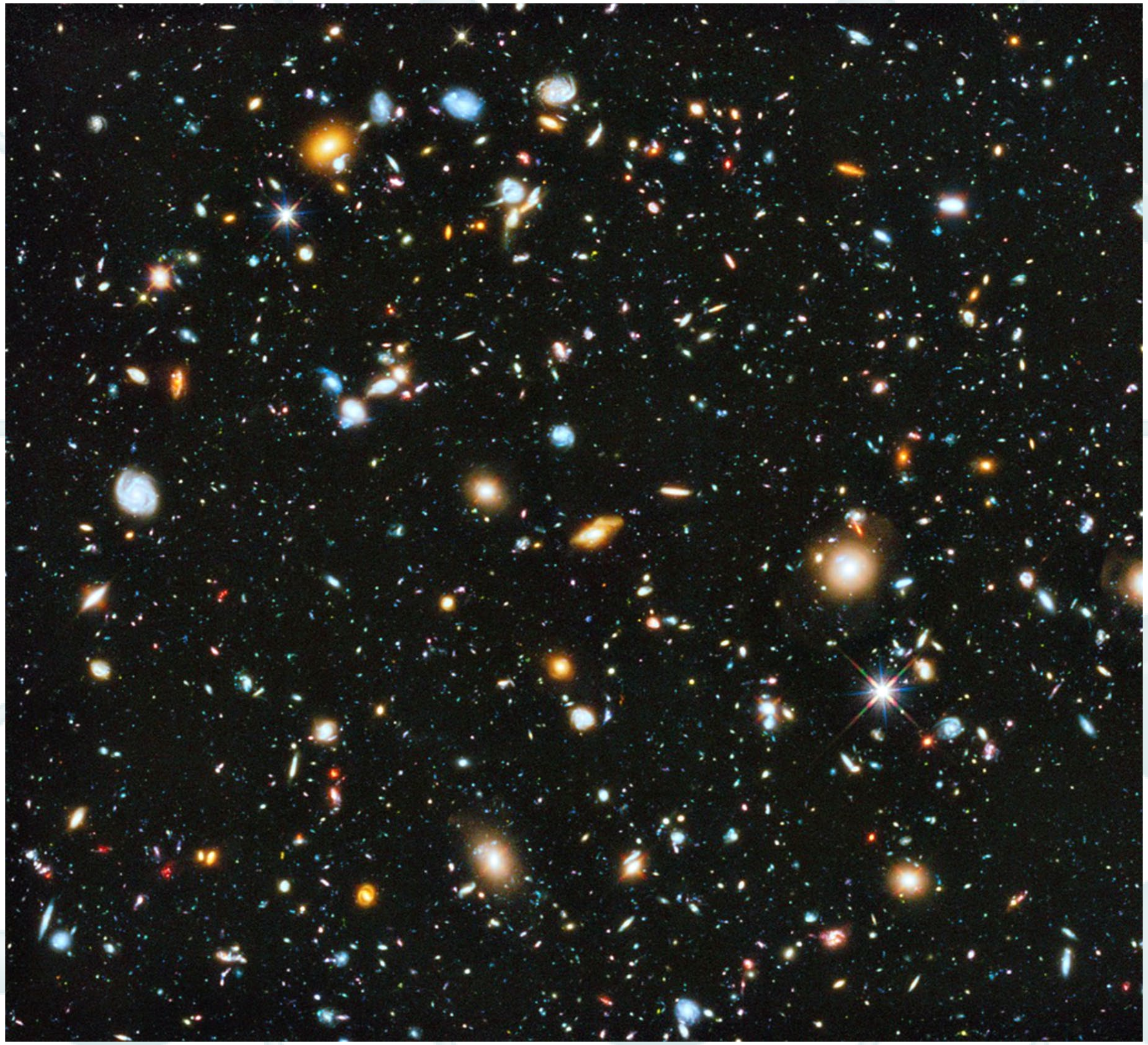
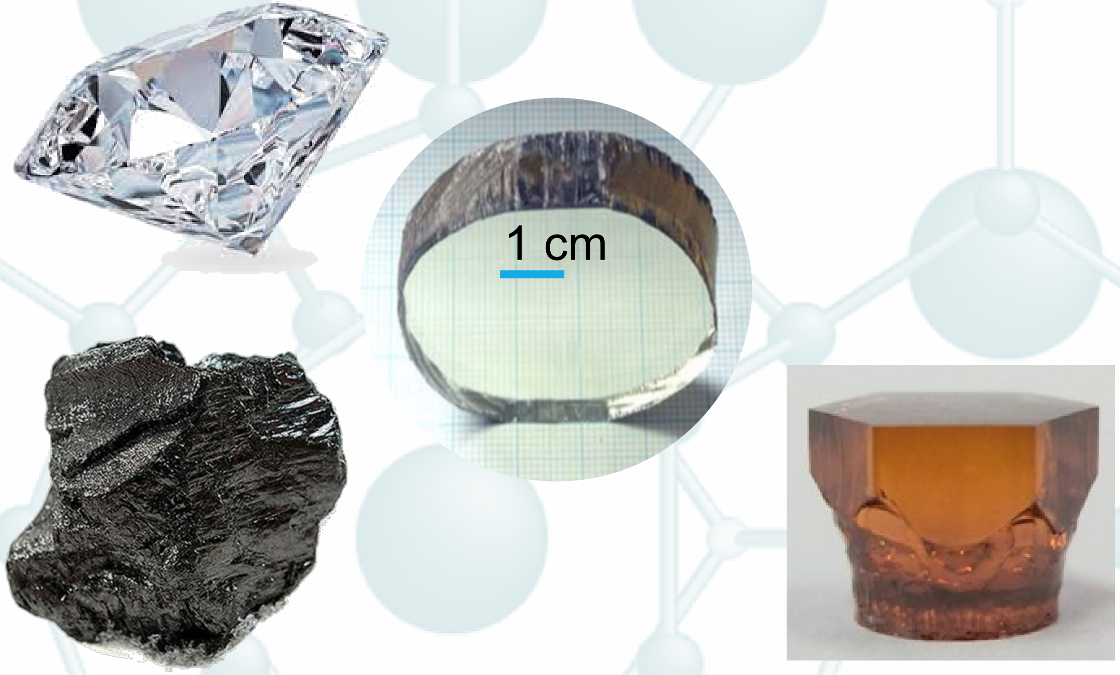
Basics of Density-functional Theory

