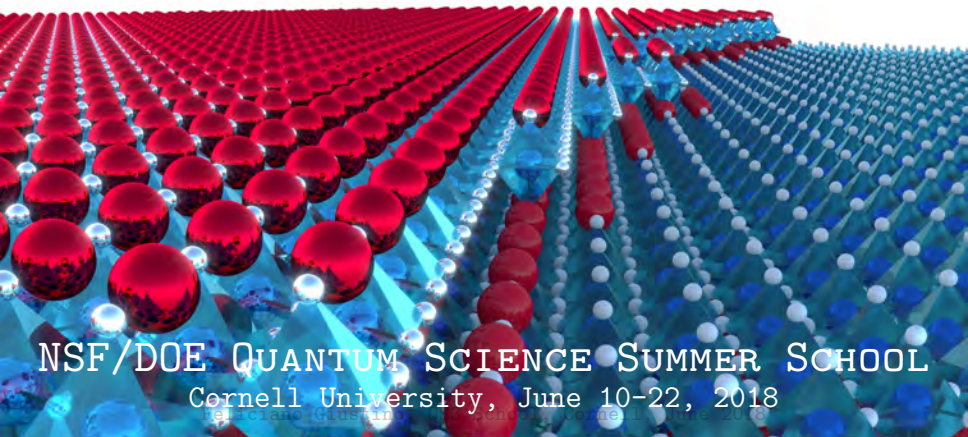


# Introduction to density functional theory

Feliciano Giustino

Department of Materials, University of Oxford

Department of Materials Science and Engineering, Cornell University



NSF/DOE QUANTUM SCIENCE SUMMER SCHOOL

Cornell University, June 10-22, 2018



Betül Pamuk



Guru Khalsa



FG



## Monday 10 June

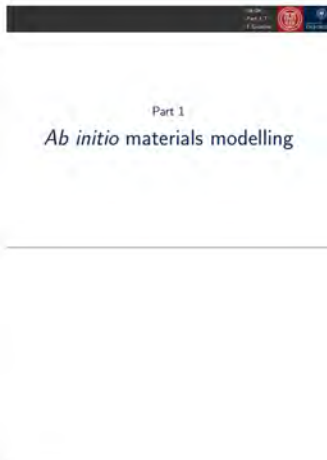
11:00–11:45	Theory Lecture 1	45m	FG
11:55–12:40	Theory Lecture 2	45m	FG
14:00–16:00	Hands-on Session 1	2h	Betül Pamuk, Guru Khalsa, FG

## Tuesday 11 June

14:00–17:30	Hands-on Session 2	3h30m	Betül Pamuk, Guru Khalsa, FG
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## Handouts

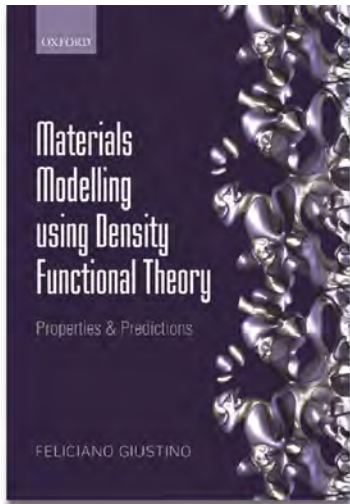


## Tutorial Sheets



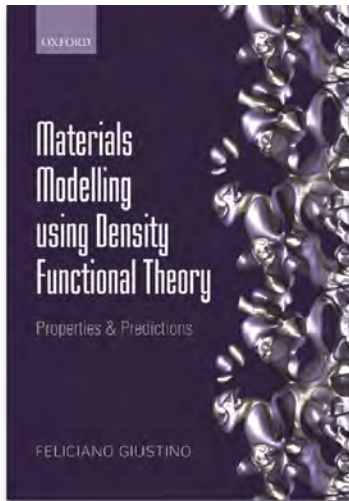


MSc and 1st year PhD level

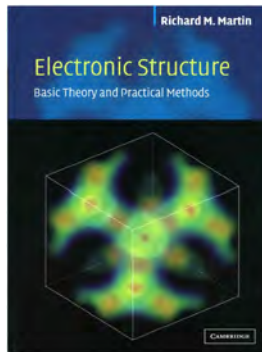




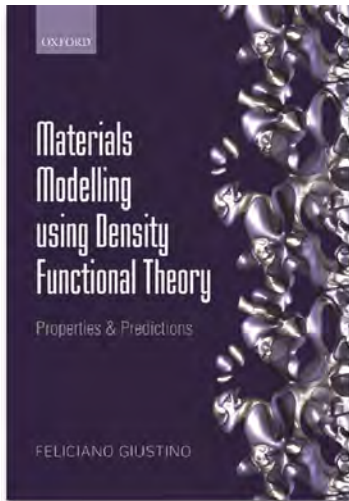
## MSc and 1st year PhD level



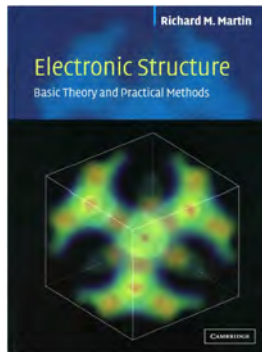
## Advanced PhD level



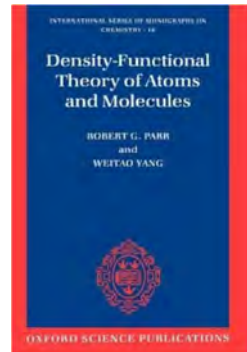
MSc and 1st year PhD level



Advanced PhD level



Theoretical foundations





**Part 1** *Ab initio* materials modelling

**Part 2** Many-body problem

**Part 3** Density-functional theory

**Part 4** Planewaves and pseudopotentials

**Part 5** Equilibrium structures

**Part 6** Band structures

**Part 7** DFT beyond the LDA





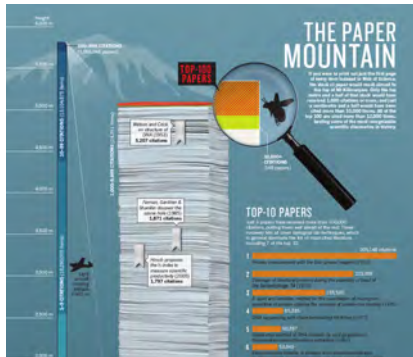
## Part 1

# *Ab initio* materials modelling

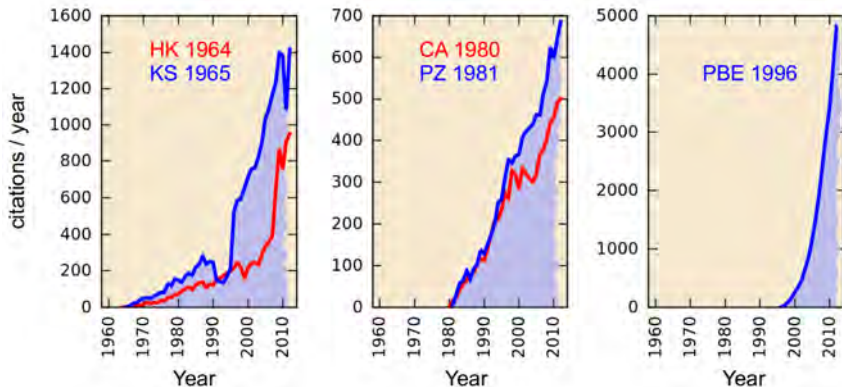


# THE TOP 100 PAPERS

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



- 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)*



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)

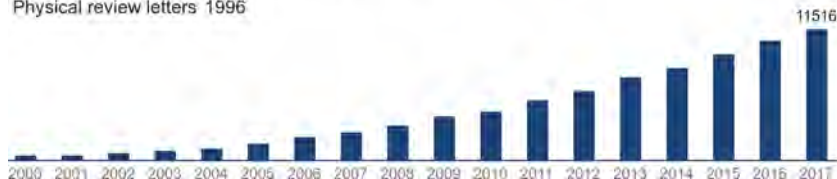


## Generalized gradient approximation made simple

John P Perdew, Kieron Burke, Matthias Ernzerhof

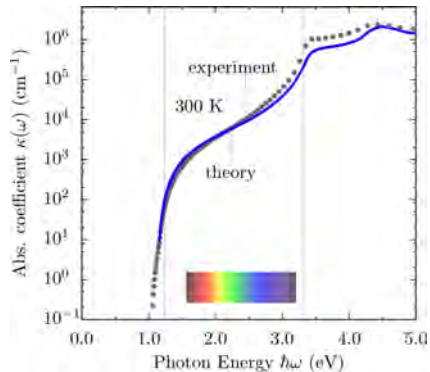
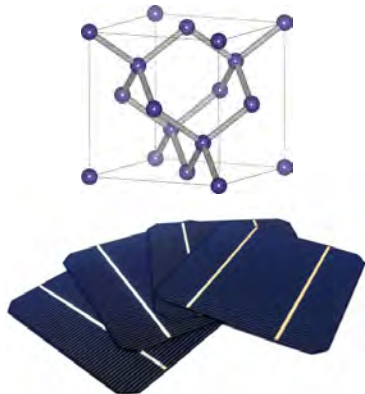
Physical review letters 1996

