Density Functional Theory: Introduction and Applications

André Schleife
Department of Materials Science and Engineering
University of Illinois Urbana-Champaign
October 5th, 2022

The Grainger College of Engineering
IBM-Illinois Discovery Accelerator Institute

Sandia National Laboratories

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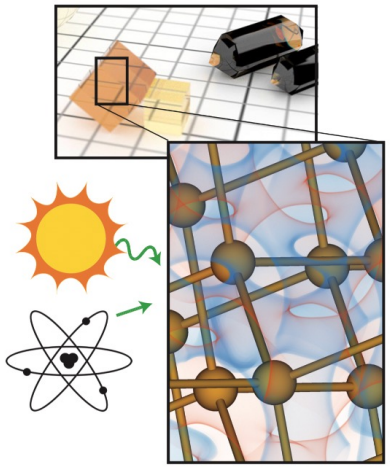
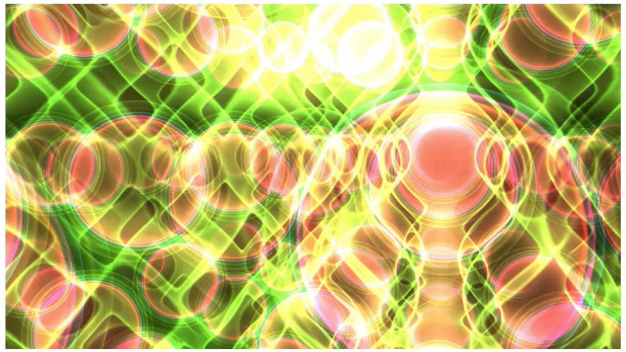
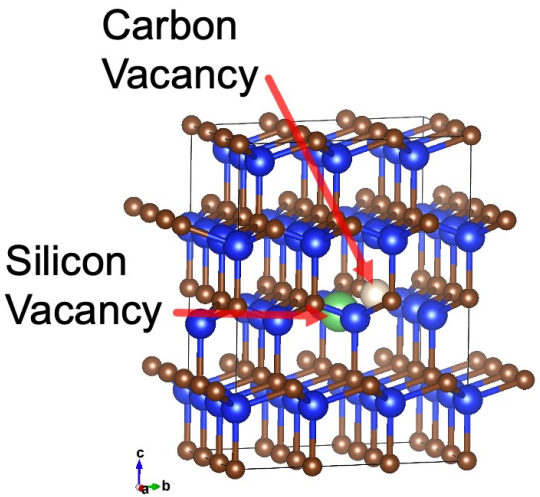


Electronic Excitations



Proton-irradiated MgO



Defects in SiC

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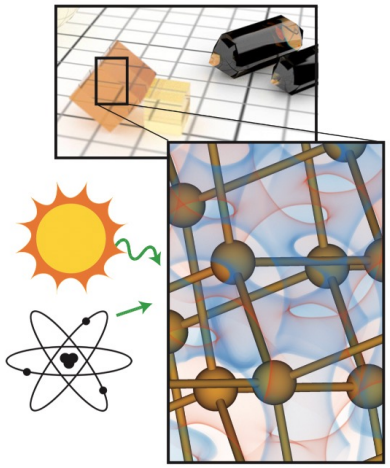

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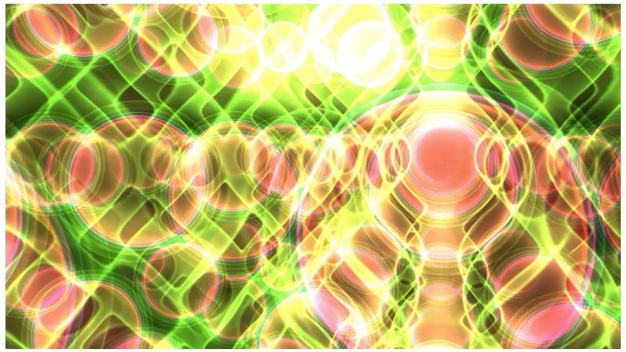

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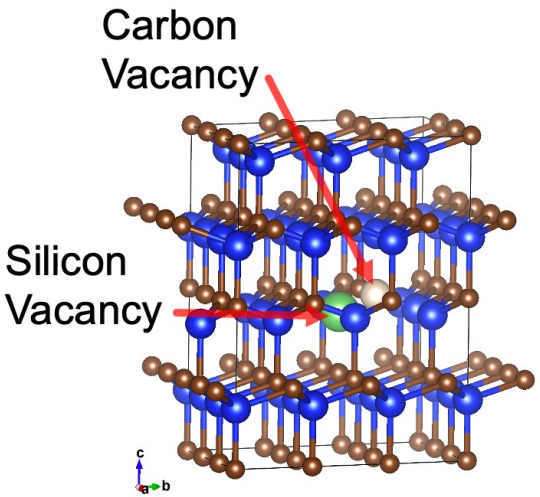

Defects in SiC

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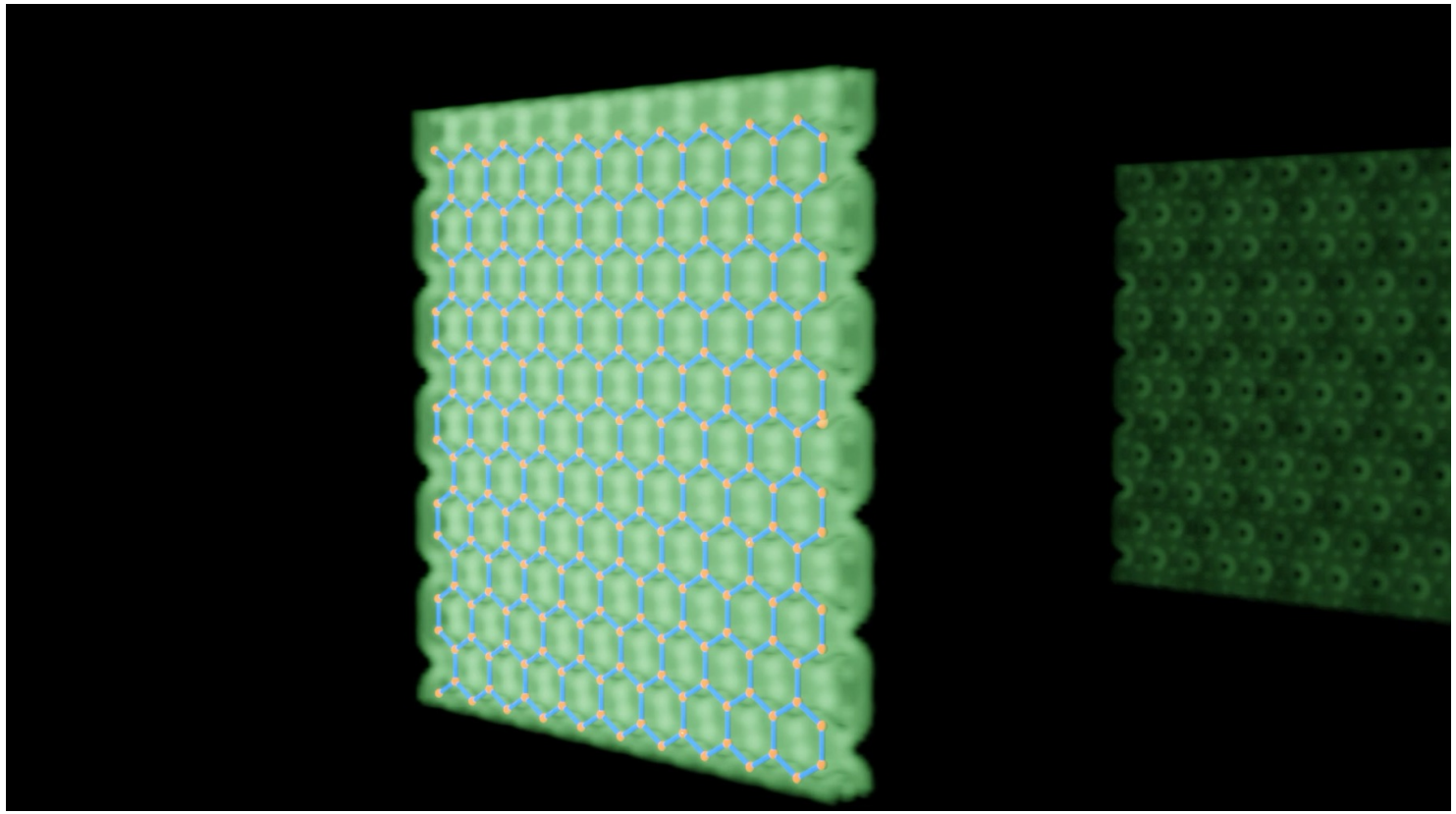
Question: What do you need Density Functional Theory for?