Claudia Draxl, HU Berlin

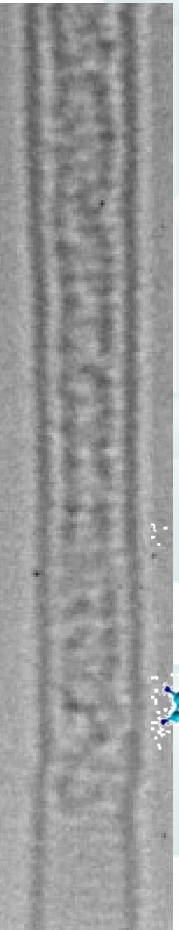
A fascinating universe

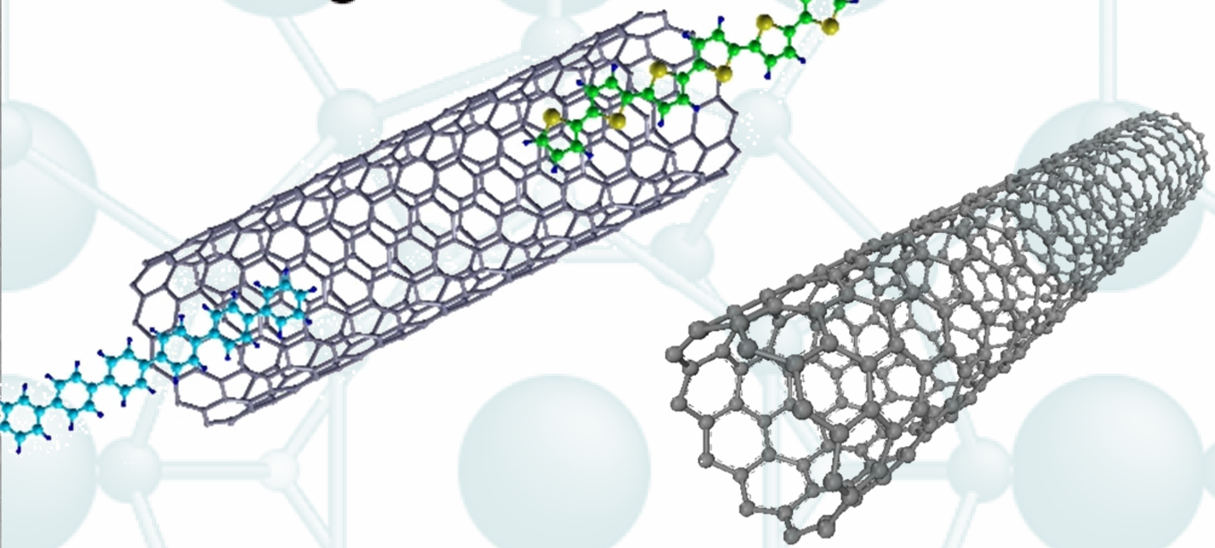




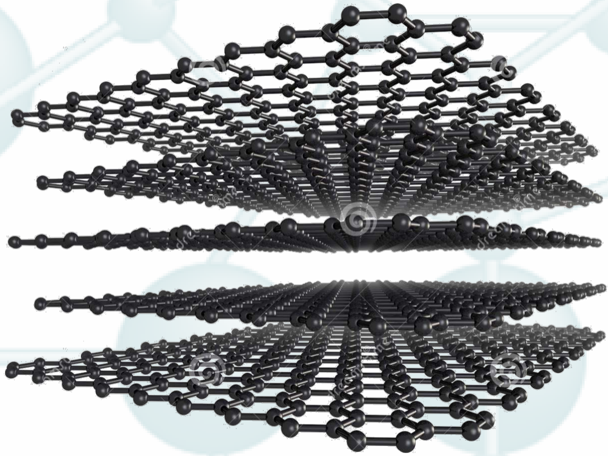
Example: C

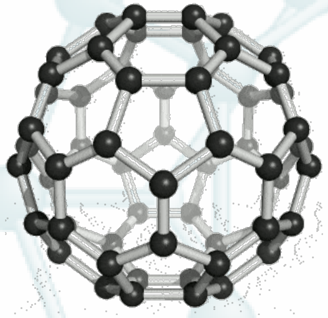
diamond



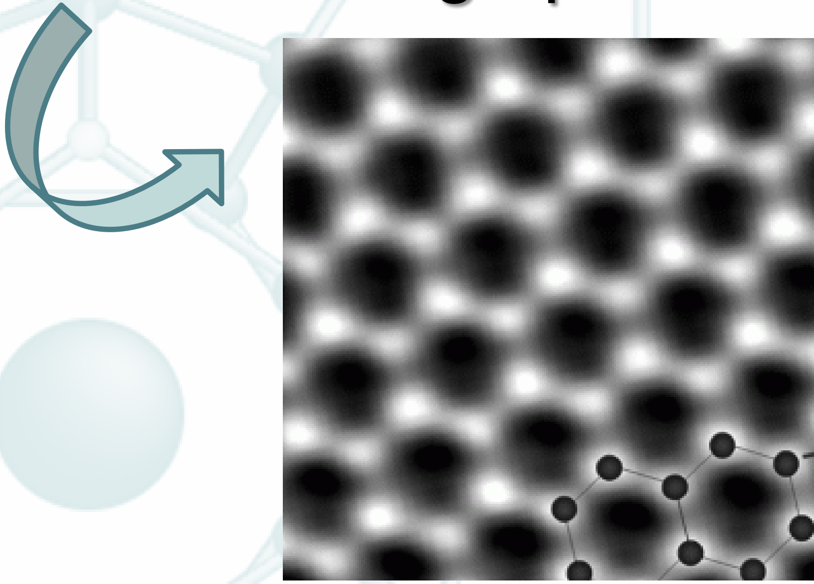


graphite

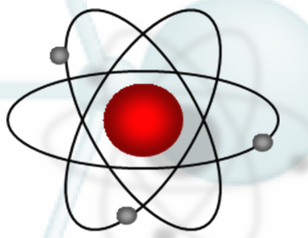


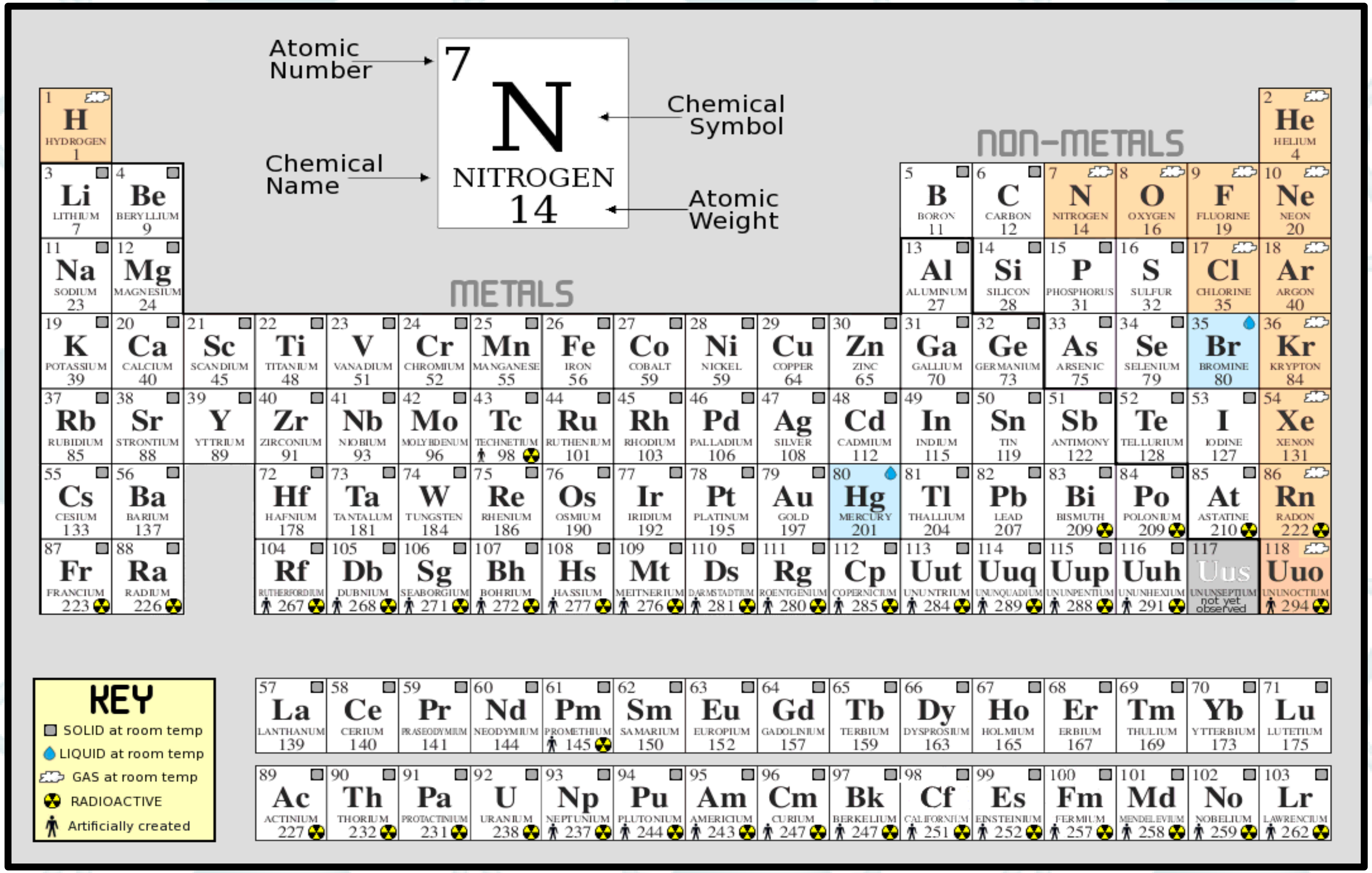


graphene



A playground of building blocks


atoms


Atomic Number

Chemical Symbol

Chemical Name

Atomic Weight

7
N
NITROGEN
14

METALS

NON-METALS

1 ☁ H HYDROGEN 1																	2 ☁ He HELIUM 4
3 ■ Li LITHIUM 7	4 ■ Be BERYLLIUM 9											5 ■ B BORON 11	6 ■ C CARBON 12	7 ☁ N NITROGEN 14	8 ☁ O OXYGEN 16	9 ☁ F FLUORINE 19	10 ☁ Ne NEON 20
11 ■ Na SODIUM 23	12 ■ Mg MAGNESIUM 24											13 ■ Al ALUMINUM 27	14 ■ Si SILICON 28	15 ■ P PHOSPHORUS 31	16 ■ S SULFUR 32	17 ☁ Cl CHLORINE 35	18 ☁ Ar ARGON 40
19 ■ K POTASSIUM 39	20 ■ Ca CALCIUM 40	21 ■ Sc SCANDIUM 45	22 ■ Ti TITANIUM 48	23 ■ V VANADIUM 51	24 ■ Cr CHROMIUM 52	25 ■ Mn MANGANESE 55	26 ■ Fe IRON 56	27 ■ Co COBALT 59	28 ■ Ni NICKEL 59	29 ■ Cu COPPER 64	30 ■ Zn ZINC 65	31 ■ Ga GALLIUM 70	32 ■ Ge GERMANIUM 73	33 ■ As ARSENIC 75	34 ■ Se SELENIUM 79	35 💧 Br BROMINE 80	36 ☁ Kr KRYPTON 84
37 ■ Rb RUBIDIUM 85	38 ■ Sr STRONTIUM 88	39 ■ Y YTTRIUM 89	40 ■ Zr ZIRCONIUM 91	41 ■ Nb NIOBIUM 93	42 ■ Mo MOLYBDENUM 96	43 ■ Tc TECHNETIUM 🚶 98 ☢	44 ■ Ru RUTHENIUM 101	45 ■ Rh RHODIUM 103	46 ■ Pd PALLADIUM 106	47 ■ Ag SILVER 108	48 ■ Cd CADMIUM 112	49 ■ In INDIUM 115	50 ■ Sn TIN 119	51 ■ Sb ANTIMONY 122	52 ■ Te TELLURIUM 128	53 ■ I IODINE 127	54 ☁ Xe XENON 131
55 ■ Cs CESIUM 133	56 ■ Ba BARIUM 137		72 ■ Hf HAFNIUM 178	73 ■ Ta TANTALUM 181	74 ■ W TUNGSTEN 184	75 ■ Re RHENIUM 186	76 ■ Os OSMIUM 190	77 ■ Ir IRIDIUM 192	78 ■ Pt PLATINUM 195	79 ■ Au GOLD 197	80 💧 Hg MERCURY 201	81 ■ Tl THALLIUM 204	82 ■ Pb LEAD 207	83 ■ Bi BISMUTH 209 ☢	84 ■ Po POLONIUM 209 ☢	85 ■ At ASTATINE 210 ☢	86 ☁ Rn RADON 222 ☢
87 ■ Fr FRANCIUM 223 ☢	88 ■ Ra RADIUM 226 ☢		104 ■ Rf RUTHERFORDIUM 🚶 267 ☢	105 ■ Db DUBNIUM 🚶 268 ☢	106 ■ Sg SEABORGIUM 🚶 271 ☢	107 ■ Bh BOHRIUM 🚶 272 ☢	108 ■ Hs HASSIUM 🚶 277 ☢	109 ■ Mt MEITNERIUM 🚶 276 ☢	110 ■ Ds DARMSTADTIUM 🚶 281 ☢	111 ■ Rg ROENTGENIUM 🚶 280 ☢	112 ■ Cp COPERNICIUM 🚶 285 ☢	113 ■ Uut UNUNTRIUM 🚶 284 ☢	114 ■ Uuq UNUNQUADIUM 🚶 289 ☢	115 ■ Uup UNUNPENTIUM 🚶 288 ☢	116 ■ Uuh UNUNHEXIUM 🚶 291 ☢	117 Uus UNUNSEPTIUM not yet observed	118 ☁ Uuo UNUNOCTIUM 🚶 294 ☢

57 ■ La LANTHANUM 139	58 ■ Ce CERIUM 140	59 ■ Pr PRASEODYMIUM 141	60 ■ Nd NEODYMIUM 144	61 ■ Pm PROMETHIUM 🚶 145 ☢	62 ■ Sm SAMARIUM 150	63 ■ Eu EUROPIUM 152	64 ■ Gd GADOLINIUM 157	65 ■ Tb TERBIUM 159	66 ■ Dy DYSPROSIUM 163	67 ■ Ho HOLMIUM 165	68 ■ Er ERBIUM 167	69 ■ Tm THULIUM 169	70 ■ Yb YTTERBIUM 173	71 ■ Lu LUTETIUM 175
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 ☢

KEY
- ■ SOLID at room temp
- 💧 LIQUID at room temp
- ☁ GAS at room temp
- ☢ RADIOACTIVE
- 🚶 Artificially created

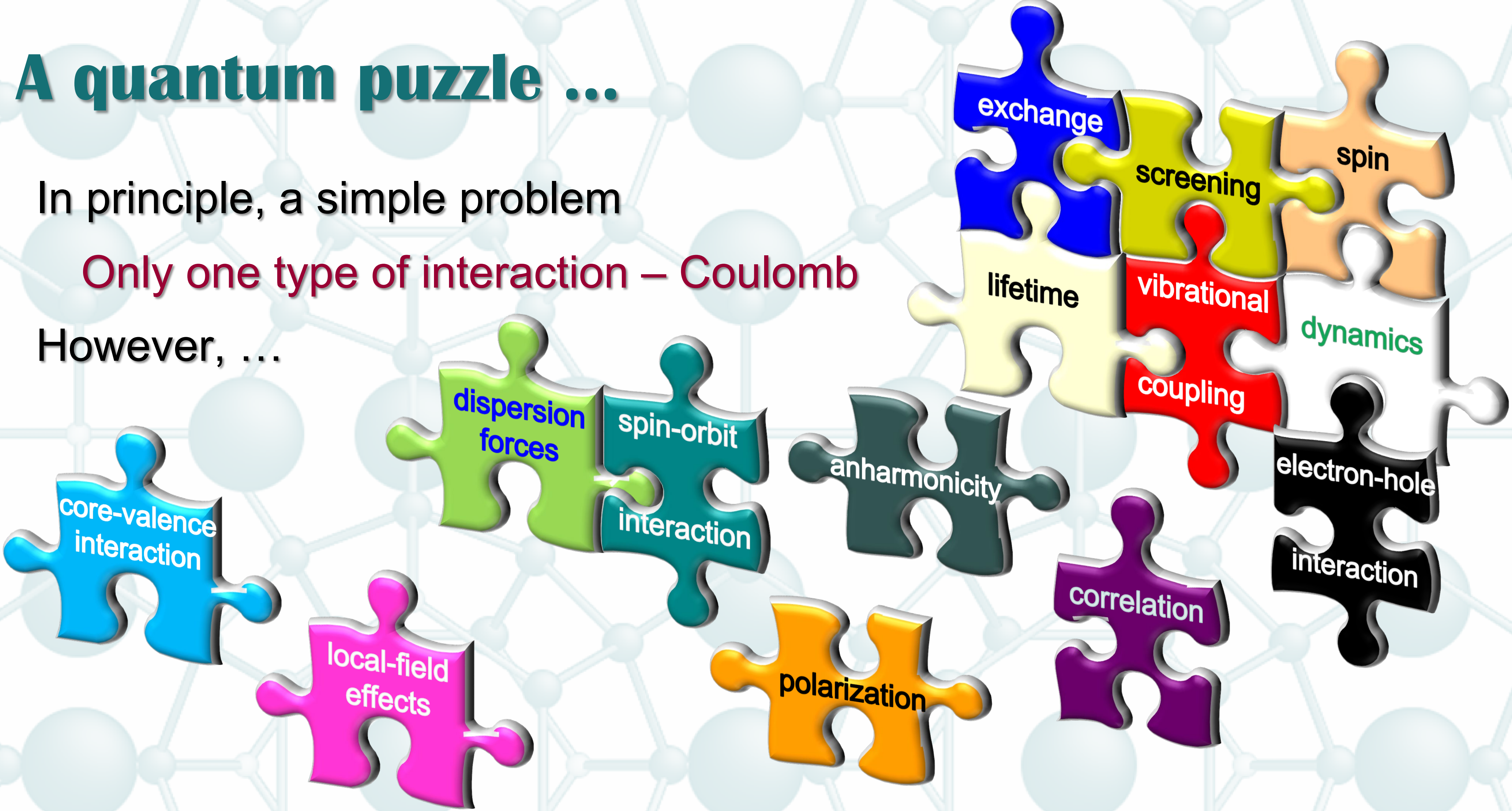
… giving rise to an infinite number of materials

A quantum puzzle …

In principle, a simple problem

Only one type of interaction – Coulomb

However, …



Why are condensed-matter systems so complicated then?

It's all about materials …

- Harder, tougher, …,
- Light-weight, ductile, …
- Flexible, ultra-thin, …
- Non-toxic, sustainable, edible, …
- Energy saving, …
- Biocompatible, …

Role of theory?





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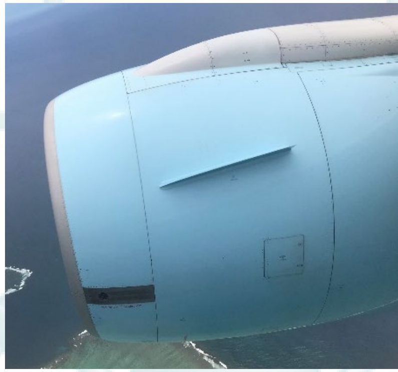
ADVANCED FUNCTIONAL MATERIALS




What do we want?

