

Density functional theory - an introduction

Anna Delin

Applied Physics, KTH, Stockholm,
Sweden

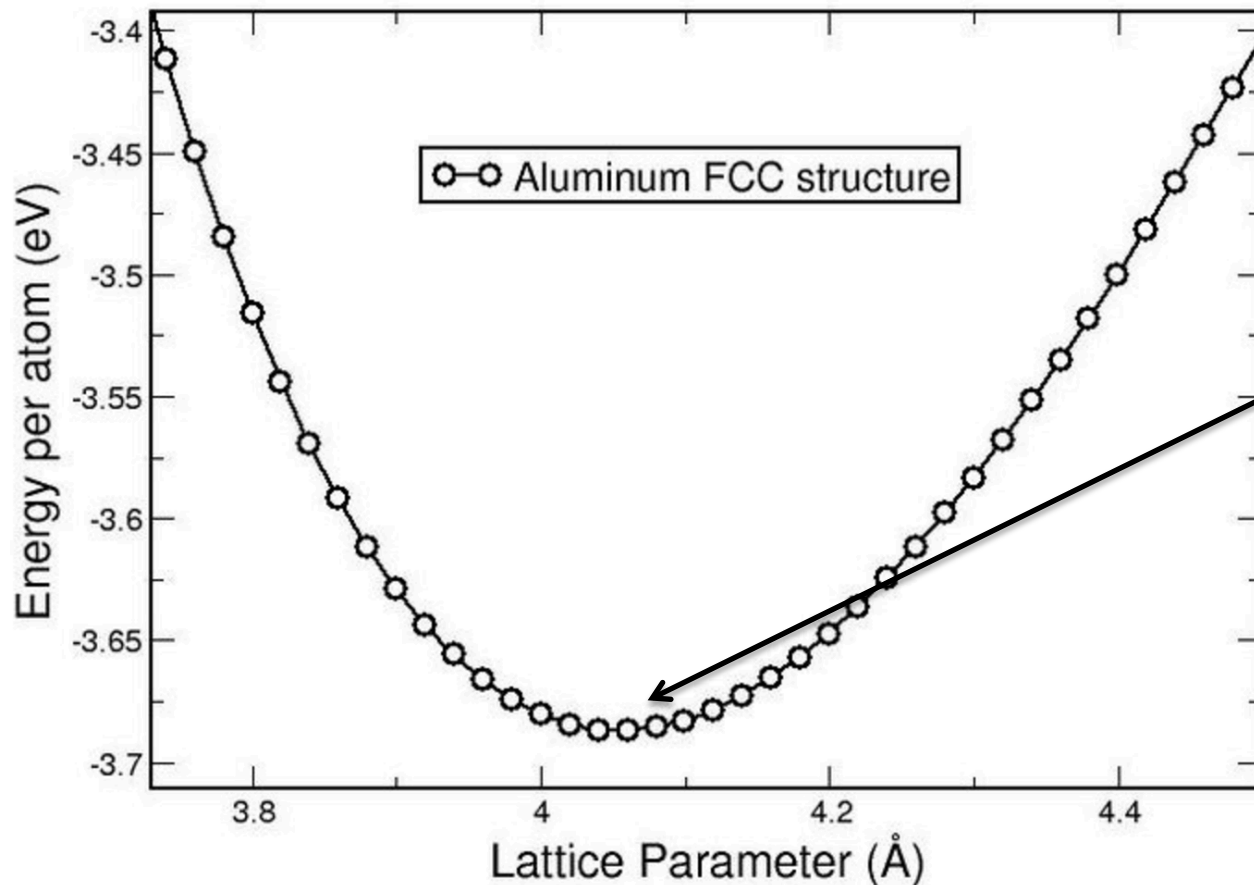
Mentimeter question 1:
How familiar are you with DFT?

What is density functional theory (DFT)?

- It's a way to calculate, using large computers, the physical properties of materials and molecules.
- It is based on quantum mechanics.
- It's free from adjustable parameters. *This is a very important point.*