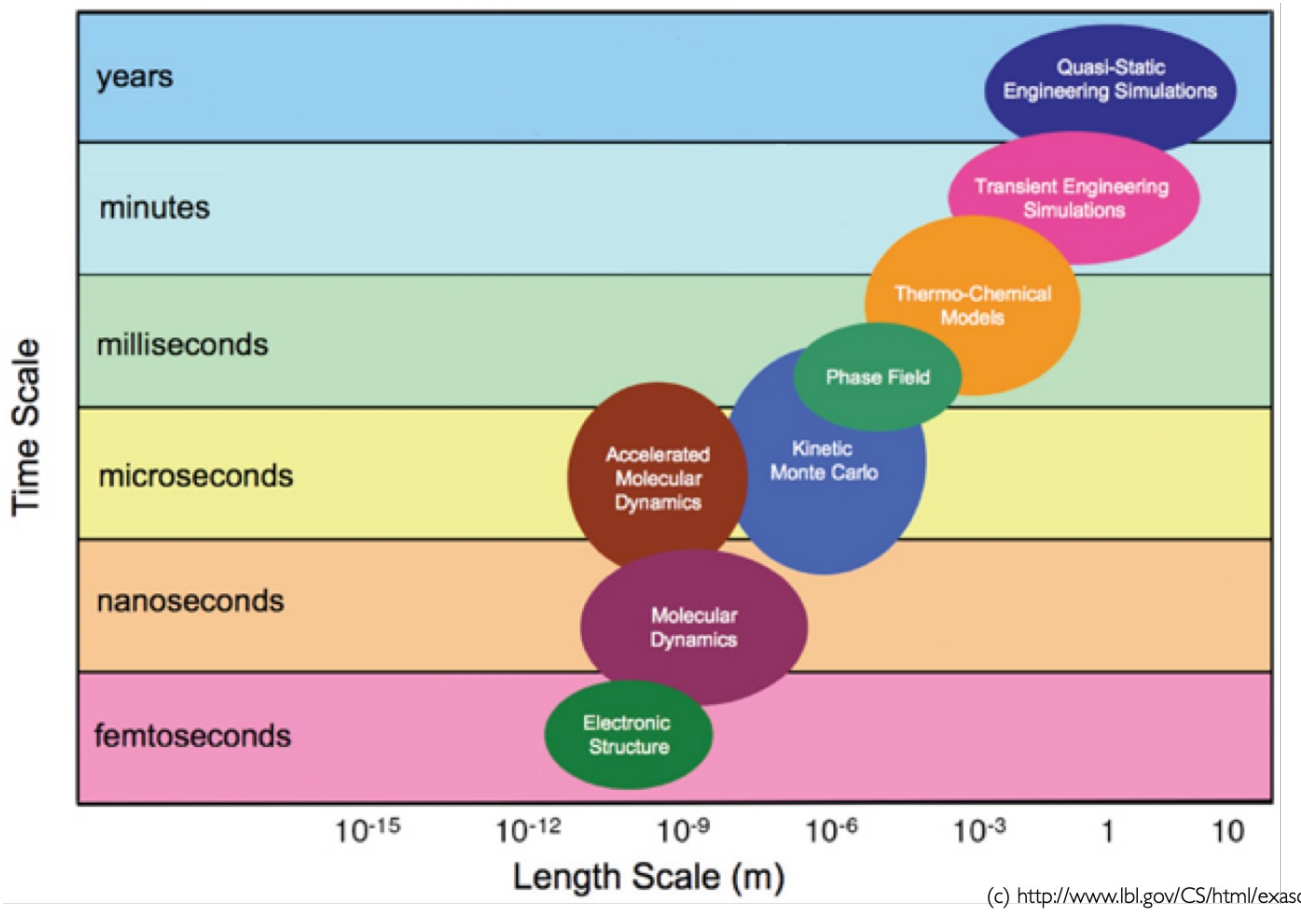
1. Use DFT
2. Develop DFT
3. Mostly to understand other people's work
4. My teaching
5. I am mostly just curious

Overview

- Motivation and Background
- Formulation and Implementation of Density Functional Theory
- Example Applications: Total Energy and Bulk Modulus, Electronic Band Structures



Computational Material Science



(c) http://www.lbl.gov/CS/html/exascale4energy/nuclear.html

- Computational cost depends on level of accuracy
- Many different approaches/codes available (depends on goal)
- Density Functional Theory: Microscopic scale

Microscopic Scale: Quantum Mechanics

Today's standard model of materials:

- Materials consist of atoms
- Atoms consist of
  - massive, point-like nuclei (protons + neutrons)
  - surrounded by tightly bound core electrons
  - held together in molecules, liquid, and solids by the bonds formed by valence electrons

Microscopic Scale: Quantum Mechanics

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Goal: Solve laws of quantum mechanics for actual materials

- Bonding and structure (structural properties)
- Electronic, magnetic, and optical properties of materials
- Chemistry and reactions

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> The general theory of quantum mechanics is now almost complete. The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, **and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble**.
> P. A. M. Dirac, Proc. R. Soc. Lond. A 1929, pg. 123

Microscopic Scale: Quantum Mechanics

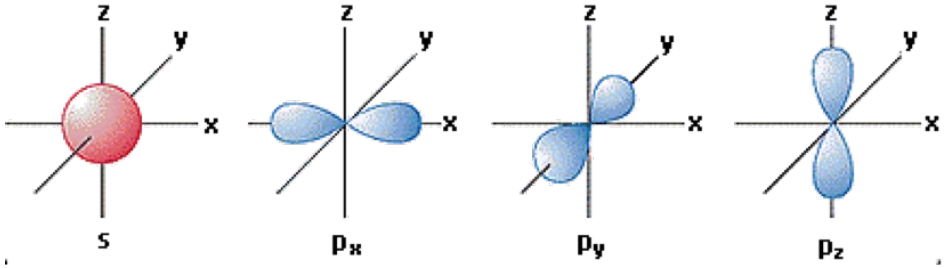
Quantum Mechanics:

1. Write Down Hamilton Operator

$$\hat{H} = \hat{T} + \hat{V}$$

2. Solve Schrödinger Equation to get *E* and ψ

$$\hat{H}\,\psi(\mathbf{r}) = (\hat{T} + \hat{V})\,\psi(\mathbf{r}) = E\,\psi(\mathbf{r})$$

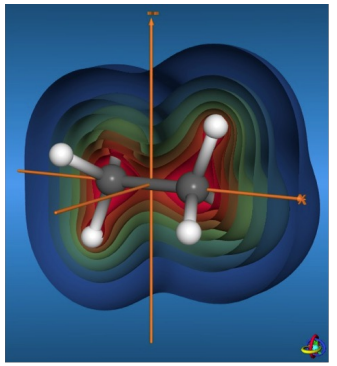


(c) https://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/Images/hybrid1.gif

3. Use this solution to compute observables

Probability of finding electron at position **r** in space

$$n(\mathbf{r}) = \sum_{k=1}^{N} n_k \left|\varphi_k(\mathbf{r})\right|^2$$



(c) http://csi.chemie.tu-darmstadt.de/ak/immel/tutorials/orbitals/molecular.html

Microscopic Scale: Quantum Mechanics

Why is Quantum Mechanics/Solving Schrödinger Equation hard?

Example: Fe atom

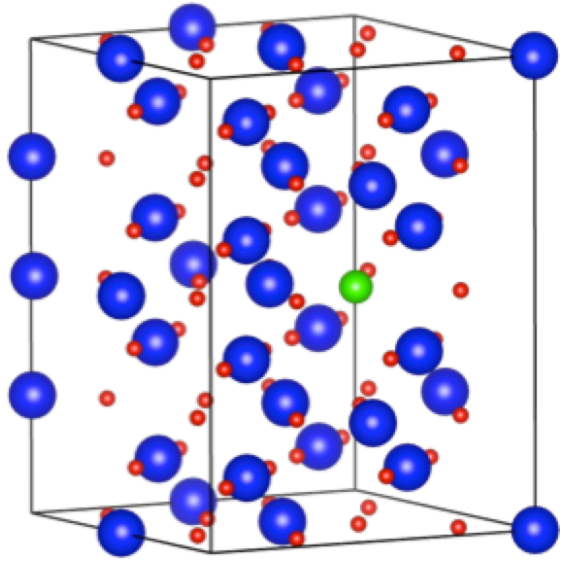
- Fe has 26 electrons ⇒ wave function has 3×26 = 78 variables
- store wave function on a grid
- coarse grid of only 10 points along each direction
- to store wave function would require storage of 10^{78} numbers
- single precision 1 number = 4 Bytes
- compare to all data stored worldwide in 2020:

  64 zettabyte = $64*10^{21}$ Bytes

$$\Psi(r_1, \ldots, r_{26})$$

(c) https://en.wikipedia.org/wiki/Iron#/media/File:Iron_electrolytic_and_1cm3_cube.jpg

Microscopic Scale: Quantum Mechanics



$TiO_{2(1-x)}S_{2x}$

Many-electron Hamiltonian of a material

- Fix ions in their positions: Born-Oppenheimer Approximation
- Leads to Electronic Hamiltonian:

$$\hat{H} = -\sum_i \frac{\hbar^2}{2m_e}\nabla^2_{\mathbf{r}_i} + \sum_i \sum_{j>i} \frac{e^2}{4\pi\varepsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} - \sum_i \sum_j \frac{Z_i e^2}{4\pi\varepsilon_0 |\mathbf{R}_i - \mathbf{r}_j|}$$

KE $e^- - e^-$ $e^- - ion$

Solution requires approximations

- Historic approaches include Hartree Approximation, Hartree-Fock Approximation, …
- In general: Balance/tradeoff between accuracy and speed
- Density Functional Theory favorable on that spectrum and is very widespread nowadays

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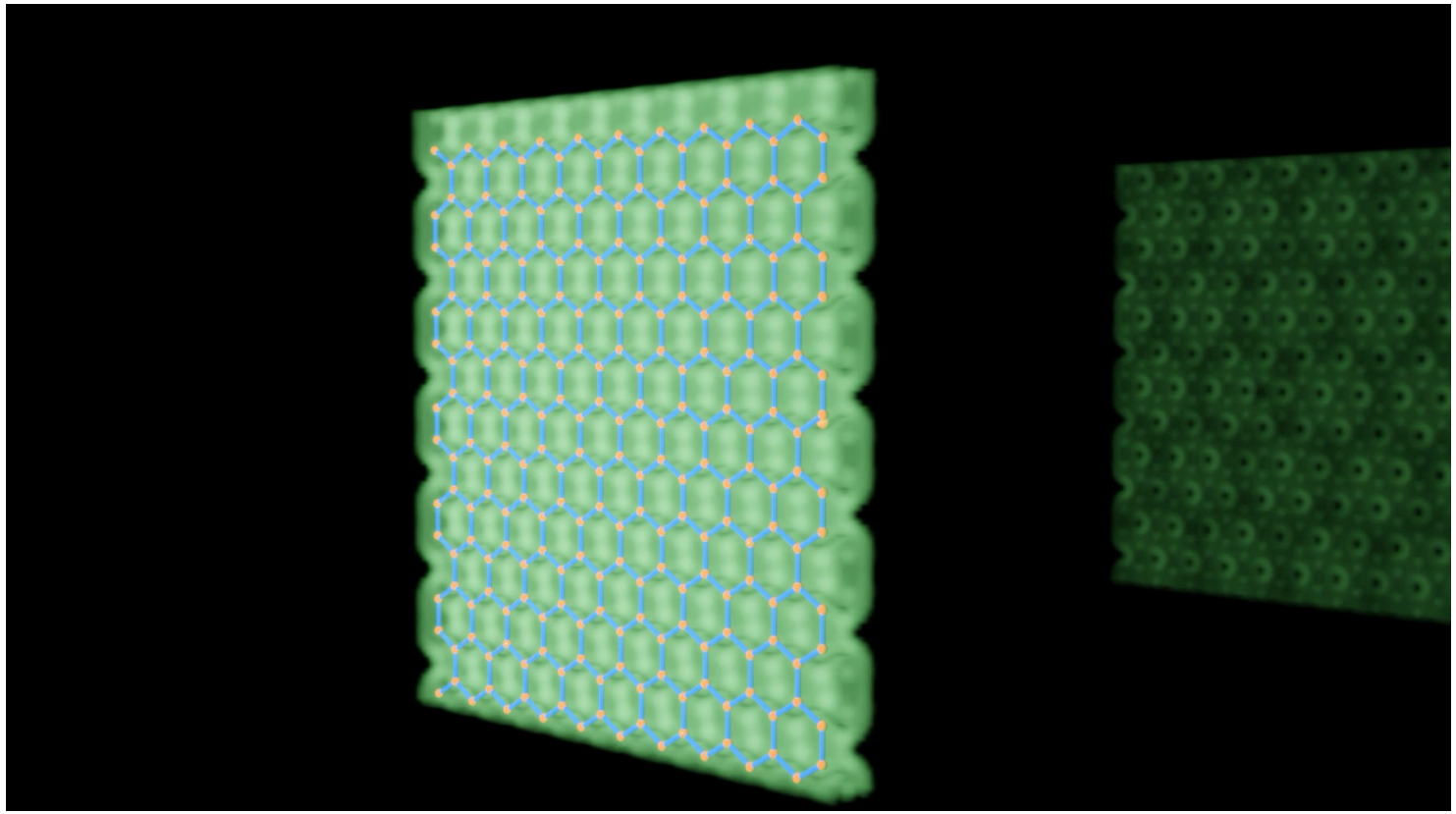
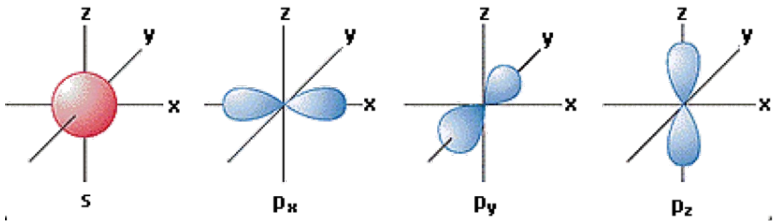