Describe all materials on the same footing – without parameters from experiment

Understand and predict all kinds of properties – from their structure to their response to electromagnetic radiation, and more …

Many-body systems

How can we describe a many-body system of interacting particles?

In principle, we know what to do …

$$H \Psi = E \Psi$$

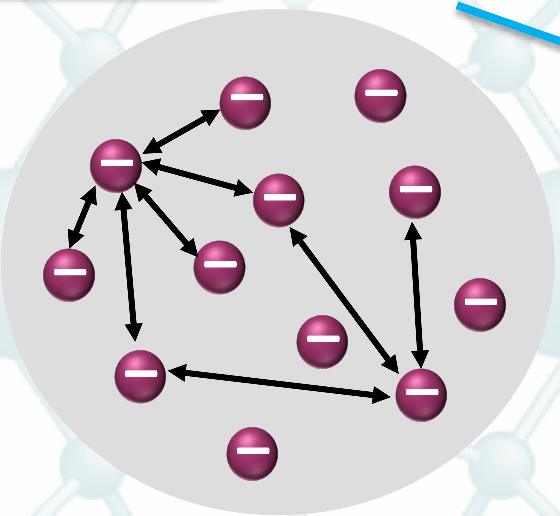
$$\Psi(R_1, R_2, \dots R_N; r_1, r_2, r_3, r_4, \dots r_M)$$

The wavefunction of steel

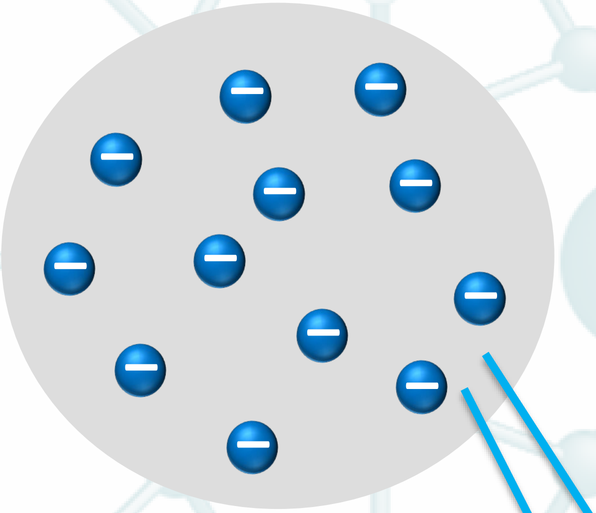
Sandviken, Sweden, 1901

DFT in a nutshell

We replace the many-body system of interacting electrons by fictitious sytem of non-interacting electrons



$n(\mathbf{r})$



Caution!

Density-functional theory

Ground state

Kohn-Sham equation

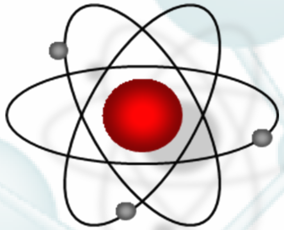
$$\left[T+V_{ext}(\mathbf{r})+V_H(\mathbf{r})+V_{xc}(\mathbf{r})\right]\psi_i^{KS}(\mathbf{r})=\epsilon_i^{KS}\psi_i^{KS}(\mathbf{r})$$

Density-functional theory

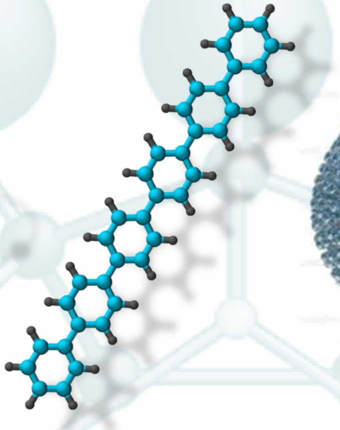
Hohenberg-Kohn theorem (1964)

The electron density is the key variable.

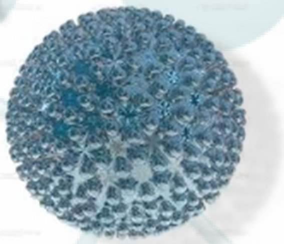
Why do we like it so much?



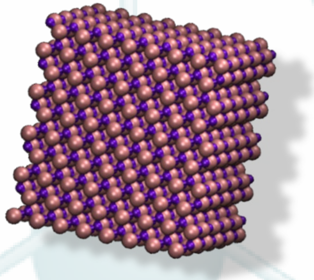
atoms



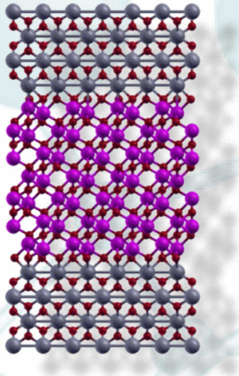
molecules



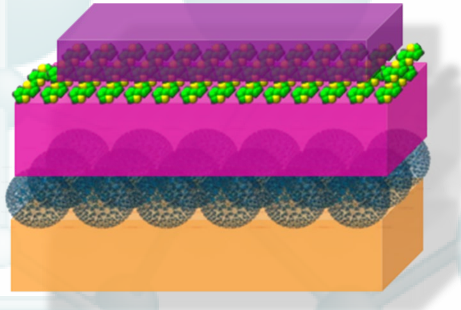
clusters



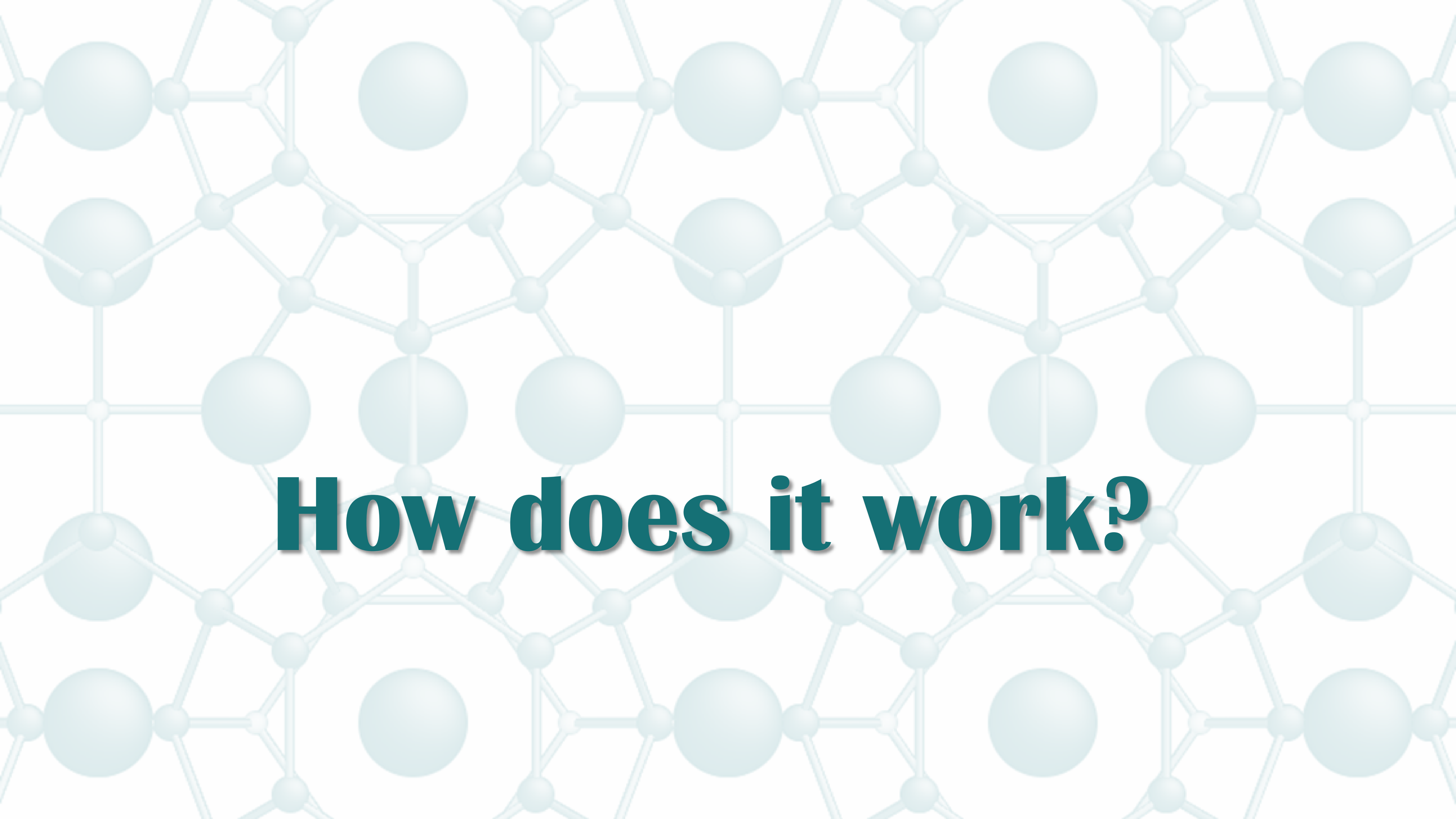
bulk crystals



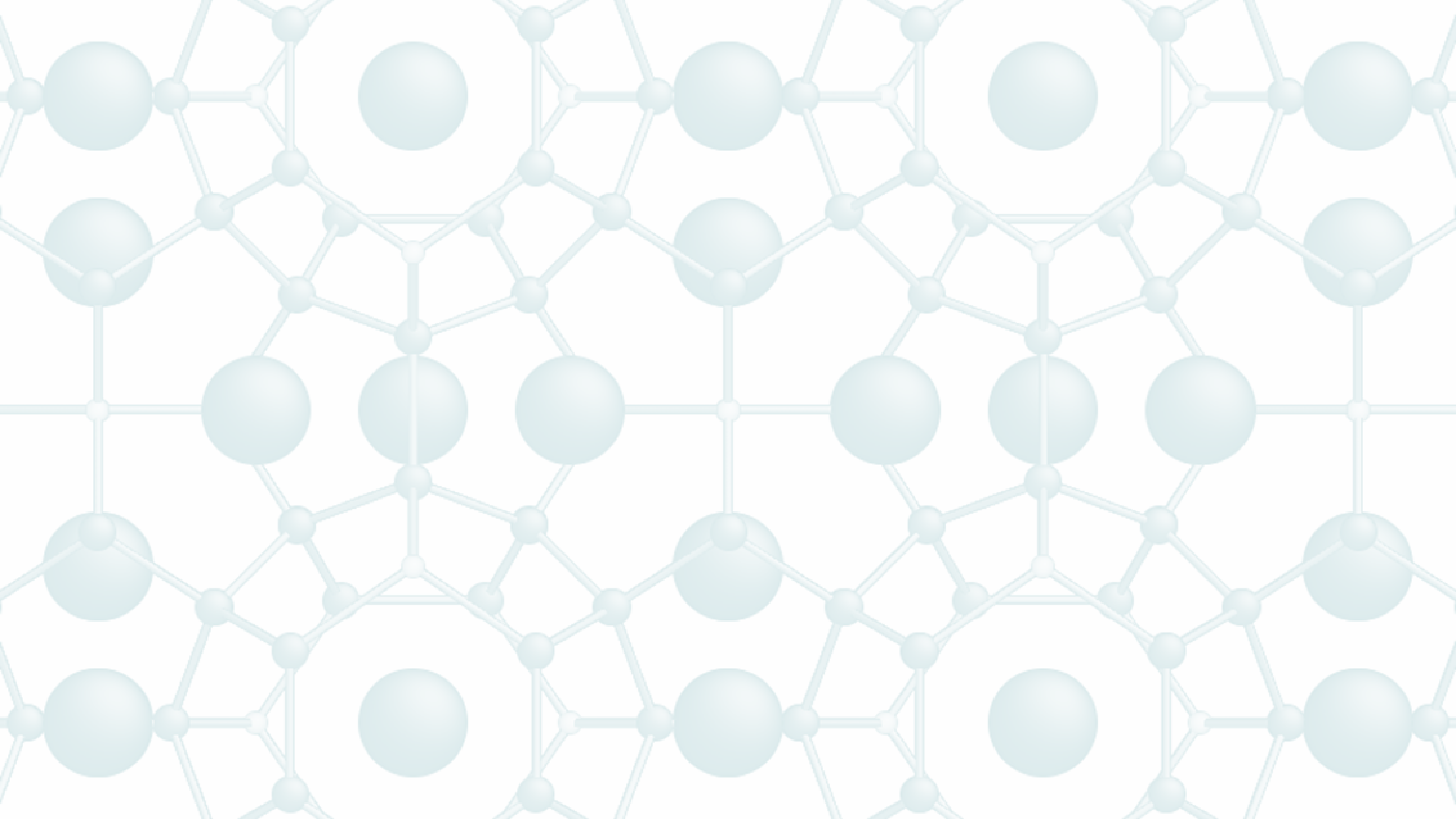
surfaces & interfaces



nanostructures



How does it work?



