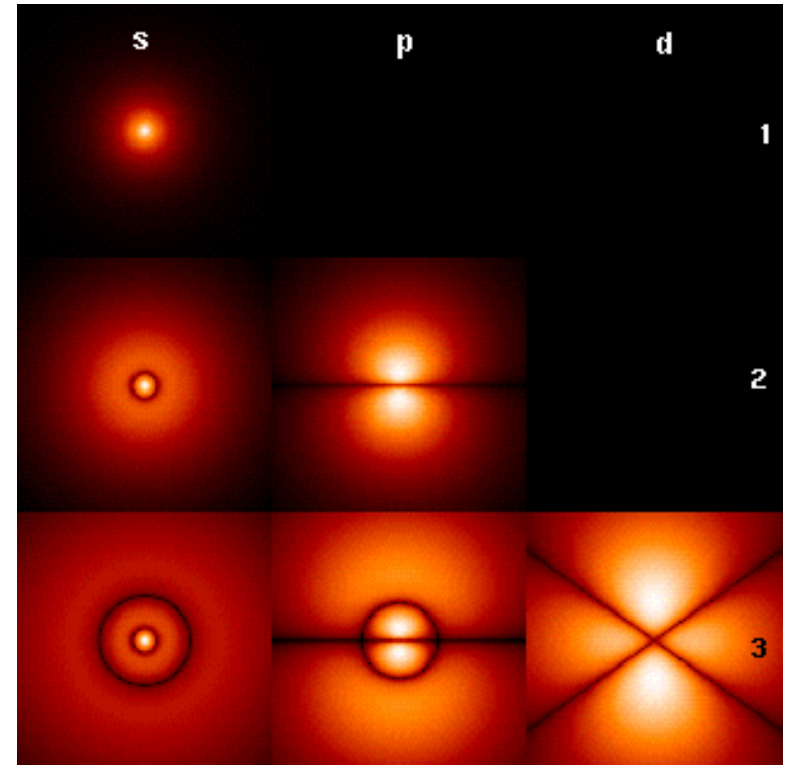
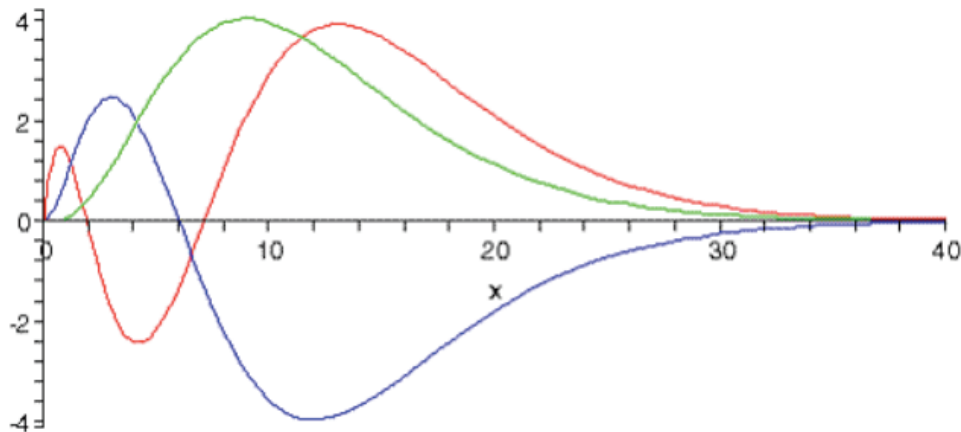


Hydrogen Atom

Wavefunctions

$$n = 1, 2, 3, \dots$$

$$l = 0 (s), 1(p), 2(d), \dots, n-1$$

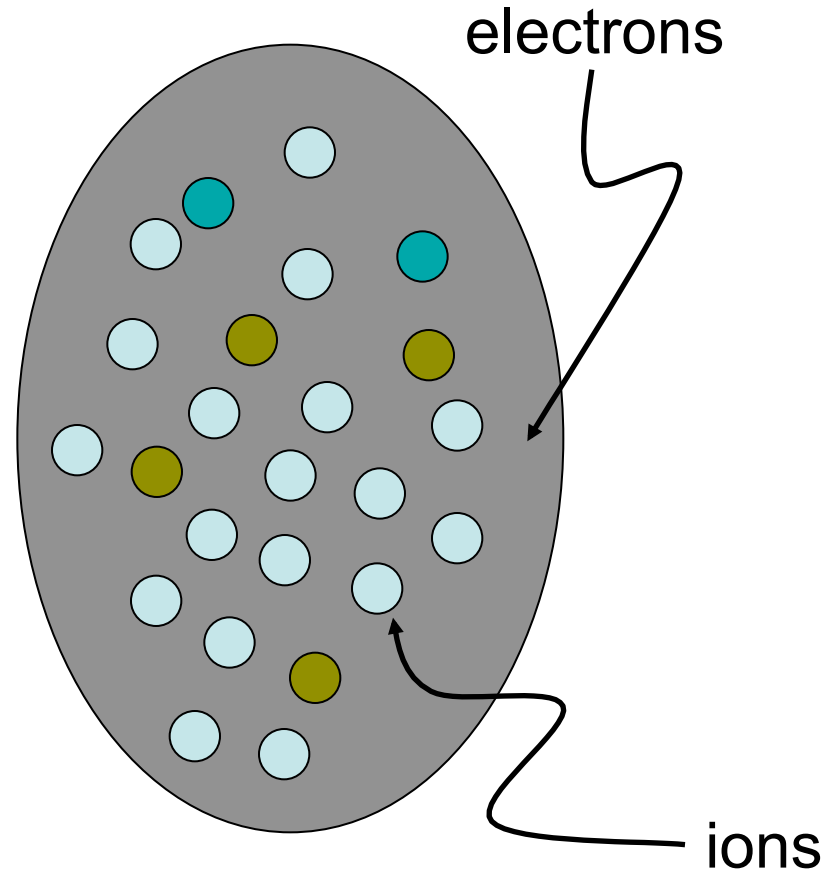


Probability densities through the xz -plane for the electron at different quantum numbers (l , across top; n , down side; $m = 0$)

http://en.wikipedia.org/wiki/Hydrogen_atom

The Many-Electron Problem

- Collection of
 - N ions
 - n electrons
- Analytical solution like that for hydrogen atom not available