Total citations  
83631



The B3LYP papers ranked #7 and #8 in 2014 are now at ~75k cites

## Predictive calculations of optical properties



Zacharias, Patrick, and FG, Phys. Rev. Lett. 115, 177401 (2015)

## Predictive calculations of transport properties

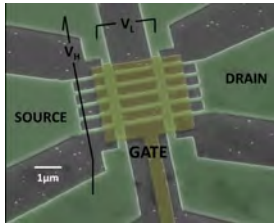
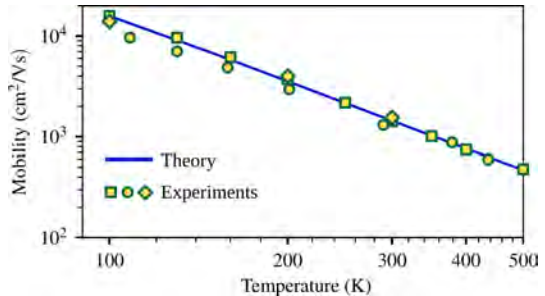


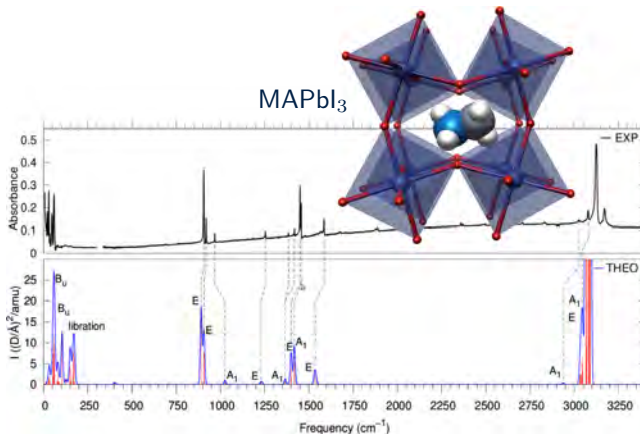
Image from Thathachary et al,  
Nano Lett. 14, 626 (2014)

### Silicon



Poncé, Margine, and FG, Phys. Rev. B(R) 97, 121201 (2018)

## Materials characterization via vibrational spectroscopy



Perez-Osorio, Milot, Filip, Patel, Herz, Johnston, and FG, J. Phys. Chem. C 119, 25703 (2015)

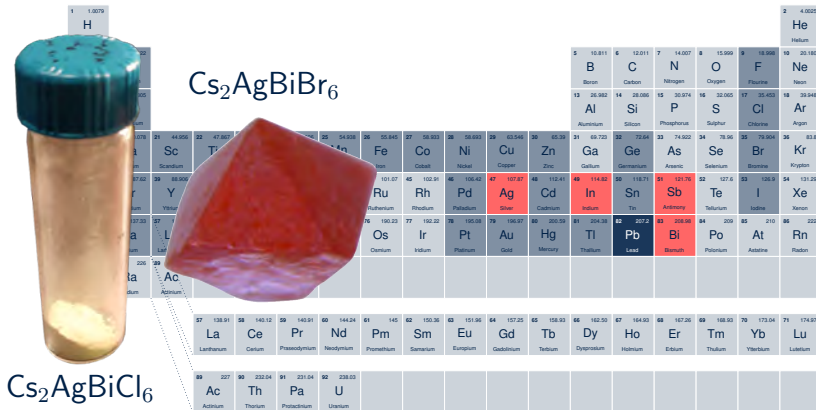


## Computational materials discovery

1 1.0079 H Hydrogen																	2 4.0026 He Helium				
3 6.941 Li Lithium	4 9.0122 Be Beryllium															5 10.811 B Boron	6 12.011 C Carbon	7 14.007 N Nitrogen	8 15.999 O Oxygen	9 18.998 F Fluorine	10 20.180 Ne Neon
11 22.990 Na Sodium	12 24.305 Mg Magnesium															13 26.982 Al Aluminum	14 28.086 Si Silicon	15 30.974 P Phosphorus	16 32.065 S Sulphur	17 35.453 Cl Chlorine	18 39.948 Ar Argon
19 39.098 K Potassium	20 40.078 Ca Calcium	21 44.956 Sc Scandium	22 47.867 Ti Titanium	23 50.942 V Vanadium	24 51.996 Cr Chromium	25 54.938 Mn Manganese	26 55.845 Fe Iron	27 58.933 Co Cobalt	28 58.933 Ni Nickel	29 63.546 Cu Copper	30 65.39 Zn Zinc	31 68.723 Ga Gallium	32 72.64 Ge Germanium	33 74.922 As Arsenic	34 78.96 Se Selenium	35 79.904 Br Bromine	36 83.8 Kr Krypton				
37 85.468 Rb Rubidium	38 87.62 Sr Strontium	39 88.906 Y Yttrium	40 91.224 Zr Zirconium	41 92.906 Nb Niobium	42 95.94 Mo Molybdenum	43 96 Tc Technetium	44 101.07 Ru Ruthenium	45 101.91 Rh Rhodium	46 106.42 Pd Palladium	47 107.87 Ag Silver	48 112.41 Cd Cadmium	49 114.82 In Indium	50 118.71 Sn Tin	51 121.76 Sb Antimony	52 127.6 Te Tellurium	53 126.9 I Iodine	54 131.29 Xe Xenon				
55 132.91 Cs Cesium	56 137.33 Ba Barium	57 138.91 La Lanthanum	58 178.49 Hf Hafnium	59 178.49 Ta Tantalum	60 183.84 W Tungsten	61 186.21 Re Rhenium	62 186.21 Os Osmium	63 190.23 Ir Iridium	64 195.08 Pt Platinum	65 196.97 Au Gold	66 200.59 Hg Mercury	67 204.38 Tl Thallium	68 207.2 Pb Lead	69 208.98 Bi Bismuth	70 209 Po Polonium	71 210 At Astatine	72 222 Rn Radon				
87 223 Fr Francium	88 226 Ra Radium	89 227 Ac Actinium																			
57 138.91 La Lanthanum	58 140.12 Ce Cerium	59 140.91 Pr Praseodymium	60 144.24 Nd Neodymium	61 145 Pm Promethium	62 150.36 Sm Samarium	63 151.96 Eu Europium	64 157.25 Gd Gadolinium	65 158.93 Tb Terbium	66 162.50 Dy Dysprosium	67 164.93 Ho Holmium	68 167.26 Er Erbium	69 168.93 Tm Thulium	70 173.04 Yb Ytterbium	71 174.97 Lu Lutetium							
89 227 Ac Actinium	90 232.04 Th Thorium	91 231.04 Pa Protactinium	92 238.03 U Uranium																		

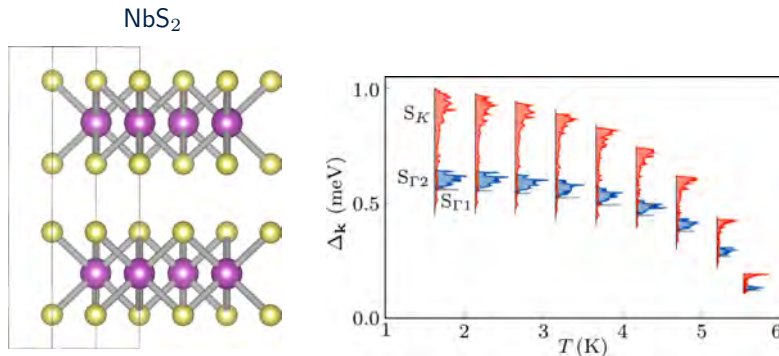
Volonakis, Filip, Haghighirad, Sakai, Wenger, Snaith, and FG, J. Phys. Chem. Lett. 7, 1254 (2016)

## Computational materials discovery



Volonakis, Filip, Haghighirad, Sakai, Wenger, Snaith, and FG, J. Phys. Chem. Lett. 7, 1254 (2016)

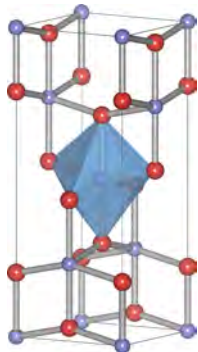
## Predictive calculations of the superconducting critical temperature



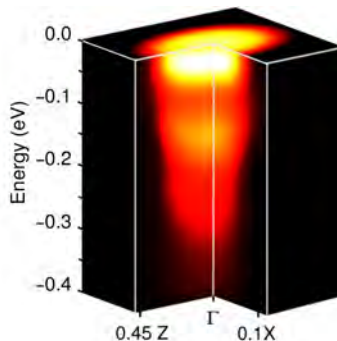
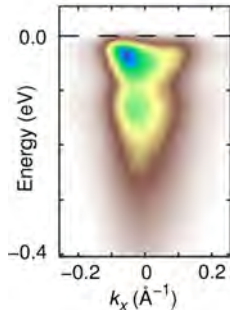
Heil, Poncé, Lambert, Schlipf, Margine, and FG, Phys. Rev. Lett., 119, 087003 (2017)

## Many-body effects in ARPES

TiO<sub>2</sub> anatase



Moser et al,  
PRL 110, 196403 (2013)



Verdi, Caruso, and FG, Nat. Commun. 8, 15769 (2017)

# Why is DFT so popular?

17/88

Part 1/7

F Giustino



- **Transferability**

We can use the same codes/methods for very different materials

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- **Robust platform**

Often the shortcomings of DFT can be cured by using more sophisticated approaches, which still use DFT as their starting point



How many papers using DFT will be published worldwide during the QS<sup>3</sup> school?