Questions

Do we really need the many-body wavefunction?

Can we compute the electron distribution without explicitly knowing the WF?

$$n(\mathbf{r}) = \left\langle \Phi(\{\mathbf{r}_i\}) \left| \sum_i^N \delta(\mathbf{r} - \mathbf{r}_i) \right| \Phi(\{\mathbf{r}_i\}) \right\rangle$$

According to Hohenberg and Kohn, only the electron density is required

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

depending on three coordinates: x, y, z

Density-functional theory

Hohenberg-Kohn theorem

P. Hohenberg, W. Kohn, Phys. Rev. 136 , B864 (1964)

I: The total energy of an interacting system of electrons is a unique functional of the density.

$$\boxed{E = F[n(\mathbf{r})] + \int V_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r}}$$

The functional *F* does not depend on the external potential !!

II: The energy takes its minimum at the ground-state density.

Walter Kohn

Nobel prize to Walter Kohn

1998 for chemistry (!)

34 years before DFT

34 years after DFT

Density-functional theory

Proof of HK theorem

I: Uniqueness: We need to show that there is only one potential that leads to a certain density

Given V_{ext} H^e $E = \langle \Phi(\{\mathbf{r}_i\}) | H^e | \Phi(\{\mathbf{r}_i\}) \rangle$ $n(\mathbf{r})$

Assume there is another potential such that we have

$$\tilde{V}_{ext} \quad \tilde{H}^e \quad \tilde{E} = \left\langle \tilde{\Phi}(\{\mathbf{r}_i\}) \middle| \tilde{H}^e \middle| \tilde{\Phi}(\{\mathbf{r}_i\}) \right\rangle \quad \tilde{n}(\mathbf{r}) = n(\mathbf{r})$$

$$\tilde{E} = \left\langle \tilde{\Phi} \middle| \tilde{H}^e \middle| \tilde{\Phi} \right\rangle < \left\langle \Phi \middle| \tilde{H}^e \middle| \Phi \right\rangle = \left\langle \Phi \middle| H^e - V_{ext} + \tilde{V}_{ext} \middle| \Phi \right\rangle$$

$$\tilde{E} < E + \left\langle \Phi \middle| \tilde{V}_{ext} - V_{ext} \middle| \Phi \right\rangle$$

Density-functional theory

$$\tilde{E} < E + \left\langle \Phi \middle| \tilde{V}_{ext} - V_{ext} \middle| \Phi \right\rangle = E + \int d\mathbf{r} \left(\tilde{V}_{ext} - V_{ext} \right) n(\mathbf{r})$$

+

$$E < \tilde{E} + \left\langle \tilde{\Phi} \middle| V_{ext} - \tilde{V}_{ext} \middle| \tilde{\Phi} \right\rangle = \boxed{\tilde{E} + \int d\mathbf{r} \left(V_{ext} - \tilde{V}_{ext} \right) \tilde{n}(\mathbf{r})}$$

$$\Updownarrow \qquad \tilde{n}(\mathbf{r}) = n(\mathbf{r})$$

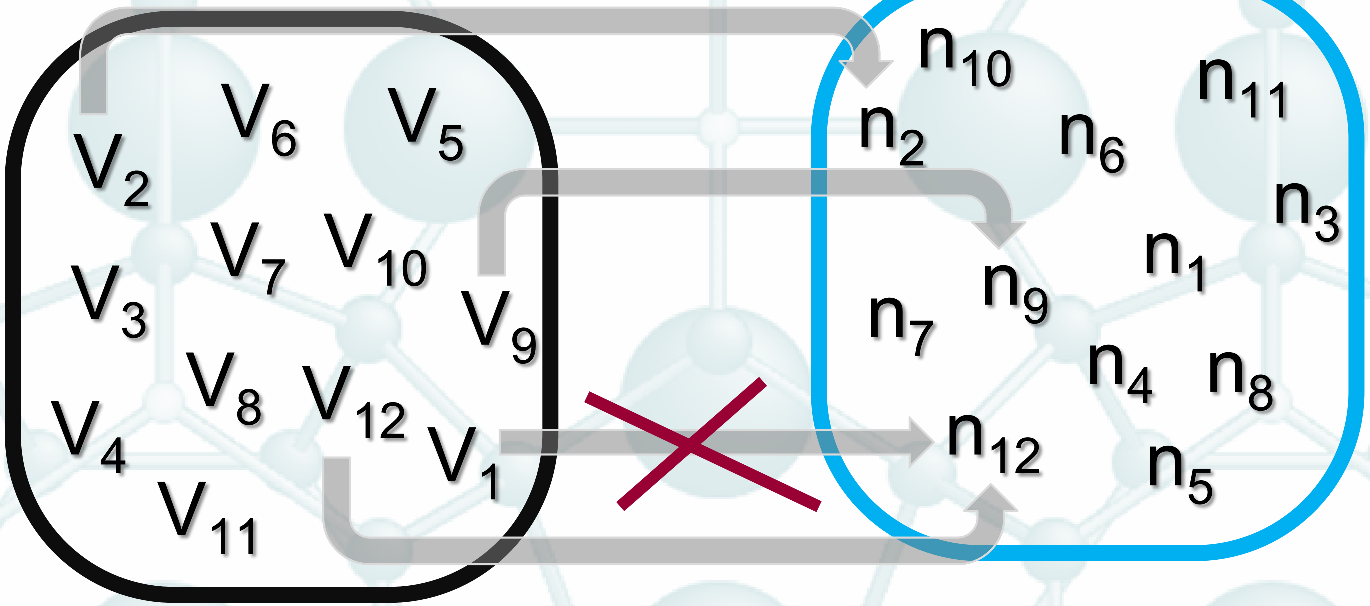
$$\boxed{\tilde{E} + \int d\mathbf{r} \left(V_{ext} - \tilde{V}_{ext} \right) n(\mathbf{r})}$$

$$\tilde{E} + E < E + \tilde{E} \quad \Longrightarrow \quad \boxed{\tilde{n}(\mathbf{r}) \neq n(\mathbf{r})}$$

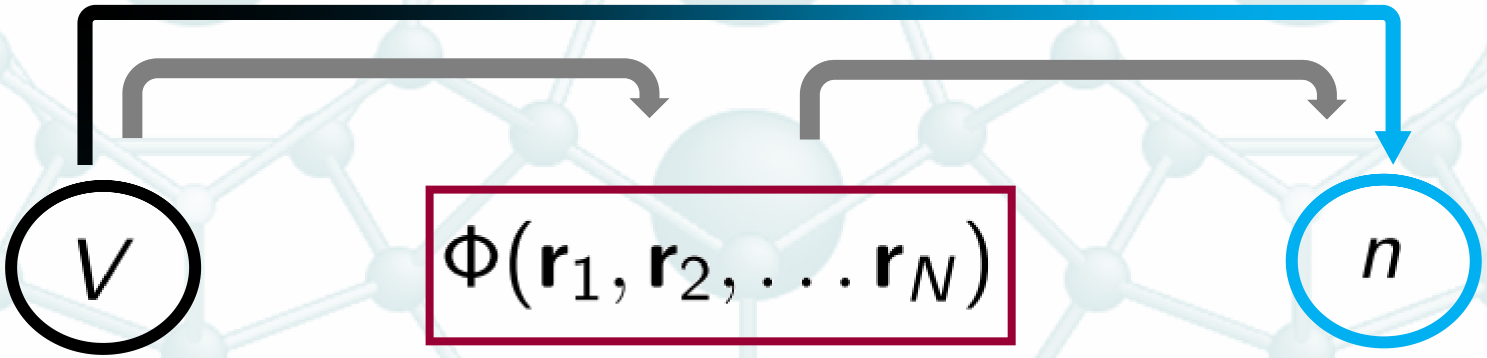
impossible!

Density-functional theory

There is a one-to-one correspondence between density and potential.



Density-functional theory



V

$\Phi(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N)$

n

single-particle potentials

ground-state wavefunctions

single-particle densities

$$n(\mathbf{r}) = \left\langle \Phi \left| \sum_{i=1}^{N} \delta\left(\mathbf{r} - \mathbf{r}_i\right) \right| \Phi \right\rangle$$

Hohenberg-Kohn:

$V(\mathbf{r}) \rightarrow \; n(\mathbf{r})$ is invertible

Consequence: Every quantum-mechanical observable is fully determined by the ground-state density.

Density-functional theory

Kohn-Sham theory

The HK theorem is exact for the ground state

It is beautiful as we only need to know one = *THE* functional to describe any system

Atoms, molecules, cluster, bulk materials, surfaces, nano-structures

The only problem is that we don't know this functional

Thus DFT is not practical so far

Kohn and Sham set the stage for the practicality of DFT

W. Kohn, L. Sham, Phys. Rev. A 140,1133 (1965)

Kohn-Sham density-functional theory

One can devide the energy functional into three contributions:

$$F[n(\mathbf{r})] = T[n(\mathbf{r})] + \frac{1}{2}\iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' + \boxed{E_{xc}[n(\mathbf{r})]}$$

unknown "*rest*"

Even if we don't know the expressions for the kinetic energy and the exchange-correlation energy, we can formally vary it with respect to the density, constraining the particle number *N*:

$$\frac{\delta(E-\mu N)}{\delta n(\mathbf{r})} = 0 = \frac{\delta T[n(\mathbf{r})]}{\delta n(\mathbf{r})} + \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + \frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})} + V_{ext}(\mathbf{r}) - \mu$$

Kohn-Sham density-functional theory

$$\frac{\delta(E-\mu N)}{\delta n(\mathbf{r})} = 0 = \frac{\delta T[n(\mathbf{r})]}{\delta n(\mathbf{r})} + \boxed{\int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \boxed{\frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})}} + V_{ext}(\mathbf{r})} - \mu$$

Introducing the exchange-correlation (xc) potential

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

and the effective potential

$$\boxed{V_{eff}(\mathbf{r}) = \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + V_{xc}(\mathbf{r}) + V_{ext}(\mathbf{r})}$$

we arrive at

$$\boxed{\frac{\delta T[n(\mathbf{r})]}{\delta n(\mathbf{r})} + V_{eff}(\mathbf{r}) - \mu = 0}$$

Kohn-Sham density-functional theory

We can now carry out the variation with respect to the density through a variation with respect to the auxiliary single-particle functions.

$$
\begin{aligned}
E[n(\mathbf{r})] - \mu N = & -\frac{1}{2}\int d\mathbf{r} \sum_i u_i^*(\mathbf{r})\nabla^2 u_i(\mathbf{r}) \\
& + \int d\mathbf{r} \quad n(\mathbf{r}) \quad V_{ext}(\mathbf{r}) \\
& + \frac{1}{2}\int d\mathbf{r} \quad n(\mathbf{r}) \quad \int d\mathbf{r}' \quad n(\mathbf{r}') \quad \frac{1}{|\mathbf{r}-\mathbf{r}'|} \\
& + \int d\mathbf{r} \quad n(\mathbf{r}) \quad \epsilon_{xc}(\mathbf{r}) \\
& - \int d\mathbf{r} \quad n(\mathbf{r}) \quad \mu
\end{aligned}
$$

kinetic energy of
non-interacting electrons

Kohn-Sham density-functional theory

Collecting contributions …

$$
\begin{aligned}
E[n(\mathbf{r})] - \mu N = & -\frac{1}{2}\boxed{\int d\mathbf{r} \sum_i u_i^*(\mathbf{r})}\nabla^2 u_i(\mathbf{r}) \\
& + \boxed{\int d\mathbf{r} \sum_i u_i^*(\mathbf{r})} u_i(\mathbf{r}) V_{ext}(\mathbf{r}) \\
& + \frac{1}{2}\boxed{\int d\mathbf{r} \sum_i u_i^*(\mathbf{r})} u_i(\mathbf{r}) \int d\mathbf{r}' \sum_j u_j^*(\mathbf{r}') u_j(\mathbf{r}') \frac{1}{|\mathbf{r}-\mathbf{r}'|} \\
& + \boxed{\int d\mathbf{r} \sum_i u_i^*(\mathbf{r})} u_i(\mathbf{r}) \epsilon_{xc}(\mathbf{r}) \\
& - \boxed{\int d\mathbf{r} \sum_i u_i^*(\mathbf{r})} u_i(\mathbf{r})\ \mu
\end{aligned}
$$

Kohn-Sham density-functional theory

Collecting contributions …

$$
\begin{aligned}
\delta\left(E[n(\mathbf{r})] - \mu N\right) = \boxed{\int d\mathbf{r} \sum_i \delta u_i^*(\mathbf{r})} \Bigg\{ & -\frac{1}{2}\nabla^2 u_i(\mathbf{r}) \\
& + u_i(\mathbf{r}) V_{ext}(\mathbf{r}) \\
& + u_i(\mathbf{r}) \int d\mathbf{r}' \sum_j u_j^*(\mathbf{r}') u_j(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \\
& + u_i(\mathbf{r}) V_{xc}(\mathbf{r}) \\
& - u_i(\mathbf{r})\, \mu \Bigg\}
\end{aligned}
$$