Born-Oppenheimer Approximation

- Mass of nuclei exceeds that of the electrons by a factor of 1000 or more
 - we can neglect the kinetic energy of the nuclei
 - treat the ion-ion interaction classically
 - significantly simplifies the Hamiltonian for the electrons
- Consider Hamiltonian for n electrons in potential of N nuclei with atomic numbers Z_i

$$H = -\frac{\hbar^2}{2m} \sum_{i=1}^n \nabla_{\mathbf{r}_i}^2 - \sum_{i=1}^N \sum_{j=1}^n \frac{Z_i e^2}{|\mathbf{R}_i - \mathbf{r}_j|} + \frac{1}{2} \sum_{i=1}^N \sum_{\substack{j=1 \\ i \neq j}}^N \frac{e^2}{|\mathbf{R}_i - \mathbf{R}_j|}$$

external potential $\equiv V_{\text{ext}}(\mathbf{r}_j)$

Density Functional Theory

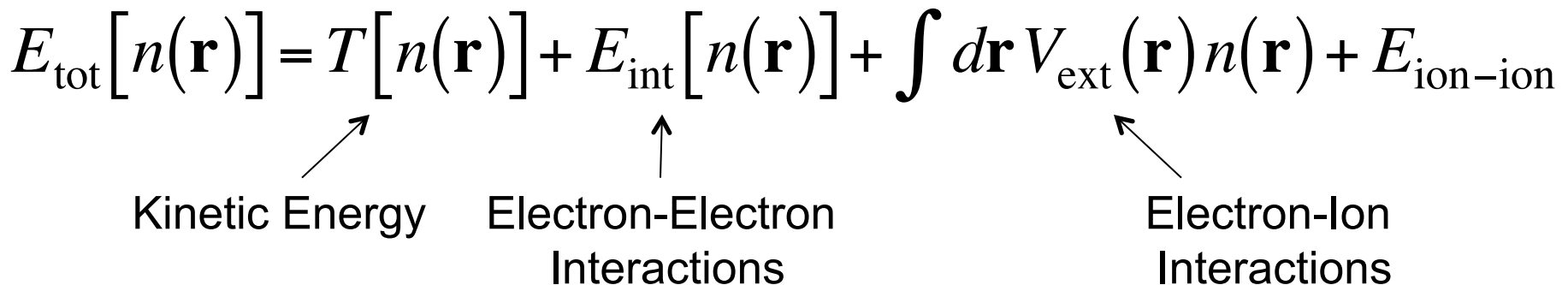
Hohenberg and Kohn (1964), Kohn and Sham (1965)

- For each external potential there is a unique ground-state electron density
- Energy can be obtained by minimizing of a *density functional with respect to density of electrons $n(r)$*

$$E_{\text{groundstate}} = \min\{E_{\text{tot}}[n(\mathbf{r})]\}$$

$$E_{\text{tot}}[n(\mathbf{r})] = T[n(\mathbf{r})] + E_{\text{int}}[n(\mathbf{r})] + \int d\mathbf{r} V_{\text{ext}}(\mathbf{r})n(\mathbf{r}) + E_{\text{ion-ion}}$$

Kinetic Energy Electron-Electron Interactions Electron-Ion Interactions



Kohn-Sham Approach

$$n(\mathbf{r}) = -e \sum_{i=1}^n |\phi_i(\mathbf{r})|^2$$

$$E[\{\phi_i\}] = -\frac{\hbar^2}{2m} \sum_{i=1}^n \int \phi_i^* \nabla_i^2 \phi_i d^3 r + \int V_{ext}(\mathbf{r}) n(\mathbf{r}) d^3 r \\ + \frac{1}{2} \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r d^3 r' + E_{xc}[n(\mathbf{r})]$$

Many-Body Electron-Electron Interactions Lumped into $E_{xc}[n(\mathbf{r})]$

“Exchange-Correlation Energy”

Kohn-Sham Equations

$$\left[-\frac{\hbar^2}{2m} \nabla_i^2 + V_{nuclei}(r) + \int \frac{n(r')}{|r-r'|} d^3 r' + V_{xc}(r) \right] \phi_i(r) = \varepsilon_i \phi_i(r)$$

$$V_{xc}(r) \equiv \frac{\delta E_{xc}[n(r)]}{\delta n(r)}$$

Local Density Approximation

(e.g., *J. P. Perdew and A. Zunger, Phys. Rev. B* **23**, 5048 (1981))

$$E_{xc}[n(r)] = \int \varepsilon_{xc}^{\text{hom}}(n(r))n(r)d^3r$$

$\varepsilon_{xc}^{\text{hom}}(n(r)) \rightarrow$ Exchange – Correlation Energy of Homogeneous
Electron Gas of Density $n(r)$

Generalized Gradient Approximation

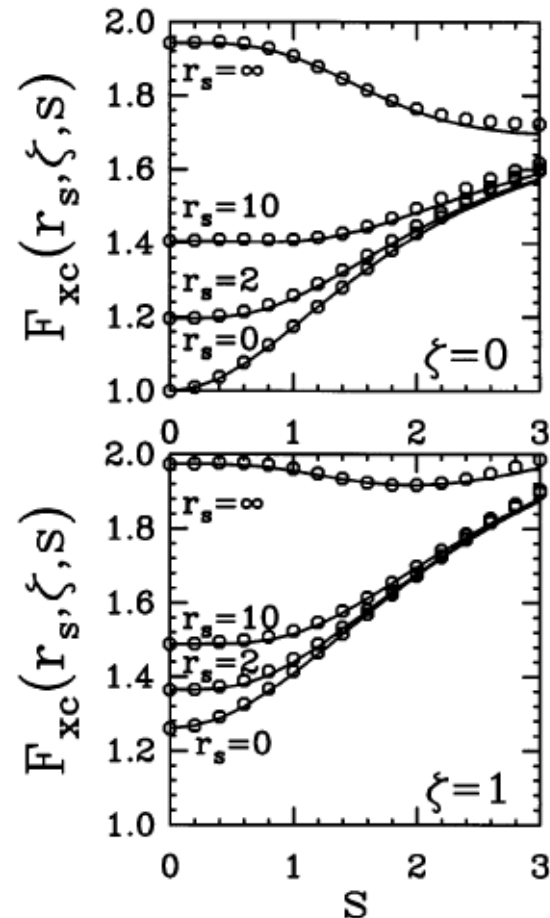
J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett. 77 (1996)