- A** Ten
- B** At least four hundred
- C** Ten thousand
- D** More than a million
- E** I have no idea



## Part 2

# Many-body problem



Materials = Electrons + Nuclei



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

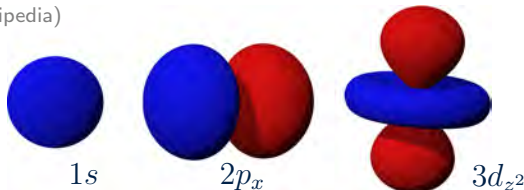
$$-\frac{\hbar^2}{2m_e} \nabla^2 \psi(\mathbf{r}) - \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r}|} \psi(\mathbf{r}) = E_{\text{tot}} \psi(\mathbf{r})$$

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- wavefunctions of H  
(from Wikipedia)





- Many-body wavefunction (keep it simple: only 3 electrons)

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



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

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





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



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- Electrons are indistinguishable

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



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



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



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- potential energy, electron-nucleus attraction

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



$$\left[ -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right. \\ \left. + \frac{1}{2} \sum_{I \neq J} \frac{e^2}{4\pi\epsilon_0} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} - \sum_{i,I} \frac{e^2}{4\pi\epsilon_0} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} \right] \Psi = E_{\text{tot}} \Psi$$





$$\left[ -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2} \sum_{I \neq J} \frac{e^2}{4\pi\epsilon_0} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} - \sum_{i,I} \frac{e^2}{4\pi\epsilon_0} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} \right] \Psi = E_{\text{tot}} \Psi$$

## 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)



$$\left[ -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right. \\ \left. + \frac{1}{2} \sum_{I \neq J} \frac{e^2}{4\pi\epsilon_0} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} - \sum_{i,I} \frac{e^2}{4\pi\epsilon_0} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} \right] \Psi = E_{\text{tot}} \Psi$$

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MBSE

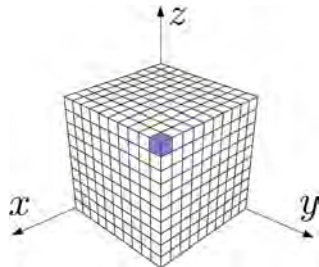


MBSE



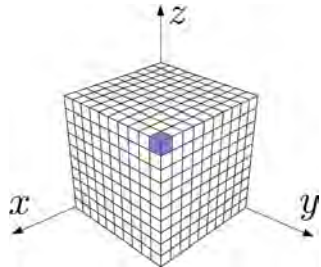
MBSE in Hartree units

Storage requirements for the many-body wavefunction  
of one unit cell of silicon in the diamond structure



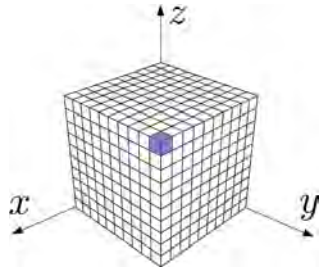
Storage requirements for the many-body wavefunction  
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- $\Delta x \sim 0.1 \text{ \AA}$



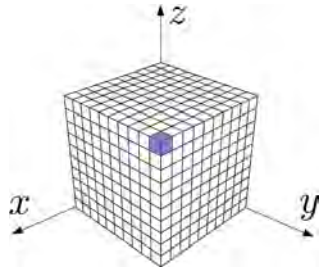
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- $\Delta x \sim 0.1 \text{ \AA}$
- $a = 5.43 \text{ \AA}$



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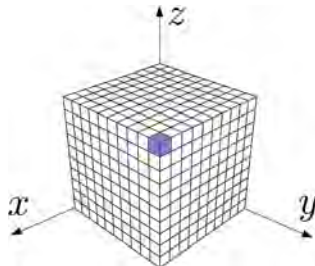
- $\Delta x \sim 0.1 \text{ \AA}$
- $a = 5.43 \text{ \AA}$
- $N_p = (a^3/4)/(\Delta x)^3 \sim 40,000$





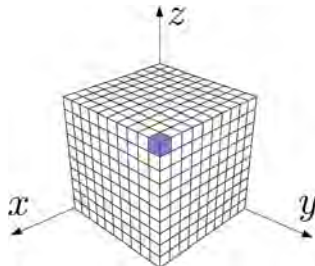
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- 8 valence electrons per unit cell



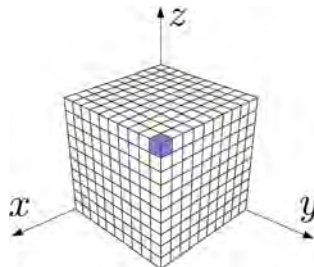
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$10^{26}$  Terabytes



Set nuclear masses  $M_I = \infty$ :

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Electronic structure theory in a nutshell



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



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- ☺ No need for the many-body wavefunction
- ☹ Requires iterative solution



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- Since the Slater determinant is really useful for practical calculations, we keep it and we describe correlations by adding a fictitious potential

$$\left[ -\frac{1}{2} \nabla^2 + V_n + V_H + V_X + V_c \right] \phi_i = \varepsilon_i \phi_i$$


**correlation  
potential**





$$\left[ -\frac{1}{2} \nabla^2 + V_n + V_H + V_{xc} \right] \phi_i = \varepsilon_i \phi_i$$

Exchange and Correlation potential



We want to study the many-body wavefunction of a unit cell of  $\text{Sr}_2\text{RuO}_4$ .  
We discretize the volume using 100,000 mesh points.

How many terabytes would we need  
to store this wavefunction?

- A** Less than 1 TB
- B** 10 TB
- C**  $10^{784}$  TB
- D** Infinity
- E** How much is a terabyte?



## Part 3

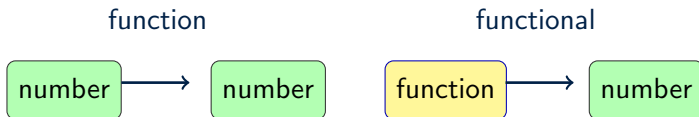
# Density-functional theory



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being a **functional** of their **density**



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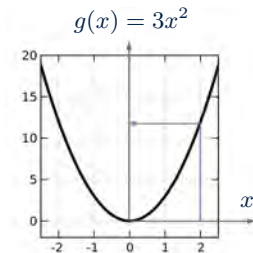


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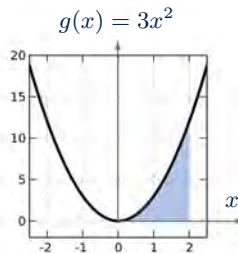
function



functional



$$g(2) = 12$$



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



The total energy is a **functional** of the **wavefunction**

$$\hat{H} \Psi = E \Psi$$



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So for a generic quantum state we have

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) \longrightarrow E$$

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In 1964 Hohenberg and Kohn noted that, for the lowest-energy state, the total energy is a **functional** of the **density**

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



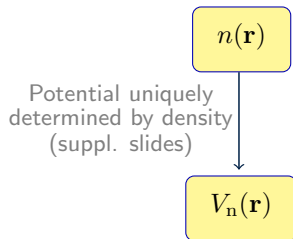
$$n(\mathbf{r})$$

# Hohenberg-Kohn theorem

37/88

Part 3/7

F Giustino

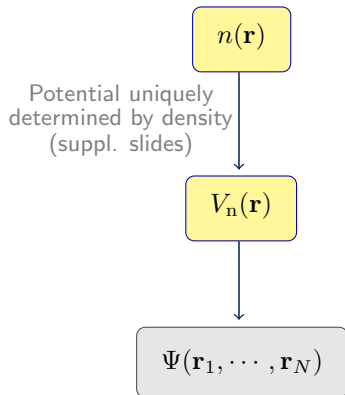


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37/88

Part 3/7

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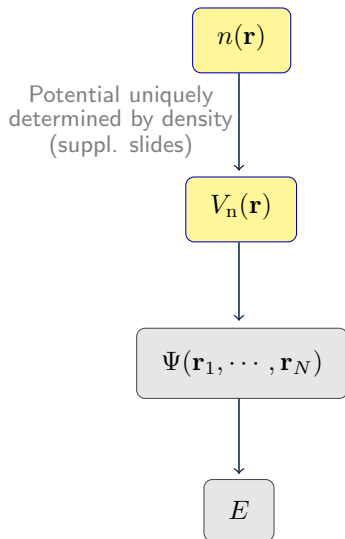