Kohn-Sham density-functional theory

$$\boxed{\delta\left(E[n(\mathbf{r})]-\mu N\right)} = \int d\mathbf{r}\sum_i \delta u_i^*(\mathbf{r})\Big\{-\frac{1}{2}\nabla^2\boxed{u_i(\mathbf{r})}$$

$$+\boxed{u_i(\mathbf{r})}V_{ext}(\mathbf{r})$$

$$+\boxed{u_i(\mathbf{r})}\int d\mathbf{r}'\sum_j u_j^*(\mathbf{r}')u_j(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}$$

$$+\boxed{u_i(\mathbf{r})}V_{xc}(\mathbf{r})$$

$$-\boxed{u_i(\mathbf{r})}\,\mu\Big\}$$

0

fulfilled for each *i*

$$\left\{-\frac{1}{2}\nabla^2+V_{ext}(\mathbf{r})+\int d\mathbf{r}'\sum_j u_j^*(\mathbf{r}')u_j(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}+V_{xc}(\mathbf{r})-\epsilon_i\right\}u_i(\mathbf{r})=0$$

Kohn-Sham density-functional theory

$$\left\{-\frac{1}{2}\nabla^2+V_{ext}(\mathbf{r})+\int d\mathbf{r}'\boxed{\sum_j u_j^*(\mathbf{r}')u_j(\mathbf{r}')}\frac{1}{|\mathbf{r}-\mathbf{r}'|}+V_{xc}(\mathbf{r})-\epsilon_i\right\}u_i(\mathbf{r})=0$$

$$\Downarrow$$

$$\left\{-\frac{1}{2}\nabla^2+V_{ext}(\mathbf{r})+\int d\mathbf{r}'\,n(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}+V_{xc}(\mathbf{r})-\epsilon_i\right\}u_i(\mathbf{r})=0$$

Kohn-Sham equations

$$\boxed{\left\{-\frac{1}{2}\nabla^2+V_{ext}(\mathbf{r})+\int d\mathbf{r}'\,n(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}+\boxed{V_{xc}[n(\mathbf{r})]}-\epsilon_i\right\}u_i(\mathbf{r})=0}$$

approximation needed – only approximation!
contains xc effects and corrections to kinetic energy

Kohn-Sham density-functional theory

Caution: The Kohn-Sham eigenvalues were derived as Lagrange parameters of the variation procedure.

They cannot *a priori* be interpreted as single-particle energies.

The Kohn-Sham orbitals are auxiliary quantities which produce the exact density.

The only approximation required for the ground state is V_{xc}.

The potential is a functional of the density which is obtained from the KS orbitals; these, in turn, give the density.

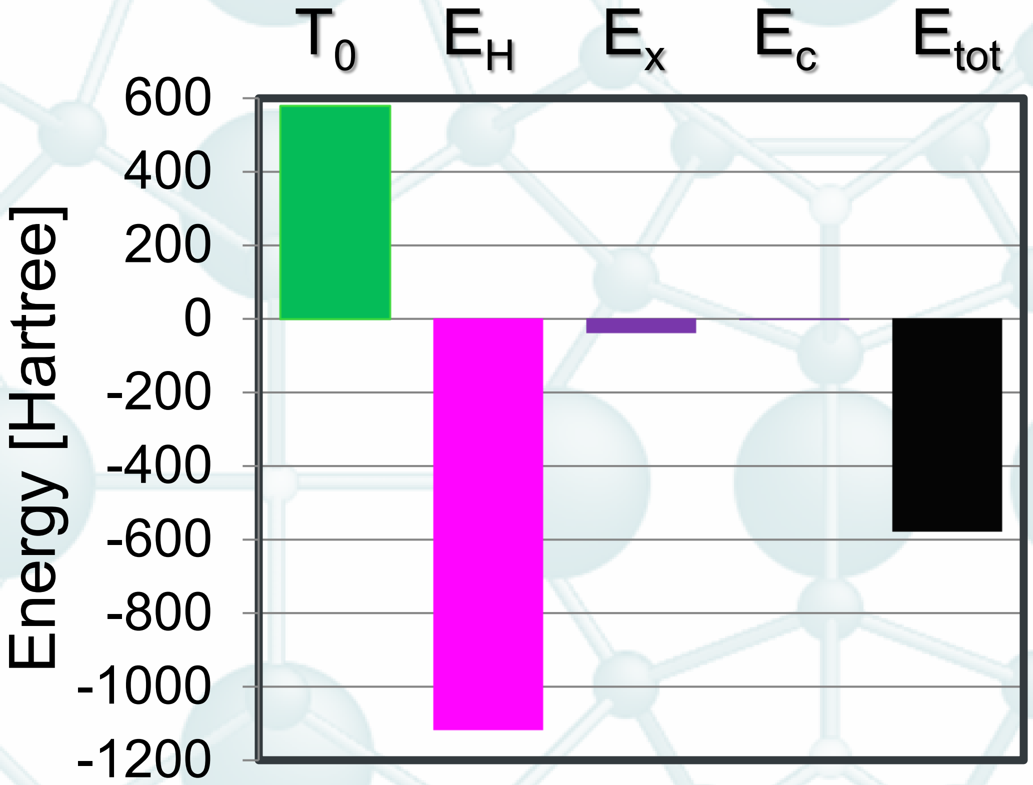
Thus the KS equation must be solved self-consistently.

Role of xc effects

Kohn-Sham density-functional theory

Energy contributions

Example: Si



Splitting into long- and short-range parts of Coulomb interaction is a good approach

Long-range part is treated exactly

Kohn-Sham density-functional theory

Exchange-correlation functionals

Local-density approximation (LDA)

xc effects taken from homogenous electron gas

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

$$\epsilon_x(r_s) = -\frac{3}{2\pi}\left(\frac{9\pi}{4}\right)^{\frac{1}{3}}\frac{1}{r_s} \qquad r_s = \left[\frac{3}{4\pi n(\mathbf{r})}\right]^{\frac{1}{3}}$$

Parametrization to exact numerical solution

e.g., Hedin & Lundquist, 1971

$$x = \frac{r_s}{21}$$

$$\epsilon_c[n(\mathbf{r})] = 0.045\left[(1+x^3)\,ln\left(1+\frac{1}{x}\right)+\frac{x}{2}-x^2-\frac{1}{3}\right]$$

Kohn-Sham density-functional theory

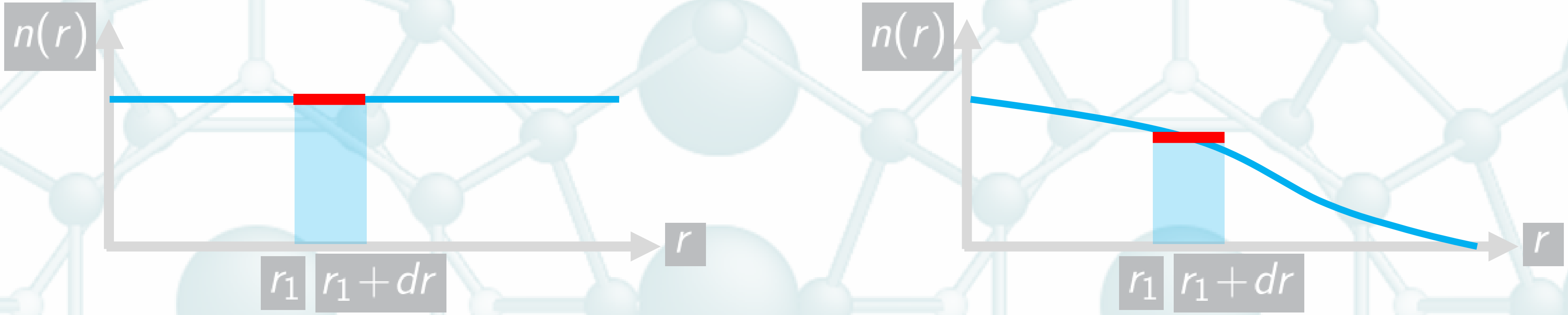
Exchange-correlation functionals

Local-density approximation (LDA)

xc effects taken from homogenous electron gas

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

Example in 1D



constant density

slowly varying density

Exchange-correlation functionals

How well does LDA work?

- In total energies, E_x is underestimated by about ~10%, E_c is overestimated by about ~200%, so E_{xc} is within ~7% compared to the exact solution
  - Cancelation of errors
  - Material-dependent!
- Bond dissociation energies: LDA overbinds by about 1 eV/bond
  - Not good for thermochemistry
- Typical bond lengths are underestimated by 1%
  - Excellent geometries and vibrational frequencies
  - Good for structural properties … but not perfect

Exchange-correlation functionals

What about more strongly varying densities?

- Generalized gradient approximation (GGA)
  - Exchange-correlation energy is functional of the density and the density gradient

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

How to design functionals?

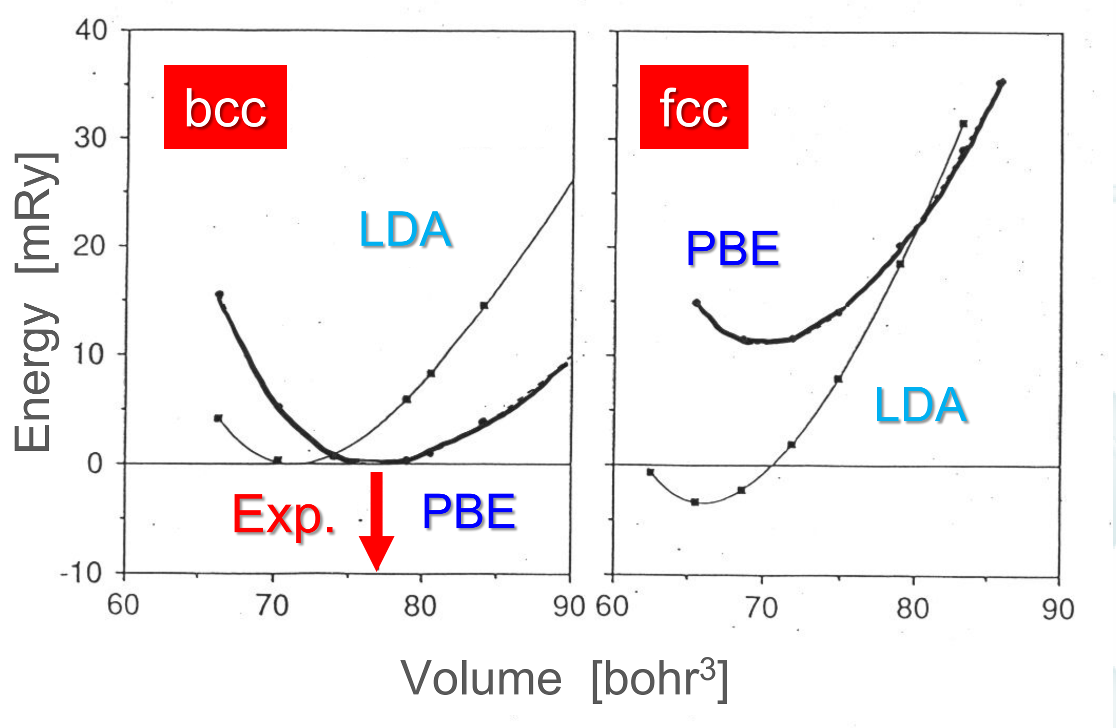
Exchange-correlation functionals

Example: Fe

It took until 1996 that the crystallographic phase of Fe could be (nearly) correctly obtained by DFT

Generalized gradient approximation

PBE



calculations by P. Blaha

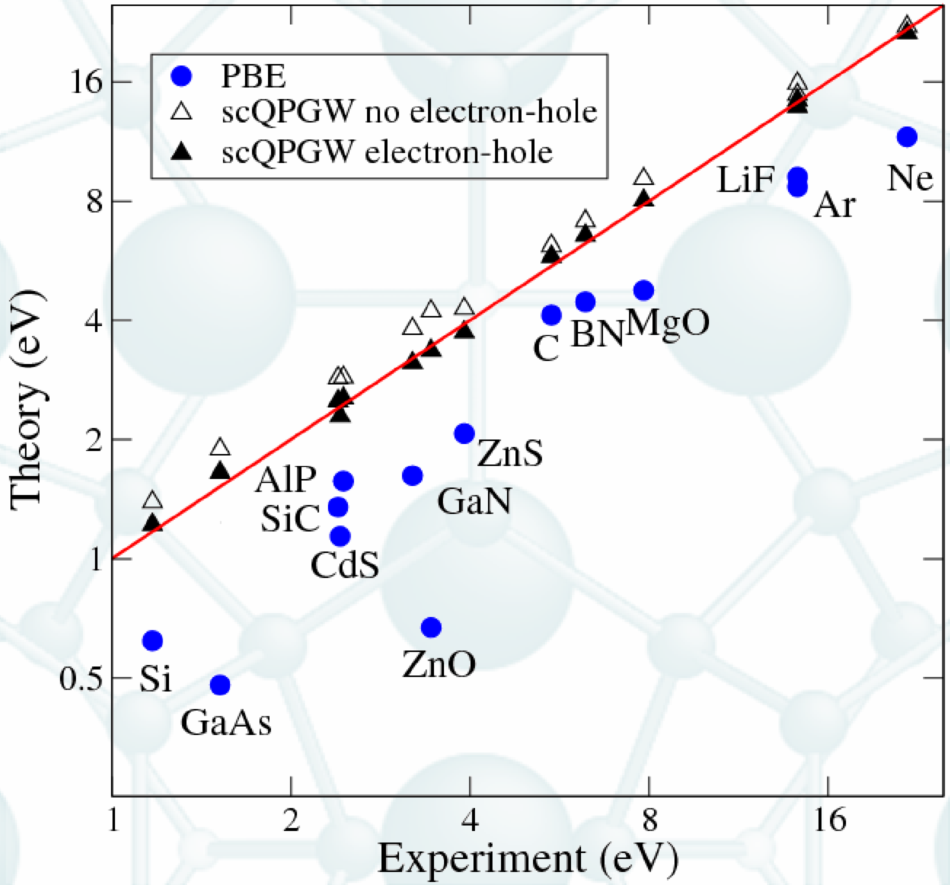
J. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).