$$E_{xc}^{GGA}[n(r)] = \int \varepsilon_x^{\text{hom}}(n(r)) n(r) F_{xc}(r_s, \zeta, s) d^3r$$

$$n = 3/4\pi r_s^3 = k_F^3 / 3\pi^2$$

$$\zeta = (n_\uparrow - n_\downarrow) / n$$

$$s = |\nabla n| / 2k_F n$$

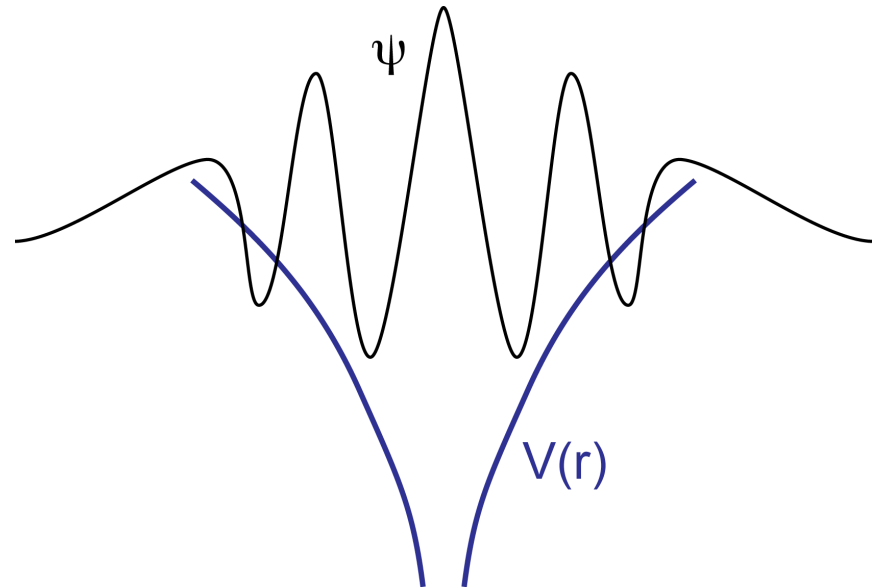


A Note on Accuracy and Ongoing Research

- LDA often leads to “overbinding”
 - Lattice constants can be 1-3 % too small, elastic constants 10-15 % too stiff, cohesive energies 5-20 % too large
- BUT, errors are largely systematic
 - Energy differences tend to be more accurate
- GGA corrects for overbinding
 - Sometimes “overcorrects”
- “Beyond DFT” Approaches
 - For “highly correlated” systems LDA & GGA perform worse and corrections required (DFT+U, Hybrid Hartree-Fock/DFT, Meta-GGA, DMFT, ...)
 - Non-bonded interactions, e.g., van der Waals interactions in graphite, require additional terms or functionals (e.g., vdW-DF)

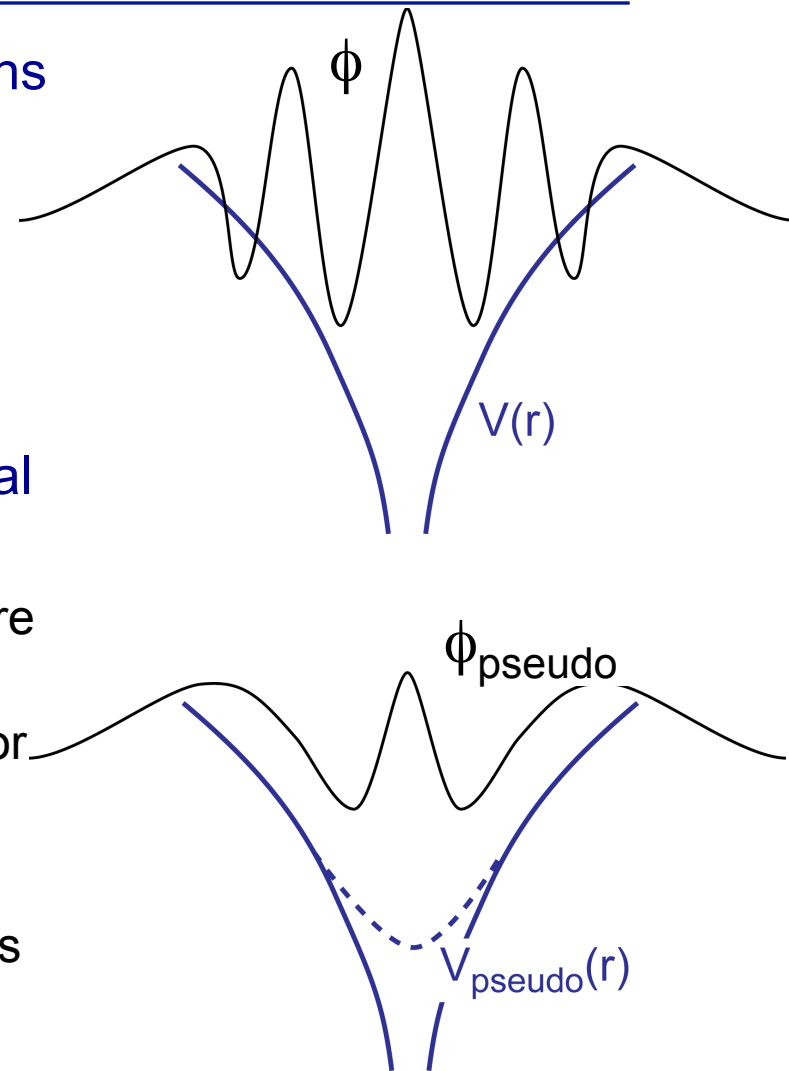
Pseudopotentials

- Potential due to ions is singular at ion core
- Eigenfunctions oscillate rapidly near singularity
- Eigenfunction in bonding region is smooth



