An introduction to density functional theory for experimentalists

Feliciano Giustino

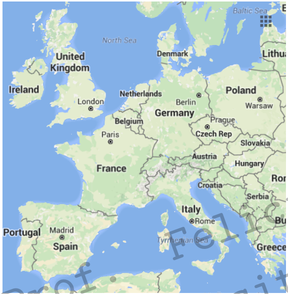
University of Oxford

25–29 July 2016

Lecture 1.1

Ab initio materials modelling

Oxford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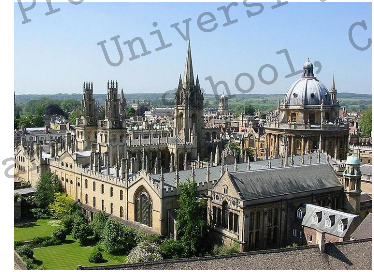

About me


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Mauritania

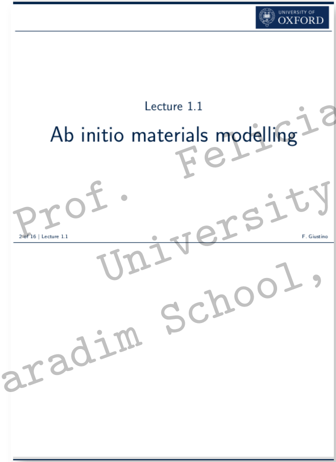
Organization of the course

Monday 25 – Friday 29

9:30–10:15	Theory Lecture 1	45 min
10:15–10:45	Coffee Break	30 min
10:45–11:30	Theory Lecture 2	45 min
11:30–13:30	Lunch Break	2 h
13:30–14:15	Practical Lecture	45 min
14:15–14:30	Short Break	15 min
14:30–16:30	Hands-on Session	2 h
18:00–19:30	Dinner	1 h
19:30–21:30	Team Problem Solving Workshops	2 h

Handouts and Tutorial Sheets

Handouts

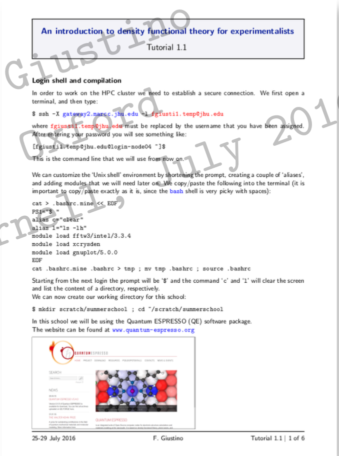


Lecture 1.1

Ab initio materials modelling

2 of 16 | Lecture 1.1 F. Giustino

Tutorial Sheets



An introduction to density functional theory for experimentalists

Tutorial 1.1

Login shell and compilation

In order to work on the HPC cluster we need to establish a secure connection. We first open a terminal, and then type:

```
$ ssh -X gateway2.marcc.jhu.edu -l fgiusti1.temp@jhu.edu
```

where fgiusti1.temp@jhu.edu must be replaced by the username that you have been assigned. After entering your password you will see something like:

```
[fgiusti1.temp@jhu.edu@login-node04 ~]$
```

This is the command line that we will use from now on.

We can customize the 'Unix shell' environment by shortening the prompt, creating a couple of 'aliases', and adding modules that we will need later on. We copy/paste the following into the terminal (it is important to copy/paste exactly as it is, since the bash shell is very picky with spaces):

```
cat > .bashrc.mine << EOF
PS1="$ "
alias c="clear"
alias l="ls -lh"
module load fftw3/intel/3.3.4
module load xcrysden
module load gnuplot/5.0.0
EOF
cat .bashrc.mine .bashrc > tmp ; mv tmp .bashrc ; source .bashrc
```

Starting from the next login the prompt will be '$' and the command 'c' and 'l' will clear the screen and list the content of a directory, respectively.
We can now create our working directory for this school:

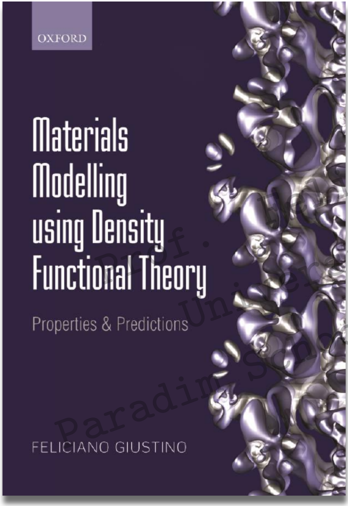
```
$ mkdir scratch/summerschool ; cd ~/scratch/summerschool
```

In this school we will be using the Quantum ESPRESSO (QE) software package.
The website can be found at www.quantum-espresso.org

25-29 July 2016 F. Giustino Tutorial 1.1 | 1 of 6

Textbooks

MSc and 1st year PhD level



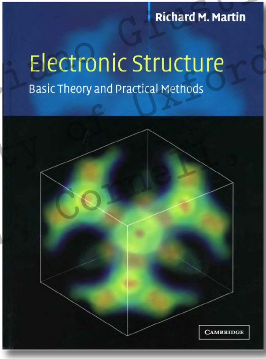
OXFORD

Materials Modelling using Density Functional Theory

Properties & Predictions

FELICIANO GIUSTINO

Advanced PhD level



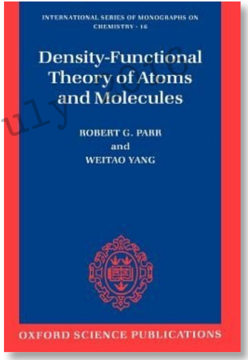
Richard M. Martin

Electronic Structure

Basic Theory and Practical Methods

CAMBRIDGE

Theoretical foundations



INTERNATIONAL SERIES OF MONOGRAPHS ON CHEMISTRY · 16

Density-Functional Theory of Atoms and Molecules

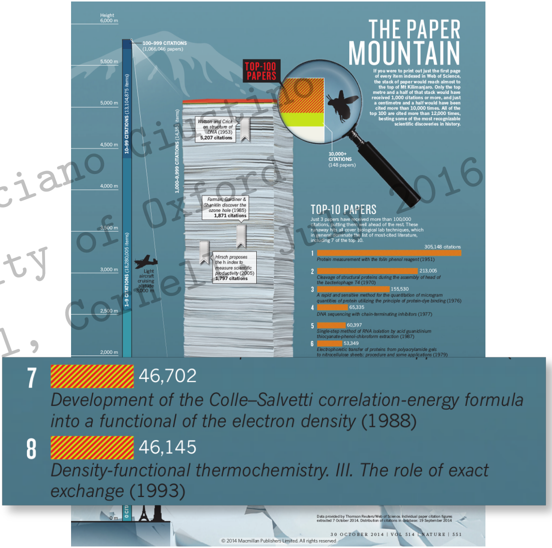
ROBERT G. PARR
and
WEITAO YANG

OXFORD SCIENCE PUBLICATIONS

Impact of DFT

THE TOP 100 PAPERS

Interview by R. Van Norden
Nature 514, 550 (2014)



Watson and Crick on structure of DNA (1953)
5,207 citations

Farman, Gardiner & Shanklin discover the ozone hole (1985)
1,871 citations

Hirsch proposes the h index to measure scientific productivity (2005)
1,797 citations

THE PAPER MOUNTAIN

If you were to print out just the first page of every item indexed in Web of Science, the stack of paper would reach almost to the top of Mt Kilimanjaro. Only the top metre and a half of that stack would have received 1,000 citations or more, and just a centimetre and a half would have been cited more than 10,000 times. All of the top 100 are cited more than 12,000 times, besting some of the most recognizable scientific discoveries in history.

TOP-10 PAPERS

Just 3 papers have received more than 100,000 citations, putting them well ahead of the rest. These runaway hits all cover biological lab techniques, which in general dominate the list of most-cited literature, including 7 of the top 10.

1 305,148 citations
Protein measurement with the folin phenol reagent (1951)

2 213,005
Cleavage of structural proteins during the assembly of head of the bacteriophage T4 (1970)

3 155,530
A rapid and sensitive method for the quantitation of microgram quantities of protein utilizing the principle of protein-dye binding (1976)

4 65,335
DNA sequencing with chain-terminating inhibitors (1977)

5 60,397
Single-step method of RNA isolation by acid guanidinium thiocyanate-phenol-chloroform extraction (1987)

6 53,349
Electrophoretic transfer of proteins from polyacrylamide gels to nitrocellulose sheets: procedure and some applications (1979)

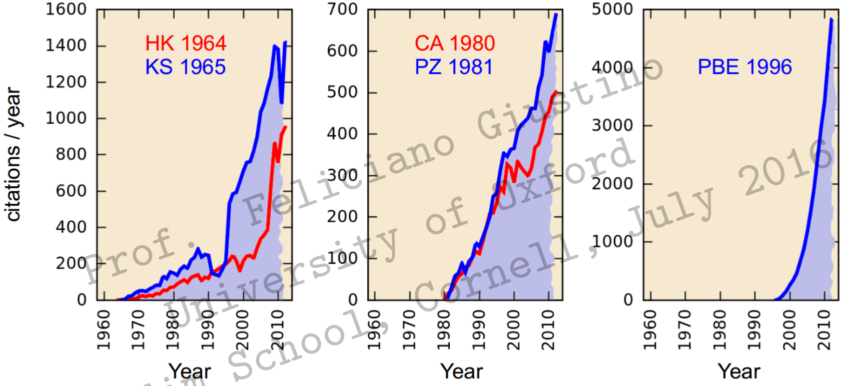
7 46,702
Development of the Colle–Salvetti correlation-energy formula into a functional of the electron density (1988)

8 46,145
Density-functional thermochemistry. III. The role of exact exchange (1993)

Data provided by Thomson Reuters/Web of Science. Individual paper citation figures extracted 7 October 2014. Distribution of citations in database: 19 September 2014

30 OCTOBER 2014 | VOL 514 | NATURE | 551

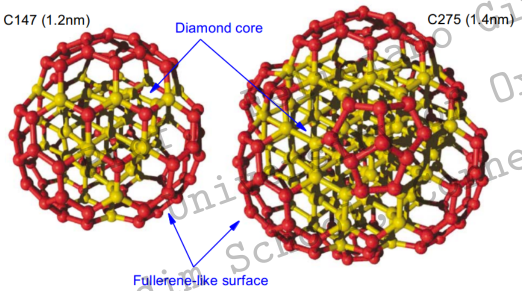
Impact of DFT

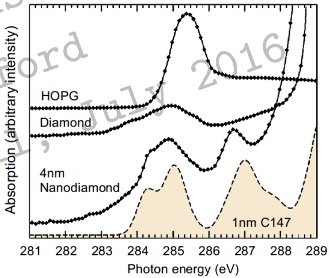


HK 1964	Hohenberg, Kohn, Phys. Rev. 136, B864 (1964)
KS 1965	Kohn, Sham, Phys. Rev. 140, A1133 (1965)
CA 1980	Ceperley, Alder, Phys. Rev. Lett. 45, 566 (1980)
PZ 1981	Perdew, Zunger, Phys. Rev. B 23, 5048 (1981)
PBE 1996	Perdew, Burke, Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996)

Examples of DFT calculations

Structure of nanodiamonds

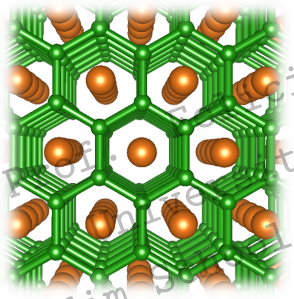


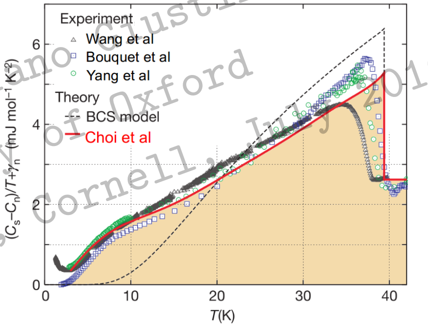


Raty, Galli, Bostedt, van Buuren, Terminello, Phys. Rev. Lett 90, 037401 (2003)

Examples of DFT calculations

Heat capacity of superconducting MgB_2

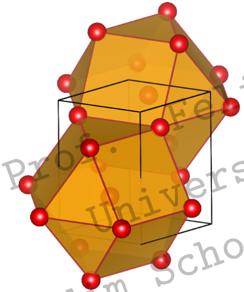


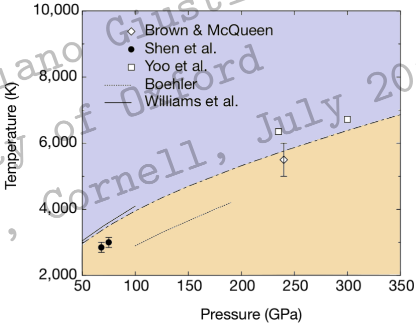


Choi, Roundy, Sun, Cohen, Louie, Nature 418, 758 (2002)

Examples of DFT calculations

Melting temperature of ϵ-Fe at the core-mantle boundary

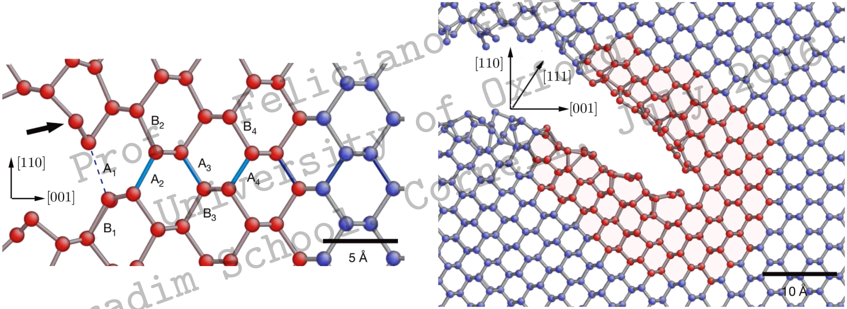




Alfe, Gillan, Price, Nature 401, 462 (1999)

Examples of DFT calculations

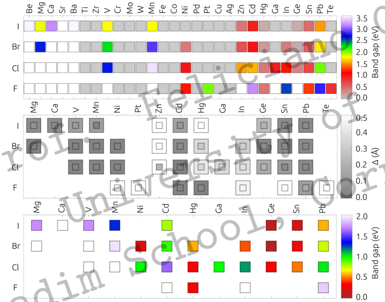
Brittle fracture in silicon

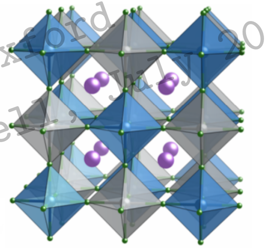


Kermode et al, Nature 455, 1224 (2008)

Examples of DFT calculations

Rational design of halide perovskites





Filip, Giustino, J. Phys. Chem. C, 120, 166 (2016)

Volonakis, Filip, Haghighirad, Sakai, Wenger, Snaith, Giustino, JPC Lett. 7, 1254 (2016)

Examples of DFT calculations

Rational design of halide perovskites

Filip, Giustino, J. Phys. Chem. C, 120, 166 (2016)
Volonakis, Filip, Haghighirad, Sakai, Wenger, Snaith, Giustino, JPC Lett. 7, 1254 (2016)

Timeline of DFT methods

1964 Hohenberg–Kohn theorem and Kohn–Sham formulation

1972 Relativistic extension of density functional theory

1980 Local density approximation for exchange and correlation

1984 Time-dependent density functional theory

1985 First-principles molecular dynamics

1986 Quasiparticle corrections for insulators

1987 Density functional perturbation theory

1988 Towards quantum chemistry accuracy

1991 Hubbard-corrected density functional theory

1996 The generalized gradient approximation

Exponential rate of progress in the past two decades...

What is DFT so popular?