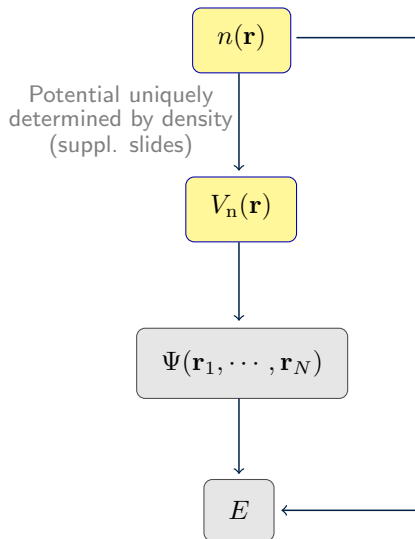
# Hohenberg-Kohn theorem

37/88

Part 3/7

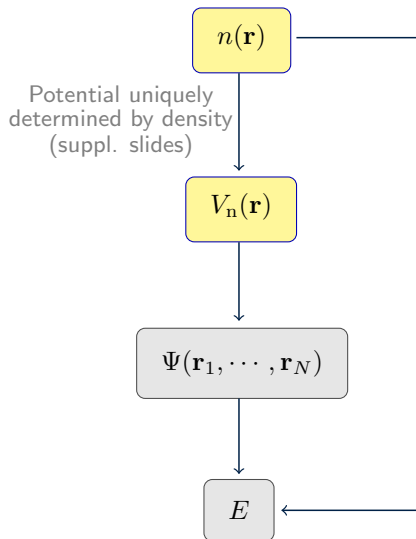
F Giustino





## HK theorem

In the ground-state the electron density  $n_0(\mathbf{r})$  uniquely determines the total energy  $E_0$



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## HK variational principle

Any  $n(\mathbf{r}) \neq n_0(\mathbf{r})$  yields  $E > E_0$ .





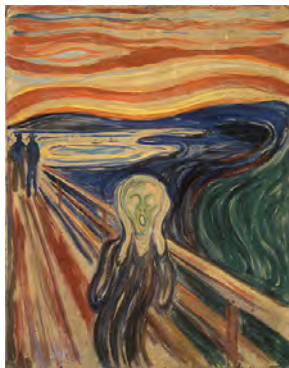
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What is this functional?

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What is this functional?

The energy functional is unknown



*The scream* by E. Munch (1910)

# The energy functional

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Part 3/7

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$$E[n] =$$

# The energy functional

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Part 3/7

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$$E[n] = \underbrace{\int d\mathbf{r} n(\mathbf{r}) V_n(\mathbf{r})}_{\text{External potential}}$$



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# The energy functional

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Part 3/7

F Giustino



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Kohn and Sham (1965) proposed to

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- (2) Take out the kinetic energy of these electrons from the “everything else”

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





Total energy

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



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

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



Total energy

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

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

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

This leads to the Kohn-Sham equations

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



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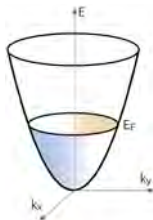
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$$V_{xc} = \frac{\delta E_{xc}}{\delta n} \text{ Exchange and Correlation Potential}$$



We consider the homogeneous electron gas (uniform gas of electrons in a positive compensating background)

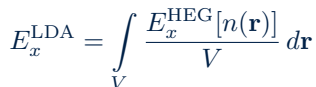


$$n(\mathbf{r}) = \text{constant}$$

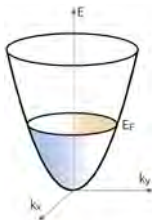
$$E_x^{\text{HEG}} = -\frac{3}{4} \left( \frac{3}{\pi} \right)^{\frac{1}{3}} n^{\frac{4}{3}} V$$

A diagram showing a parabolic energy band structure. The vertical axis is labeled  $E$  and the horizontal axis is labeled  $k_y$ . The parabola opens upwards. A horizontal line at energy  $E_F$  intersects the parabola. The region below  $E_F$  is shaded blue, and the region above  $E_F$  is shaded yellow.

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

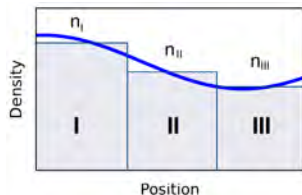


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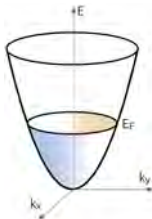
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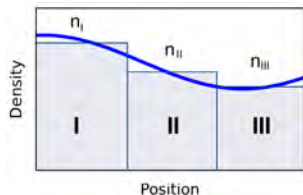
$$E_x^{\text{LDA}} = \int_V \frac{E_x^{\text{HEG}}[n(\mathbf{r})]}{V} d\mathbf{r} = -\frac{3}{4} \left( \frac{3}{\pi} \right)^{\frac{1}{3}} \int_V n^{\frac{4}{3}}(\mathbf{r}) d\mathbf{r}$$

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

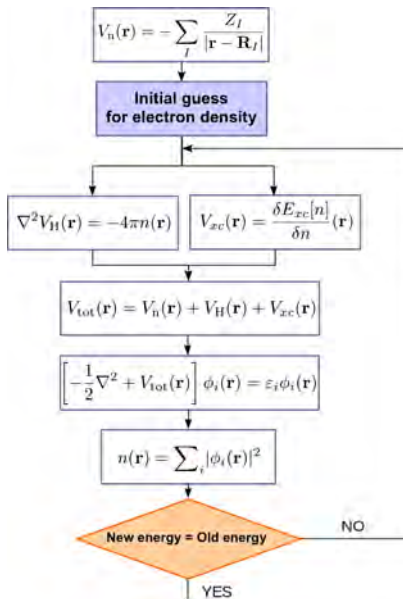


# Self-consistent field calculations (SCF)

42/88

Part 3/7

F Giustino





How many terabytes would we need in DFT to study wavefunctions in a unit cell of  $\text{Sr}_2\text{RuO}_4$ ?

- A** 10 TB
- B**  $10^{784}$  TB
- C** 1 MB
- D** 250 MB
- E** I need coffee



## Part 4

# Planewaves and pseudopotentials



DFT calculations require the numerical solution of the KS equations

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



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2nd order PDE  $\rightarrow$  for every  $y$  and  $z$  we need **two boundary conditions** on  $x$



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- **Localized system**

atom, molecule, quantum dot, nanowire, nanoslab

$$\phi_i(x, y, z) = 0 \quad \text{for } x = -\infty, \quad \phi_i(x, y, z) = 0 \quad \text{for } x = +\infty$$



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- **Extended system**

solid, liquid

$$\phi_i(x + a, y, z) = \phi_i(x, y, z), \quad \nabla\phi_i(x + a, y, z) = \nabla\phi_i(x, y, z)$$



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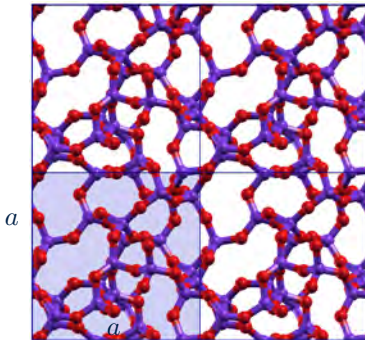
$$\phi_i(x + a, y, z) = \phi_i(x, y, z), \quad \nabla\phi_i(x + a, y, z) = \nabla\phi_i(x, y, z)$$

**Periodic (BvK) boundary conditions**



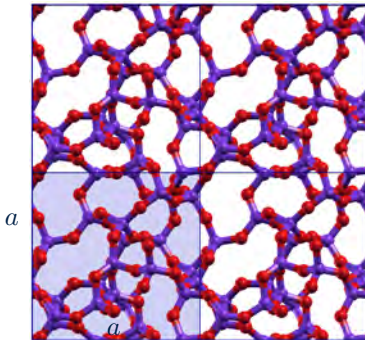
DFT calculations for **solids**, **liquids**, **interfaces**, and **nanostructures** are performed using BvK boundary conditions

amorphous  $\text{SiO}_2$

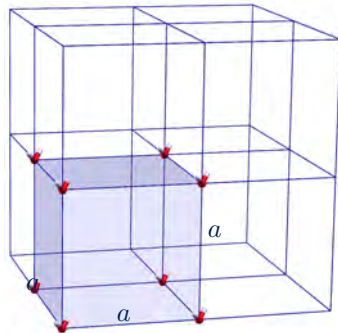


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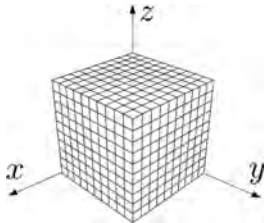


$\text{H}_2\text{O}$  molecule



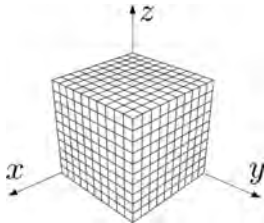


A convenient way of handling the KS wavefunctions is by expanding them in a basis of **planewaves**  $\longrightarrow$  standard Fourier transform