Pseudopotentials

- For plane-wave basis sets, rapid oscillations require large number of basis functions
 - expensive
 - unnecessary
 - these oscillations don't alter bonding properties
- Replace potential with nonsingular potential
 - preserve bonding tails of eigenfunction
 - preserve distribution of charge between core and tail regions
 - reduces number of plane waves required for accurate expansion of wavefunction
- Transferable
 - developed from properties of isolated atoms
 - applied in other situations



Summary of Approaches

- Pseudopotentials
 - Core electrons removed from problem and enter only in their effect of the pseudopotential felt by the valence electrons
 - Kohn-Sham equations solved for valence electrons only
- “Augment” Plane Waves with atomic-like orbitals
 - An efficient basis set that allows all electrons to be treated in the calculations
 - Basis for “all-electron” codes
- Projector-Augmented-Wave method
 - Combines features of both methods
 - Generally accepted as the basis for the most accurate approach for calculations requiring consideration of valence electrons only

Some of the Widely Used Codes

- **VASP** (<http://cms.mpi.univie.ac.at/vasp/>)
 - Commercial, Plane-Wave Basis, Pseudopotentials and PAW
- **PWSCF** (<http://www.quantum-espresso.org/>)
 - Free (**and available to run on nanohub**), Plane-Wave Basis, Pseudopotentials and PAW
- **CASTEP** (<http://ccpforge.cse.rl.ac.uk/gf/project/castep/>)
 - Free in UK, licensed by Accelrys elsewhere, Plane-Wave Basis, Pseudopotentials
- **ABINIT** (<http://www.abinit.org/>)
 - Free (**and available to run on nanohub**), plane-wave basis, pseudopotentials and PAW
- **WIEN2K** (<http://www.wien2k.at/>)
 - Commercial (modest license fee), all-electron augmented wave method

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Total Energy in Density Functional Theory

$$E[\{\phi_i\}] = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{N_e} \int \phi_i^* \nabla_i^2 \phi_i d^3 r + \int V_{ext}(r) n(r) d^3 r \\ + \frac{1}{2} \int \frac{n(r)n(r')}{|r-r'|} d^3 r d^3 r' + E_{xc}[n(r)]$$

Electron Density $n(r) = -e \sum_{i=1}^n |\phi_i(r)|^2$

Electron Wavefunctions $\phi_i(r)$

Potential Electrons Feel from Nuclei $V_{ext}(r)$

Exchange-Correlation Energy $E_{xc}[n(r)]$



Form depends on whether you use LDA or GGA

Kohn-Sham Equations

Schrödinger Equation for Electron Wavefunctions

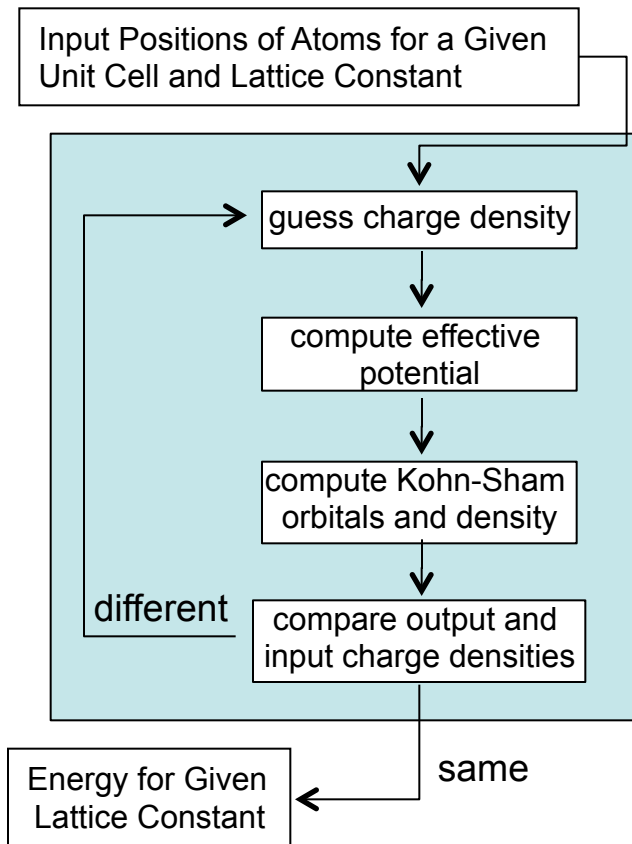
$$\left[-\frac{\hbar^2}{2m_e} \nabla_i^2 + V_{ext}(r) + \int \frac{n(r')}{|r-r'|} d^3r' + V_{xc}(r) \right] \phi_i(r) = \varepsilon_i \phi_i(r)$$

Exchange-Correlation Potential $V_{xc}(r) \equiv \frac{\delta E_{xc}[n(r)]}{\delta n(r)}$

Electron Density $n(r) = -e \sum_{i=1}^n |\phi_i(r)|^2$

Note: ϕ_i depends on $n(r)$ which depends on $\phi_i \rightarrow$
Solution of Kohn-Sham equations must be done iteratively

Self-Consistent Solution to DFT Equations



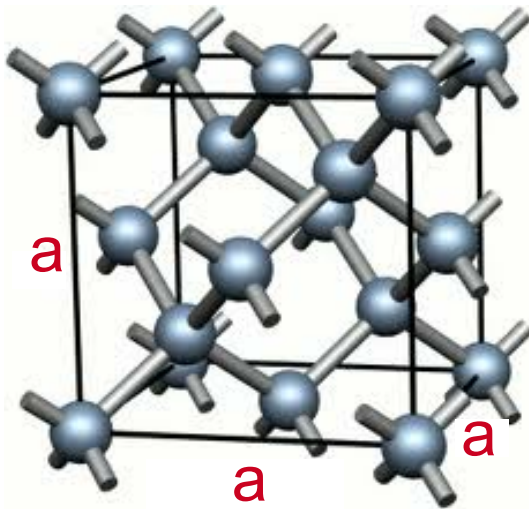
1. Set up atom positions
2. Make initial guess of “input” charge density (often overlapping atomic charge densities)
3. Solve Kohn-Sham equations with this input charge density
4. Compute “output” charge density from resulting wavefunctions
5. If energy from input and output densities differ by amount greater than a chosen threshold, mix output and input density and go to step 2
6. Quit when energy from input and output densities agree to within prescribed tolerance (e.g., 10^{-5} eV)

Note: In your exercise, positions of atoms are dictated by symmetry. If this is not the case another loop must be added to minimize energy with respect to atomic positions.