- **Transferability**
  We can use the same code/methods for very different materials
- **Simplicity**
  The Kohn-Sham equations are the closest thing to the usual Schrödinger equation that we can think of
- **Reliability**
  Often we can predict materials properties with high accuracy, sometimes even before the actual experiment
- **Software sharing**
  The development of DFT has become a global enterprise, eg open source and collaborative software development
- **Reasonable starting point**
  Often the shortcomings of DFT can be cured by using more sophsticated approaches, which still use DFT as their starting point

PARADIM

An introduction to density functional theory for experimentalists

Feliciano Giustino

University of Oxford

25–29 July 2016

Lecture 1.2

Many-body problem

Many-body Schrödinger equation

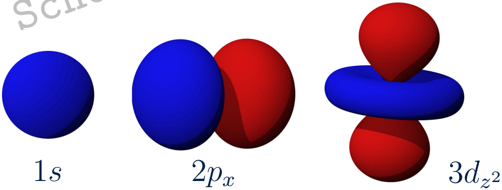
Materials = Electrons + Nuclei

- Schrödinger equation for the H atom (nucleus at $\mathbf{r} = 0$)

$$-\frac{\hbar^2}{2m_e}\nabla^2\psi(\mathbf{r}) - \frac{e^2}{4\pi\epsilon_0}\frac{1}{|\mathbf{r}|}\psi(\mathbf{r}) = E_{\text{tot}}\psi(\mathbf{r})$$

- wavefunctions of H

[from Wikipedia]



Many-body Schrödinger equation

- Many-body wavefunction (to fix ideas: only 3 electrons)

$$\psi(\mathbf{r}) \to \Psi = \Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$$

- Probability of finding electron #1 at the point $\mathbf{r}$

$$\mathrm{prob}(\mathbf{r}_1 = \mathbf{r}) = \int |\Psi(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3)|^2 \, d\mathbf{r}_2 d\mathbf{r}_3$$

- Electron density at the point $\mathbf{r}$

$$n(\mathbf{r}) = \mathrm{prob}(\mathbf{r}_1 = \mathbf{r}) + \mathrm{prob}(\mathbf{r}_2 = \mathbf{r}) + \mathrm{prob}(\mathbf{r}_3 = \mathbf{r})$$

- Electrons are indistinguishable

$$n(\mathbf{r}) = 3 \int |\Psi(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3)|^2 \, d\mathbf{r}_2 d\mathbf{r}_3$$

Many-body Schrödinger equation

$$(\,\text{kinetic energy} + \text{potential energy}\,)\,\Psi = E_{\text{tot}}\Psi$$

- kinetic energy, electrons and nuclei

$$-\sum_{i=1}^{N}\frac{\hbar^2}{2m_e}\nabla_i^2-\sum_{I=1}^{M}\frac{\hbar^2}{2M_I}\nabla_I^2$$

- potential energy, electron-electron repulsion

$$\frac{1}{2}\sum_{i\neq j}\frac{e^2}{4\pi\epsilon_0}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}$$

- potential energy, nucleus-nucleus repulsion

$$\frac{1}{2}\sum_{I\neq J}\frac{e^2}{4\pi\epsilon_0}\frac{Z_I Z_J}{|\mathbf{R}_I-\mathbf{R}_J|}$$

- potential energy, electron-nucleus attraction

$$-\sum_{i,I}\frac{e^2}{4\pi\epsilon_0}\frac{Z_I}{|\mathbf{r}_i-\mathbf{R}_I|}$$

Many-body Schrödinger equation

$$\left[-\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{4\pi\epsilon_0}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}\right.$$

$$\left.+\frac{1}{2}\sum_{I\neq J}\frac{e^2}{4\pi\epsilon_0}\frac{Z_I Z_J}{|\mathbf{R}_I-\mathbf{R}_J|} - \sum_{i,I}\frac{e^2}{4\pi\epsilon_0}\frac{Z_I}{|\mathbf{r}_i-\mathbf{R}_I|}\right]\Psi = E_{\mathrm{tot}}\Psi$$

Hartree atomic units

- masses in units of m_{e} (electron mass)
- lengths in units of a_0 (Bohr radius)
- energies in units of $e^2/4\pi\epsilon_0 a_0$ (Hartree)

$$\left[-\sum_i \frac{1}{2}\nabla_i^2 - \sum_I \frac{1}{2M_I}\nabla_I^2 + \frac{1}{2}\sum_{i\neq j}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}\right.$$

$$\left.+\frac{1}{2}\sum_{I\neq J}\frac{Z_I Z_J}{|\mathbf{R}_I-\mathbf{R}_J|} - \sum_{i,I}\frac{Z_I}{|\mathbf{r}_i-\mathbf{R}_I|}\right]\Psi = E_{\mathrm{tot}}\Psi$$

Many-body Schrödinger equation

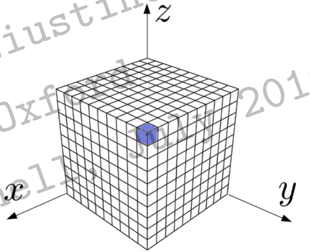
MBSE

MBSE in Hartree units

Exponential wall

Storage requirements for the many-body wavefunction of a unit cell of silicon (diamond structure)

- $\Delta x \sim 0.1$ Å
- $a = 5.43$ Å
- $N_{\rm p} = (a^3/4)/(\Delta x)^3 \sim 40,000$
- 8 valence electrons per unit cell
- $\Psi = 40,000^8$ complex numbers



$$\boxed{10^{26} \text{ Terabytes}}$$

Clamped nuclei approximation

Set nuclear masses $M_I = \infty$:

$$\left[-\sum_i \frac{1}{2}\nabla_i^2 - \cancel{\sum_I \frac{1}{2M_I}\nabla_I^2} + \frac{1}{2}\sum_{i\neq j}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}\right.$$

$$\left. + \cancel{\frac{1}{2}\sum_{I\neq J}\frac{Z_I Z_J}{|\mathbf{R}_I-\mathbf{R}_J|}} - \sum_{i,I}\frac{Z_I}{|\mathbf{r}_i-\mathbf{R}_I|}\right]\Psi = E_{\mathrm{tot}}\Psi$$

$$\boxed{\left[-\sum_i \frac{\nabla_i^2}{2} + \sum_i V_{\mathrm{n}}(\mathbf{r}_i) + \frac{1}{2}\sum_{i\neq j}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}\right]\Psi = E\,\Psi}$$

Electronic structure theory in a nutshell

Independent electrons approximation

- Independent particle Hamiltonian

$$\hat{H}_0(\mathbf{r}) = -\frac{1}{2}\nabla^2 + V_{\mathrm{n}}(\mathbf{r})$$

- Independent particles + Coulomb

$$\sum_i \hat{H}_0(\mathbf{r}_i)\Psi(\mathbf{r}_1,\dots\mathbf{r}_N) + \cancel{\frac{1}{2}\sum_{i\neq j}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}}\Psi(\mathbf{r}_1,\dots\mathbf{r}_N) = E\ \Psi(\mathbf{r}_1,\dots\mathbf{r}_N)$$

- If we neglect this electron-electron Coulomb repulsion, then electrons will not ‘feel’ each other → probability of independent events

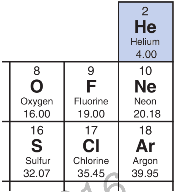
$$\Psi(\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{r}_N) = \phi_1(\mathbf{r}_1)\cdots\phi_N(\mathbf{r}_N)$$

$$\hat{H}_0(\mathbf{r})\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r})$$

$$\sum_i \hat{H}_0(\mathbf{r}_i)\Psi(\mathbf{r}_1,\dots\mathbf{r}_N) = E\ \Psi(\mathbf{r}_1,\dots\mathbf{r}_N)$$

$$\boxed{E = \varepsilon_1 + \cdots + \varepsilon_N}$$

Example: Ground state of He



		2 **He** Helium 4.00
8 **O** Oxygen 16.00	9 **F** Fluorine 19.00	10 **Ne** Neon 20.18
16 **S** Sulfur 32.07	17 **Cl** Chlorine 35.45	18 **Ar** Argon 39.95

- Idependent particle equation ($Z = 2$)

$$-\frac{1}{2}\nabla^2\phi(\mathbf{r}) - \frac{2}{|\mathbf{r}|}\phi(\mathbf{r}) = \varepsilon\phi(\mathbf{r})$$

- Lowest-energy solution

$$\phi_{1s}(\mathbf{r}) = \frac{2^{3/2}}{\sqrt{\pi}}\exp\left(-2|\mathbf{r}|\right) \quad \text{with} \quad E_{1s} = -\frac{2^2}{2}$$

- Ground-state many-body wavefunction in the *independent-electrons approximation*

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \phi_{1s}(\mathbf{r}_1)\phi_{1s}(\mathbf{r}_2) = \frac{8}{\pi}\exp\left[-2(|\mathbf{r}_1| + |\mathbf{r}_2|)\right]$$

- Ground-state energy in the *independent-electrons approximation*

$$E = 2E_{1s} = -4 \text{ Ha} = -108.8 \text{ eV}$$

Exclusion principle

- Let us calculate the electron density for 2 electrons in the independent-electron approximation

$$n(\mathbf{r}) = 2\int |\Psi(\mathbf{r},\mathbf{r}_2)|^2\, d\mathbf{r}_2 = 2\int |\phi_1(\mathbf{r})|^2 |\phi_2(\mathbf{r}_2)|^2\, d\mathbf{r}_2 = 2\,|\phi_1(\mathbf{r})|^2$$

- Admissible wavefunctions must be *antisymmetric* w.r.t. exchange of space/spin variables. 'Slater determinant' for a spin-compensated system

$$\Psi(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{\sqrt{2}}\left[\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) - \phi_1(\mathbf{r}_2)\phi_2(\mathbf{r}_1)\right]$$

- Let us try the density again

$$n(\mathbf{r}) = 2\int |\Psi(\mathbf{r},\mathbf{r}_2)|^2\, d\mathbf{r}_2 = \boxed{|\phi_1(\mathbf{r})|^2 + |\phi_2(\mathbf{r})|^2}$$

Mean-field approximation

- The electron density can be used to determine the electrostatic field generated by the electrons

$$\left[-\frac{1}{2}\nabla^2 + V_\mathrm{n}(\mathbf{r})\right]\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2$$

$$V_\mathrm{H}(\mathbf{r}) = \int d\mathbf{r}'\,\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

$$\left[-\frac{1}{2}\nabla^2 + V_\mathrm{n}(\mathbf{r}) + V_\mathrm{H}(\mathbf{r})\right]\phi_i'(\mathbf{r}) = \varepsilon_i'\phi_i'(\mathbf{r})$$

- This is Hartree's **self-consistent field approximation** (1928)

Advantages	No need for the many-body wavefunction
Shortcomings	Requires iterative solution

Exchange energy

- The Hartree approximation does not incorporate the constraint on the antisymmetry of the many-body wavefunction, $\Psi(\mathbf{r}_2, \mathbf{r}_1) = -\Psi(\mathbf{r}_{,}\mathbf{r}_2)$

- Incorporating this constraint in the mean-field equation leads to a new potential energy contribution, the **Fock exchange**
  [Sec. 2.8 and App. A of book]

$$\left[-\frac{\nabla^2}{2} + V_\mathrm{n}(\mathbf{r}) + V_\mathrm{H}(\mathbf{r})\right] \phi_i(\mathbf{r}) + \int d\mathbf{r}' V_\mathrm{X}(\mathbf{r}, \mathbf{r}')\, \phi_i(\mathbf{r}') = \varepsilon_i\, \phi_i(\mathbf{r})$$

$$V_\mathrm{X}(\mathbf{r}, \mathbf{r}') = -\sum_{j\in\mathrm{occ}} \frac{\phi_j^*(\mathbf{r}')\phi_j(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|}$$

- The Fock potential ‘enforces’ Pauli’s principle by making sure that
  - same-spin electrons repel each other
  - opposite-spin electrons attract each other

- The Fock potential is **non-local**

Correlation energy

- So far we assumed that electrons are independent, that is *uncorrelated*

$$\mathrm{prob}(\mathbf{r}_1, \mathbf{r}_2) = \mathrm{prob}(\mathbf{r}_1) \times \mathrm{prob}(\mathbf{r}_2)$$

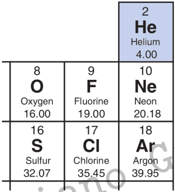
- This is not true since electrons do repel each other, therefore the 'true' wavefunction cannot be expressed as a Slater determinant

$$\Psi_{\mathrm{true}}(\mathbf{r}_1, \mathbf{r}_2) \neq \frac{1}{\sqrt{2}} \left[\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) - \phi_1(\mathbf{r}_2)\phi_2(\mathbf{r}_1) \right]$$

- Since the Slater determinant is really useful for practical calculations, we keep using it, but we **pay the price** of adding yet another potential

$$\left[-\frac{1}{2}\nabla^2 + V_{\mathrm{n}} + V_{\mathrm{H}} + V_{\mathrm{X}} + \underset{\substack{\uparrow \\ \text{correlation} \\ \text{potential}}}{V_{\mathrm{c}}} \right] \phi_i = \varepsilon_i \, \phi_i$$

Example: Ground state of He



Kinetic energy + electron-nucleus interaction	-3.89 Ha	-105.8 eV
Hartree energy	$+2.05$ Ha	$+55.8$ eV
Fock exchange energy	-1.02 Ha	-27.8 eV
Correlation energy	-0.04 Ha	-1.1 eV
Total energy	-2.90 Ha	-78.9 eV

Kohn-Sham equations

$$\boxed{\left[-\frac{1}{2}\nabla^2 + V_{\rm n} + V_{\rm H} + \underset{\uparrow}{V_{xc}}\right]\phi_i = \varepsilon_i\,\phi_i}$$

Exchange and Correlation

An introduction to density functional theory for experimentalists

Feliciano Giustino

University of Oxford

25–29 July 2016

Lecture 2.1

Density-functional theory

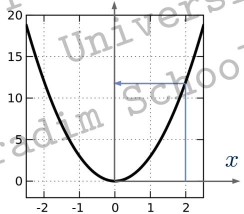
Functionals

Density **F**unctional **T**heory = theory about the energy of electrons being a functional of their density

Function

number ⟶ number

$g(x) = 3x^2$

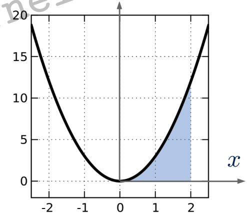


$g(2) = 12$

Functional

function ⟶ number

$g(x) = 3x^2$



$F[g] = \int_0^2 dx\, g(x) = 8$

Functionals

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The total energy is a functional of the wavefunction

$$\hat{H}\,\Psi = E\,\Psi \;\longrightarrow\; E = \int d\mathbf{r}_1 \dots d\mathbf{r}_N\; \Psi^*(\mathbf{r}_1,\dots,\mathbf{r}_N)\,\hat{H}\,\Psi(\mathbf{r}_1,\dots,\mathbf{r}_N)$$

So for a generic quantum state we have

$$\Psi(\mathbf{r}_1,\dots,\mathbf{r}_N) \longrightarrow E \qquad\qquad E = E[\Psi(\mathbf{r}_1,\dots,\mathbf{r}_N)]$$

Hohenberg and Kohn (1964) discovered that, if we are talking about the lowest-energy state, we also have

$$n(\mathbf{r}) \longrightarrow E \qquad\qquad E = E[n(\mathbf{r})]$$

The total energy is a functional of the density

Hohenberg-Kohn theorem

In Lecture 1.2 we had:

$$\left[-\sum_i \frac{\nabla_i^2}{2} + \sum_i V_{\rm n}(\mathbf{r}_i) + \frac{1}{2}\sum_{i\neq j}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}\right]\Psi = E\,\Psi$$

In order to prove the HK theorem we rewrite the energy more compactly

$$E = \int d\mathbf{r}\, n(\mathbf{r}) V_{\rm n}(\mathbf{r}) + \langle\Psi|\hat{U}|\Psi\rangle, \qquad \hat{U} = -\sum_i \frac{\nabla_i^2}{2} + \frac{1}{2}\sum_{i\neq j}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}$$

Now we want to show the following

Theorem

In the ground-state, the electron density $n(\mathbf{r})$ uniquely determines the external potential $V_{\rm n}(\mathbf{r})$

Hohenberg-Kohn theorem

- Assume there are two potentials V_1 and V_2 for the same density
  [For clarity we temporarily suppress the subscript 'n' in V_{n}]
- By solving the MBSE for each potential we find the lowest-energy states E_1, Ψ_1 and E_2, Ψ_2, respectively
- Since Ψ_1 **is** the ground state of V_1 we have

$$\int nV_1 + \langle \Psi_1 | \hat{U} | \Psi_1 \rangle = E_1$$

- Since Ψ_1 **is not** the ground state of V_2 we have

$$\int nV_2 + \langle \Psi_1 | \hat{U} | \Psi_1 \rangle > E_2$$

- The difference gives

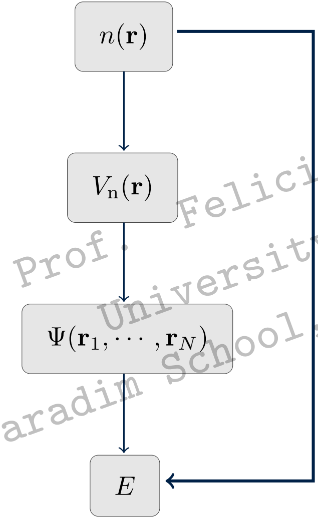
$$\int n(V_1 - V_2) > E_1 - E_2$$

- By repeating the same argument starting from Ψ_2 we have

$$\int n(V_2 - V_1) > E_2 - E_1$$

- The sum of the last two equations yields the contradiction $0 > 0$

Hohenberg-Kohn theorem



HK theorem

In the ground-state the electron density $n(\mathbf{r})$ uniquely determines the total energy E

HK variational principle

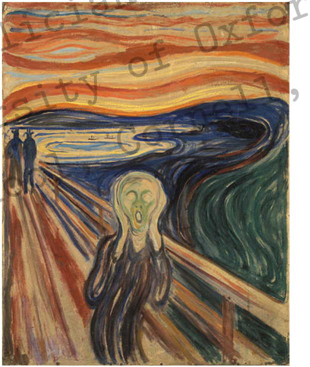
Any $n'(\mathbf{r}) \neq n(\mathbf{r})$ yields $V' \neq V$ and $\Psi' \neq \Psi$, therefore $E' > E$.