Density Functional Theory: Formulation and Implementation

- Walter Kohn proved: Ground state energy of the electronic system can be written as functional of electron density (instead of wave function)



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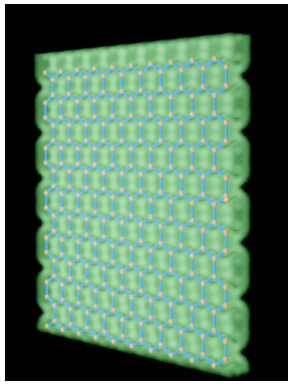
$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n)$	Function of 3N variables
$n(\mathbf{r})$	Function of 3 variables



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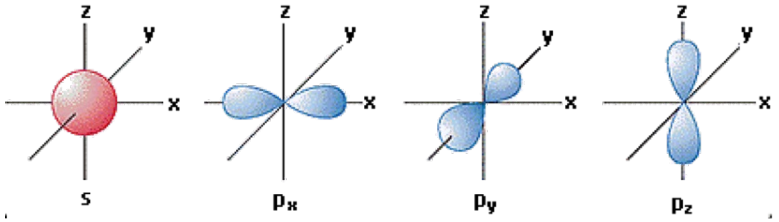

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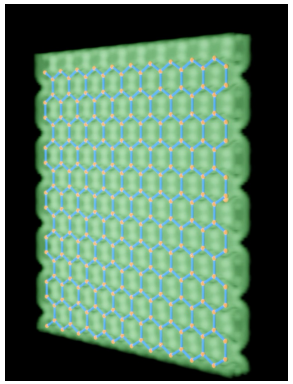
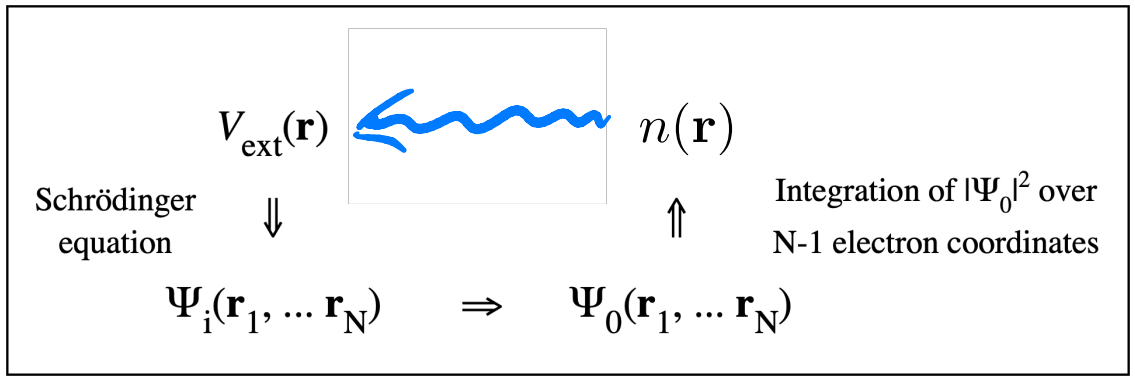


First Hohenberg-Kohn theorem

external potential is a unique functional of density



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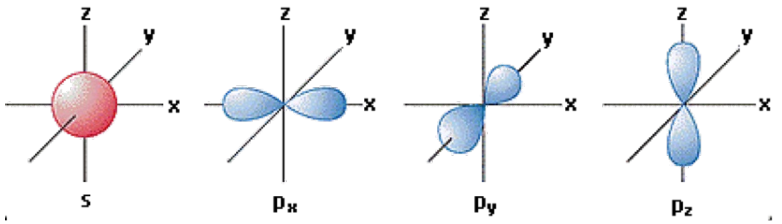

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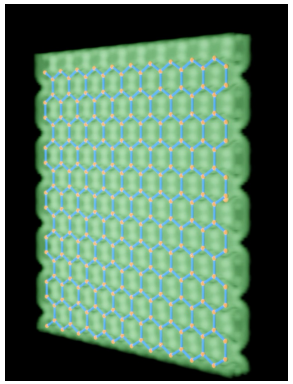

First Hohenberg-Kohn theorem

external potential is a unique functional of density

$V_{ext}(\mathbf{r})$ $\quad\quad$ $n(\mathbf{r})$

Schrödinger equation $\Downarrow$ $\quad\quad$ $\Uparrow$ Integration of $|\Psi_0|^2$ over N-1 electron coordinates

$\Psi_i(\mathbf{r}_1, \ldots \mathbf{r}_N) \Rightarrow \Psi_0(\mathbf{r}_1, \ldots \mathbf{r}_N)$

Second Hohenberg-Kohn theorem

density that minimizes the total energy is the exact groundstate density

$$E[n(\mathbf{r})] = E_{\text{kin}}[n(\mathbf{r})] + V_{\text{ext}}[n(\mathbf{r})] + V_{ee}[n(\mathbf{r})] \geq E_0$$

Question: Have we made an approximation yet?

1. Yes
2. No
3. I am not sure

Density Functional Theory: Formulation and Implementation

Find the solution in practice: Map to a non-interacting (Kohn-Sham) system

- Reason: We know the kinetic energy of non-interacting electrons

$$n(\mathbf{r}) = \sum_{k=1}^{N} n_k |\varphi_k(\mathbf{r})|^2 \qquad E_{\text{kin}}[n(\mathbf{r})] = -\frac{1}{2}\sum_{i=1}^{N} \int \varphi_i^*(\mathbf{r}) \nabla^2 \varphi_i(\mathbf{r})$$

- Determine the Hamiltonian of that system, such that the ground-state electron density of interacting and non-interacting system are the same
- But: We replaced the interacting by the non-interacting kinetic energy
- And: We also replaced full electron-electron interaction by the Hartree potential
- Make up for the resulting error by introducing an exchange-correlation functional

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$$\underbrace{\left[-\frac{1}{2}\nabla^2 + V_{\text{H}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}) + V_{\text{ext}}(\mathbf{r})\right]}_{\mathcal{H}_{\text{KS}}} \varphi_i(\mathbf{r}) = \epsilon_i \varphi_i(\mathbf{r})$$

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- Kinetic energy of non-interacting electrons
- Hartree energy (classical electron-electron interaction)
- External potential (Coulomb potential of ions)

$$V_{xc} = \hat{T} - \hat{T}_S + \hat{U} - V_H$$

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- Kinetic energy of non-interacting electrons
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All quantum effects in exchange-correlation potential

- Exact form not known, but reliable approximations available
- Examples: Local-density approximation (take from free-electron gas of same density), generalized-gradient approximation, self-interaction correction, Hubbard *U*, hybrid functionals, exact exchange, Van der Waals, Machine-Learned Functionals, …
- Accuracy: depends on approximation used and material to be studied