Implementation of DFT for a Single Crystal

Crystal Structure Defined by Unit Cell Vectors and Positions of Basis Atoms

Example: Diamond Cubic Structure of Si



Unit Cell Vectors

$$\mathbf{a}_1 = a \left(-\frac{1}{2}, \frac{1}{2}, 0\right)$$

$$\mathbf{a}_2 = a \left(-\frac{1}{2}, 0, \frac{1}{2}\right)$$

$$\mathbf{a}_3 = a \left(0, \frac{1}{2}, \frac{1}{2}\right)$$

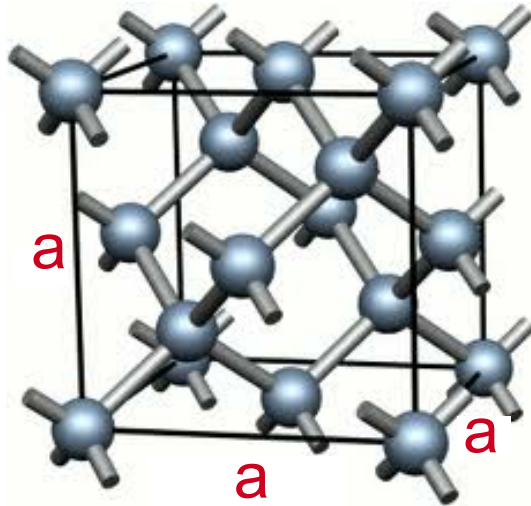
Basis Atom Positions

$$0 \ 0 \ 0$$

$$\frac{1}{4} \ \frac{1}{4} \ \frac{1}{4}$$

All atoms in the crystal can be obtained by adding integer multiples of unit cell vectors to basis atom positions

Electron Density in Crystal Lattice



Unit-Cell Vectors

$$\mathbf{a}_1 = a \left(-\frac{1}{2}, \frac{1}{2}, 0 \right)$$

$$\mathbf{a}_2 = a \left(-\frac{1}{2}, 0, \frac{1}{2} \right)$$

$$\mathbf{a}_3 = a \left(0, \frac{1}{2}, \frac{1}{2} \right)$$

Electron density is periodic with periodicity given by \mathbf{R}_{uvw}

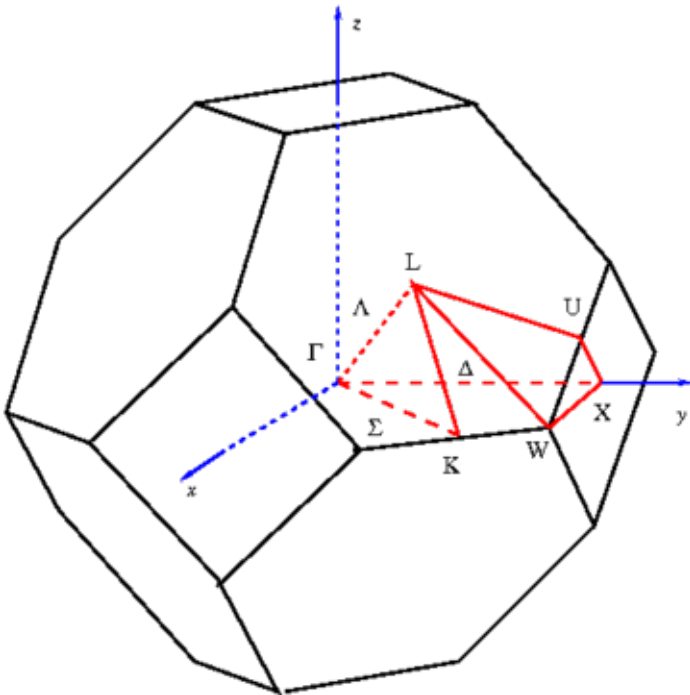
$$n(\mathbf{r}) = n(\mathbf{r} + \mathbf{R}_{uvw})$$

Translation Vectors: $\mathbf{R}_{uvw} = u\mathbf{a}_1 + v\mathbf{a}_2 + w\mathbf{a}_3$

Electronic Bandstructure

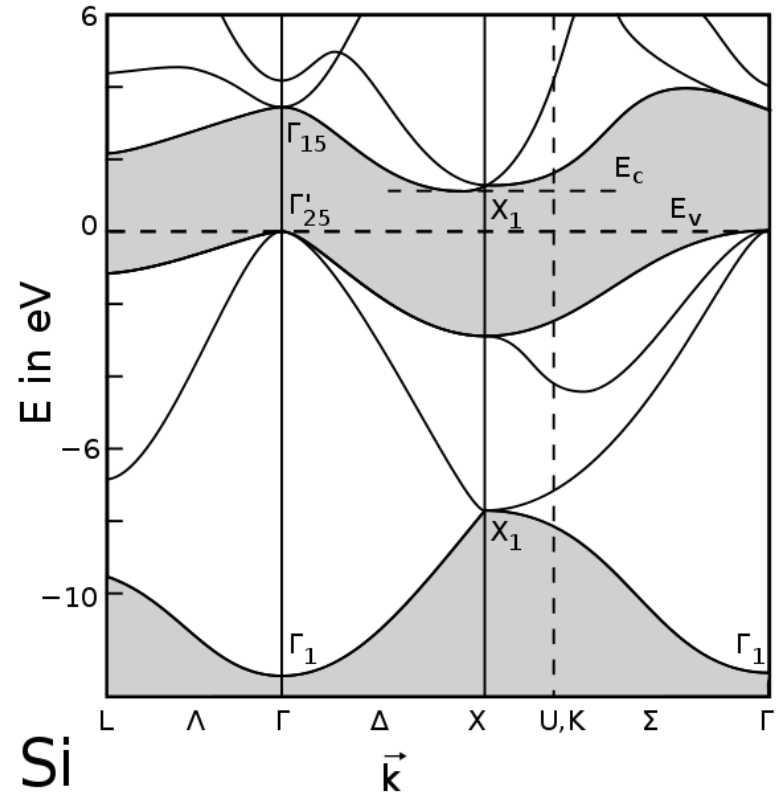
Example for Si

Brillouin Zone



http://en.wikipedia.org/wiki/Brillouin_zone

Bandstructure



http://de.wikipedia.org/wiki/Datei:Band_structure_Si_schematic.svg

Electronic wavefunctions in a crystal can be indexed by point in reciprocal space (\vec{k}) and a band index (β)

Why?