The energy functional

The HK theorem states that, in the ground state, the total energy of many electrons is a functional of their density, $E = E[n(\mathbf{r})]$.

But what is the form of this functional?

The energy functional is unknown



The scream by E. Munch (1910)

The energy functional

$$E[n] = \underbrace{\int d\mathbf{r}\, n(\mathbf{r}) V_{\rm n}(\mathbf{r})}_{\text{External potential}} + \underbrace{\frac{1}{2}\int d\mathbf{r}\, d\mathbf{r}' \,\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}}_{\text{Hartree energy}} + \boxed{\text{Everything Else}}$$

Kohn and Sham (1965) proposed to

(1) express the electron density
<u>as if</u> we had a system of independent electrons

$$n(\mathbf{r}) = \sum_{i\in\text{occ}} |\phi_i(\mathbf{r})|^2$$

(2) isolate the kinetic energy of these independent electrons from the 'Everything Else' above

$$\boxed{\text{Everything Else}} = -\sum_i \int d\mathbf{r}\, \phi_i^*(\mathbf{r}) \frac{\nabla^2}{2} \phi_i(\mathbf{r}) + \boxed{\textbf{Unknown Terms}}$$

Exchange and Correlation

E_{xc}

Kohn-Sham equations

Total energy

$$E[n] = \int d\mathbf{r}\, n(\mathbf{r}) V_{\rm n}(\mathbf{r}) + \frac{1}{2}\int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} - \sum_i \int d\mathbf{r}\, \phi_i^*(\mathbf{r}) \frac{\nabla^2}{2} \phi_i(\mathbf{r}) + E_{xc}[n]$$

We find the lowest energy state by looking for stationary points of $E[n]$

[the derivation can be found in Appendix B of the book]

$$\begin{cases} \dfrac{\delta E}{\delta n} = 0 \\ \langle \phi_i | \phi_j \rangle = \delta_{ij} \end{cases}$$

This leads to the Kohn-Sham equations

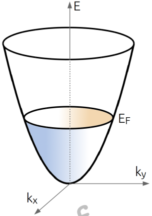
$$\boxed{\left[-\frac{1}{2}\nabla^2 + V_{\rm n}(\mathbf{r}) + V_{\rm H}(\mathbf{r}) + V_{xc}(\mathbf{r})\right] \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r})}$$

$$V_{xc} = \frac{\delta E_{xc}}{\delta n}$$

Exchange and Correlation Potential

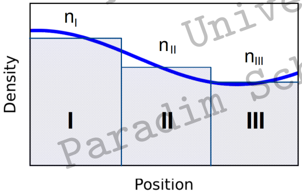
LDA – Local Density Approximation

Homogeneous electron gas



$$n(\mathbf{r}) = \text{constant}$$

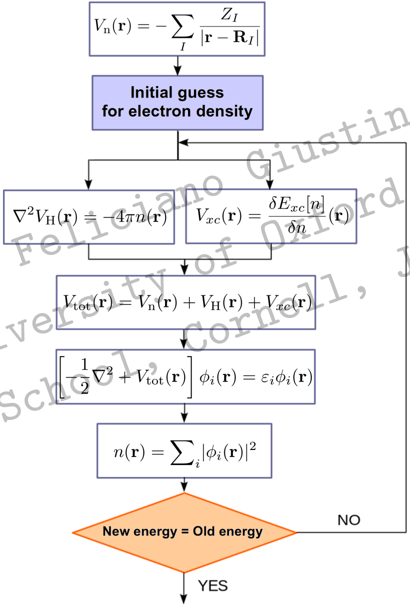
$$E_x^{\text{HEG}} = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{\frac{1}{3}} n^{\frac{4}{3}} V$$



$$E_x^{\text{LDA}} = \int_V \frac{E_x^{\text{HEG}}[n(\mathbf{r})]}{V} d\mathbf{r} = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{\frac{1}{3}} \int_V n^{\frac{4}{3}}(\mathbf{r}) d\mathbf{r}$$

$$V_x^{\text{LDA}} = \frac{\delta E_x^{\text{LDA}}}{\delta n} = -\left(\frac{3}{\pi}\right)^{\frac{1}{3}} n^{\frac{1}{3}}(\mathbf{r})$$

SCF – Self-consistent field calculations



$$V_{\mathrm{n}}(\mathbf{r}) = -\sum_I \frac{Z_I}{|\mathbf{r}-\mathbf{R}_I|}$$

Initial guess for electron density

$$\nabla^2 V_{\mathrm{H}}(\mathbf{r}) = -4\pi n(\mathbf{r})$$

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

$$V_{\mathrm{tot}}(\mathbf{r}) = V_{\mathrm{n}}(\mathbf{r}) + V_{\mathrm{H}}(\mathbf{r}) + V_{xc}(\mathbf{r})$$

$$\left[-\frac{1}{2}\nabla^2 + V_{\mathrm{tot}}(\mathbf{r})\right]\phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2$$

New energy = Old energy

Successes and failures

	1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8	9 8B	10	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1	1 **H** Hydrogen 1.01																	2 **He** Helium 4.00
2	3 **Li** Lithium 6.94	4 **Be** Beryllium 9.01											5 **B** Boron 10.81	6 **C** Carbon 12.01	7 **N** Nitrogen 14.01	8 **O** Oxygen 16.00	9 **F** Fluorine 19.00	10 **Ne** Neon 20.18
3	11 **Na** Sodium 22.99	12 **Mg** Magnesium 24.31											13 **Al** Aluminum 26.98	14 **Si** Silicon 28.09	15 **P** Phosphorus 30.97	16 **S** Sulfur 32.07	17 **Cl** Chlorine 35.45	18 **Ar** Argon 39.95
4	19 **K** Potassium 39.10	20 **Ca** Calcium 40.08	21 **Sc** Scandium 44.96	22 **Ti** Titanium 47.87	23 **V** Vanadium 50.94	24 **Cr** Chromium 52.00	25 **Mn** Manganese 54.94	26 **Fe** Iron 55.85	27 **Co** Cobalt 58.93	28 **Ni** Nickel 58.69	29 **Cu** Copper 63.55	30 **Zn** Zinc 65.39	31 **Ga** Gallium 69.72	32 **Ge** Germanium 72.61	33 **As** Arsenic 74.92	34 **Se** Selenium 78.96	35 **Br** Bromine 79.90	36 **Kr** Krypton 83.80
5	37 **Rb** Rubidium 85.47	38 **Sr** Strontium 87.62	39 **Y** Yttrium 88.91	40 **Zr** Zirconium 91.22	41 **Nb** Niobium 92.91	42 **Mo** Molybdenum 95.94	43 **Tc** Technetium (98)	44 **Ru** Ruthenium 101.07	45 **Rh** Rhodium 102.91	46 **Pd** Palladium 106.42	47 **Ag** Silver 107.87	48 **Cd** Cadmium 112.41	49 **In** Indium 114.82	50 **Sn** Tin 118.71	51 **Sb** Antimony 121.76	52 **Te** Tellurium 127.60	53 **I** Iodine 126.90	54 **Xe** Xenon 131.29
6	55 **Cs** Cesium 132.91	56 **Ba** Barium 137.33	57 **La** Lanthanum 138.91	72 **Hf** Hafnium 178.49	73 **Ta** Tantalum 180.95	74 **W** Tungsten 183.84	75 **Re** Rhenium 186.21	76 **Os** Osmium 190.23	77 **Ir** Iridium 192.22	78 **Pt** Platinum 195.08	79 **Au** Gold 196.97	80 **Hg** Mercury 200.59	81 **Tl** Thallium 204.38	82 **Pb** Lead 207.2	83 **Bi** Bismuth 208.98	84 **Po** Polonium (209)	85 **At** Astatine (210)	86 **Rn** Radon (222)
7	87 **Fr** Francium (223)	88 **Ra** Radium (226)	89 **Ac** Actinium (227)	104 **Rf** Rutherfordium (261)	105 **Db** Dubnium (262)	106 **Sg** Seaborgium (266)	107 **Bh** Bohrium (264)	108 **Hs** Hassium (269)	109 **Mt** Meitnerium (268)									

58 **Ce** Cerium 140.12	59 **Pr** Praseodymium 140.91	60 **Nd** Neodymium 144.24	61 **Pm** Promethium (145)	62 **Sm** Samarium 150.36	63 **Eu** Europium 151.96	64 **Gd** Gadolinium 157.25	65 **Tb** Terbium 158.93	66 **Dy** Dysprosium 162.50	67 **Ho** Holmium 164.93	68 **Er** Erbium 167.26	69 **Tm** Thulium 168.93	70 **Yb** Ytterbium 173.04	71 **Lu** Lutetium 174.97
90 **Th** Thorium 232.04	91 **Pa** Protactinium 231.04	92 **U** Uranium 238.03	93 **Np** Neptunium (237)	94 **Pu** Plutonium (244)	95 **Am** Americium (243)	96 **Cm** Curium (247)	97 **Bk** Berkelium (247)	98 **Cf** Californium (251)	99 **Es** Einsteinium (252)	100 **Fm** Fermium (257)	101 **Md** Mendelevium (258)	102 **No** Nobelium (259)	103 **Lr** Lawrencium (262)

An introduction to density functional theory for experimentalists

Feliciano Giustino

University of Oxford

25–29 July 2016

Lecture 2.2

Planewaves and pseudopotentials

Born-von Kármán boundary conditions

DFT calculations require the numerical solution of the KS equations

$$\boxed{-\frac{1}{2}\nabla^2\phi_i(\mathbf{r}) + V_{\mathrm{tot}}(\mathbf{r})\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r})}$$

2^{nd} order PDE ⟶ for every y and z we need 2 boundary conditions on x

- **Localized system**
  atom | molecule | nanocrystal
  $\phi_i(x,y,z) = 0 \;\text{ for }\; x = -\infty, \qquad \phi_i(x,y,z) = 0 \;\text{ for }\; x = +\infty$

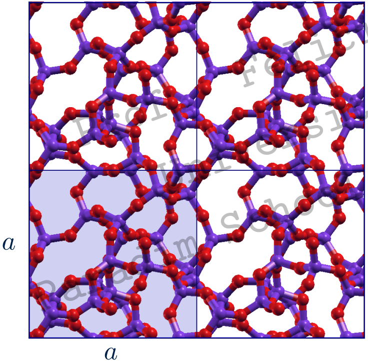
- **Extended system**
  solid | liquid
  $\phi_i(x+a,y,z) = \phi_i(x,y,z), \qquad \nabla\phi_i(x+a,y,z) = \nabla\phi_i(x,y,z)$

Periodic (BvK) boundary conditions

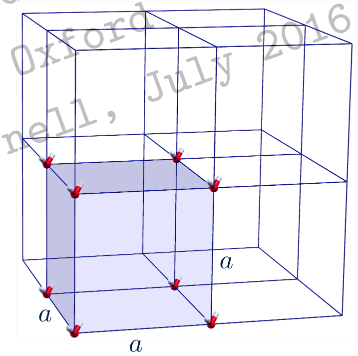
Born-von Kármán boundary conditions

DFT calculations for solids, liquids, interfaces, and nanostructures
are performed using BvK boundary conditions

amorphous SiO_2

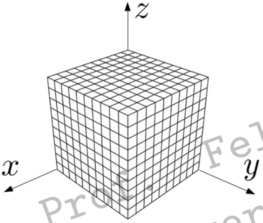


H_2O molecule

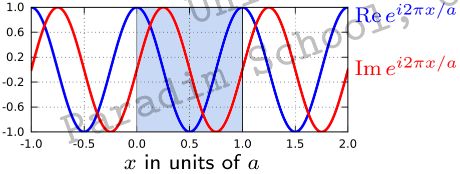


Planewaves

A convenient way of handling the KS wavefunctions is by expanding them in a basis of planewaves ⟶ standard Fourier transform



1D case $\phi(x) = \sum_{n=-\infty}^{+\infty} c_n \, \mathrm{e}^{i2\pi nx/a}$



BvK conditions built in

$$\phi(x+a) = \phi(x)$$

$$\nabla\phi(x+a) = \nabla\phi(x)$$

Planewaves

In 2D and 3D we replace $2\pi/a$ by the primitive vectors of the reciprocal lattice, eg

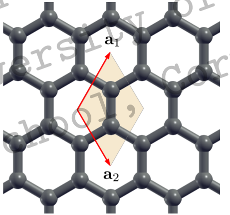
$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3}$$

Reciprocal lattice vectors

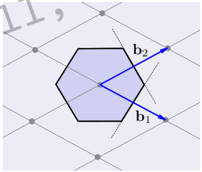
$$\mathbf{G} = m_1\mathbf{b}_1 + m_2\mathbf{b}_2 + m_3\mathbf{b}_3, \text{ with } m_1, m_2, m_3 \text{ integers}$$

Example: graphene

direct lattice



reciprocal lattice



Planewave in 2D or 3D

$$\boxed{\exp(i\mathbf{G}\cdot\mathbf{r})}$$

Planewaves

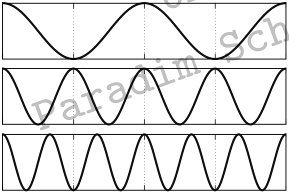
Kohn-Sham wavefunction in a basis of planewaves

$$\phi_i(\mathbf{r}) = \sum_{\mathbf{G}} c_i(\mathbf{G}) \exp(i\mathbf{G}\cdot\mathbf{r})$$

By replacing in the KS equations we obtain

$$\boxed{\frac{|\mathbf{G}|^2}{2} c_i(\mathbf{G}) + \sum_{\mathbf{G}'} V_{\mathrm{tot}}(\mathbf{G}-\mathbf{G}') c_i(\mathbf{G}') = \varepsilon_i\, c_i(\mathbf{G})}$$

How many planewave **G**-vectors should we include in the expansion?