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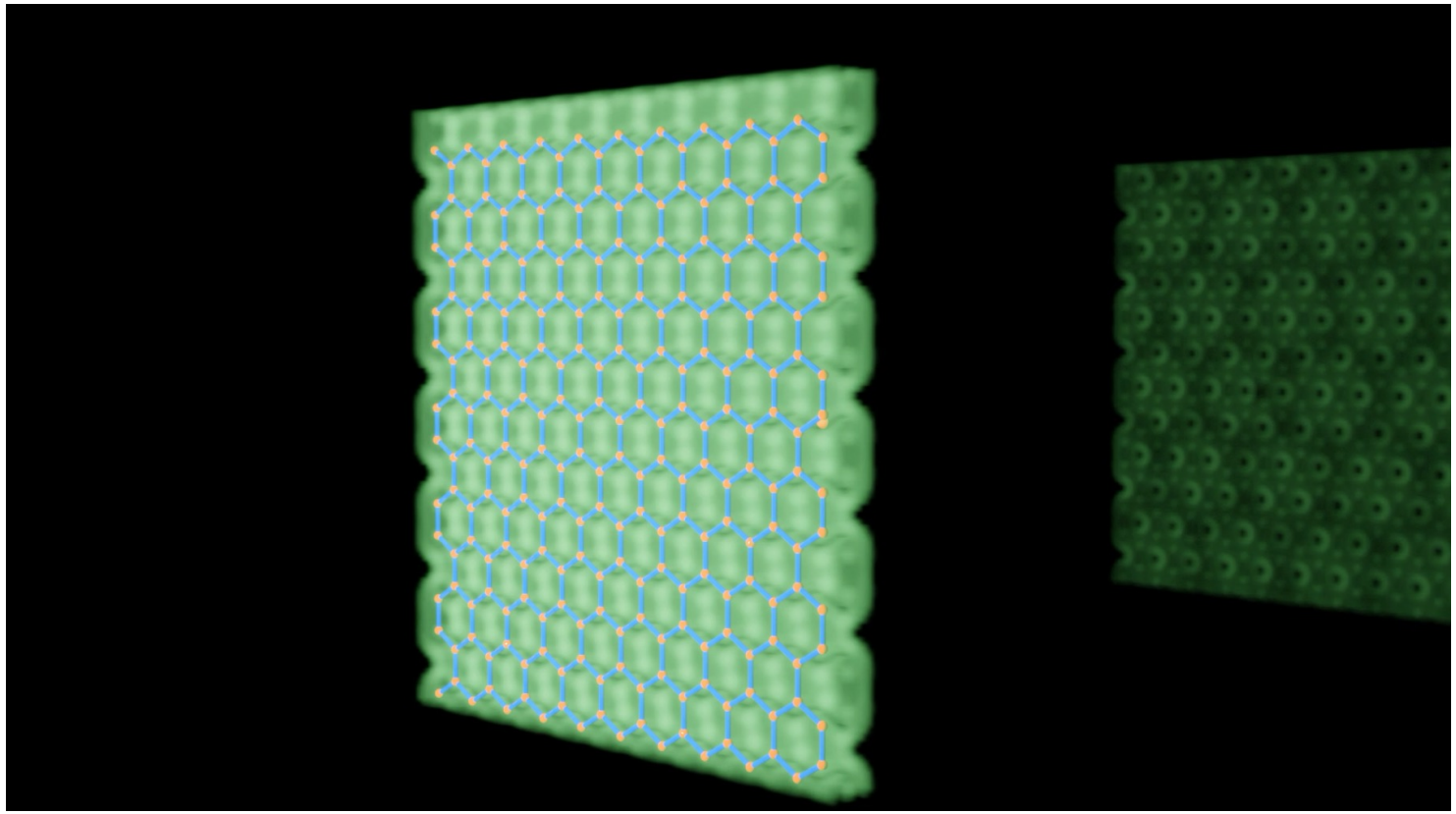
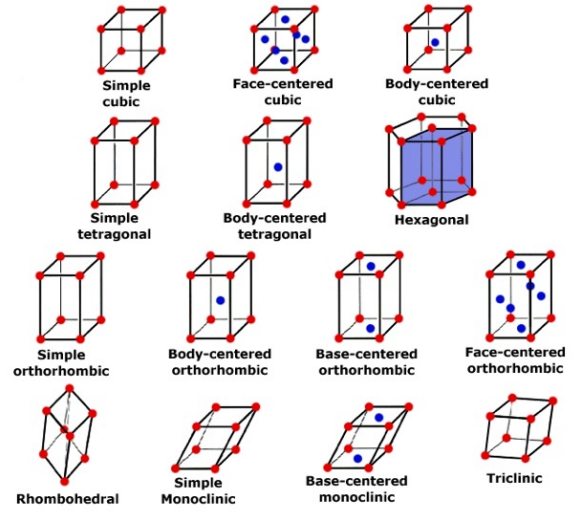
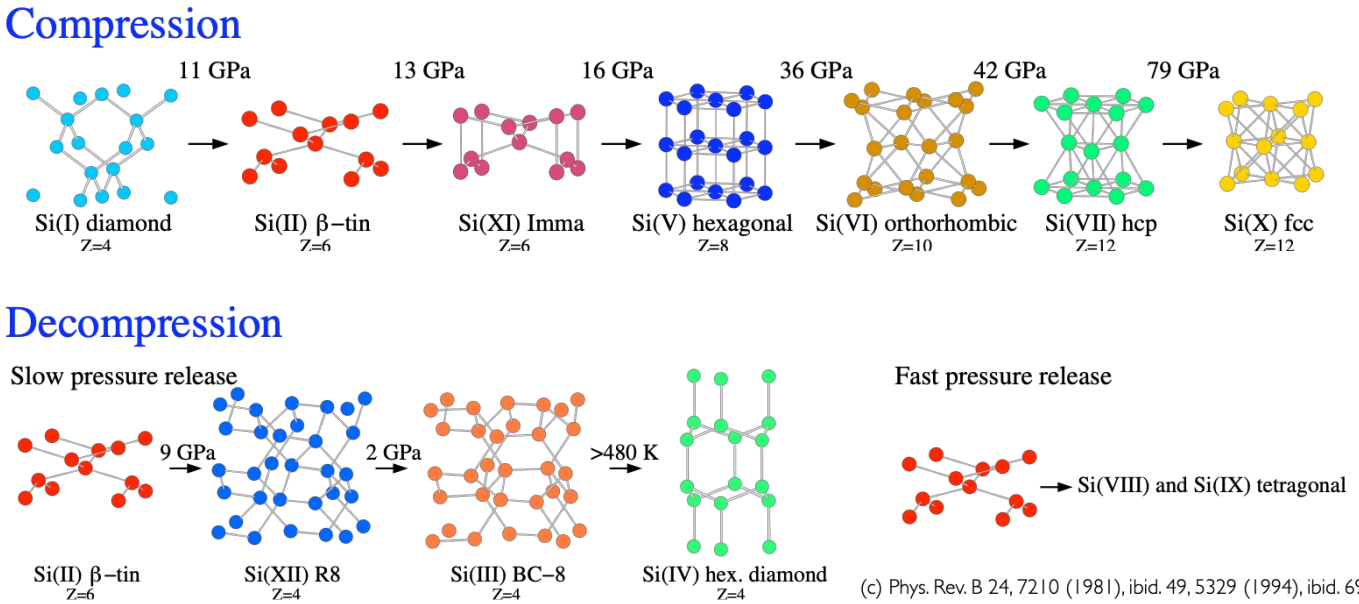