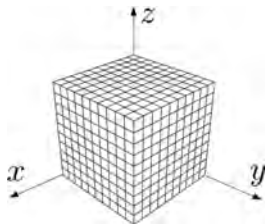


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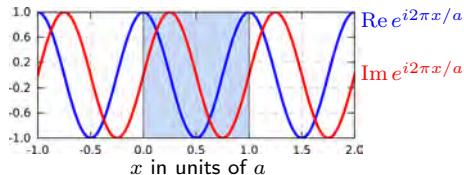


$$\text{1D case } \phi(x) = \sum_{n=-\infty}^{+\infty} c_n e^{i2\pi nx/a}$$

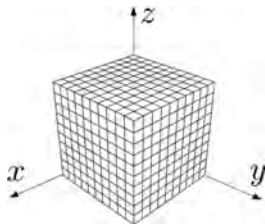
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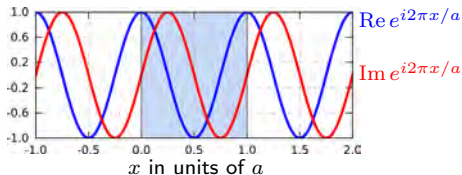
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$$\text{1D case } \phi(x) = \sum_{n=-\infty}^{+\infty} c_n e^{i2\pi nx/a}$$



BvK conditions built in

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

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

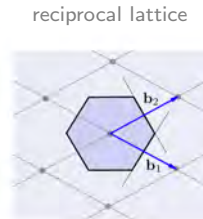
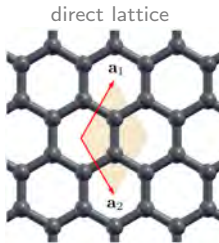
In 2D and 3D we replace  $2\pi/a$  by the primitive vectors of the reciprocal lattice

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

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



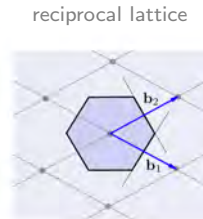
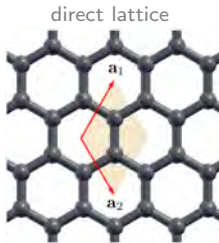
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Example: graphene



Planewave in 2D or 3D

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





Kohn-Sham wavefunction in a basis of planewaves

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



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How many planewave  $\mathbf{G}$ -vectors should we include in the **expansion**?

Kohn-Sham wavefunction in a basis of planewaves

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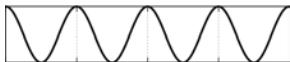
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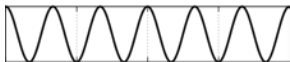
How many planewave  $\mathbf{G}$ -vectors should we include in the **expansion**?



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



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



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

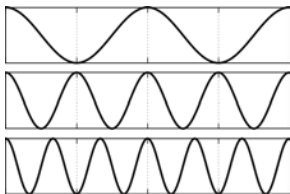
Kohn-Sham wavefunction in a basis of planewaves

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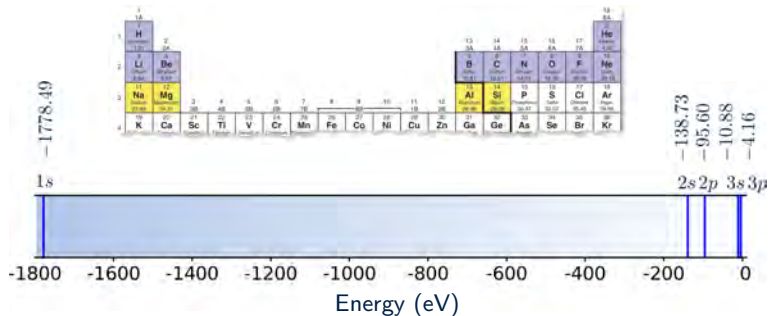
$$|\mathbf{G}| = 3 \cdot 2\pi/a$$

$$E_{\text{cut}} = \frac{\hbar^2 |\mathbf{G}_{\text{max}}|^2}{2m_e}$$

planewaves kinetic energy cutoff

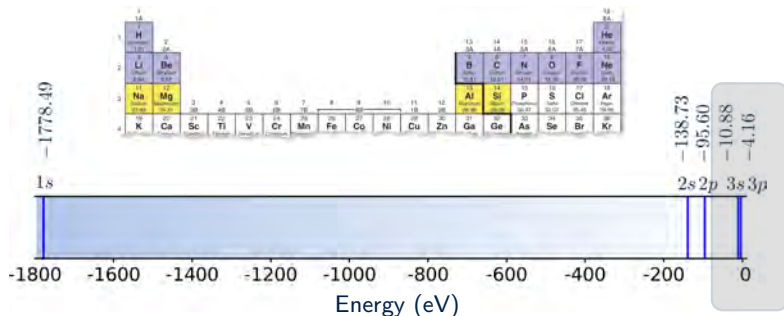


## Atomic wavefunctions of **silicon** (DFT/LDA)



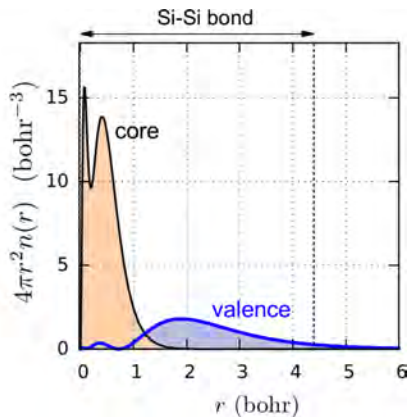
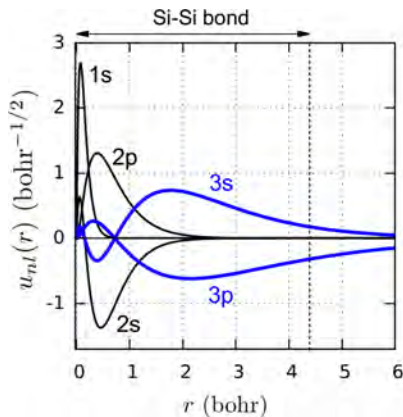


## Atomic wavefunctions of silicon (DFT/LDA)



Only valence electrons  
important for bonding

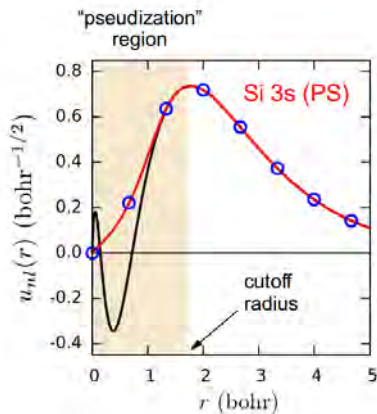
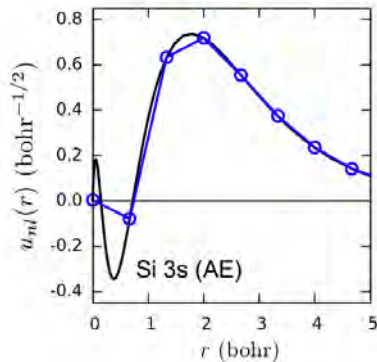
## Atomic wavefunctions of silicon (DFT/LDA)



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



**Pseudization:** make wavefunctions smooth by removing the nodes





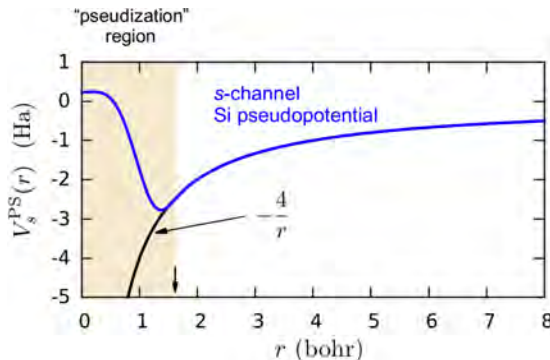
Reverse-engineer the **pseudo-potential** potential which yields the **pseudo-wavefunction** as solution of the atomic Schrödinger equation

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



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

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



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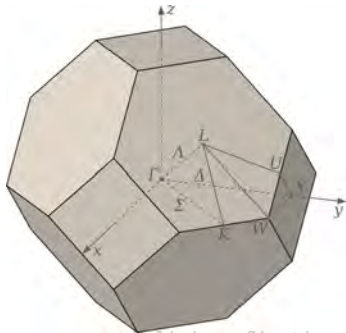
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$$n(\mathbf{r}) = \sum_{i \in \text{occ}} |\phi_i(\mathbf{r})|^2 \longrightarrow \sum_{i \in \text{occ}} \int_{\text{BZ}} \frac{d\mathbf{k}}{\Omega_{\text{BZ}}} |u_{i\mathbf{k}}(\mathbf{r})|^2 \simeq \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k} \in \text{BZ}}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

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Brillouin zone of fcc crystal (e.g. Si, Cu)

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



## What is a pseudopotential?

- A** An effective atomic potential describing nucleus & core electrons
- B** A potential describing the pseudo spin
- C** A false potential
- D** The potential in the Kohn-Sham equations of DFT
- E** This question is too easy