$|\mathbf{G}| = 2\pi/a$

$|\mathbf{G}| = 2\cdot 2\pi/a$

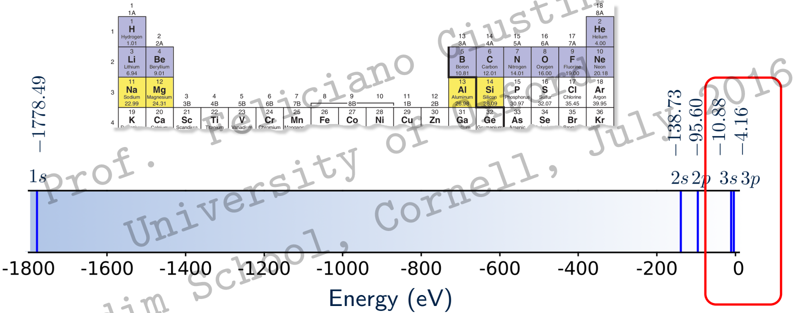
$|\mathbf{G}| = 3\cdot 2\pi/a$

$$\boxed{E_{\mathrm{cut}} = \frac{|\mathbf{G}_{\mathrm{max}}|^2}{2}}$$

planewaves kinetic energy cutoff

Pseudopotentials

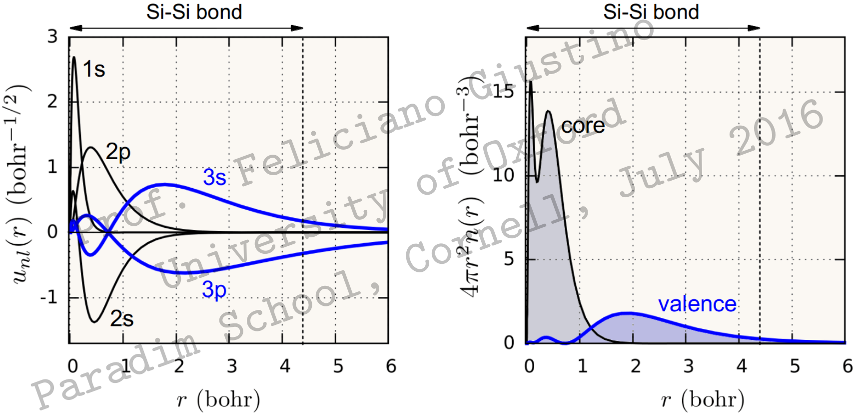
Atomic levels of silicon (DFT/LDA)



Only valence electrons are important for bonding and structure

Pseudopotentials

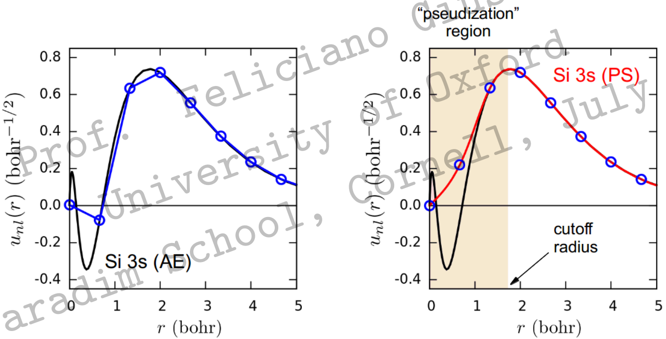
Atomic wavefunctions of silicon (DFT/LDA)



$$\psi_{nl}(\mathbf{r}) = \frac{u_{nl}(r)}{r} Y_{lm}\left(\frac{\mathbf{r}}{r}\right)$$

Pseudopotentials

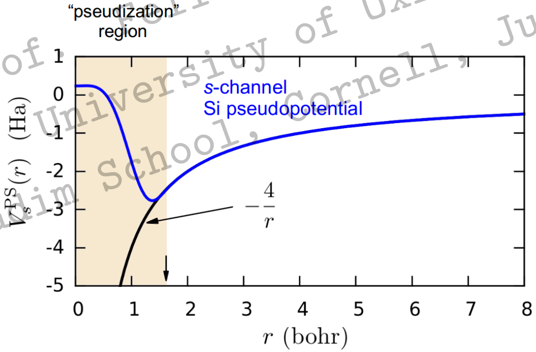
Contain planewaves cutoff by removing nodes ⟶ pseudization



Pseudopotentials

Reverse-engineer the pseudo-potential potential which gives the pseudo-wavefunction as solution of the atomic Schrödinger equation

$$-\frac{1}{2}\frac{d^2}{dr^2}\,u_{3s}^{\mathrm{PS}} + V_{3s}^{\mathrm{PS}}\,u_{3s}^{\mathrm{PS}} = E_{3s}\,u_{3s}^{\mathrm{PS}} \longrightarrow V_{3s}^{\mathrm{PS}} = E_{3s} + \frac{1}{2u_{3s}^{\mathrm{PS}}}\frac{d^2u_{3s}^{\mathrm{PS}}}{dr^2}$$



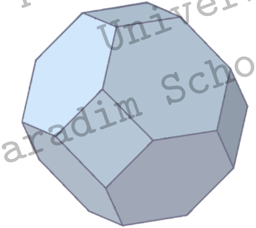
Brillouin zone sampling

In **crystalline** solids we label electronic states by their Bloch wavevector $\mathbf{k}$

[see books by Kittel or Ashcroft & Mermin]

Bloch theorem $\phi_{i\mathbf{k}}(\mathbf{r}) = \mathrm{e}^{i\mathbf{k}\cdot\mathbf{r}} u_{i\mathbf{k}}(\mathbf{r})$ with $u_{i\mathbf{k}}(\mathbf{r}+\mathbf{R}) = u_{i\mathbf{k}}(\mathbf{r})$

$$n(\mathbf{r}) = \sum_{i\in occ} |\phi_i(\mathbf{r})|^2 \longrightarrow \sum_{i\in occ} \int_{\mathrm{BZ}} \frac{d\mathbf{k}}{\Omega_{\mathrm{BZ}}} |u_{i\mathbf{k}}(\mathbf{r})|^2 \simeq \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k}\in\mathrm{BZ}} \sum_{i\in occ} |u_{i\mathbf{k}}(\mathbf{r})|^2$$



Brillouin zone of *fcc* crystal (eg silicon)

DFT codes use a uniform discretization of this volume, and reduce the number of $\mathbf{k}$-vectors using the crystal symmetry operations

An introduction to density functional theory for experimentalists

Feliciano Giustino

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25–29 July 2016

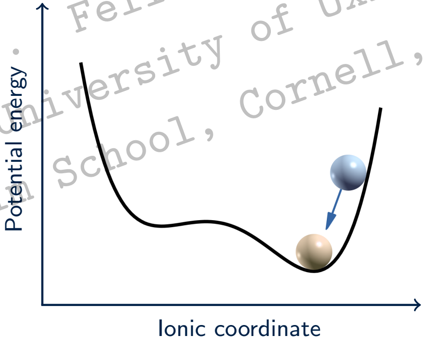
Lecture 3.1

Equilibrium structures

Equilibrium structures

In order to find the equilibrium structures of materials

1) We determine the **potential energy surface** of the ions
2) We look for the minima of this surface $\longrightarrow$ zero net forces on the ions



Born-Oppenheimer approximation

~~Clamped nuclei approximation~~

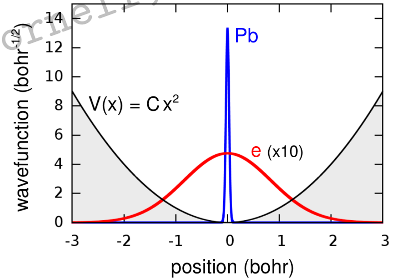
Back to the complete many-body Schrödinger equation for electrons & nuclei

$$\left[-\sum_i \frac{\nabla_i^2}{2} - \sum_I \frac{\nabla_I^2}{2M_I} - \sum_{i,I}\frac{Z_I}{|\mathbf{r}_i-\mathbf{R}_I|} + \frac{1}{2}\sum_{i\neq j}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|} + \frac{1}{2}\sum_{I\neq J}\frac{Z_I Z_J}{|\mathbf{R}_I-\mathbf{R}_J|}\right]\Psi = E_{\rm tot}\Psi$$

Here $\Psi = \Psi(\mathbf{r}_1,\dots,\mathbf{r}_N,\mathbf{R}_1,\dots,\mathbf{R}_M)$

Example: the wavefunction of an electron vs the wavefunction of the Pb nucleus

$$-\frac{1}{2M}\frac{d^2\psi(x)}{dx^2} + Cx^2\psi(x) = E\psi(x)$$



Born-Oppenheimer approximation

Born and Oppenheimer (1927) proposed the following approximation

- Factorize the electron-nuclear wavefunction

$$\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N,\mathbf{R}_1,\ldots,\mathbf{R}_M) \simeq \Psi_{\mathbf{R}}(\mathbf{r}_1,\ldots,\mathbf{r}_N)\,\chi(\mathbf{R}_1,\ldots,\mathbf{R}_M)$$

- Find the electronic part as the ground state of Schrödinger equation with the nuclei clamped at $\mathbf{R}_1,\ldots,\mathbf{R}_M$

$$\left[-\sum_i \frac{\nabla_i^2}{2} + \sum_i V_{\rm n}(\mathbf{r}_i;\mathbf{R}) + \frac{1}{2}\sum_{i\neq j}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}\right]\Psi_{\mathbf{R}} = E(\mathbf{R}_1,\ldots,\mathbf{R}_M)\,\Psi_{\mathbf{R}}$$

- Replace the result in the complete MBSE of the previous slide

$$\boxed{\left[-\sum_I \frac{\nabla_I^2}{2M_I} + \frac{1}{2}\sum_{I\neq J}\frac{Z_I Z_J}{|\mathbf{R}_I-\mathbf{R}_J|} + E(\mathbf{R}_1,\ldots,\mathbf{R}_M)\right]\chi = E_{\rm tot}\,\chi}$$

Schrödinger equation for nuclei

Potential energy surface

$$\underbrace{-\sum_I \frac{\nabla_I^2}{2M_I}}_{\text{Kinetic Energy}} \chi + \underbrace{\left[\frac{1}{2}\sum_{I\neq J}\frac{Z_I Z_J}{|\mathbf{R}_I-\mathbf{R}_J|} + E(\mathbf{R}_1,\ldots,\mathbf{R}_M)\right]}_{\text{Potential Energy}} \chi = E_{\rm tot}\,\chi$$

Potential energy surface

$$U(\mathbf{R}_1,\ldots,\mathbf{R}_M) = \frac{1}{2}\sum_{I\neq J}\frac{Z_I Z_J}{|\mathbf{R}_I-\mathbf{R}_J|} + E(\mathbf{R}_1,\ldots,\mathbf{R}_M)$$

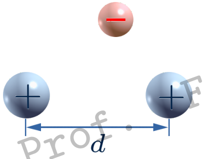
Coulomb repulsion
between positive nuclei

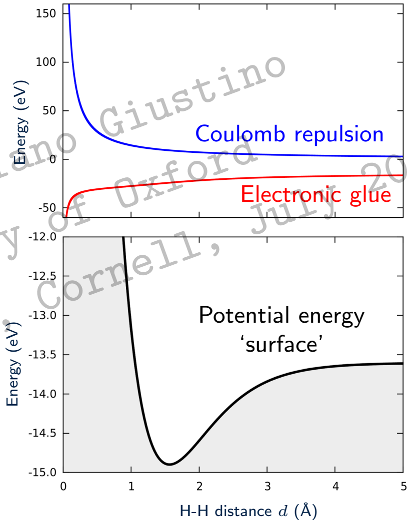
Glue resulting from the
negative charge of the electrons
(we get this from **DFT**)

Potential energy surface

H_2^+ molecular ion

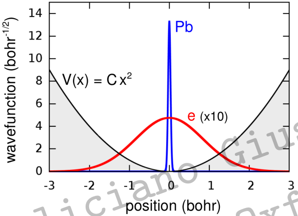
Example from Exercise 4.4 of the book





Classical nuclei

From slide #4



$$-\sum_I \frac{\nabla_I^2}{2M_I} + U(\mathbf{R}_1,\ldots,\mathbf{R}_M) \xrightarrow{\text{classical nuclei}} \sum_I \frac{\mathbf{P}_I^2}{2M_I} + U(\mathbf{R}_1,\ldots,\mathbf{R}_M)$$

$$\boxed{M_I \frac{d^2\mathbf{R}_I}{dt^2} = \mathbf{F}_I = -\frac{\partial U}{\partial \mathbf{R}_I}}$$

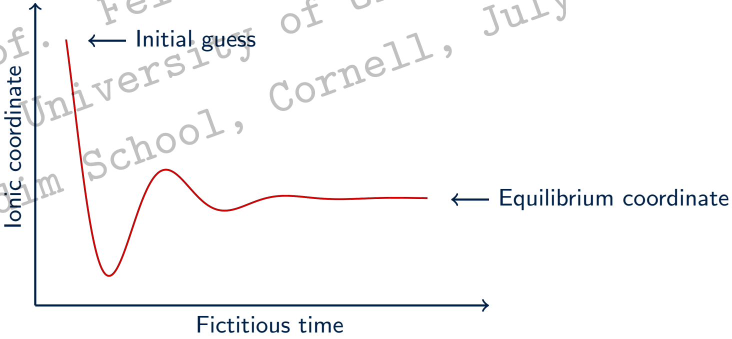
Newton's equation for nuclei

Structural optimization

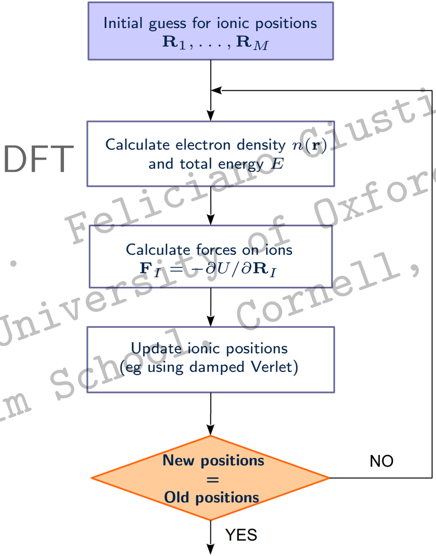
Finding the minima of the PES using damped molecular dynamics

$$M\frac{d^2x}{dt^2} = -\frac{\partial U}{\partial x} \underbrace{-\frac{2M}{\tau}\frac{dx}{dt}}_{\text{Friction term}}$$

(Verlet) $M\frac{x_{i+1}-2x_i+x_{i-1}}{\Delta t^2} = -\frac{U(x_i)-U(x_{i-1})}{x_i-x_{i-1}} - \frac{2M}{\tau}\frac{x_{i+1}-x_{i-1}}{2\Delta t}$



Structural optimization



Initial guess for ionic positions
$\mathbf{R}_1, \ldots, \mathbf{R}_M$

DFT

Calculate electron density $n(\mathbf{r})$
and total energy E

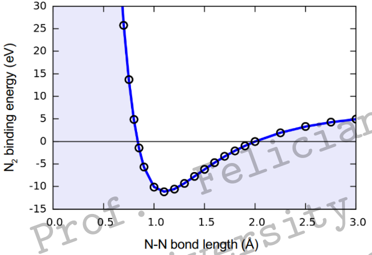
Calculate forces on ions
$\mathbf{F}_I = -\partial U / \partial \mathbf{R}_I$

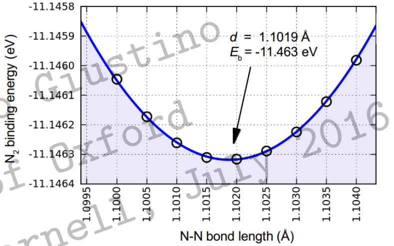
Update ionic positions
(eg using damped Verlet)

New positions
=
Old positions

Examples

Simplest case of structural optimization: N_2 diatomic molecule



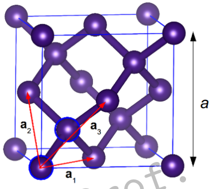


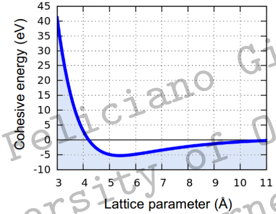
	DFT/LDA	Experiment	Rel. Error
bond length (Å)	1.102	1.098	0.4%
binding energy (eV)	11.46	9.76	17%

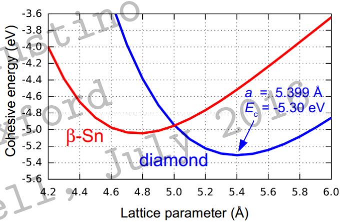
Note Nitrogen is $[1s^2]2s^2p^3$, therefore it has a spin $S = 3/2$ after the first Hund's rule. These calculations are spin-unpolarized (N_2 has 14 electrons), therefore the result at large separation is higher than twice the energy of one N atom