Density Functional Theory: Applications

Predict atomic geometries and crystal structure, e.g. Si



(c) http://www.seas.upenn.edu/~chem101/sschem/bravais.gif



(c) Phys. Rev. B 24, 7210 (1981), ibid. 49, 5329 (1994), ibid. 69, 134112 (2004)

Other examples include:

- Ab-initio molecular dynamics
- Vibrational properties
- Defect geometries and energetics
- …

Density Functional Theory: Applications

Quantum Espresso

- Integrated suite of Open-Source computer codes for electronic-structure calculations and materials modeling at the nanoscale
- Core set of codes, plugins for more advanced tasks and third-party packages
- Contributed to by developers across the world
- Can be run on nanoHUB, including for teaching
- Uses plane wave expansion for Kohn-Sham states and pseudo-potentials for electron-ion interaction

Example I: Total-energy calculations and convergence

- Compute total energies for bulk fcc silicon, change either plane-wave cutoff and/or k-point grid

https://nanohub.org/tools/dftqe

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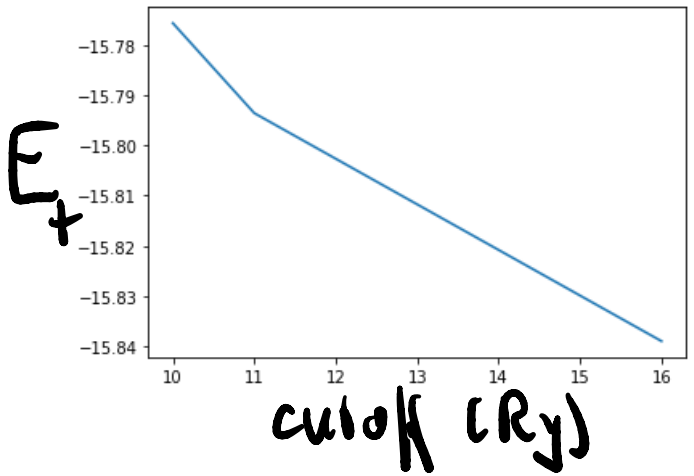

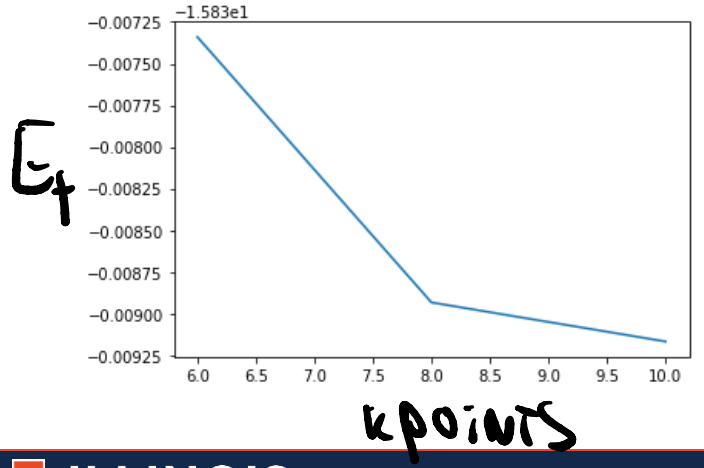

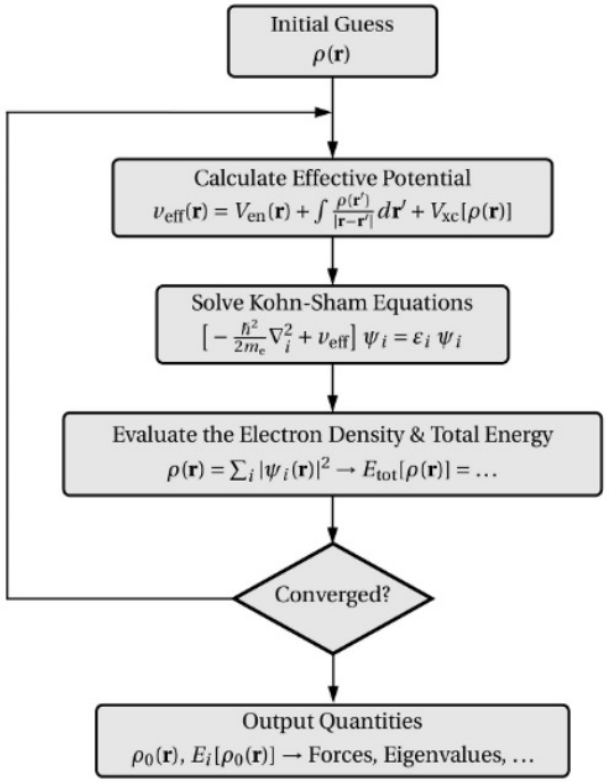

https://nanohub.org/tools/dftqe

(c) Wolfgang Goes, TU Vienna

Density Functional Theory: Applications

Example II: Bulk modulus

- At constant temperature, bulk modulus relates change in volume with a change in pressure:

$$B = -V\frac{dP}{dV}$$

- Decreasing the volume corresponds to positive external pressure on the material
- Pressure and energy are related via:

$$P = -\frac{dE}{dV}$$

- This leads to the following expression for the bulk modulus:

$$B = V\frac{d^2E}{dV^2}$$

- Produce an $E(V)$ curve with nanoHUB by varying volume around $0.9V_0 < V_0 < 1.1V_0$, V_0 follows from the lattice parameter of Si (5.43 Angstrom)

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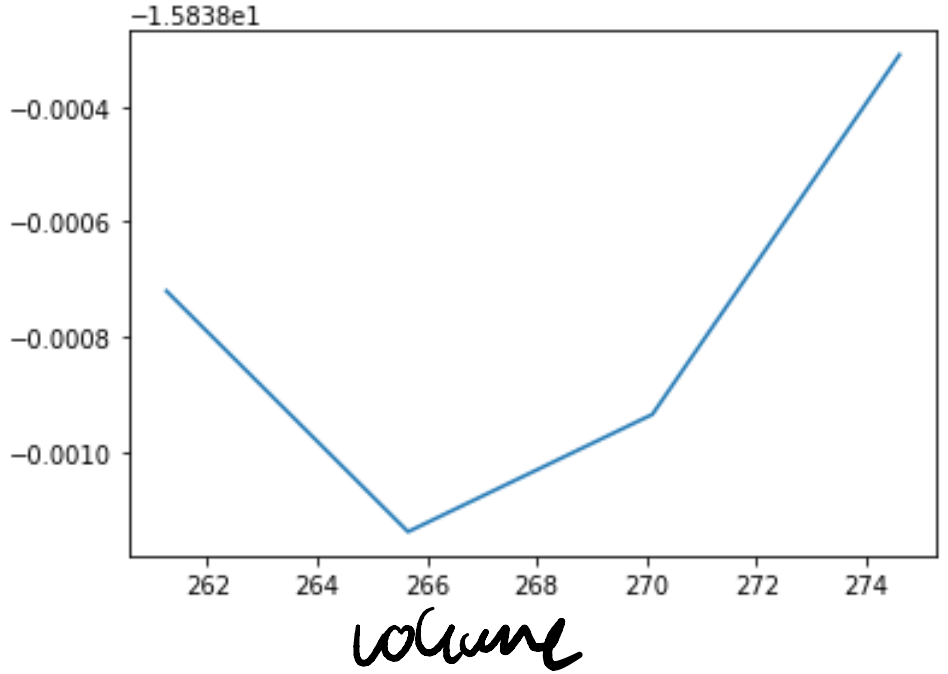
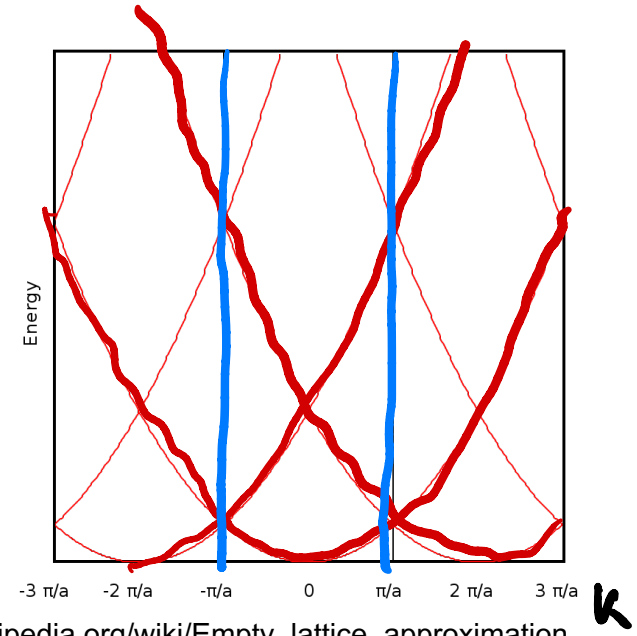