More than 136,000 citations

Exchange-correlation functionals

Improvement over LDA?

How well does PBE work for band gaps?



M. Shishkin, M. Marsman, Phys. Rev. Lett. 95, 246403 (2007).

Exchange-correlation functionals

How to design functionals?

Going higher …

Gradient-corrected density functionals (GGA's)

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

Meta- GGA‘s

kinetic energy density

$$E_{xc}^{meta-GGA} = \int d\mathbf{r}\ g[n(\mathbf{r}),\nabla n(\mathbf{r}),\tau(r)]$$

Orbital-dependent functionals

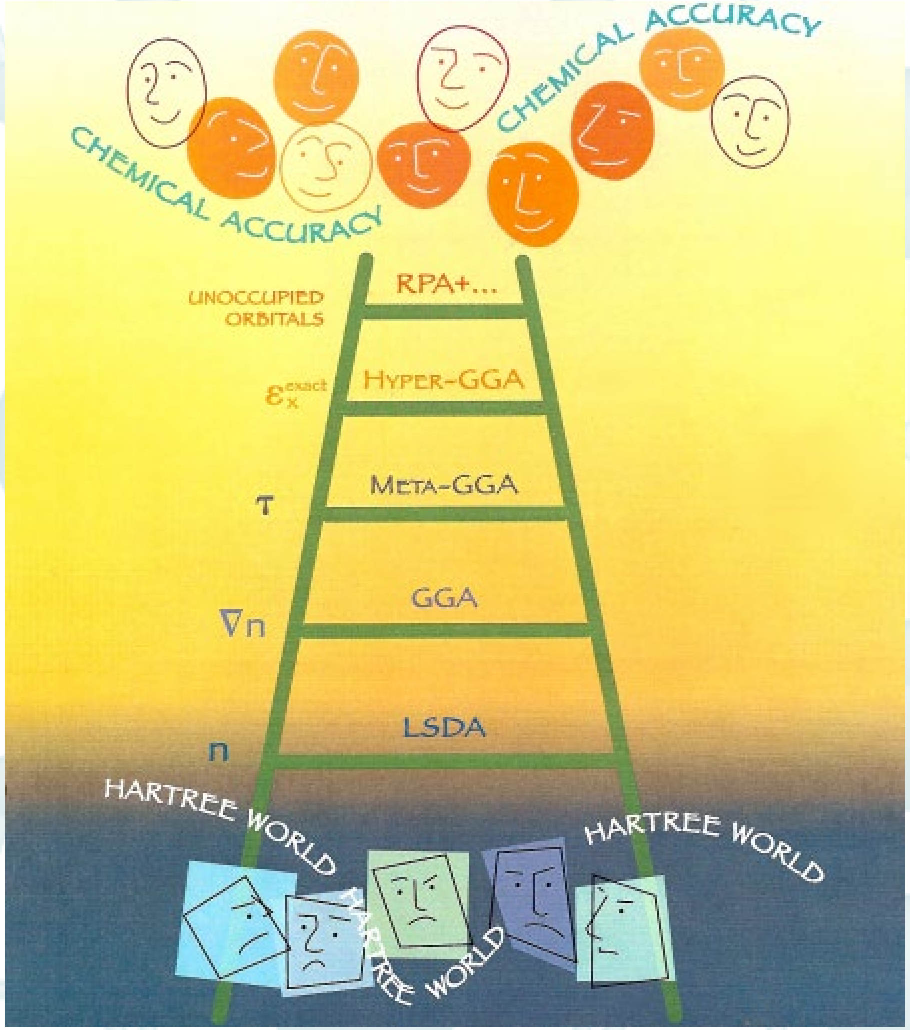
E.g., *exact* exchange

Same as HF theory?

$$E_x^{EX} = -\frac{1}{2}\sum_{i,j}^{\text{occ}}\int d\mathbf{r}\ d\mathbf{r}'\frac{u_i^*(\mathbf{r})u_j^*(\mathbf{r}')u_j(\mathbf{r})u_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

Kohn-Sham density-functional theory

- Exchange-correlation functionals
  - Jacob's ladder
    - by John Perdew



from Kieron Burke

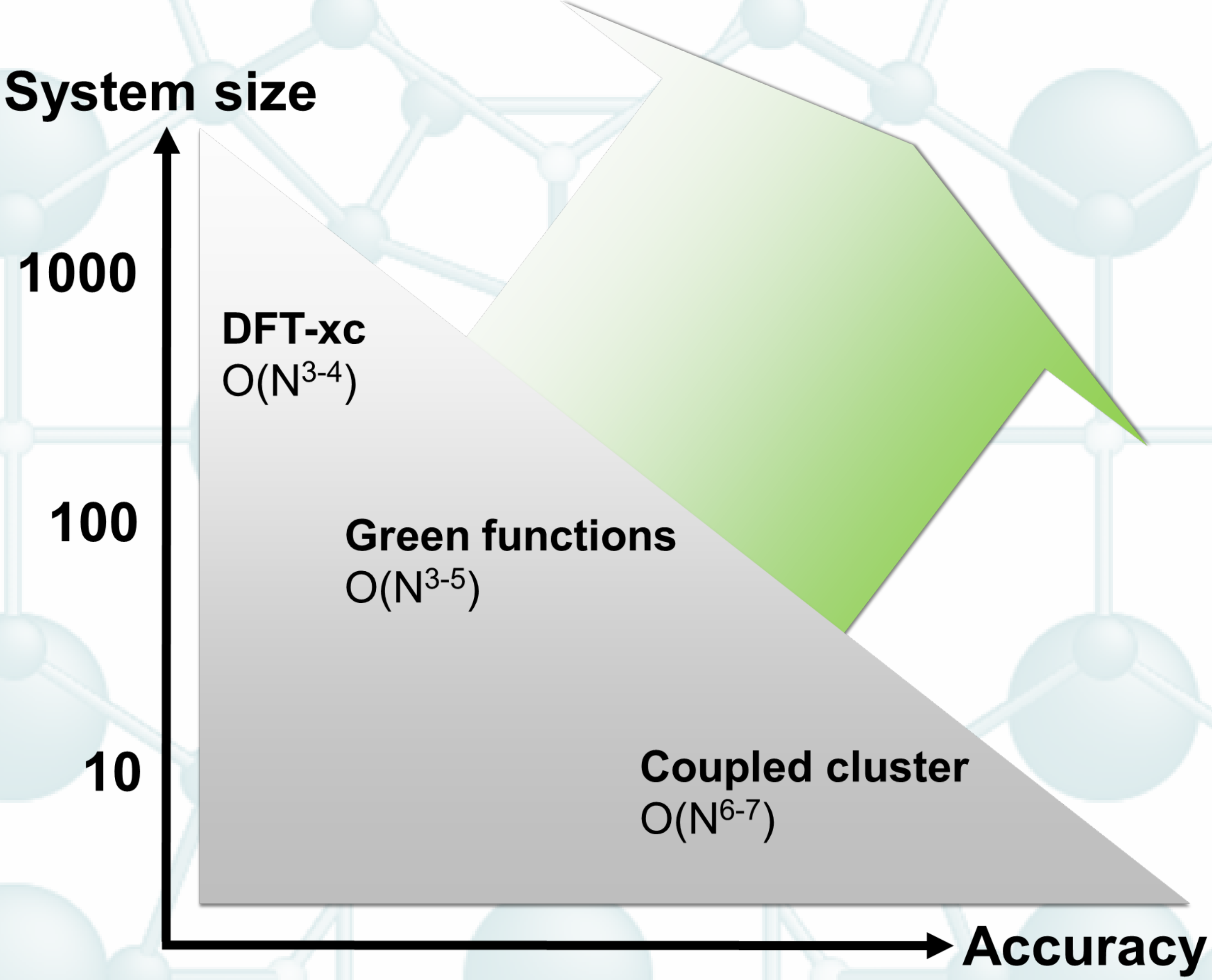
Accuracy

Many materials and/or properties require methods better than semi-local DFT

Complex systems require larger simulation cells

to avoid finite-size effects

… and/or better methodology



How to solve it?

From a PDE to the eigenvalue problem

Multiply KS equation from the left with the complex conjugate KS wavefunction

Integrate over space:

$$\int \psi_{\mathbf{k}}^{*}(\mathbf{r}) \left[-\frac{1}{2}\nabla^{2} + V_{eff}(\mathbf{r}) \right] \psi_{\mathbf{k}}(\mathbf{r}) d^{3}r = \varepsilon_{\mathbf{k}} \int \psi_{\mathbf{k}}^{*}(\mathbf{r}) \psi_{\mathbf{k}}(\mathbf{r}) d^{3}r$$

Ansatz: linear combination of arbitrary basis functions

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{j} c_{j}(\mathbf{k}) \chi_{j\mathbf{k}}(\mathbf{r})$$

From a PDE to the eigenvalue problem

Inserting ansatz for the KS functions in the KS equation leads to secular equation

$$\boxed{\sum_j \Big[\langle i|H|j\rangle - \varepsilon\langle i|j\rangle\Big] c_j = 0}$$

with the matrix elements

$$\langle i|H|j\rangle = \int \chi^*_{i\mathbf{k}}(\mathbf{r})\, H\, \chi_{j\mathbf{k}}(\mathbf{r}) d^3 r$$

$$\langle i|j\rangle = \int \chi^*_{i\mathbf{k}}(\mathbf{r}) \chi_{j\mathbf{k}}(\mathbf{r}) d^3 r$$

Choices of basis sets

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_j c_j(\mathbf{k}) \chi_{j\mathbf{k}}(\mathbf{r})$$

How do they compare?

Planewaves

- Easy to handle
- Require pseudopotentials
  - VASP, Abinit, Quantum ESPRESSO, CASTEP, ...

Atomic-like functions

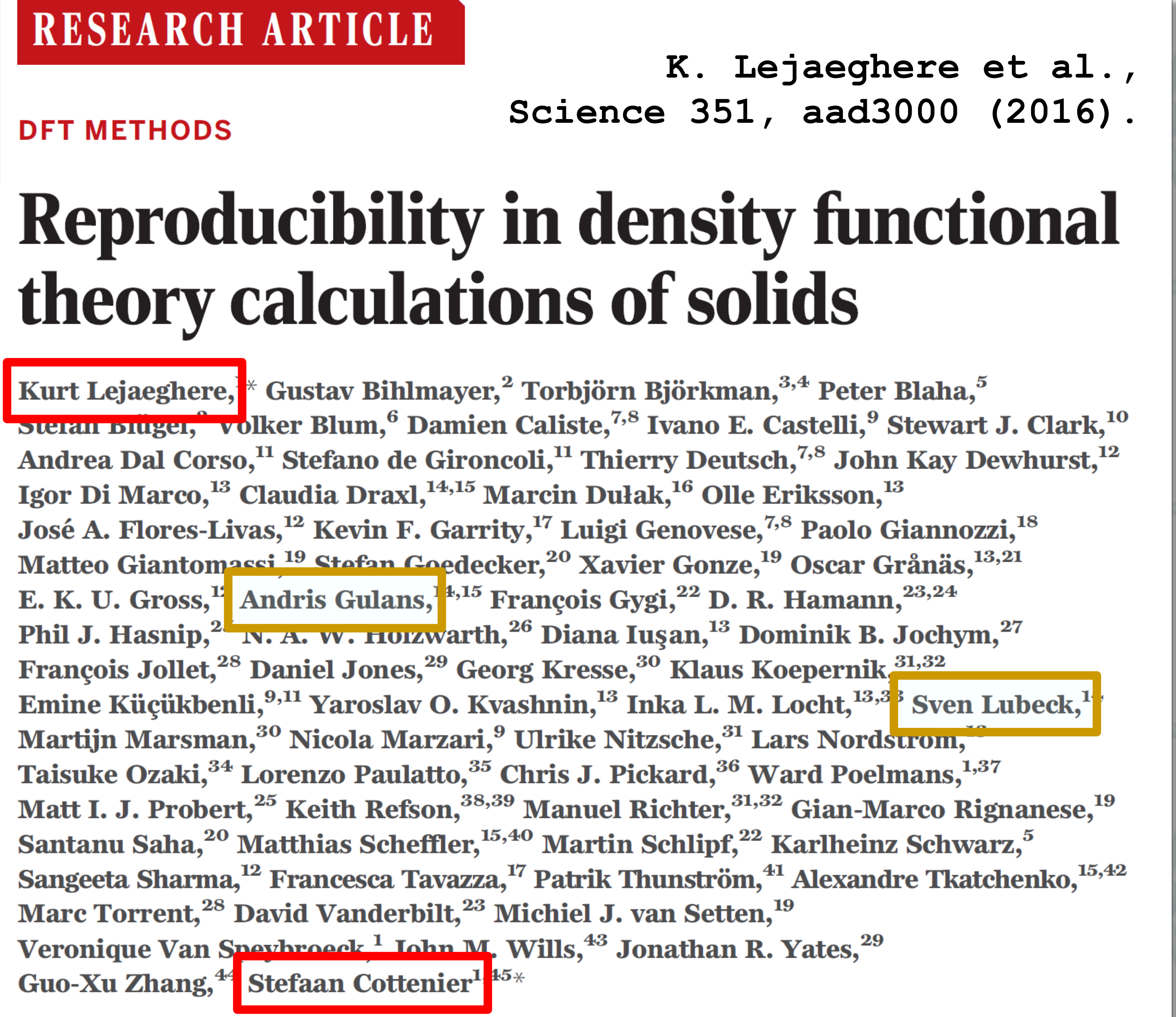
- Numerically very efficient
  - SIESTA, FHI-aims, …