Examples

Structural optimization of bulk crystals: Silicon



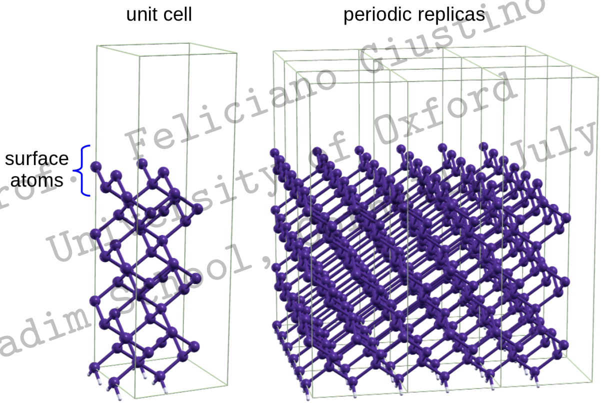




	DFT/LDA	Experiment	Rel. Error
lattice parameter (Å)	5.40	5.43	0.6%
cohesive energy (eV)	5.30	4.62	15%

Examples

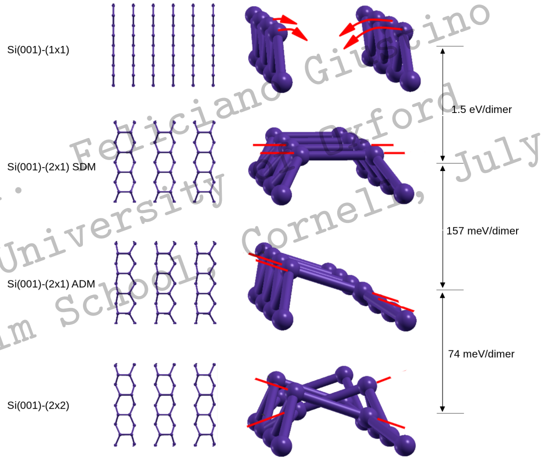
Structural optimization of surfaces: Clean Si(001) surface



52 Si atoms | 13 layers | 8 H atoms for passivation | 4 layers kept fixed

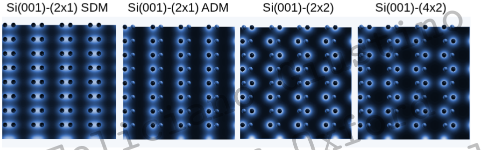
Examples

Structural optimization of surfaces: Clean Si(001) surface

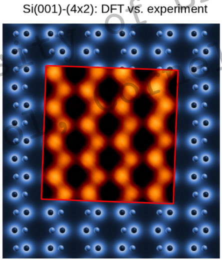


Examples

Comparison between calculated and measured STM images



Si(001)-(2x1) SDM Si(001)-(2x1) ADM Si(001)-(2x2) Si(001)-(4x2)



Si(001)-(4x2): DFT vs. experiment

Experimental STM image courtesy of T. Yokoyama
`http://dx.doi.org/10.1103/PhysRevB.61.R5078`

An introduction to density functional theory for experimentalists

Feliciano Giustino

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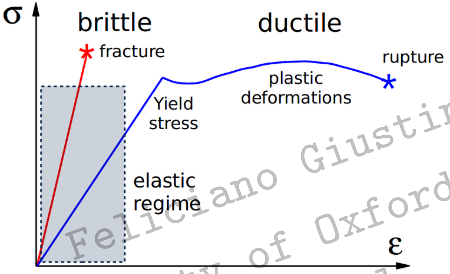
25–29 July 2016

Lecture 3.2

Elastic properties

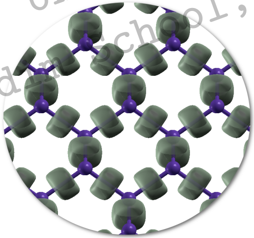
Elastic properties

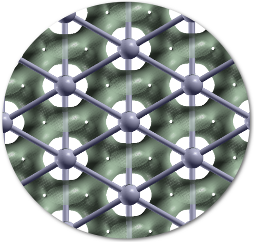


silicon (diamond structure)

bcc tungsten

brittle

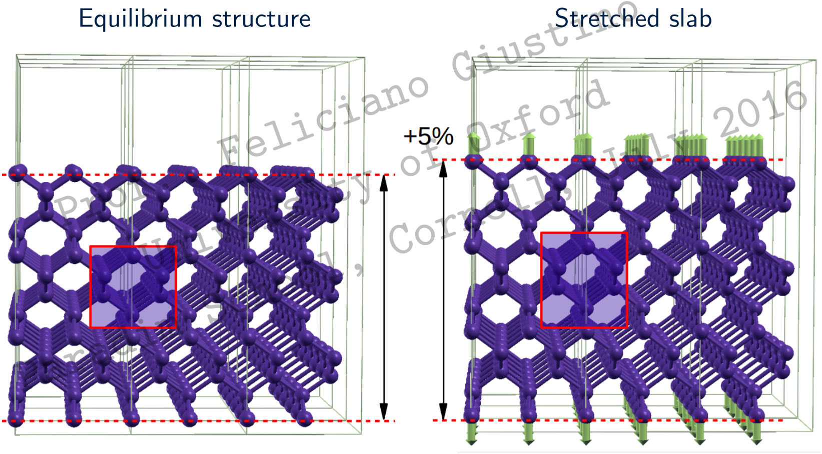




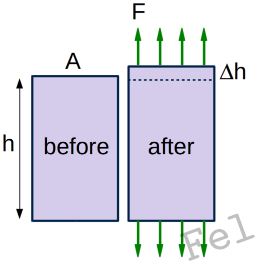
ductile

Heuristic approach

Notion of stress and strain: a **computer experiment** on silicon



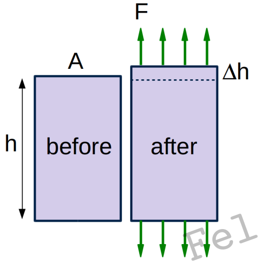
Heuristic approach



$$\sigma = \frac{F_{\text{tot}}}{A} \qquad \epsilon = \frac{\Delta h}{h} \qquad \sigma = Y\epsilon$$

transverse size	7.635 Å
no. of surface atoms	4
force per atom	0.682 eV/Å
σ	7.5 GPa
ϵ	5%
Y	150 GPa
experiment	166 GPa
deviation	11%

General theory



Work-energy theorem

The work of external forces on a system equals the increase of its total potential and kinetic energies

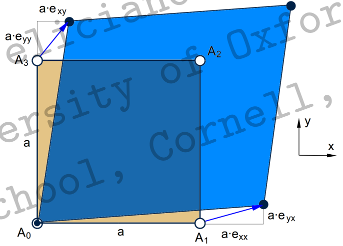
$$\Delta U = \int_h^{h+\Delta h} F(z)dz = Ah \int_h^{h+\Delta h} \frac{F(z)}{A}\frac{dz}{h} = \Omega \int_0^{\epsilon} \sigma\, d\epsilon = \Omega \int_0^{\epsilon} C\,\epsilon\, d\epsilon = \frac{1}{2}\Omega\, C\, \epsilon^2$$

$$\frac{1}{\Omega}\frac{\partial U}{\partial \epsilon} = C\epsilon = \sigma \qquad \frac{1}{\Omega}\frac{\partial^2 U}{\partial \epsilon^2} = C$$

General theory

General transformation of the atomic coordinates: the **strain tensor**

$$R'_{I\alpha} = \sum_{\beta} (\delta_{\alpha\beta} + \mathrm{e}_{\alpha\beta}) R_{I\beta}$$



$$\sigma_{\alpha\beta} = \frac{1}{\Omega} \frac{\partial U}{\partial \epsilon_{\alpha\beta}} \qquad \frac{\Delta U}{\Omega} = \frac{1}{2}\, \epsilon_{\alpha\beta}\, \epsilon_{\gamma\delta}$$

General theory

Voigt notation

$$\epsilon_{\alpha\beta} = \begin{pmatrix} \epsilon_{xx} & \epsilon_{xy} & \epsilon_{xz} \\ \epsilon_{xy} & \epsilon_{yy} & \epsilon_{yz} \\ \epsilon_{xz} & \epsilon_{yz} & \epsilon_{zz} \end{pmatrix} \longrightarrow \epsilon_i = \begin{pmatrix} \epsilon_1 & \epsilon_6 & \epsilon_5 \\ & \epsilon_2 & \epsilon_4 \\ & & \epsilon_3 \end{pmatrix}$$

Engineering strain

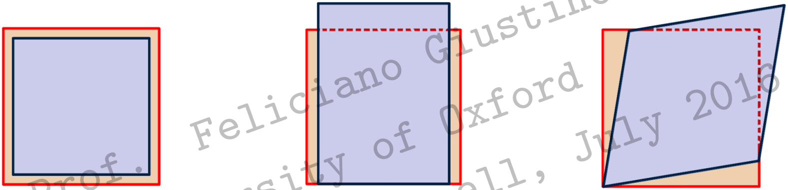
$$\frac{\Delta U}{\Omega} = \frac{1}{2} C_{ij} u_i u_j \qquad \text{with} \qquad u_i = \begin{cases} \epsilon_i & \text{if } i = 1,2,3 \\ 2\epsilon_i & \text{if } i = 4,5,6 \end{cases}$$

$6^2 = 36$ constants
(21 independent)

Example: Cubic system

$$C_{ij} = \begin{pmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{pmatrix}$$

Practical calculations



Isotropic deformation

$$u_1 = u_2 = u_3 = \eta$$
$$u_4 = u_5 = u_6 = 0$$

$$\frac{\Delta U}{\Omega} = \frac{3}{2}(C_{11} + 2C_{12})\,\eta^2$$

Tetragonal deformation

$$u_1 = u_2 = -\eta$$
$$u_3 = 2\eta$$
$$u_4 = u_5 = u_6 = 0$$

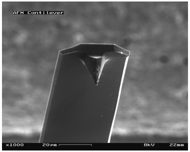
$$\frac{\Delta U}{\Omega} = 3(C_{11} - C_{12})\,\eta^2$$

Trigonal deformation

$$u_1 = u_2 = u_3 = 0$$
$$u_4 = u_5 = 0$$
$$u_6 = \eta$$

$$\frac{\Delta U}{\Omega} = \frac{1}{2}C_{44}\,\eta^2$$

Practical calculations



en.wikipedia.org/wiki/Cantilever

Elastic constants of silicon in GPa

	DFT/LDA	Experiment	Rel. Error
C_{11}	161	165.6	3%
C_{12}	62	63.9	3%
C_{44}	78	79.5	2%

en.wikipedia.org/wiki/Tungsten

Bulk modulus of tungsten in GPa

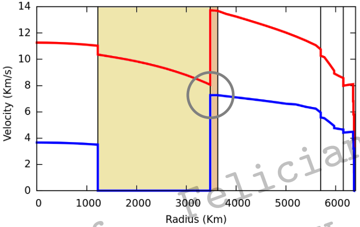
$$B = \Omega \frac{\partial^2 U}{\partial \Omega^2} = \frac{1}{3}(C_{11} + 2C_{12})$$

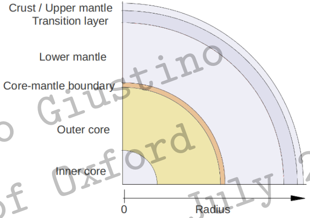
	DFT/LDA	Experiment	Rel. Error
B	328	314	4%

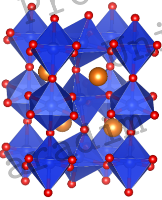
Practical calculations

- The stress tensor can also be calculated in DFT w/o considering explicit distortions (stress theorem)
  Nielsen and Martin, Phys. Rev. Lett. 50, 697 (1983)
- It is possible to perform DFT calculations for an abritrary external load → common to study pressure-dependence
  Parrinello and Rahman, J. Appl. Phys. 52, 7182 (1981)

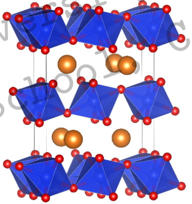
Example: Post-perovskite $MgSiO_3$



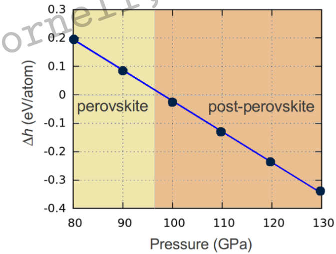




perovskite



post-perovskite



Iitaka et al, Nature 430, 442 (2004)

PARADIM

An introduction to density functional theory for experimentalists

Feliciano Giustino

University of Oxford

25–29 July 2016

Lecture 4.1

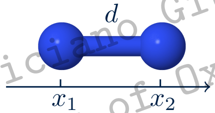
Phonons in DFT

Harmonic approximation

From Lecture 3.1 (slide 8): Newton's equation for classical ions

$$M_I \frac{d^2\mathbf{R}_I}{dt^2} = -\frac{\partial U}{\partial \mathbf{R}_I} \longleftarrow \text{Potential energy surface from DFT}$$

N$_2$ molecule



$$M_\mathrm{N}\frac{d^2x_1}{dt^2} = -\frac{\partial U}{\partial x_1}$$

$$M_\mathrm{N}\frac{d^2x_2}{dt^2} = -\frac{\partial U}{\partial x_2}$$

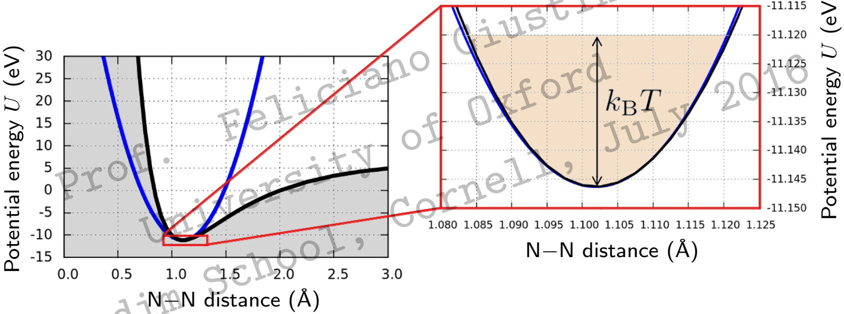
mathematical detail

$$\begin{aligned}\frac{\partial U}{\partial x_1} &= \frac{\partial U}{\partial \overline{x}}\frac{\partial \overline{x}}{\partial x_1} - \frac{\partial U}{\partial d}\frac{\partial d}{\partial x_1} \\ &= \frac{1}{2}\frac{\partial U}{\partial \overline{x}} - \frac{\partial U}{\partial d}\end{aligned}$$

$$M_\mathrm{N}\,\ddot{d} = M_\mathrm{N}\frac{d^2}{dt^2}(x_2 - x_1) = -\left(\frac{\partial U}{\partial x_2} - \frac{\partial U}{\partial x_1}\right) = -2\frac{\partial U}{\partial d}$$

Harmonic approximation

$$\frac{M_{\rm N}}{2}\,\ddot{d} = -\frac{\partial U}{\partial d}$$



$$U(d) = U_0 + \frac{1}{2}K(d-d_0)^2 \longrightarrow \frac{\partial U}{\partial d} = K(d-d_0)$$

Harmonic approximation (Hooke's law)

Harmonic approximation

Stretching frequency of N_2

$$\ddot{d} = -\frac{2K}{M_\mathrm{N}}(d - d_0)$$

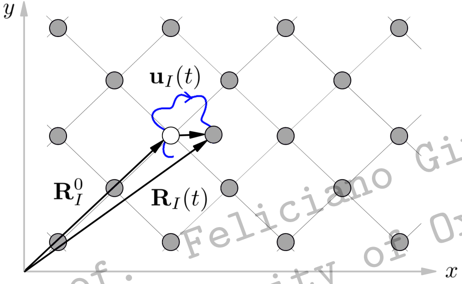
$$\omega_{\mathrm{N}_2} = \sqrt{\frac{2K}{M_\mathrm{N}}}$$

	DFT/LDA	experiment	deviation
$\hbar\omega_{\mathrm{N}_2}$ (meV)	288.9	300.4	4%

	harmonic	anharmonic	deviation
$\hbar\omega_{\mathrm{N}_2}$ (meV)	288.9	304.2	5%

[Excercise 8.1 of Book]