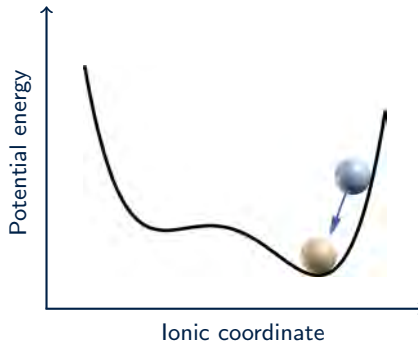
## Part 5

# 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





## Clamped nuclei approximation



~~Clamped nuclei approximation~~



## ~~Clamped nuclei approximation~~

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

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

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



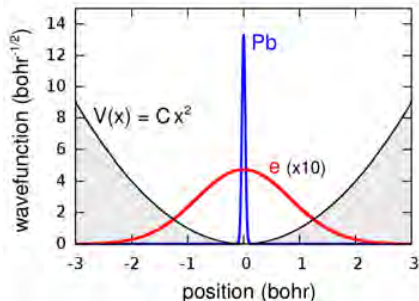
## ~~Clamped nuclei approximation~~

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

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

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





Born and Oppenheimer (1927) proposed the following approximation



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- Factorize the electron-nuclear wavefunction

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



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

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





Born and Oppenheimer (1927) proposed the following approximation

- Factorize the electron-nuclear wavefunction

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

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

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

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

Schrödinger equation for nuclei



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



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

Potential energy surface

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



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

Potential energy surface

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

↑  
Coulomb repulsion  
between positive nuclei

↑  
Glue resulting from the  
negative charge of the electrons

# Potential energy surface

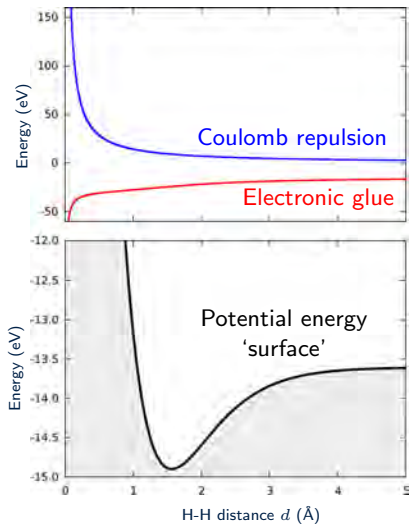
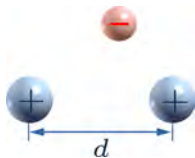
61/88

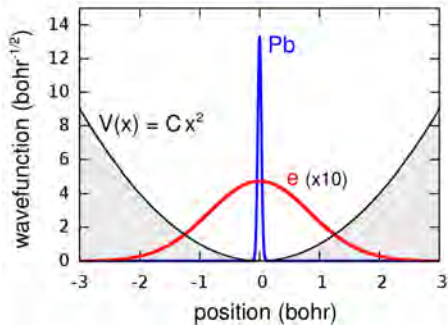
Part 5/7

F Giustino

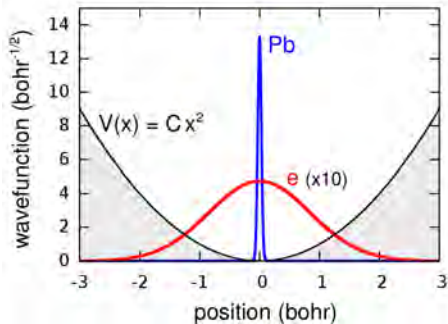


$\text{H}_2^+$  molecular ion





$$-\sum_I \frac{\nabla_I^2}{2M_I} + U(\mathbf{R}_1, \dots, \mathbf{R}_M)$$

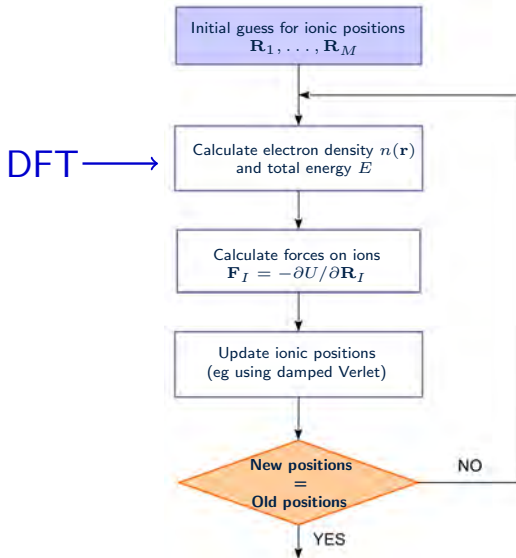


$$-\sum_I \frac{\nabla_I^2}{2M_I} + U(\mathbf{R}_1, \dots, \mathbf{R}_M)$$



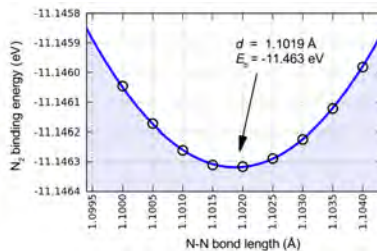
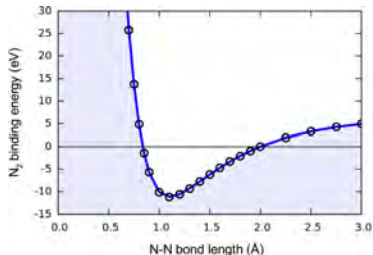
$$M_I \frac{d^2 \mathbf{R}_I}{dt^2} = \mathbf{F}_I = -\frac{\partial U}{\partial \mathbf{R}_I}$$

Newton's equation for nuclei



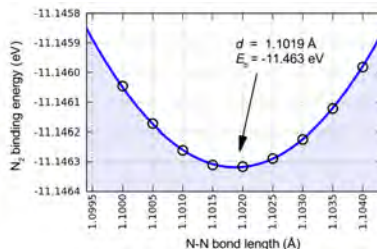
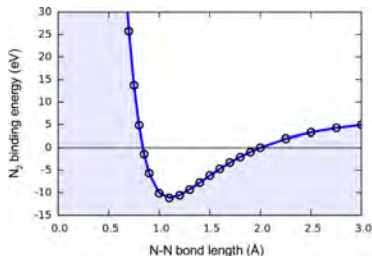


## Simplest case of structural optimization: $\text{N}_2$ diatomic molecule





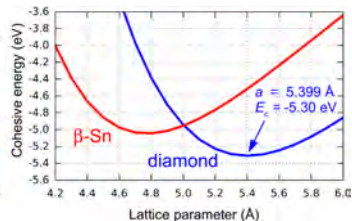
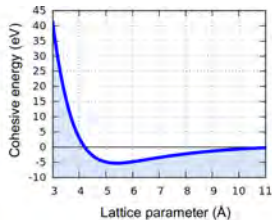
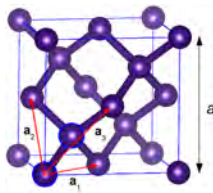
## Simplest case of structural optimization: $\text{N}_2$ diatomic molecule



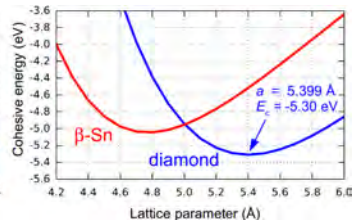
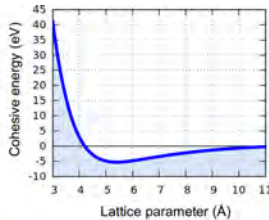
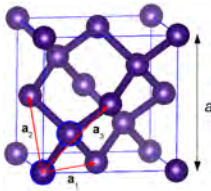
	DFT/LDA	Experiment	Rel. Error
bond length (Å)	1.102	1.098	0.4%
binding energy (eV)	11.46	9.76	17%

**Note** Nitrogen is  $[1s^2]2s^2p^3$ , therefore it has a spin  $S = 3/2$  after the Hund's first rule. As the above calculations are spin-unpolarized, the energy at infinity is higher than twice the energy of one N atom.

## Structural optimization of bulk crystals: **Silicon**



## 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%



In which of the following systems the Born-Oppenheimer approximation breaks down?

- A** Organic-inorganic lead halide perovskites
- B** Sulfur hydride high-temperature superconductors
- C** Diamond
- D** Graphene
- E** What is the Born-Oppenheimer approximation?