Wavefunctions in a Crystal Obey Bloch's Theorem

For a given band β

$$\phi_{\mathbf{k}}^{\beta}(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r}) u_{\mathbf{k}}^{\beta}(\mathbf{r})$$

Where $u_{\mathbf{k}}^{\beta}(\mathbf{r})$ is periodic in real space: $u_{\mathbf{k}}^{\beta}(\mathbf{r}) = u_{\mathbf{k}}^{\beta}(\mathbf{r} + \mathbf{R}_{uvw})$

Translation Vectors: $\mathbf{R}_{uvw} = u\mathbf{a}_1 + v\mathbf{a}_2 + w\mathbf{a}_3$

Representation of Electron Density

$$\phi_{\mathbf{k}}^{\beta}(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r}) u_{\mathbf{k}}^{\beta}(\mathbf{r})$$

$$n(\mathbf{r}) = -e \sum_{i=1}^{N_e} |\phi_i(\mathbf{r})|^2 \longrightarrow n(\mathbf{r}) = -e \sum_{\beta} \int_{\Omega_{BZ}} |\phi_{\mathbf{k}}^{\beta}(\mathbf{r})|^2 f(\epsilon_{\mathbf{k}}^{\beta} - \epsilon_F) \frac{d^3k}{\Omega_{BZ}}$$

Integral over k-points in first Brillouin zone

$f(\epsilon - \epsilon_F)$ is Fermi-Dirac distribution function with Fermi energy ϵ_F

In practice the integral over the Brillouin zone is replaced with a sum over a finite number of k-points (N_{kpt})

$$n(\mathbf{r}) \approx -e \sum_{\beta} \sum_{j=1}^{N_{kpt}} w_j |\phi_{\mathbf{k}_j}^{\beta}(\mathbf{r})|^2 f(\epsilon_{\mathbf{k}_j}^{\beta} - \epsilon_F)$$

One parameter that needs to be checked for numerical convergence is number of k-points

Representation of Wavefunctions

Fourier-Expansion as Series of Plane Waves

For a given band: $\phi_{\mathbf{k}}^{\beta}(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r}) u_{\mathbf{k}}^{\beta}(\mathbf{r})$

Recall that $u_{\mathbf{k}}^{\beta}(\mathbf{r})$ is periodic in real space: $u_{\mathbf{k}}^{\beta}(\mathbf{r}) = u_{\mathbf{k}}^{\beta}(\mathbf{r} + \mathbf{R}_{uvw})$

$u_{\mathbf{k}}^{\beta}(\mathbf{r})$ can be written as a Fourier Series:

$$u_{\mathbf{k}}^{\beta}(\mathbf{r}) = \sum_{lmn} u_{\mathbf{k}}^{\beta}(\mathbf{G}_{lmn}) \exp(i\mathbf{G}_{lmn} \cdot \mathbf{r})$$

$$\mathbf{G}_{lmn} = l\mathbf{a}_1^* + m\mathbf{a}_2^* + n\mathbf{a}_3^*$$

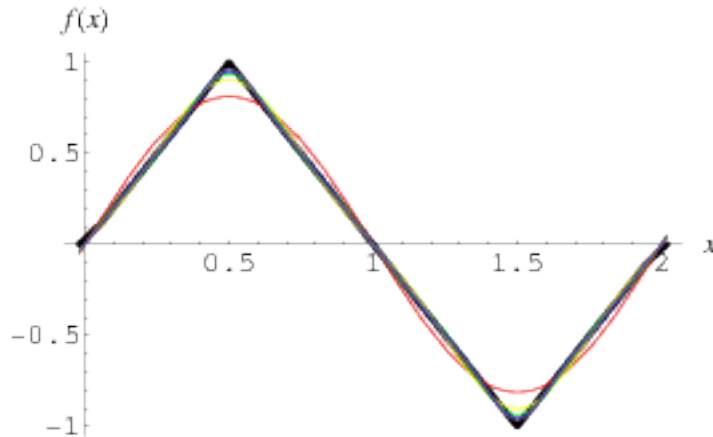
where the \mathbf{a}_i^* are primitive *reciprocal lattice vectors*

$$\mathbf{a}_1^* \cdot \mathbf{a}_1 = 2\pi \quad \mathbf{a}_1^* \cdot \mathbf{a}_2 = 0 \quad \mathbf{a}_1^* \cdot \mathbf{a}_3 = 0$$

$$\mathbf{a}_2^* \cdot \mathbf{a}_1 = 0 \quad \mathbf{a}_2^* \cdot \mathbf{a}_2 = 2\pi \quad \mathbf{a}_2^* \cdot \mathbf{a}_3 = 0$$

$$\mathbf{a}_3^* \cdot \mathbf{a}_1 = 0 \quad \mathbf{a}_3^* \cdot \mathbf{a}_2 = 0 \quad \mathbf{a}_3^* \cdot \mathbf{a}_3 = 2\pi$$

Recall Properties of Fourier Series



Black line = (exact) triangular wave

Colored lines = Fourier series truncated at different orders

<http://mathworld.wolfram.com/FourierSeriesTriangleWave.html>

General Form of Fourier Series:
$$f(x) = \frac{1}{2} a_0 + \sum_{n=1}^{\infty} a_n \cos(nx) + \sum_{n=1}^{\infty} b_n \sin(nx),$$

For Triangular Wave:
$$f(x) = \frac{8}{\pi^2} \sum_{n=1,3,5,\dots}^{\infty} \frac{(-1)^{(n-1)/2}}{n^2} \sin\left(\frac{n\pi x}{L}\right).$$

Typically we expect the accuracy of a truncated Fourier series to improve as we increase the number of terms