Vibrational eigenmodes and eigenvalues



$$\mathbf{R}_I(t) = \mathbf{R}_I^0 + \mathbf{u}_I(t)$$

$$M_I \ddot{\mathbf{u}}_I = -\frac{\partial U}{\partial \mathbf{u}_I}$$

Taylor expansion of potential energy surface for small displacements

$$U = U_0 + \cancel{\sum_{I\alpha} u_{I\alpha} \frac{\partial U}{\partial R_{I\alpha}}} + \frac{1}{2} \underbrace{\boxed{\sum_{I\alpha,J\beta} \frac{\partial^2 U}{\partial R_{I\alpha} \partial R_{J\beta}}}}_{K_{I\alpha,J\beta}} u_{I\alpha} u_{J\beta} + \cancel{\mathcal{O}(u^3)}$$

matrix of force constants

Vibrational eigenmodes and eigenvalues

Equation of motion in the harmonic approximation

$$M_I\, \ddot{u}_{I\alpha} = -\sum_{J\beta} K_{I\alpha,J\beta}\; u_{J\beta}$$

Try with $u_{I\alpha}(t) = u^0_{I\alpha} \exp(i\omega t)$ and rearrange

$$\sum_{J\beta} K_{I\alpha,J\beta}\; u^0_{J\beta} = M_I \omega^2 u^0_{I\alpha}$$

Get rid of masses

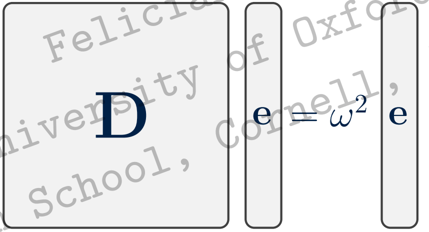
$$\sum_{J\beta} \underbrace{\boxed{\frac{K_{I\alpha,J\beta}}{\sqrt{M_I M_J}}}}_{D_{I\alpha,J\beta}} \underbrace{\boxed{\sqrt{M_J}u^0_{J\beta}}}_{e_{J\beta}} = \omega^2 \underbrace{\boxed{\sqrt{M_I}\, u^0_{I\alpha}}}_{e_{I\alpha}}$$

dynamical matrix — mass-scaled eigenmode

Vibrational eigenmodes and eigenvalues

Dynamical matrix

$$D_{I\alpha,J\beta} = \frac{1}{\sqrt{M_I M_J}} \left.\frac{\partial^2 U}{\partial R_{I\alpha}\partial R_{J\beta}}\right|_{\text{Eq.}}$$



$$\mathbf{D}\,\mathbf{e} = \omega^2\,\mathbf{e}$$

$3M \times 3M$
(M atoms)

Standard matrix eigenvalue problem

Calculations of vibrational frequencies

Frozen-phonon method

$$\frac{\partial^2 U}{\partial R_{I\alpha}^2} \simeq \frac{U(R_{I\alpha}^0 + u) - 2U_0 + U(R_{I\alpha}^0 - u)}{u^2}$$

or alternatively using the forces

$$\frac{\partial^2 U}{\partial R_{I\alpha}^2} \simeq - \frac{F_{I\alpha}(R_{I\alpha}^0 + u) - F_{I\alpha}(R_{I\alpha}^0 - u)}{2u}$$

Density-functional perturbation theory (DFPT)

The method of choice for crystals

[Baroni et al, Rev. Mod. Phys. 73, 515 (2001)]

Calculations of vibrational frequencies

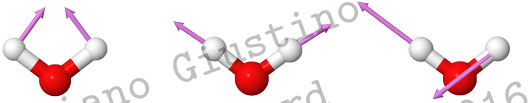
Example: water molecule

$$\hbar^2\mathbf{D} = \begin{pmatrix} 82 & 82 & -0 & -164 & -164 & -176 & -164 & -164 & 176 \\ & 82 & -0 & -164 & -164 & -176 & -164 & -164 & 176 \\ & & 103 & -136 & -136 & -206 & 136 & 136 & -206 \\ & & & 710 & 711 & 625 & -55 & -55 & -81 \\ & & & & 710 & 625 & -55 & -55 & -81 \\ & & & & & 791 & 81 & 81 & 31 \\ & & & & & & 710 & 711 & -625 \\ & & & & & & & 710 & -625 \\ & & & & & & & & 791 \end{pmatrix} \cdot 100\,\mathrm{meV}^2$$

$$\text{9 eigenvalues}\left\{\begin{array}{ll} 3 & \text{rigid-body translations} \\ 2 & \text{rigid-body librations} \\ 1 & \text{rigid-body spinning} \\ 3 & \text{internal vibrations} \end{array}\right.$$

Calculations of vibrational frequencies

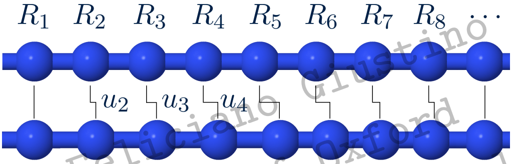
Example: water molecule



	bending	symmetric stretching	asymmetric stretching
DFT frequency (meV)	189	453	466
Expt. frequency (meV)	198	458	473
deviation	4.8%	1.1%	1.5%

Vibrations in crystals

Simplest model: 1D chain of atoms moving along 1 direction



$$M\ddot{u}_I = -\sum_J K_{IJ}\, u_J$$

Sound waves $\frac{1}{v_s^2}\frac{\partial^2 p}{\partial t^2} = \frac{\partial^2 p}{\partial x^2} \longrightarrow p(x,t) = p_0\, e^{i(qx-\omega t)}$

By analogy we can try $u_I(t) = u_0\, \mathrm{e}^{i(qR_I-\omega t)}$

Vibrations in crystals

$$M\,\omega^2\,\mathrm{e}^{iqR_I} = \sum_J K_{IJ}\,\mathrm{e}^{iqR_J}$$

$$\omega^2 = \frac{1}{M}\sum_J K_{IJ}\,\mathrm{e}^{iq(R_J-R_I)}$$

In crystals the force constants are **translationally invariant**, ie $K_{IJ} = K_{I+N,J+N}$

$$\omega^2(q) = \frac{1}{M}\sum_J K_{0J}\,\mathrm{e}^{iqR_J}$$

The eigenfrequencies are obtained as the Fourier transform of the force constants

Dynamical matrix for 2D/3D crystals

$$\boxed{D_{I\alpha,J\beta}(\mathbf{q}) = \frac{1}{\sqrt{M_I M_J}}\sum_{\mathbf{R}} e^{i\mathbf{q}\cdot\mathbf{R}}\mathrm{e}^{i\mathbf{q}\cdot(\tau_J-\tau_I)}\,K_{0I\alpha,\mathbf{R}J\beta}}$$

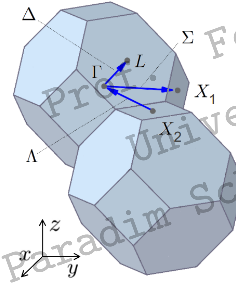
$\mathbf{R}$ reciprocal lattice vector

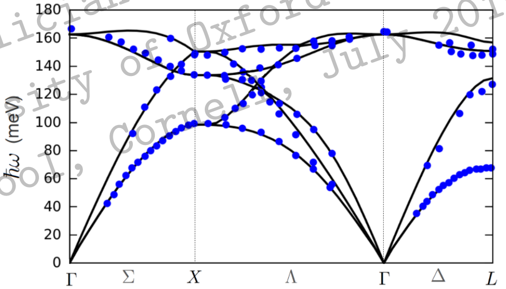
τ_I position of atom I in the primitive unit cell

Phonon dispersion relations

Example: diamond

en.wikipedia.org/wiki/Oppenheimer_Diamond



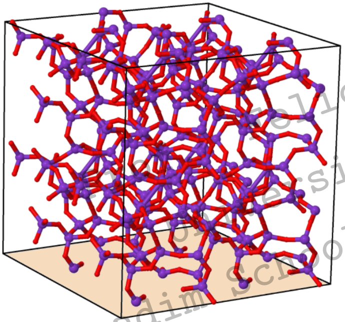


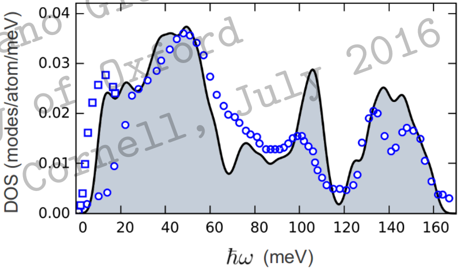
▬ DFT/LDA calculation

● Inelastic neutron scattering

Phonon density of states

Example: a-SiO_2





- ○ Inelastic neutron scattering
- ▬ DFT/LDA calculation

An introduction to density functional theory for experimentalists

Feliciano Giustino

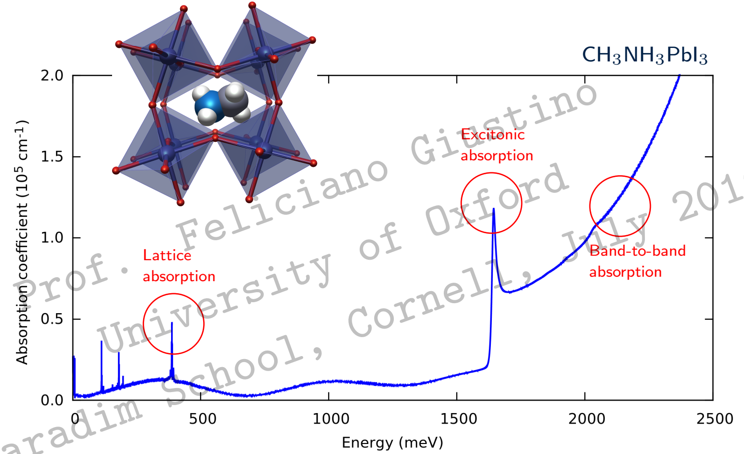
University of Oxford

25–29 July 2016

Lecture 4.2

IR spectra & dielectric constants

Infrared absorption spectrum



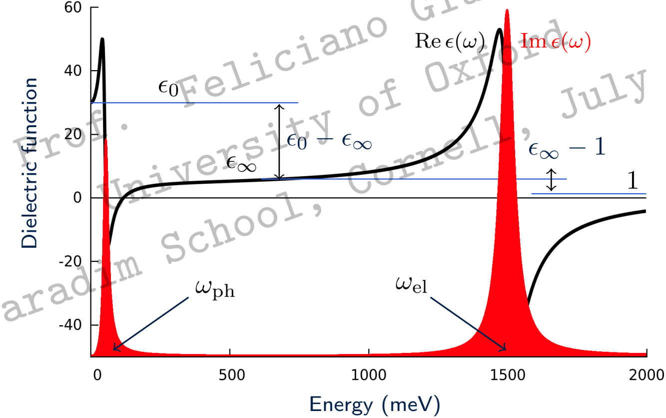
Experiment by R. Milot & M. Johnston

Perez et al, J. Phys. Chem. C 119, 25703 (2015)

Dielectric function

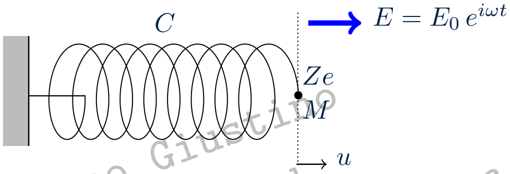
General structure of the frequency-dependent dielectric function

$$\epsilon(\omega) = 1 + \frac{\epsilon_\infty - 1}{1-(\omega/\omega_{\rm el})^2} + \frac{\epsilon_0 - \epsilon_\infty}{1-(\omega/\omega_{\rm ph})^2}$$



Simplified model

Classical point charge attached to spring



Equation of motion $M\ddot{u}(t) = -C\,u(t) + Ze\,E(t)$

Set $u(t) = u_0\, e^{i\omega t}$

We obtain $-M\omega^2 u_0 = -C\,u_0 + Ze\,E_0$

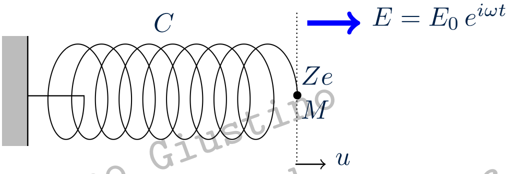
W/o electric field $-M\omega_0^2 u_0 = -C\,u_0$

Difference $M(\omega_0^2 - \omega^2)u_0 = Ze\,E_0$

Induced displacement $u_0 = \dfrac{e}{M}\dfrac{Z}{\omega_0^2 - \omega^2}E_0$

Simplified model

Classical point charge attached to spring



Induced displacement $u_0 = \dfrac{e}{M}\dfrac{Z}{\omega_0^2-\omega^2}E_0$

Macroscopic polarization
1 oscillator per unit cell of volume Ω

$$P(t) = \frac{1}{\Omega} Ze\, u(t) = P_0\, e^{i\omega t} \to P_0 = \frac{1}{\Omega} Ze\, u_0$$

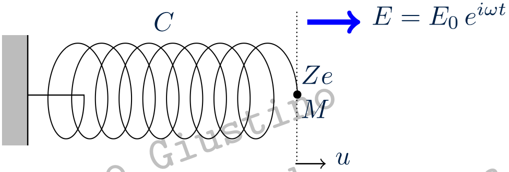
Dielectric function $P_0 + P_{\mathrm{el}} = \epsilon_0 \epsilon_1(\omega) E_0, \qquad P_{\mathrm{el}} = \epsilon_0 \epsilon^{\infty} E_0$

$$\epsilon_1(\omega) = \epsilon^{\infty} + \frac{e^2}{4\pi\epsilon_0}\frac{4\pi}{\Omega}\frac{1}{M}\frac{Z^2}{\omega_0^2-\omega^2}$$

Born charge $Z = \dfrac{\Omega}{e}\dfrac{\partial P_0}{\partial u_0}$ or $Z = \dfrac{1}{e}\dfrac{\partial F}{\partial E}$

Simplified model

Classical point charge attached to spring



Dielectric function
$$\epsilon_1(\omega) = \epsilon^\infty + \frac{e^2}{4\pi\epsilon_0}\frac{4\pi}{\Omega}\frac{1}{M}\frac{Z^2}{\omega_0^2-\omega^2}$$

Static dielectric constant
$$\epsilon_0 = \epsilon^\infty + \frac{e^2}{4\pi\epsilon_0}\frac{4\pi}{\Omega}\frac{1}{M}\frac{Z^2}{\omega_0^2}$$

IR intensity
[see Sec. 10.2.1 of Book]
$$I(\omega) \propto \omega\epsilon_2(\omega) \propto Z^2\delta(\omega-\omega_0)$$

DFT calculations

Low-frequency dielectric constant tensor $(\mathbf{q} \to 0)$

$$\epsilon_{1,\alpha\beta}(\omega) = {\epsilon_1}^{\infty}_{\alpha\beta} + \frac{e^2}{4\pi\varepsilon_0}\frac{4\pi}{\Omega}\frac{1}{M_0}\sum_n \frac{Z_{\alpha n} Z_{\beta n}}{\omega_n^2 - \omega^2}$$

high-frequency
dielectric constant

phonon frequencies
at $\mathbf{q} = 0$

DFT calculations

Low-frequency dielectric constant tensor ($\mathbf{q} \to 0$)

$$\epsilon_{1,\alpha\beta}(\omega) = \epsilon_{1}{}^{\infty}_{\alpha\beta} + \frac{e^2}{4\pi\varepsilon_0}\frac{4\pi}{\Omega}\frac{1}{M_0}\sum_n \frac{Z_{\alpha n} Z_{\beta n}}{\omega_n^2 - \omega^2}$$

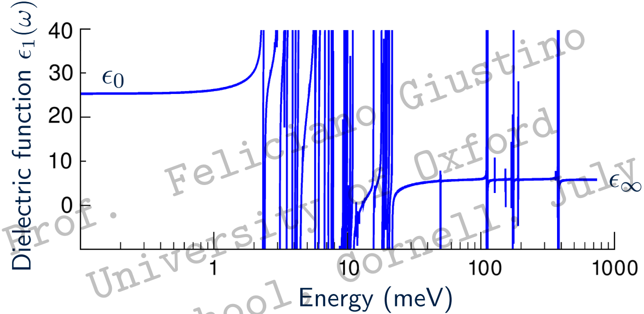
Mode effective charge vector $Z_{\alpha n} = \sum_{J\beta} Z^*_{J,\alpha\beta} \sqrt{\frac{M_0}{M_J}}\, e_{J\beta,n}$

Born effective charge tensor $Z^*_{J,\alpha\beta} = \frac{\Omega}{e}\,\frac{\partial P_\alpha}{\partial R_{J\beta}}$