Density Functional Theory: Applications

Example III: Electronic band structure

- Remember from free-electron gas (one-dimensional periodic lattice):

$$E(\mathbf{k}) = \hbar^2 \frac{\mathbf{k}^2}{2m} = \hbar^2 \frac{(\mathbf{k}_{\text{reduced}} + \mathbf{K})^2}{2m}$$



(c) https://en.wikipedia.org/wiki/Empty_lattice_approximation

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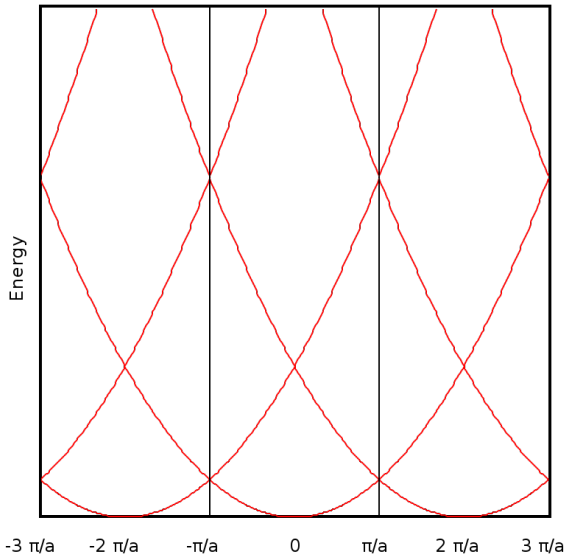

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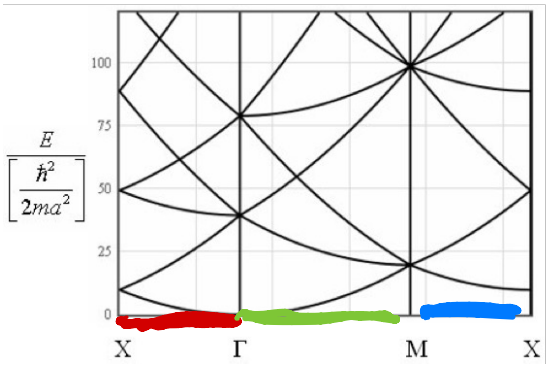
- in 2D or 3D path in k-space more complicated
- in a real material: electron-ion interaction

2D (square)



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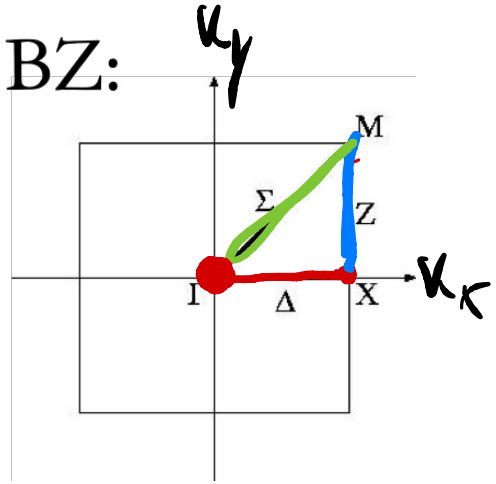


(c) http://lamp.tu-graz.ac.at/~hadley/ss1/empty/empty.php

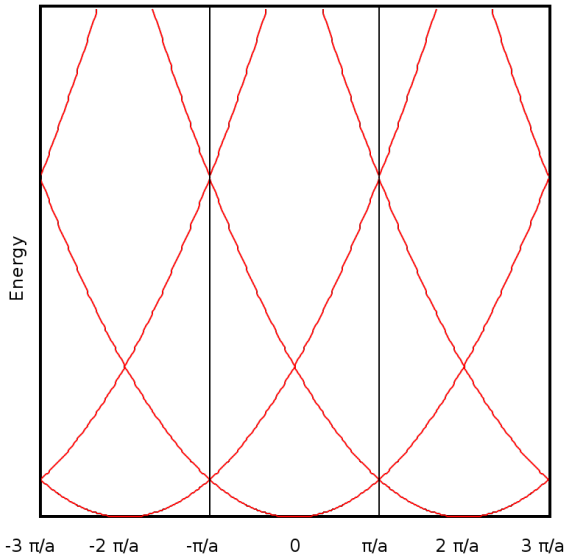
Density Functional Theory: Applications

Example III: Electronic band structure

- Remember from free-electron gas (one-dimensional periodic lattice):

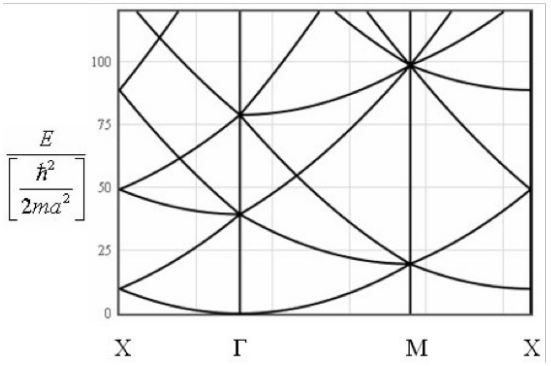
$$E(\mathbf{k}) = \hbar^2 \frac{\mathbf{k}^2}{2m} = \hbar^2 \frac{(\mathbf{k}_{\text{reduced}} + \mathbf{K})^2}{2m}$$

- in 2D or 3D path in k-space more complicated
- in a real material: electron-ion interaction

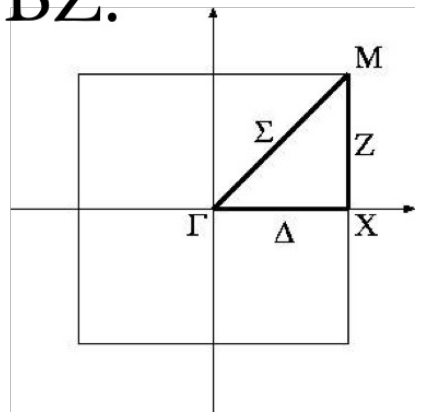


(c) https://en.wikipedia.org/wiki/Empty_lattice_approximation

2D (square)