Augmented planewaves

- Highly precise
  - WIEN2k, **`exciting`**, FLEUR, ELK, …

Precision …

K. Lejaeghere et al.,
Science 351, aad3000 (2016).



Science
AAAS

RESEARCH ARTICLE

DFT METHODS

Reproducibility in density functional theory calculations of solids

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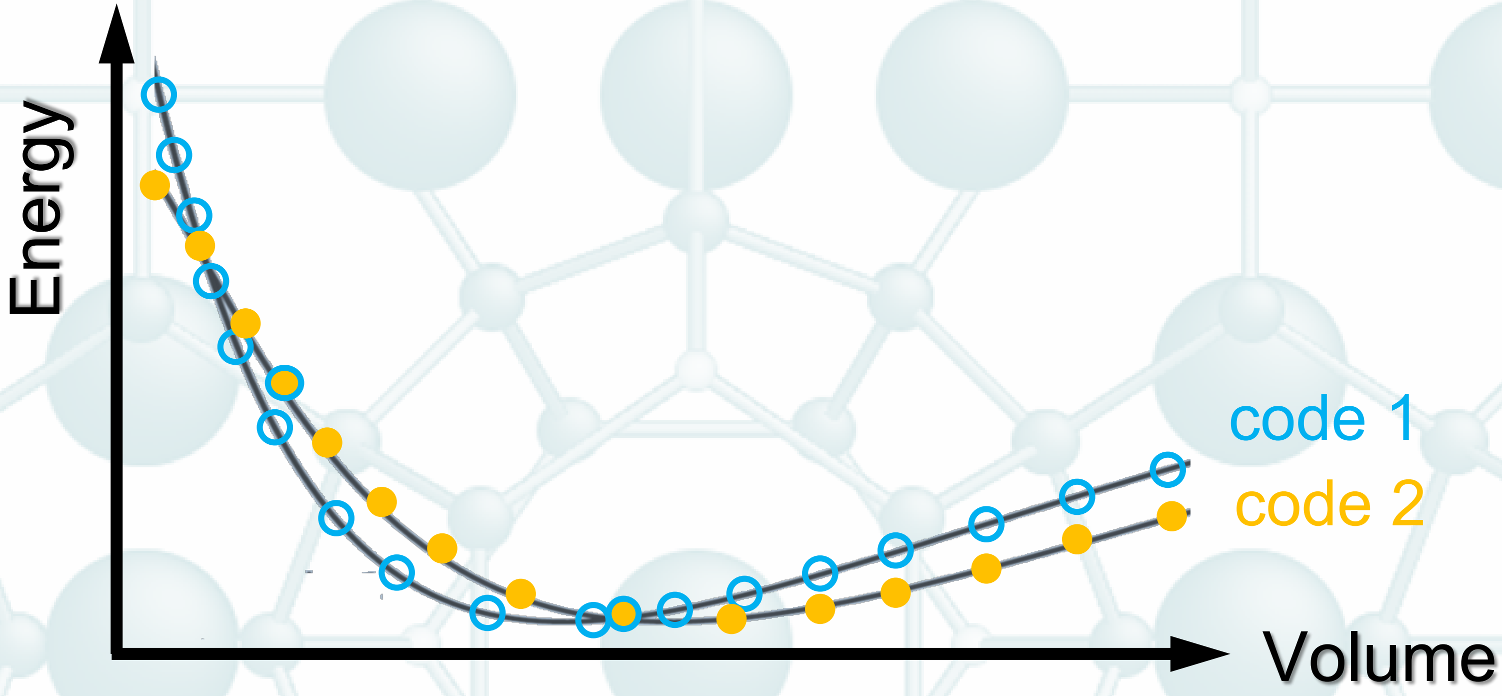
Delta test

Compute E(V) using PBE

Do the same with other code



Quality factor

$$\Delta = \left\langle \sqrt{\frac{\int \Delta E^2(V)dV}{\Delta V}} \right\rangle$$

Delta test

https://molmod.ugent.be/deltacodesdft

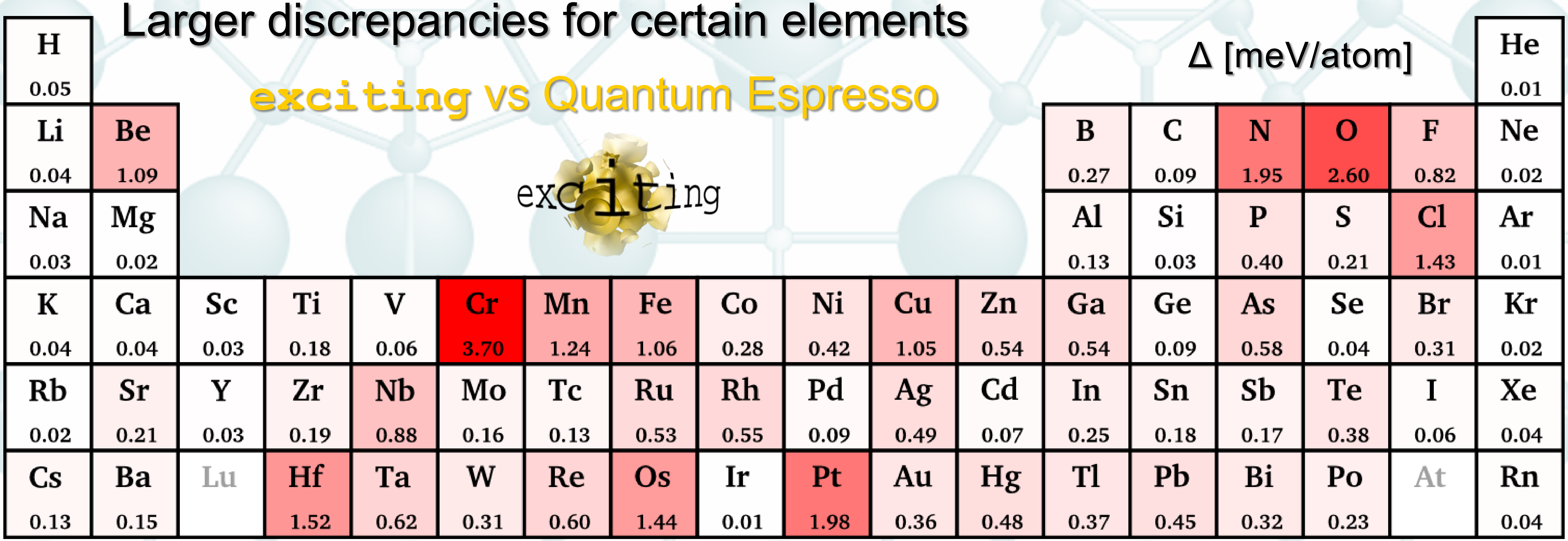
Code	Version	Basis	Electron treatment	Δ-value	Authors
Exciting	development version	LAPW+xlo	all-electron	0 meV/atom	Exciting [10,16]
FHI-aims	081213	tier2 numerical orbitals	all-electron (relativistic atomic_zora scalar)	0.1 meV/atom	ASE [2,16]
WIEN2k	13.1	LAPW/APW+lo	all-electron	0.2 meV/atom	S. Cottenier [16]
FHI-aims	081213	tier2 numerical orbitals	all-electron (relativistic zora scalar 1e-12)	0.3 meV/atom	ASE [2]
Elk	3.1.5	APW+lo	all-electron	0.3 meV/atom	Elk [14,16]
VASP	5.2.12	plane waves	PAW 2015 GW-ready	0.4	K. Lejaeghere [16]

Data quality

Excellent overall agreement between codes – great!

Larger discrepancies for certain elements

exciting vs Quantum Espresso



Δ [meV/atom]

H 0.05																	He 0.01
Li 0.04	Be 1.09											B 0.27	C 0.09	N 1.95	O 2.60	F 0.82	Ne 0.02
Na 0.03	Mg 0.02											Al 0.13	Si 0.03	P 0.40	S 0.21	Cl 1.43	Ar 0.01
K 0.04	Ca 0.04	Sc 0.03	Ti 0.18	V 0.06	Cr 3.70	Mn 1.24	Fe 1.06	Co 0.28	Ni 0.42	Cu 1.05	Zn 0.54	Ga 0.54	Ge 0.09	As 0.58	Se 0.04	Br 0.31	Kr 0.02
Rb 0.02	Sr 0.21	Y 0.03	Zr 0.19	Nb 0.88	Mo 0.16	Tc 0.13	Ru 0.53	Rh 0.55	Pd 0.09	Ag 0.49	Cd 0.07	In 0.25	Sn 0.18	Sb 0.17	Te 0.38	I 0.06	Xe 0.04
Cs 0.13	Ba 0.15	Lu	Hf 1.52	Ta 0.62	W 0.31	Re 0.60	Os 1.44	Ir 0.01	Pt 1.98	Au 0.36	Hg 0.48	Tl 0.37	Pb 0.45	Bi 0.32	Po 0.23	At	Rn 0.04

Average over 71 elemental solids: ~10 codes within 0.5 meV/atom

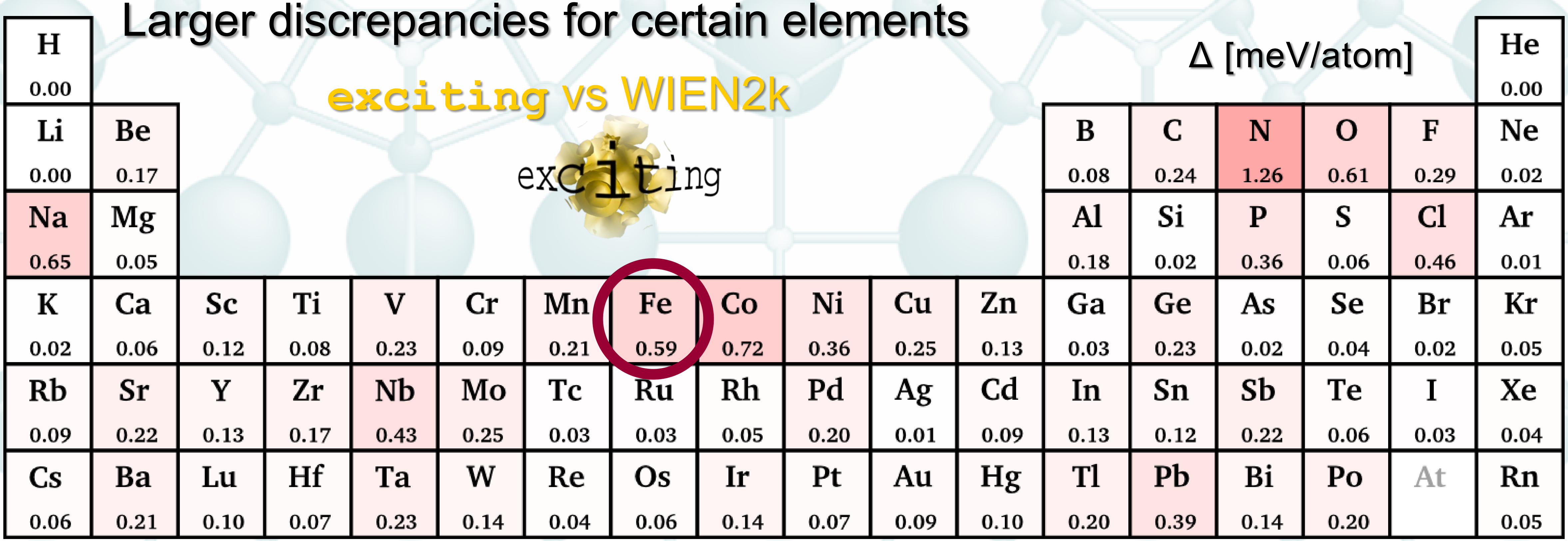
Data quality

Excellent overall agreement between codes – great!