Phonon eigenmodes at $\mathbf{q} = 0$

DFT calculations

Example: Dielectric constant of $CH_3NH_3PbI_3$

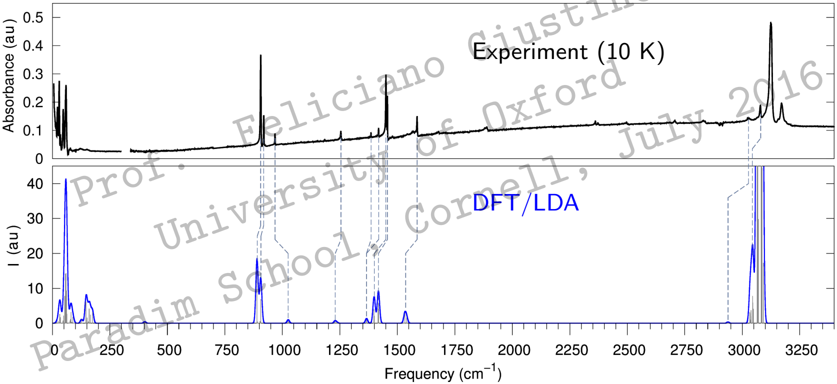


	DFT/LDA	Experiment	deviation
ϵ_∞	5.9	6.5	10%
ϵ_0	25.3	30.5	20%

Perez et al, J. Phys. Chem. C 119, 25703 (2015)

DFT calculations

Example: IR absorption of $CH_3NH_3PbI_3$



Perez et al, J. Phys. Chem. C 119, 25703 (2015)

Born effective charges

$$Z^*_{I,\alpha\beta} = \begin{cases} \dfrac{\Omega}{e}\dfrac{\partial P_\alpha}{\partial R_{I\beta}} & \text{Change of electronic polarization upon atomic displacement} \\ \boxed{\dfrac{1}{e}\dfrac{\partial F_{I\alpha}}{\partial E_\beta} \quad \text{Change of force on atom induced by macroscopic electric field}} \end{cases}$$

Most convenient for DFT calculations

MAPbI$_3$ (MA=CH$_3$NH$_3$)

	Nominal charge	Born charge tensor	Isotropic Born charge
Pb	+2	$\begin{matrix} 4.52 & -0.14 & -0.77 \\ -0.19 & 4.42 & 0.60 \\ 0.66 & -0.27 & 4.31 \end{matrix}$	+4.42
I	−1	$\begin{matrix} -0.58 & 0.00 & 0.08 \\ 0.01 & -4.15 & 0.01 \\ 0.16 & 0.01 & -0.92 \end{matrix}$	−1.88

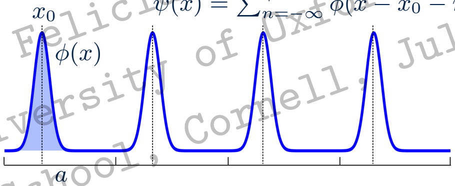
Polarization in extended systems

- A uniform electric field yields a potential which is unbounded in infinite crystals $V(x) = eEx \to \infty$ when $x \to \infty$
- Replace the position operator x by the **Berry-phase formula**

R.D. King-Smith and D. Vanderbilt, Phys. Rev. B (R) 47, 1651 (1993)

Simplified model

$$\psi(x) = \sum_{n=-\infty}^{+\infty} \phi(x - x_0 - na)$$



$$\langle\psi|e^{i\frac{2\pi x}{L}}|\psi\rangle = e^{i\frac{2\pi x_0}{L}}\langle\psi|e^{i\frac{2\pi(x-x_0)}{L}}|\psi\rangle = e^{i\frac{2\pi x_0}{L}}\left[1 + A/L^2 + iB/L^3 + \cdots\right]$$

$$\boxed{\frac{L}{2\pi}\mathrm{Im}\,\log\langle\psi|e^{i\frac{2\pi x}{L}}|\psi\rangle = x_0 \text{ mod L} + \mathcal{O}(1/L^2)}$$

An introduction to density functional theory for experimentalists

Feliciano Giustino

University of Oxford

25–29 July 2016

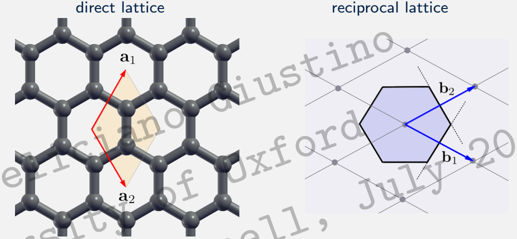
Lecture 5.1

Band structures & optical spectra

Band structures

From Lecture 2.2

Example: graphene



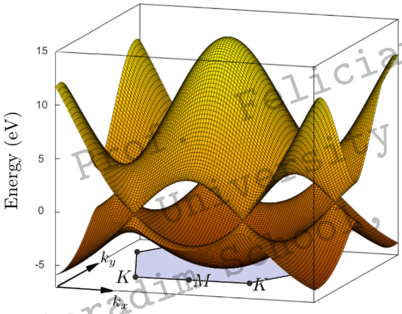
$$\phi_{i\mathbf{k}}(\mathbf{r}) = \mathrm{e}^{i\mathbf{k}\cdot\mathbf{r}} u_{i\mathbf{k}}(\mathbf{r}) \text{ with } u_{i\mathbf{k}}(\mathbf{r}) \text{ periodic}$$

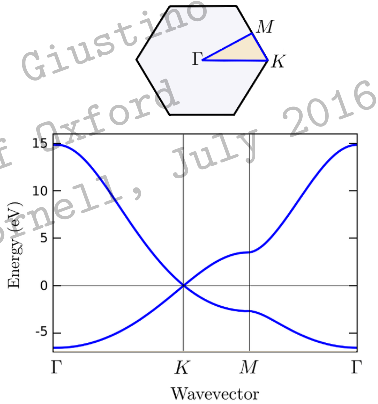
$$-\frac{1}{2}\nabla^2\phi_{i\mathbf{k}}(\mathbf{r})+V_{\text{tot}}(\mathbf{r})\phi_{i\mathbf{k}}(\mathbf{r}) = \boxed{\varepsilon_{i\mathbf{k}}}\phi_{i\mathbf{k}}(\mathbf{r})$$

k-dependent
KS eigenvalue

Band structures

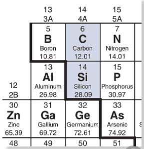
Example: simplified tight-binding model of graphene

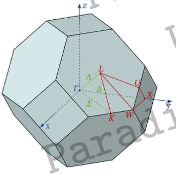


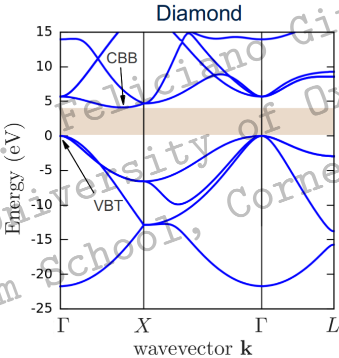


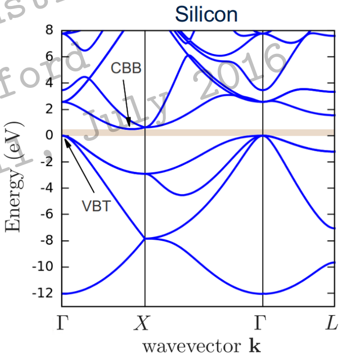
Band structures

Example: DFT/LDA band structures of common semiconductors



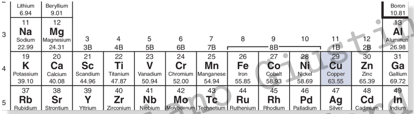




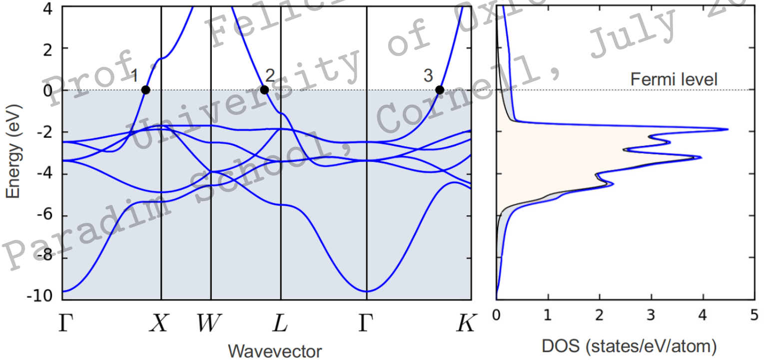


Fermi surfaces

Example: DFT/LDA band structure and Density of States of copper

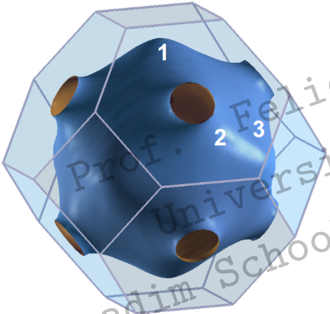


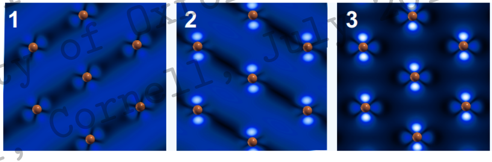
	Lithium 6.94	Beryllium 9.01											Boron 10.81
3	11 **Na** Sodium 22.99	12 **Mg** Magnesium 24.31	3 3B	4 4B	5 5B	6 6B	7 7B	8	9 8B	10	11 1B	12 2B	13 **Al** Aluminum 26.98
4	19 **K** Potassium 39.10	20 **Ca** Calcium 40.08	21 **Sc** Scandium 44.96	22 **Ti** Titanium 47.87	23 **V** Vanadium 50.94	24 **Cr** Chromium 52.00	25 **Mn** Manganese 54.94	26 **Fe** Iron 55.85	27 **Co** Cobalt 58.93	28 **Ni** Nickel 58.69	29 **Cu** Copper 63.55	30 **Zn** Zinc 65.39	31 **Ga** Gallium 69.72
5	37 **Rb** Rubidium	38 **Sr** Strontium	39 **Y** Yttrium	40 **Zr** Zirconium	41 **Nb** Niobium	42 **Mo** Molybdenum	43 **Tc** Technetium	44 **Ru** Ruthenium	45 **Rh** Rhodium	46 **Pd** Palladium	47 **Ag** Silver	48 **Cd** Cadmium	49 **In** Indium



Fermi surfaces

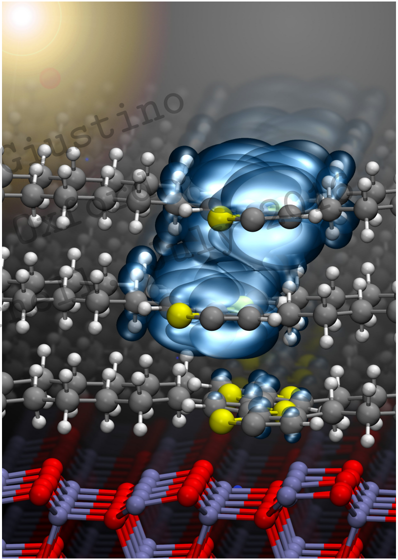
Example: DFT/LDA Fermi surface and wavefunctions of copper





Kohn-Sham wavefunctions

Example: Highest-occupied orbital
of P3HT on ZnO

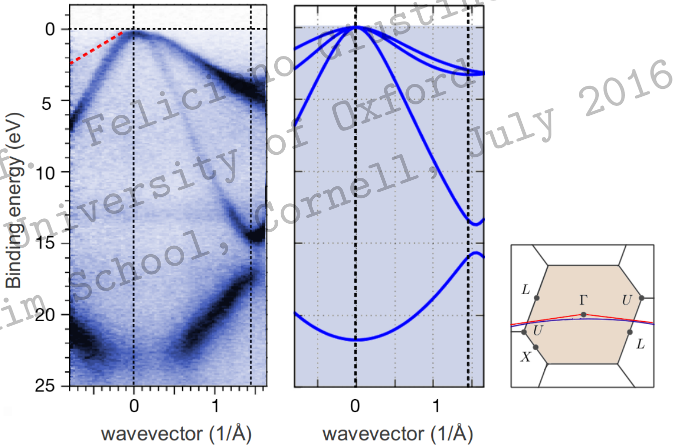


Noori & Giustino, Adv. Func. Mater. 22, 5089 (2012)

Meaning of band structures

- Are band structures real?

ARPES spectrum of diamond and DFT/LDA bands



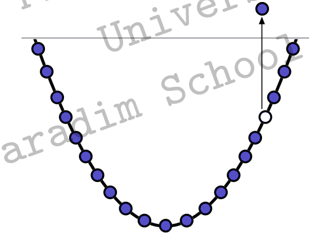
Experiment by
Prof. T. Yokoya
Okayama University

Meaning of band structures

The DFT total energy (Lecture 2.1) can be rewritten as

$$E[n] \; = \; \underbrace{\sum_i \frac{d\mathbf{k}}{\Omega_{\mathrm{BZ}}} f_{i\mathbf{k}}\, \varepsilon_{i\mathbf{k}}}_{\text{band structure term}} \; - \; \underbrace{\left[E_{\mathrm{H}} + \int d\mathbf{r}\, V_{xc}(\mathbf{r}) n(\mathbf{r}) - E_{xc} \right]}_{\text{double counting term}}$$

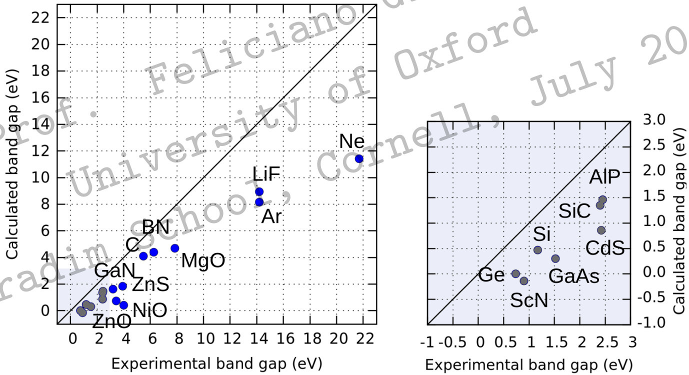
$f_{i\mathbf{k}}$ electron occupation



- If the double-counting term vanished, $\varepsilon_{i\mathbf{k}}$ would give the change of energy upon adding/removing one electron
- KS levels can be thought of as very rough approximations to addition/removal energies

Band gap problem

- DFT/LDA typically underestimates the band gaps of insulators and semiconductors
- Major challenge in materials design

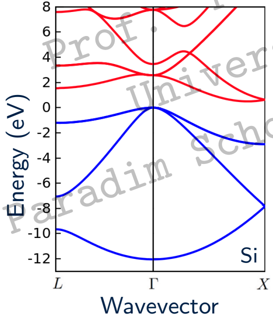


Dielectric function and optical spectra

From band structure & wavefunctions we can calculate UV/Vis spectra

$$\epsilon_2(\omega) = \frac{\pi\, e^2}{\varepsilon_0 m_e^2 \Omega} \frac{1}{\omega^2} \sum_{cv} \int \frac{d\mathbf{k}}{\Omega_{\mathrm{BZ}}} |\langle u_{c\mathbf{k}}|p_x|u_{v\mathbf{k}}\rangle|^2 \delta(\varepsilon_{c\mathbf{k}} - \varepsilon_{v\mathbf{k}} - \hbar\omega)$$

Independent-particle approximation

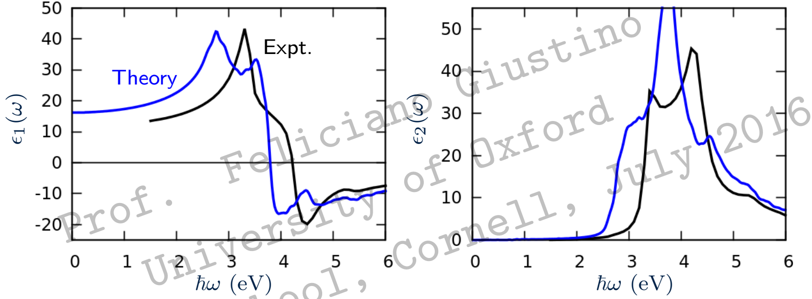


For a derivation see Chapter 10 of the Book

- Transitions from occupied to empty states
- Energy conservation
- Momentum conservation
- Oscillator strength given by electric dipole matrix element $\langle u_{c\mathbf{k}}|x|u_{v\mathbf{k}}\rangle$