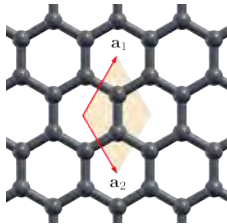


## Part 6

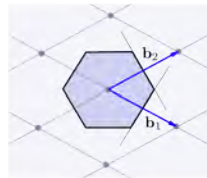
# Band structures

## Example: graphene

direct lattice



reciprocal lattice



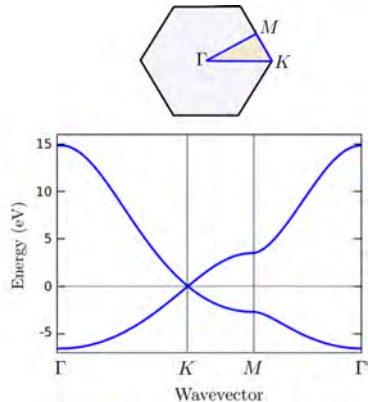
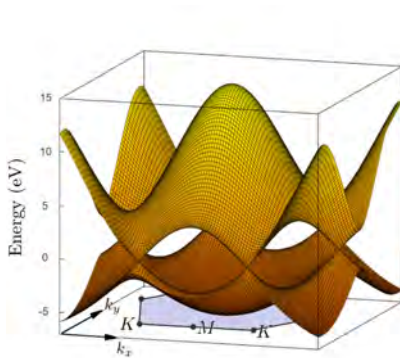
$$\phi_{i\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{i\mathbf{k}}(\mathbf{r}) \text{ with } u_{i\mathbf{k}}(\mathbf{r}) \text{ periodic}$$

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

$\mathbf{k}$ -dependent

KS eigenvalue

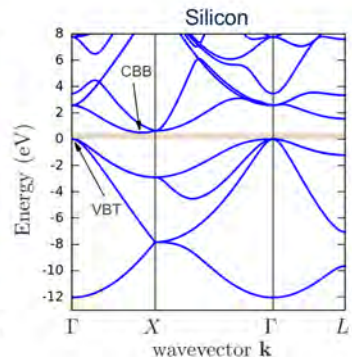
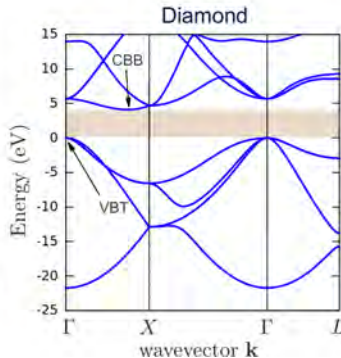
Example: simplified tight-binding model of graphene





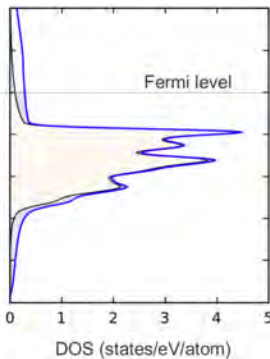
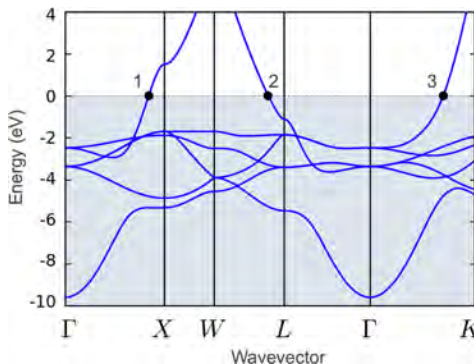
## Example: DFT/LDA band structures of common semiconductors

	13	14	15
	3A	4A	5A
	<b>B</b>	<b>C</b>	<b>N</b>
	Boron	Carbon	Nitrogen
	10.81	12.01	14.01
12	13	14	15
25	26	27	28
	<b>Al</b>	<b>Si</b>	<b>P</b>
	Aluminum	Silicon	Phosphorus
	26.98	28.09	30.97
30	31	32	33
	<b>Zn</b>	<b>Ga</b>	<b>Ge</b>
	Zinc	Gallium	Germanium
	65.38	69.72	72.64
48	49	50	51
			<b>As</b>
			Arsenic
			74.92

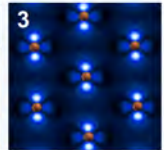
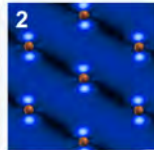
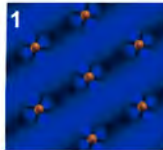
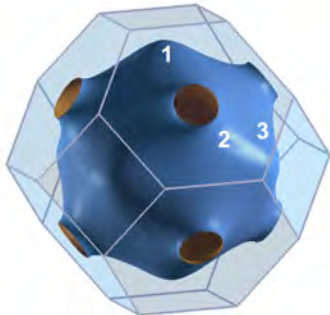


## Example: DFT/LDA band structure and Density of States of copper

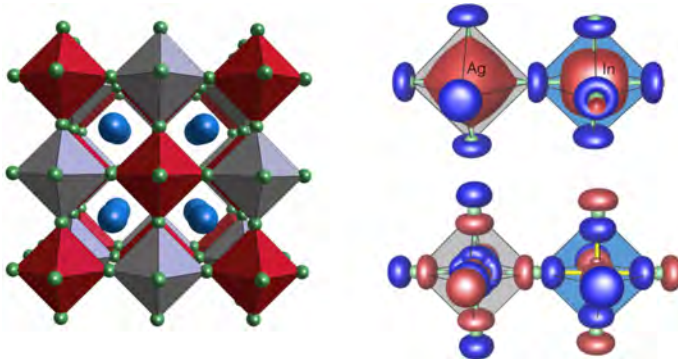
1	2	3	4	5	6	7	8	9	10	11	12	13
11 Na [22.99]	12 Mg [24.31]	13 Al [26.98]	14 Si [28.09]	15 P [30.97]	16 S [32.07]	17 Cl [35.45]	18 Ar [39.95]	19 K [39.10]	20 Ca [40.08]	21 Sc [44.96]	22 Ti [47.87]	23 V [50.94]
21 K [39.10]	22 Ca [40.08]	23 Sc [44.96]	24 Ti [47.87]	25 V [50.94]	26 Cr [51.99]	27 Mn [54.94]	28 Fe [55.85]	29 Co [58.93]	30 Ni [58.69]	31 Cu [63.55]	32 Zn [65.38]	33 Ga [69.72]
37 Rb [85.47]	38 Sr [87.62]	39 Y [88.91]	40 Zr [91.22]	41 Nb [92.91]	42 Mo [95.94]	43 Tc [98.91]	44 Ru [101.07]	45 Rh [102.91]	46 Pd [106.42]	47 Ag [107.87]	48 Cd [112.41]	49 In [114.82]



Example: DFT/LDA Fermi surface and wavefunctions of copper



Example: Elpasolite  $\text{Cs}_2\text{InAgCl}_6$



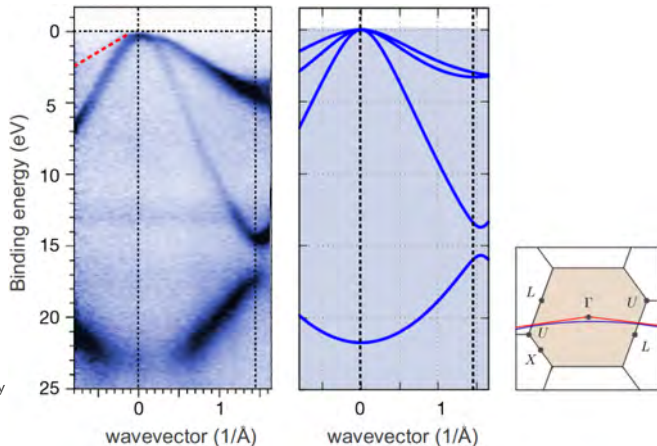
Volonakis et al, J. Phys. Chem. Lett., 8, 772 (2017)



- Are band structures real?

- Are band structures real?

ARPES spectrum of diamond and DFT/LDA bands



Experiment by  
Prof. T. Yokoya  
Okayama University

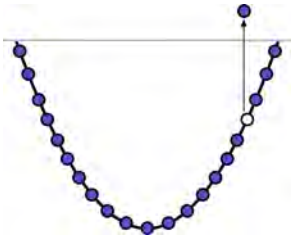


The DFT total energy can be rewritten as

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

The DFT total energy can be rewritten as

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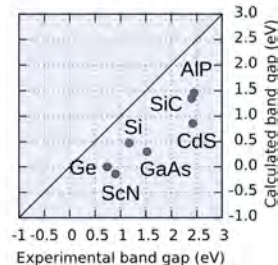
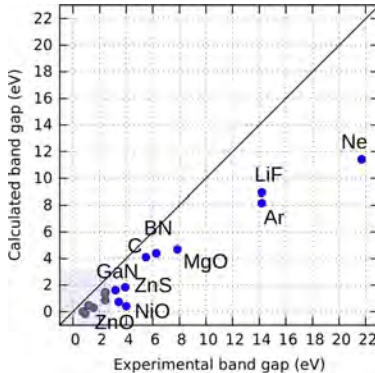


- If the double-counting term could be neglected, the eigenvalues would give the change of total energy upon adding or removing one electron
- The KS levels can be thought of as **very rough** approximations to addition or removal energies





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





Which of the following statements is true ?