Representation of Wavefunctions

Plane-Wave Basis Set

For a given band $\phi_{\mathbf{k}}^{\beta}(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r}) u_{\mathbf{k}}^{\beta}(\mathbf{r})$

Use Fourier Expansion

$$\phi_{\mathbf{k}}^{\beta}(\mathbf{r}) = \sum_{\mathbf{G}} u_{\mathbf{k}}^{\beta}(\mathbf{G}) \exp[i(\mathbf{G} + \mathbf{k}) \cdot \mathbf{r}]$$

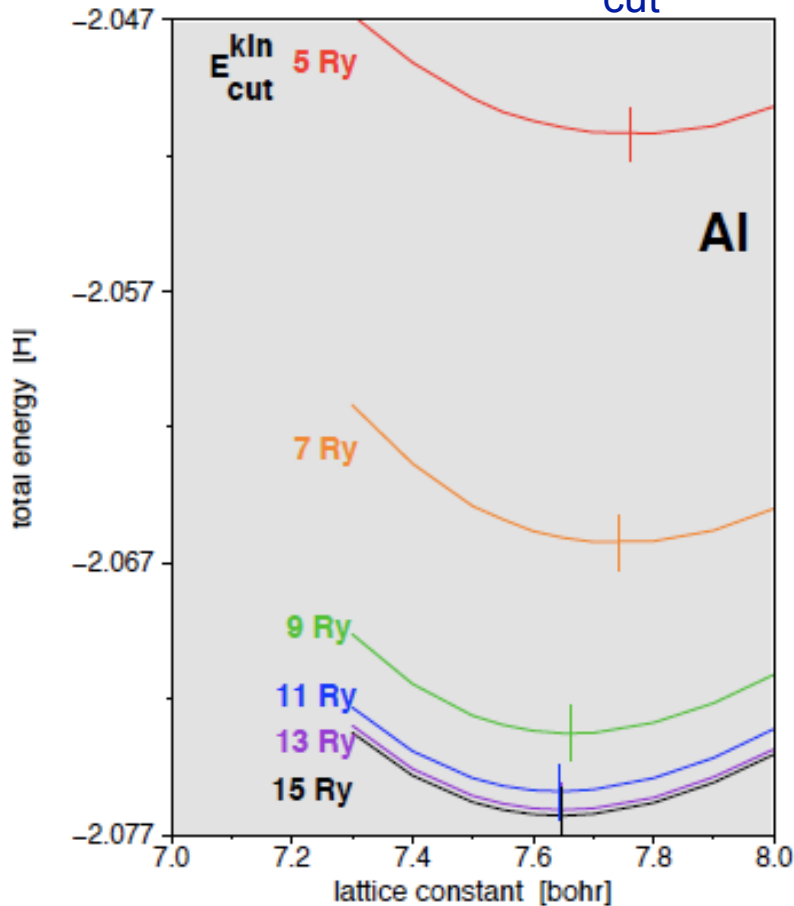
In practice the Fourier series is truncated to include all \mathbf{G} for which:

$$\frac{\hbar^2}{2m} (\mathbf{G} + \mathbf{k})^2 < E_{\text{cut}}$$

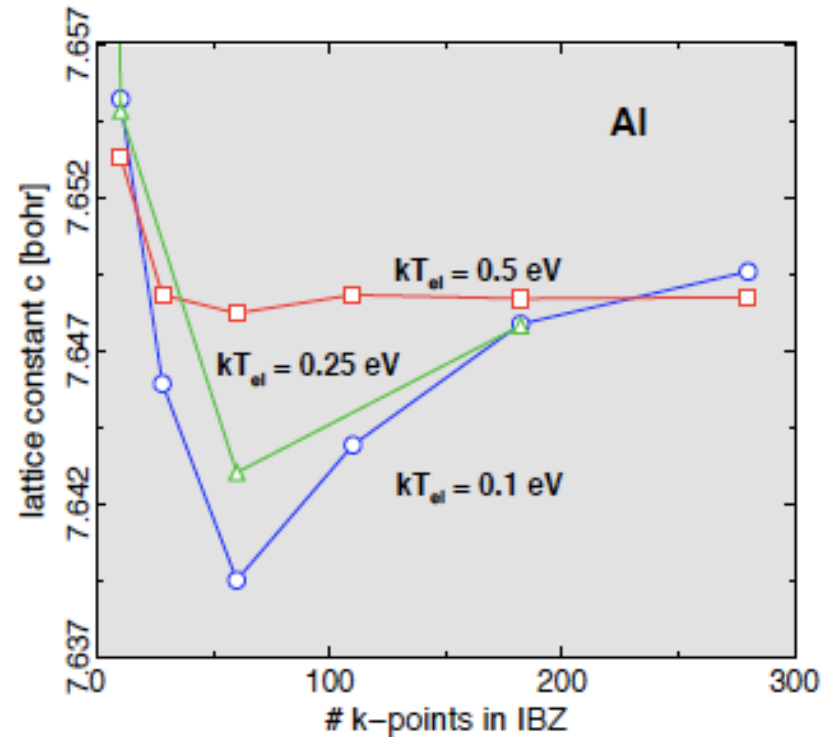
Another parameter that needs to be checked for convergence is the “plane-wave cutoff energy” E_{cut}

Examples of Convergence Checks

Effect of $E_{\text{cut}}^{\text{kin}}$



Effect of Number of k Points

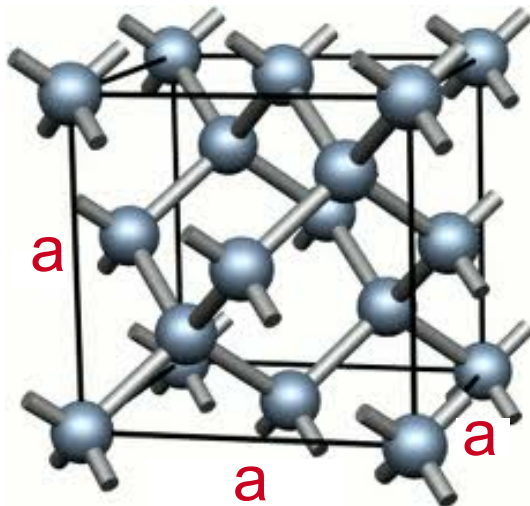


Outline

- Formalism
 - Hydrogen Atom
 - Density Functional Theory
 - Exchange-Correlation Potentials
 - Pseudopotentials and Related Approaches
 - Some Commercial and Open Source Codes
- Practical Issues
 - Implementation
 - Periodic boundary conditions
 - k-Points
 - Plane-wave basis sets
 - Parameters controlling numerical precision
- Example Exercise