Larger discrepancies for certain elements

exciting vs WIEN2k

Δ [meV/atom]



H 0.00																	He 0.00
Li 0.00	Be 0.17											B 0.08	C 0.24	N 1.26	O 0.61	F 0.29	Ne 0.02
Na 0.65	Mg 0.05											Al 0.18	Si 0.02	P 0.36	S 0.06	Cl 0.46	Ar 0.01
K 0.02	Ca 0.06	Sc 0.12	Ti 0.08	V 0.23	Cr 0.09	Mn 0.21	Fe 0.59	Co 0.72	Ni 0.36	Cu 0.25	Zn 0.13	Ga 0.03	Ge 0.23	As 0.02	Se 0.04	Br 0.02	Kr 0.05
Rb 0.09	Sr 0.22	Y 0.13	Zr 0.17	Nb 0.43	Mo 0.25	Tc 0.03	Ru 0.03	Rh 0.05	Pd 0.20	Ag 0.01	Cd 0.09	In 0.13	Sn 0.12	Sb 0.22	Te 0.06	I 0.03	Xe 0.04
Cs 0.06	Ba 0.21	Lu 0.10	Hf 0.07	Ta 0.23	W 0.14	Re 0.04	Os 0.06	Ir 0.14	Pt 0.07	Au 0.09	Hg 0.10	Tl 0.20	Pb 0.39	Bi 0.14	Po 0.20	At	Rn 0.05

What about other systems or quantities?

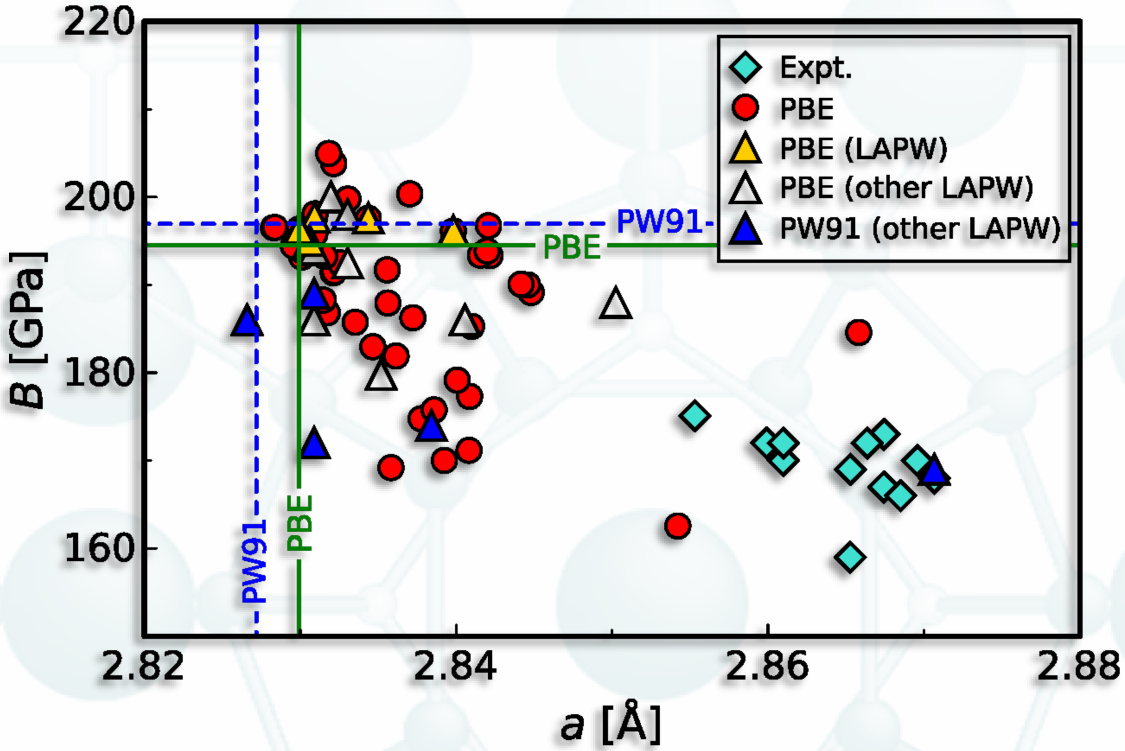
Surfaces, defects, molecules, alloys, … band gaps, barriers, spectra, …

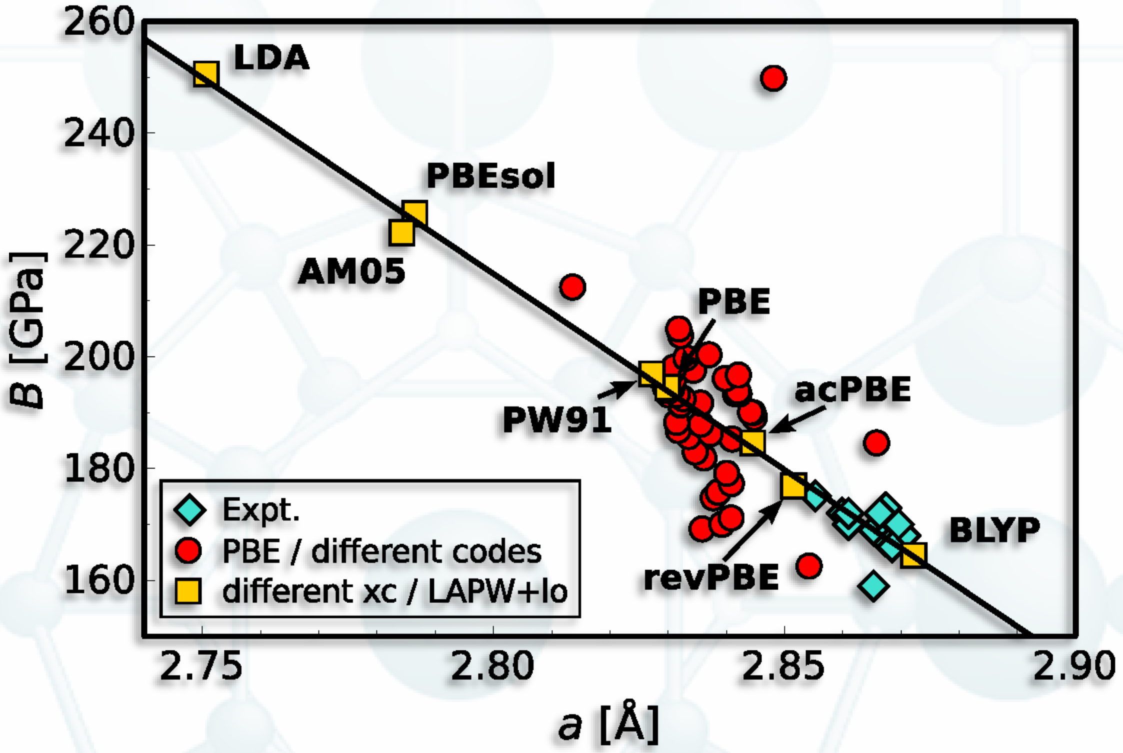
Accuracy vs precision

A. Gulans, A. Kozhevnikov, and C. Draxl
Phys. Rev. B **97**, 161105(R) (2018).

Example bcc Fe

Distinction between numerical precision of a calculation and accuracy of an xc funtional

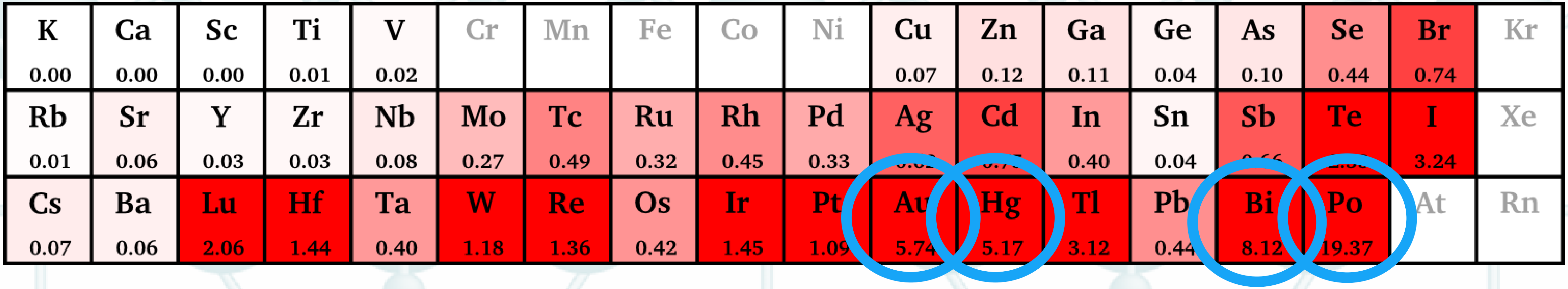




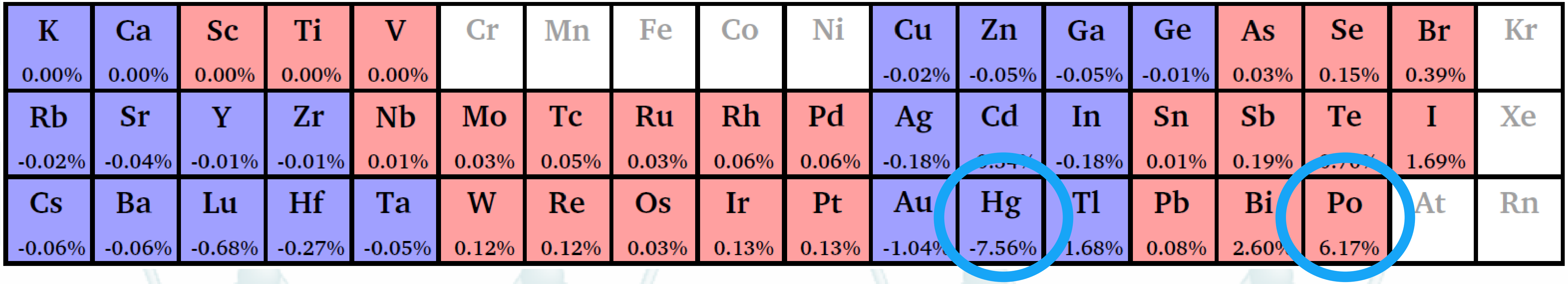
Impact of spin-orbit coupling

A. Gulans

Total energy: Δ [meV/atom] (red: Δ > 1)



K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
0.00	0.00	0.00	0.01	0.02						0.07	0.12	0.11	0.04	0.10	0.44	0.74	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
0.01	0.06	0.03	0.03	0.08	0.27	0.49	0.32	0.45	0.33	0.62	0.75	0.40	0.04	0.66	2.38	3.24	
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
0.07	0.06	2.06	1.44	0.40	1.18	1.36	0.42	1.45	1.09	5.74	5.17	3.12	0.44	8.12	19.37		



K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
0.00%	0.00%	0.00%	0.00%	0.00%						-0.02%	-0.05%	-0.05%	-0.01%	0.03%	0.15%	0.39%	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
-0.02%	-0.04%	-0.01%	-0.01%	0.01%	0.03%	0.05%	0.03%	0.06%	0.06%	-0.18%	-0.34%	-0.18%	0.01%	0.19%	0.70%	1.69%	
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
-0.06%	-0.06%	-0.68%	-0.27%	-0.05%	0.12%	0.12%	0.03%	0.13%	0.13%	-1.04%	-7.56%	1.68%	0.08%	2.60%	6.17%		

DFT in practice

It‘s all about materials …

Harder, tougher, …,

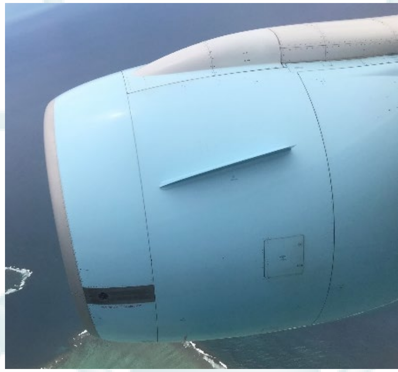
Light-weight, ductile, …

Flexible, ultra-thin, …

Non-toxic, sustainable, edible, …

Energy saving, …

Biocompatible, …



Structure

Mechanical properties

Magnetism

Vibrational properties

Electronic properties (caution!)

Thermodynamics

… and more

Role of theory?

Teamwork

exciting

Thanks!