- A** DFT band structures are generally good for *sp* semiconductors
- B** DFT predicts accurate band gaps in semiconductors and insulators
- C** DFT performs poorly for metals
- D** The DFT band gap problem has to do with pseudopotentials
- E** The Kohn-Sham eigenvalues correspond to electron addition or removal energies



## Part 7

# DFT beyond the LDA



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

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

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

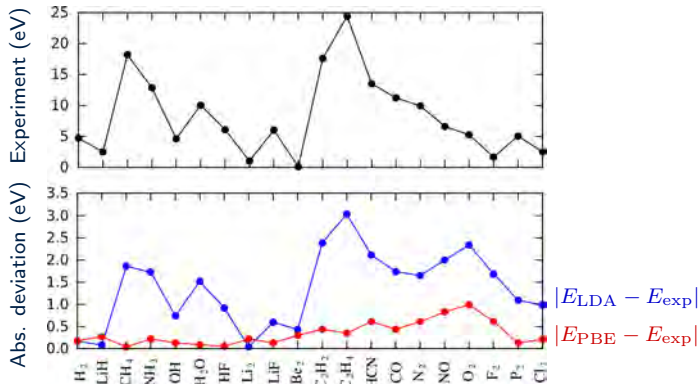
- Generalized gradient approximations (GGA) like PBE incorporate also information about the **density gradient**

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



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

## Atomization energies



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

Anisimov, Zaanen & Andersen, Phys. Rev. B 44, 943 (1991)

1 H Hydrogen 1.01																	2 He Helium 4.00				
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 15.99	9 F Fluorine 18.99	10 Ne Neon 20.18
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
19 K Potassium 39.10	20 Ca Calcium 40.08	21 Sc Scandium 44.96	22 Ti Titanium 47.88	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 65.38	31 Ga Gallium 69.72	32 Ge Germanium 72.64	33 As Arsenic 74.92	34 Se Selenium 78.96	35 Br Bromine 79.90	36 Kr Krypton 83.80				
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				
55 Cs Cesium 132.91	56 Ba Barium 137.33	57 La Lanthanum 138.91	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 173.05	71 Lu Lutetium 174.97					
87 Fr Francium (223)	88 Ra Radium (226)	89 Ac Actinium (227)	90 Th Thorium (232)	91 Pa Protactinium (231)	92 U Uranium (238)	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)					

72 Ge Germanium 72.64	73 As Arsenic 74.92	74 Se Selenium 78.96	75 Br Bromine 79.90	76 Kr Krypton 83.80	77 Rb Rubidium 85.47	78 Sr Strontium 87.62	79 Y Yttrium 88.91	80 Zr Zirconium 91.22	81 Nb Niobium 92.91	82 Mo Molybdenum 95.94	83 Tc Technetium (98)	84 Ru Ruthenium 101.07	85 Rh Rhodium 102.91	86 Pd Palladium 106.42	87 Ag Silver 107.87	88 Cd Cadmium 112.41	89 In Indium 114.82	90 Sn Tin 118.71	91 Sb Antimony 121.76	92 Te Tellurium 127.60	93 I Iodine 126.90	94 Xe Xenon 131.29	95 Cs Cesium 132.91	96 Ba Barium 137.33	97 La Lanthanum 138.91	98 Ce Cerium 140.12	99 Pr Praseodymium 140.91	100 Nd Neodymium 144.24	101 Pm Promethium (145)	102 Sm Samarium 150.36	103 Eu Europium 151.96	104 Gd Gadolinium 157.25	105 Tb Terbium 158.93	106 Dy Dysprosium 162.50	107 Ho Holmium 164.93	108 Er Erbium 167.26	109 Tm Thulium 168.93	110 Yb Ytterbium 173.05	111 Lu Lutetium 174.97
102 Th Thorium 232.04	103 Pa Protactinium 231.04	104 U Uranium 238.03	105 Np Neptunium 237.05	106 Pu Plutonium 244.06	107 Am Americium 243.06	108 Cm Curium 247.07	109 Bk Berkelium 247.07	110 Cf Californium 251.08	111 Es Einsteinium 252.08	112 Fm Fermium 257.10	113 Md Mendelevium 258.10	114 No Nobelium 259.10	115 Lr Lawrencium 262.11																										

- **3d transition metal** and **4f rare earth**
- LDA and PBE underestimate on-site Coulomb energy
- DFT+U adds Hubbard-like correction to remedy this deficiency
- Important for strongly-correlated materials

Anisimov, Zaanen & Andersen, Phys. Rev. B 44, 943 (1991)

FeO (AF-II phase)

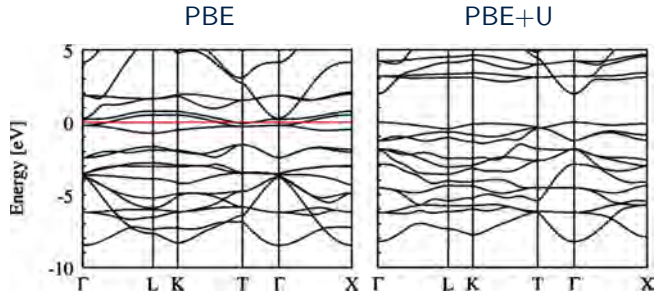
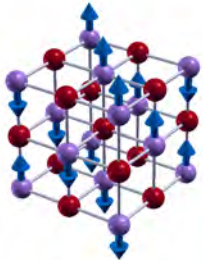


Figure from: Cococcioni & De Gironcoli, PRB 2005

Anisimov, Zaanen & Andersen, Phys. Rev. B 44, 943 (1991)

FeO (AF-II phase)

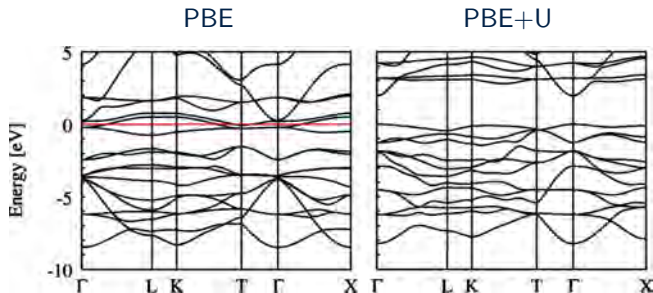
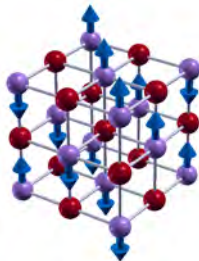


Figure from: Cococcioni & De Gironcoli, PRB 2005

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





- PBE0** Perdew, Burke & Ernzerhof, J. Chem. Phys. 105 (1996)
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- Improve upon semilocal GGA by including fully non-local Fock exchange

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



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



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- Requires the evaluation of the **non-local** Fock exchange potential (expensive)

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



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

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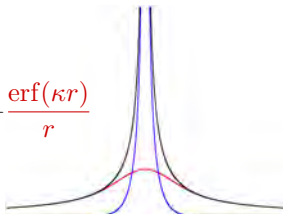
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- The separation is carried out by breaking the Coulomb potential in two parts

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





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- **Band gaps**

Typically PBE underestimates band gaps while Hartree-Fock overestimates. Mixing PBE and HF yields values closer to experiments.



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- **Correlation**

The correlation energy is still described at the PBE level.  
Misses van der Waals effects and dynamical renormalization effects.



## GW method

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

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

$$\text{KS} \quad -\frac{1}{2}\nabla^2\phi_i(\mathbf{r}) + [V_n(\mathbf{r}) + V_H(\mathbf{r})]\phi_i(\mathbf{r}) + \boxed{V_{xc}(\mathbf{r})}\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r})$$



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$$\Sigma = \textcolor{blue}{G}\textcolor{red}{W}$$



Screened Coulomb interaction

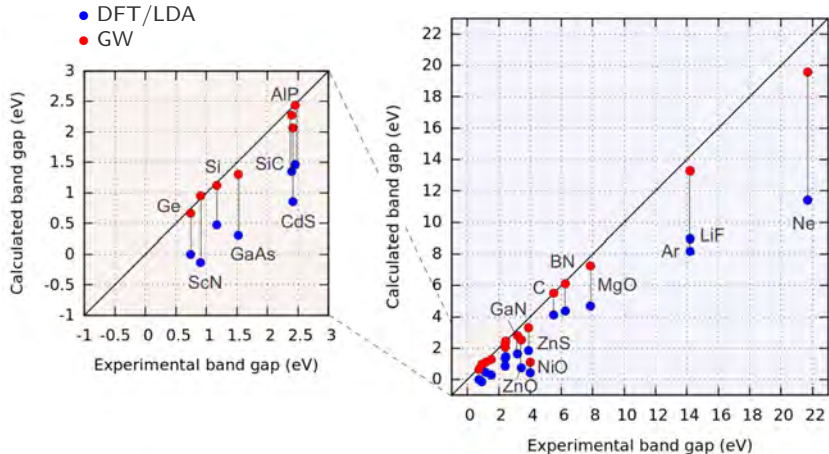
Electron Green's function



## GW method

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Ready to start DFT calculations?

NSF/DOE QUANTUM SCIENCE SUMMER SCHOOL

Cornell University, June 10-22, 2018

Veronica Giustino, Quantum Science Summer School, Cornell, June 2018



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



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

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





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Now we want to show the following

## Theorem

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



- Assume there are two potentials  $V_1$  and  $V_2$  for the same density  
[For clarity we temporarily suppress the subscript 'n' in  $V_n$ ]



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



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



# Example: Ground state of He

03/09

Part 7/7

F Giustino



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

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Total energy

$-2.90 \text{ Ha}$

$-78.9 \text{ eV}$

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Kinetic energy + electron-nucleus interaction     $-3.89 \text{ Ha}$      $-105.8 \text{ eV}$

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Correlation energy     $-0.04$  Ha     $-1.1$  eV

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