Your Exercise: Part 1

- Calculate equation of state of diamond cubic Si using Quantum Espresso on Nanohub (<http://nanohub.org/>)
- You will compare accuracy of LDA and GGA
- You will check numerical convergence with respect to number of k-points and plane-wave cutoff
- You will make use of the following unit cell for diamond-cubic structure



Lattice Vectors

$$a_1 = a \left(-\frac{1}{2}, \frac{1}{2}, 0\right)$$

$$a_2 = a \left(-\frac{1}{2}, 0, \frac{1}{2}\right)$$

$$a_3 = a \left(0, \frac{1}{2}, \frac{1}{2}\right)$$

Basis Atom Positions

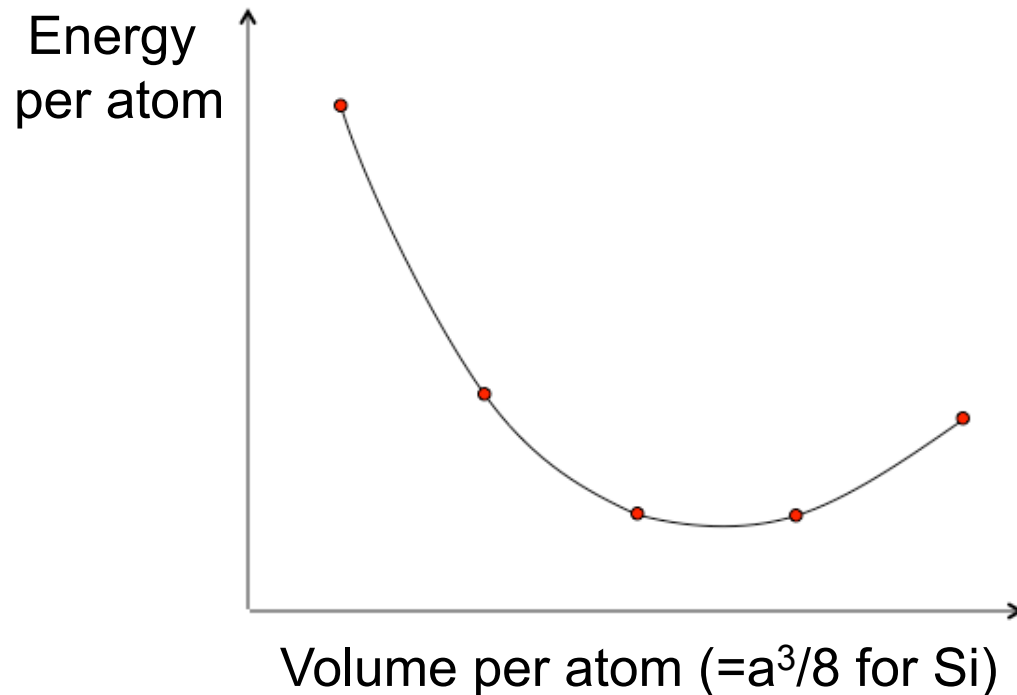
$$0 \ 0 \ 0$$

$$\frac{1}{4} \ \frac{1}{4} \ \frac{1}{4}$$

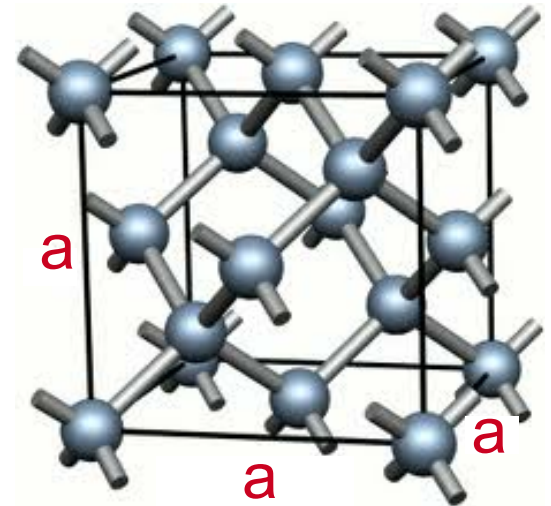
Equation of State

A Probe of Interatomic Interactions

Schematic Energy vs. Volume Relation



Diamond Cubic Structure of Si



<http://www.e6cvd.com/cvd/page.jsp?pageid=361>

Equation of State

What Properties Can we Learn from It?

Pressure versus Volume Relation

$$P = -\frac{\partial E}{\partial V}$$

Given $E(V)$ one can compute $P(V)$ by taking derivative

Recall 1st Law of Thermo: $dE = T dS - P dV$ and consider $T = 0 K$

Equilibrium Volume (or Lattice Constant)

Volume corresponding to zero pressure = Volume where slope of $E(V)$ is zero
 \approx Volume measured experimentally at $P = 1$ atm

Bulk Modulus

$$B = -V \frac{\partial P}{\partial V} = V \frac{\partial^2 E}{\partial V^2}$$

B related to curvature of $E(V)$ Function

Your Exercise: Part 2

Non-hydrostatic Stress and Strain

Stress-Strain Relations in Linear Elasticity

$$\sigma_{ij} = \sum_{k,l} C_{ijkl} \varepsilon_{kl}$$

Stress Strain

C_{ijkl} \longrightarrow *Single-Crystal Elastic Constants*

Stress-Strain Relations in Linear Elasticity

Consider Single Strain $\varepsilon_{33} = \varepsilon$

$$\sigma_{33} = C_{11} \varepsilon$$

$$\sigma_{22} = C_{12} \varepsilon$$

Voigt Notation (for Cubic Crystal)

$$C_{3333} = C_{2222} = C_{1111} = C_{11}$$

$$C_{2233} = C_{1133} = C_{1122} = C_{2211} = C_{3311} = C_{3322} = C_{12}$$