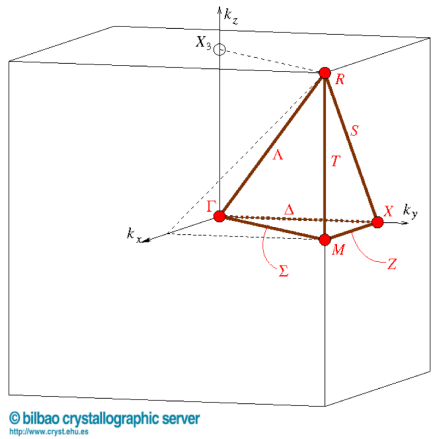


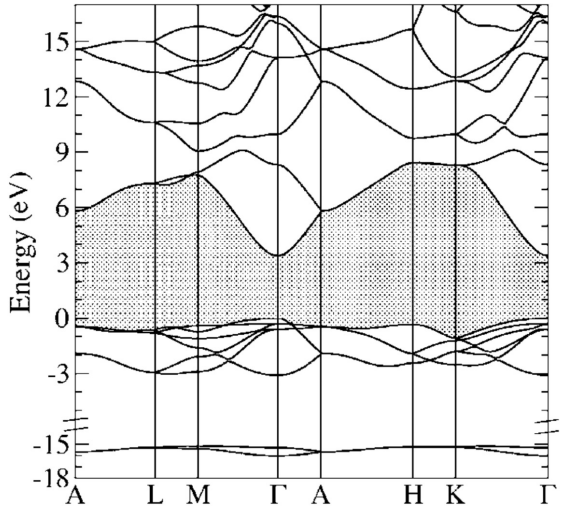
BZ:



(c) http://lamp.tu-graz.ac.at/~hadley/ss1/empty/empty.php

3D (schematic)





(c) Phys. Rev. B 73, 245212 (2006)

Density Functional Theory: Applications

Example III: Electronic band structure

- Restart the DFT tool on nanoHUB
- Use 15 to 20 band structure points
- Pick high-symmetry k-points for your band structure path, e.g. (0.5, 0.5, 0.5); (0.0, 0.0, 0.0); (1.0, 0.0, 0.0)
- Compute the band structure and density of states

https://nanohub.org/tools/dftqe

Density Functional Theory: Applications

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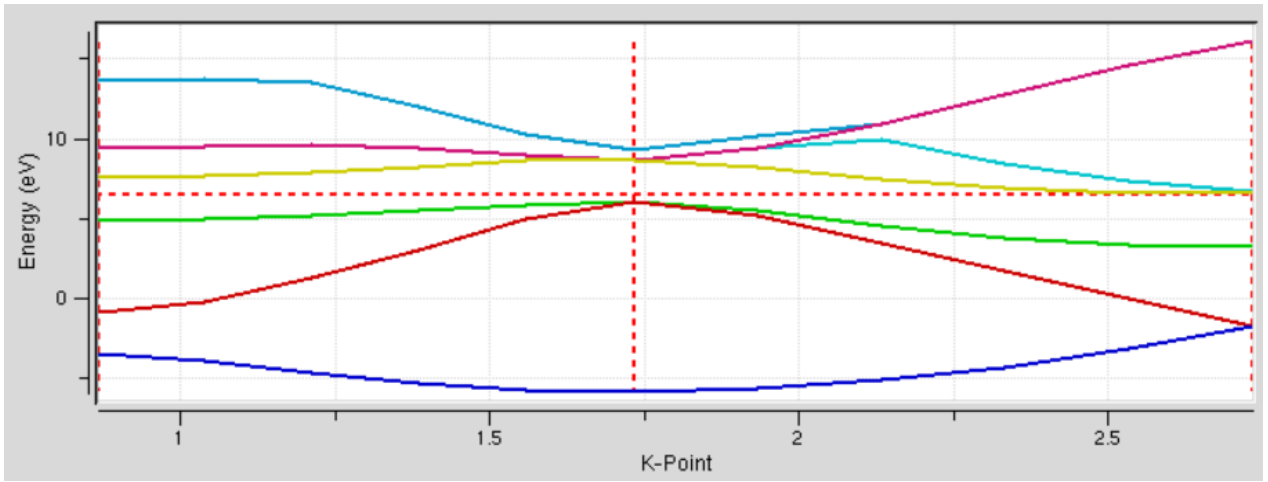
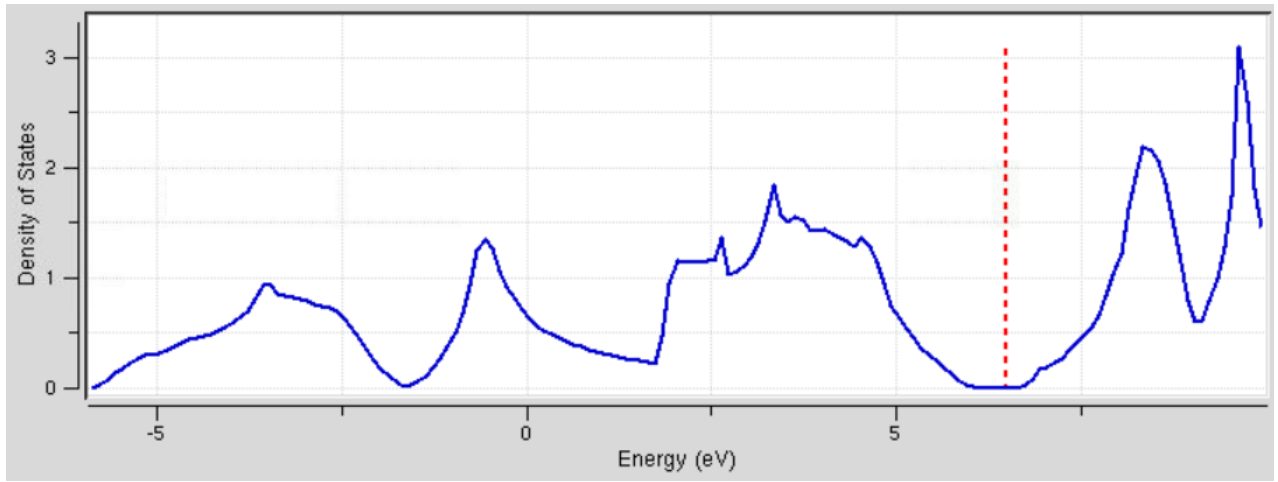
- Illustrate the corresponding Brillouin zone path (with the help of the Bilbao Crystallographic Server)
- Label direct and indirect band gaps
- Connect band structure and density of states
- Extract effective masses of electrons and holes





Summary

Literature on Density Functional Theory:

- “Electronic Structure: Basic Theory and Practical Methods”, Richard Martin, Cambridge
- “Density Functional Theory: An Approach to the Quantum Many-Body Problem”, Dreizler and Gross, Springer
- “Density Functional Theory: A Practical Introduction”, David Sholl, Wiley

Literature on Excited Electronic States:

- “Time-Dependent Density-Functional Theory: Concepts and Applications”, Carsten Ullrich, Oxford
- “Many-Body Approach to Electronic Excitations: Concepts and Applications”, Friedhelm Bechstedt, Springer
- “Interacting Electrons: Theory and Computational Approaches”, Reining, Martin, Ceperley, Cambridge

https://nanohub.org/groups/dft_users

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