Dielectric function and optical spectra

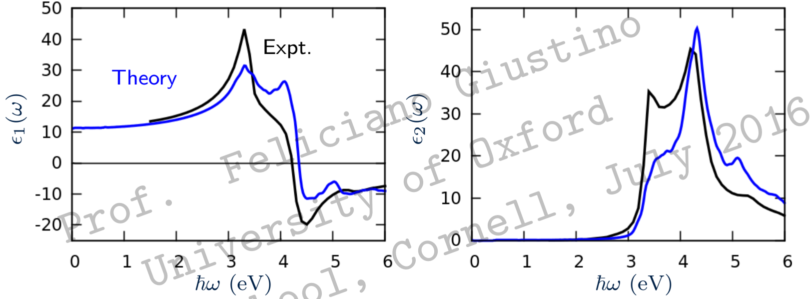
Example: Dielectric function of silicon



- DFT/LDA in the independent-particle approximation

Dielectric function and optical spectra

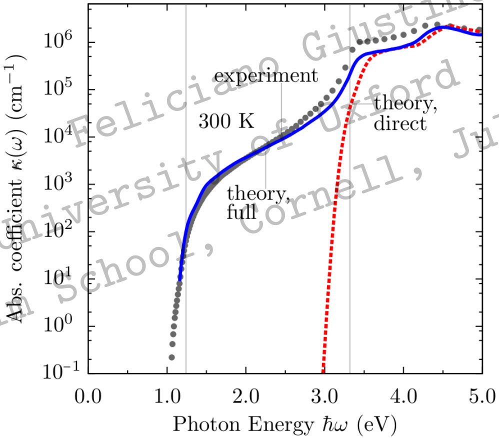
Example: Dielectric function of silicon



- DFT/LDA in the independent-particle approximation
- 'Scissor correction' of 0.55 eV
- Excitonic peak observed at 3.2 eV missing in the calculation
- Phonon-assisted absorption below 3 eV missing in the calculation

Dielectric function and optical spectra

Example: Optical absorption coefficient of silicon
including phonon-assisted processes



Zacharias, Patrick & Giustino, PRL 2015

PARADIM

An introduction to density functional theory for experimentalists

Feliciano Giustino

University of Oxford

25–29 July 2016

Lecture 5.2

DFT beyond the LDA

PBE exchange and correlation

Perdew, Burke & Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996)

- Within the LDA the XC energy is approximated using the local density

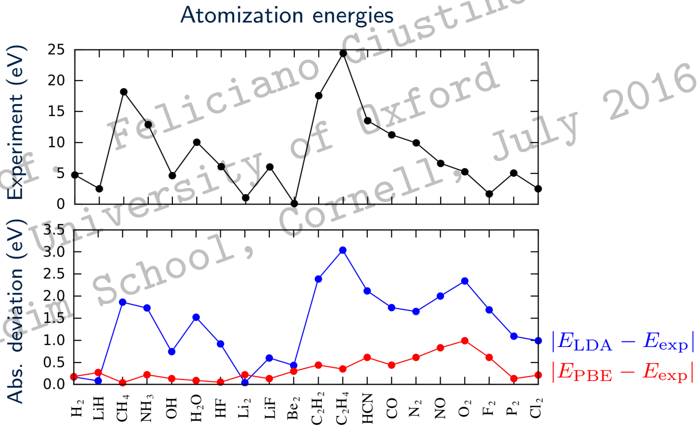
$$E_{xc}^{\mathrm{LDA}} = \int d\mathbf{r}\, n(\mathbf{r})\, \epsilon_{xc}^{\mathrm{HEG}}[n(\mathbf{r})]$$

- ‘Generalized gradient’ approximations (GGA) incorporate information about the density gradient

$$E_{xc}^{\mathrm{GGA}} = \int d\mathbf{r}\, f[n(\mathbf{r}), \nabla n(\mathbf{r})]$$

PBE exchange and correlation

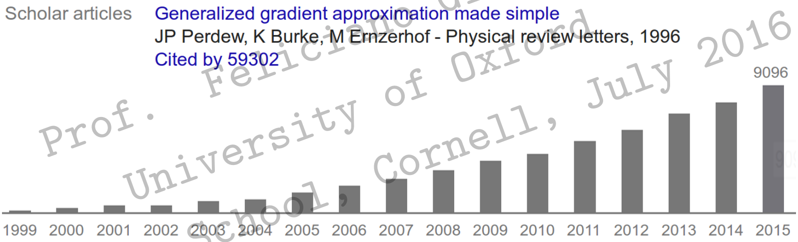
Perdew, Burke & Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996)



From Table 1 of Perdew, Burke, Ernzerhof, PRL 1996

PBE exchange and correlation

Perdew, Burke & Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996)



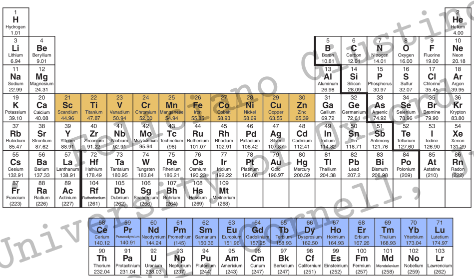
Scholar articles Generalized gradient approximation made simple

JP Perdew, K Burke, M Ernzerhof - Physical review letters, 1996

Cited by 59302

Hubbard-corrected DFT

Anisimov, Zaanen & Andersen, Phys. Rev. B 44, 943 (1991)
Cococcioni & De Gironcoli, Phys. Rev. B 71, 035105 (2005)

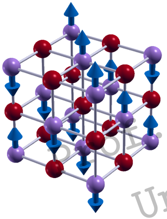


- $3d$ transition metal and $4f$ rare earth
- LDA underestimates the on-site Coulomb energy between electrons
- DFT+U adds Hubbard-like corrections to remedy this deficiency
- Important for strongly-correlated materials

Hubbard-corrected DFT

Anisimov, Zaanen & Andersen, Phys. Rev. B 44, 943 (1991)
Cococcioni & De Gironcoli, Phys. Rev. B 71, 035105 (2005)

FeO (AF-II phase)



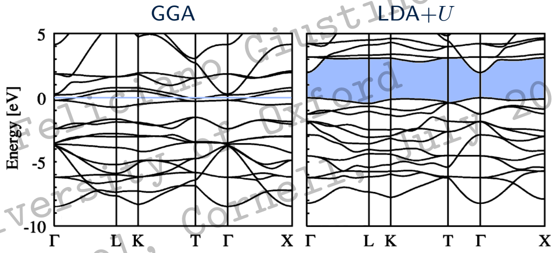


Figure from: Cococcioni & De Gironcoli, PRB 2005

- Computationally efficient
- Hubbard U often used as an adjustable parameter
- Results can be very sensitive to U

Hybrid functionals

PBE0: Perdew, Burke & Ernzerhof, J. Chem. Phys. 105 (1996)
HSE: Heyd, Scuseria & Ernzerhof, J. Chem. Phys. 118, 8207 (2003)

- Improve upon semilocal GGA by including fully non-local Fock exchange [see Lecture 1.2, slide 14]

$$E_x^{\mathrm{HF}} = -\sum_{j\in\mathrm{occ}} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\phi_i^*(\mathbf{r}_1)\phi_j^*(\mathbf{r}_2)\phi_i(\mathbf{r}_2)\phi_j(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

- PBE0 prescription

$$E_{xc}^{\mathrm{PBE0}} = \frac{3}{4} E_x^{\mathrm{PBE}} + \frac{1}{4} E_x^{\mathrm{F}} + E_c^{\mathrm{PBE}}$$

- Requires the evaluation of the non-local Fock exchange potential → Very expensive

$$V_{\mathrm{X}}(\mathbf{r},\mathbf{r}') = -\sum_{j\in\mathrm{occ}} \frac{\phi_j(\mathbf{r})\phi_j^*(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

Hybrid functionals

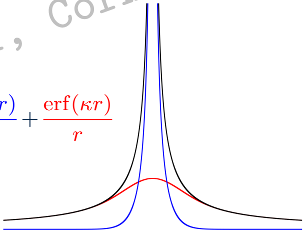
PBE0: Perdew, Burke & Ernzerhof, J. Chem. Phys. 105 (1996)
HSE: Heyd, Scuseria & Ernzerhof, J. Chem. Phys. 118, 8207 (2003)

- HSE prescription: separate short-range and long-range coulomb interactions

$$E_{xc}^{\mathrm{HSE}} = \left[\frac{3}{4}E_x^{\mathrm{PBE,sr}} + \frac{1}{4}E_x^{\mathrm{F,sr}}\right] + E_x^{\mathrm{PBE,lr}} + E_c^{\mathrm{PBE}}$$

- The separation is carried our by breaking the Coulomb potential in two parts

$$\frac{1}{r} = \frac{\mathrm{erfc}(\kappa r)}{r} + \frac{\mathrm{erf}(\kappa r)}{r}$$



Hybrid functionals

PBE0: Perdew, Burke & Ernzerhof, J. Chem. Phys. 105 (1996)
HSE: Heyd, Scuseria & Ernzerhof, J. Chem. Phys. 118, 8207 (2003)

- **Band gaps**
  Typically PBE underestimates band gaps while Hartree-Fock overestimates. Mixing PBE and HF yields values closer to experiment
- **Exchange fraction**
  Widespread practice of using the mixing fraction as an adjustable empirical parameter
- **Correlation**
  The correlation energy is still described at the PBE level. This misses van der Waals corrections (slide 13) and dynamical effects (slide 14)

van der Waals interaction

Example: Two H atoms far away from each other

- Electronic ground-state wavefunction for non-interacting atoms

$$\Psi_0(\mathbf{r}_1,\mathbf{r}_2) = \phi_{1s}^A(\mathbf{r}_1)\,\phi_{1s}^B(\mathbf{r}_2)$$

- Electron density

- This is (roughly) what we would obtain within DFT/LDA

van der Waals interaction

Example: Two H atoms far away from each other

- We can obtain a lower-energy wavefunction by using
  [Exercise 4.5 of Book]

$$\Psi(\mathbf{r}_1,\mathbf{r}_2) = \Psi_0(\mathbf{r}_1,\mathbf{r}_2) + \frac{\alpha/4\pi\epsilon_0}{d^3}\,\phi^A_{2p_x}(\mathbf{r}_1)\,\phi^B_{2p_x}(\mathbf{r}_2)$$

α = atomic polarizability

- The ground-state electron density is polarized

van der Waals interaction

Example: Two H atoms far away from each other

- The density redistribution leads to an additional attractive potential energy between the nuclei, the van der Waals interaction

$$U = -\frac{C}{d^6}$$

- Not included in standard DFT
- Important for graphitic materials, biological systems, molecular crystals

Andersson, Langreth & Lundqvist, Phys. Rev. Lett. 76, 102 (1996)

Dion, Rydberg, Schröder, Langreth & Lundqvist, Phys. Rev. Lett. 92, 246401 (2004)

Grimme, J. Comp. Chem. 27, 1787 (2006)

Tkatchenko & Scheffler, Phys. Rev. Lett. 102, 073005 (2009)

Many-body perturbation theory

The GW method

Hedin & Lundqvist, Solid State Physics 23, 1 (1969)

Hybertsen & Louie, Phys Rev B 34, 5390 (1986)

KS $$-\frac{1}{2}\nabla^2\phi_i(\mathbf{r}) + \left[V_\mathrm{n}(\mathbf{r}) + V_\mathrm{H}(\mathbf{r})\right]\phi_i(\mathbf{r}) + \boxed{V_{xc}(\mathbf{r})}\,\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r})$$

$$\downarrow$$

GW $$-\frac{1}{2}\nabla^2\phi_i(\mathbf{r}) + \left[V_\mathrm{n}(\mathbf{r}) + V_\mathrm{H}(\mathbf{r})\right]\phi_i(\mathbf{r}) + \boxed{\int d\mathbf{r}'\Sigma(\mathbf{r},\mathbf{r}',\varepsilon_i)}\,\phi_i(\mathbf{r}') = \varepsilon_i\phi_i(\mathbf{r})$$

$$\Sigma = GW$$

Screened Coulomb interaction

Electron Green's function

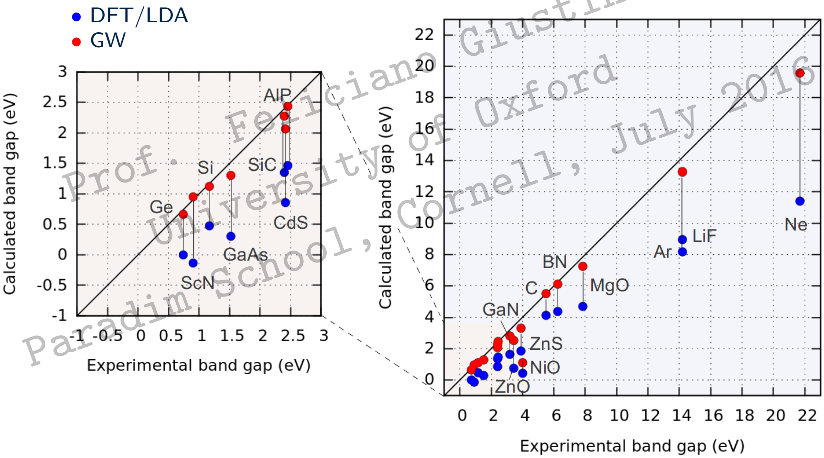
- Based on quantum-field theory
- Mostly used to correct KS eigenvalues
- Scales as N^4 (N number of atoms)

Many-body perturbation theory

The GW method

Hedin & Lundqvist, Solid State Physics 23, 1 (1969)

Hybertsen & Louie, Phys Rev B 34, 5390 (1986)



Many-body perturbation theory

Bethe-Salpeter approach

G. Strinati, Phys. Rev. B 29, 5718 (1984)

Onida, Reining & Rubio, Rev. Mod. Phys. 74, 601 (2002)

Rohlfing & Louie, Phys. Rev. Lett. 81. 2312 (1998)

- Excited states described as coherent superposition of electron-hole excitations

$$|S\rangle = \sum_{cv\mathbf{k}} A^S_{cv\mathbf{k}} \hat{a}^\dagger_{v\mathbf{k}} \hat{b}^\dagger_{c\mathbf{k}+\mathbf{Q}} |0\rangle$$

- Bethe-Salpeter equation (BSE)

$$(\varepsilon_{c\mathbf{k}+\mathbf{Q}} - \varepsilon_{v\mathbf{k}}) A^S_{cv\mathbf{k}} + \sum_{c'v'\mathbf{k}'} \langle cv\mathbf{k}|K^{\mathrm{eh}}|c'v'\mathbf{k}'\rangle A^S_{c'v'\mathbf{k}'} = E_S A^S_{cv\mathbf{k}}$$

- The eigenvalues E_S yield the energies of electron-hole excitations (eg excitons)

- Used in combination with the GW method

Many-body perturbation theory

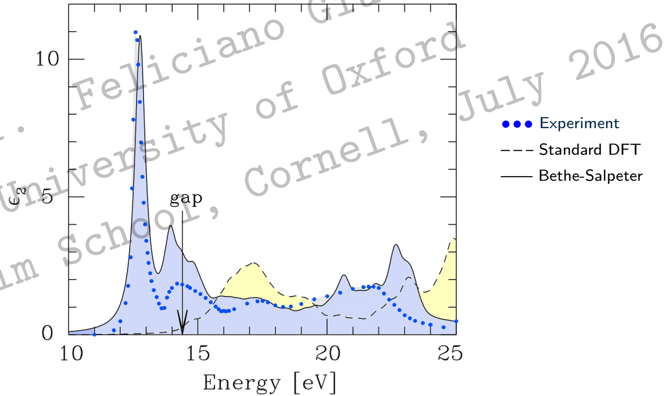
Bethe-Salpeter approach

G. Strinati, Phys. Rev. B 29, 5718 (1984)

Onida, Reining & Rubio, Rev. Mod. Phys. 74, 601 (2002)

Rohlfing & Louie, Phys. Rev. Lett. 81. 2312 (1998)

Example: Optical absorption of LiF



From: Rohlfing & Louie, Phys. Rev. Lett. 81. 2312 (1998)