Example: With DFT we can calculate the lattice parameter

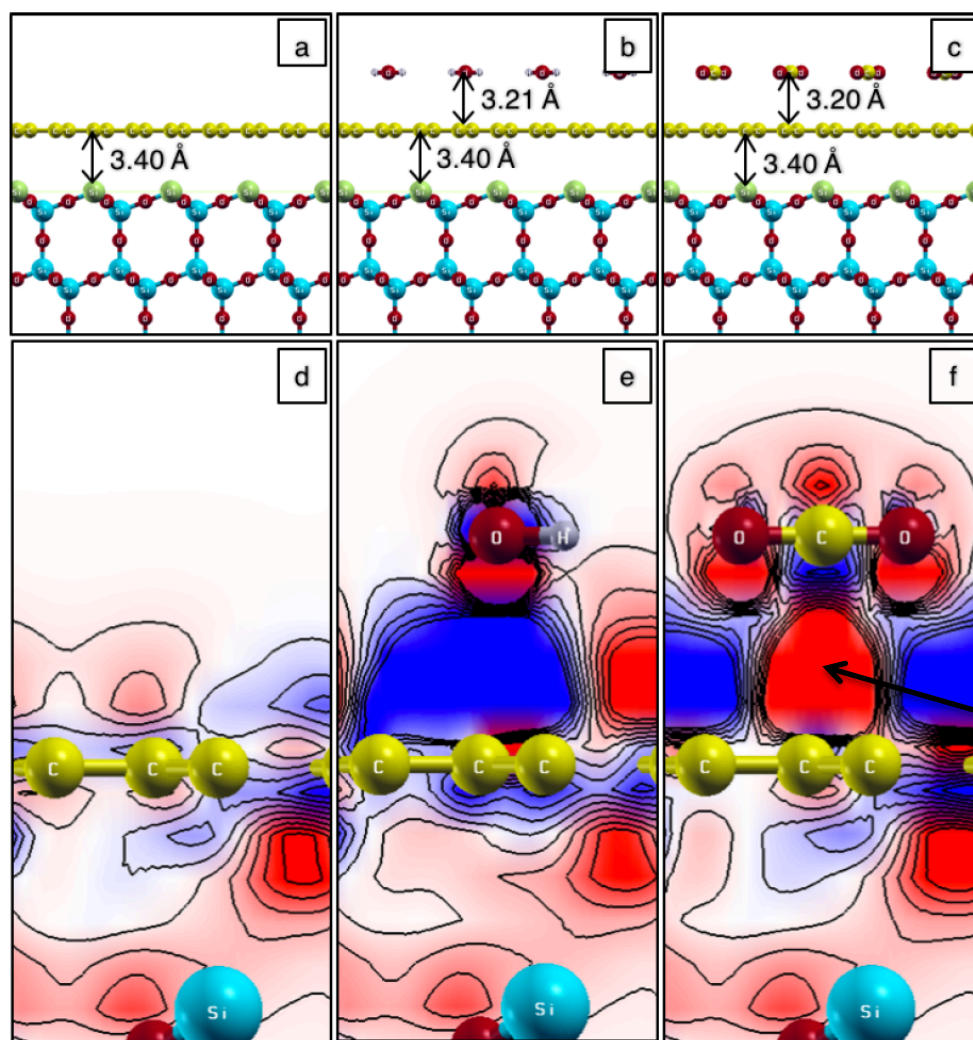
(and the bulk modulus, formation energy, elastic constants, and so forth, all without using any input parameters from experiments)



The energy minimum gives the theoretical equilibrium lattice parameter

(Experimental lattice parameter = 4.046 Å)

Example: With DFT we can see how atoms interact and bond



Charge density difference plots of molecules on top of graphene. This shows how the molecules interact with the graphene.

Bond (electron accumulation)

What is that density in density functional theory?

Use the **electron density** n as the basic variable instead of the wave function

Electron density,
or
charge density

$$n \longleftrightarrow \psi$$

Quantum
mechanical
wave function

I will say “charge density” most of the time.

Quantum mechanics reminders

- If we know the quantum mechanical wave function ψ , we know everything about the system that is possible to know.
- We find ψ by solving the Schrödinger equation $H\psi = E\psi$.

H is an operator and E is the energy of the system

- The electron density $n = |\psi|^2$

“function” vs “functional”

- A *function* $y=f(x)$ is a rule for going from a number x to another number y .
- A *functional* is a rule for mapping a function $n(r)$ to a number N :

a functional is a function from a vector space into its underlying field of scalars. Commonly the vector space is a space of functions; thus the functional takes a function for its input argument, then it is sometimes considered a function of a function (a higher-order function). Its use originates in the calculus of variations, where one searches for a function that minimizes a given functional. A particularly important application in physics is searching for a state of a system that minimizes the energy functional.

$$N = \int d^3r n(\mathbf{r}) = N[n]$$

Functional derivatives are used in Lagrangian mechanics. They are derivatives of functionals: i.e. they carry information on how a functional changes when the input function changes by a small amount.

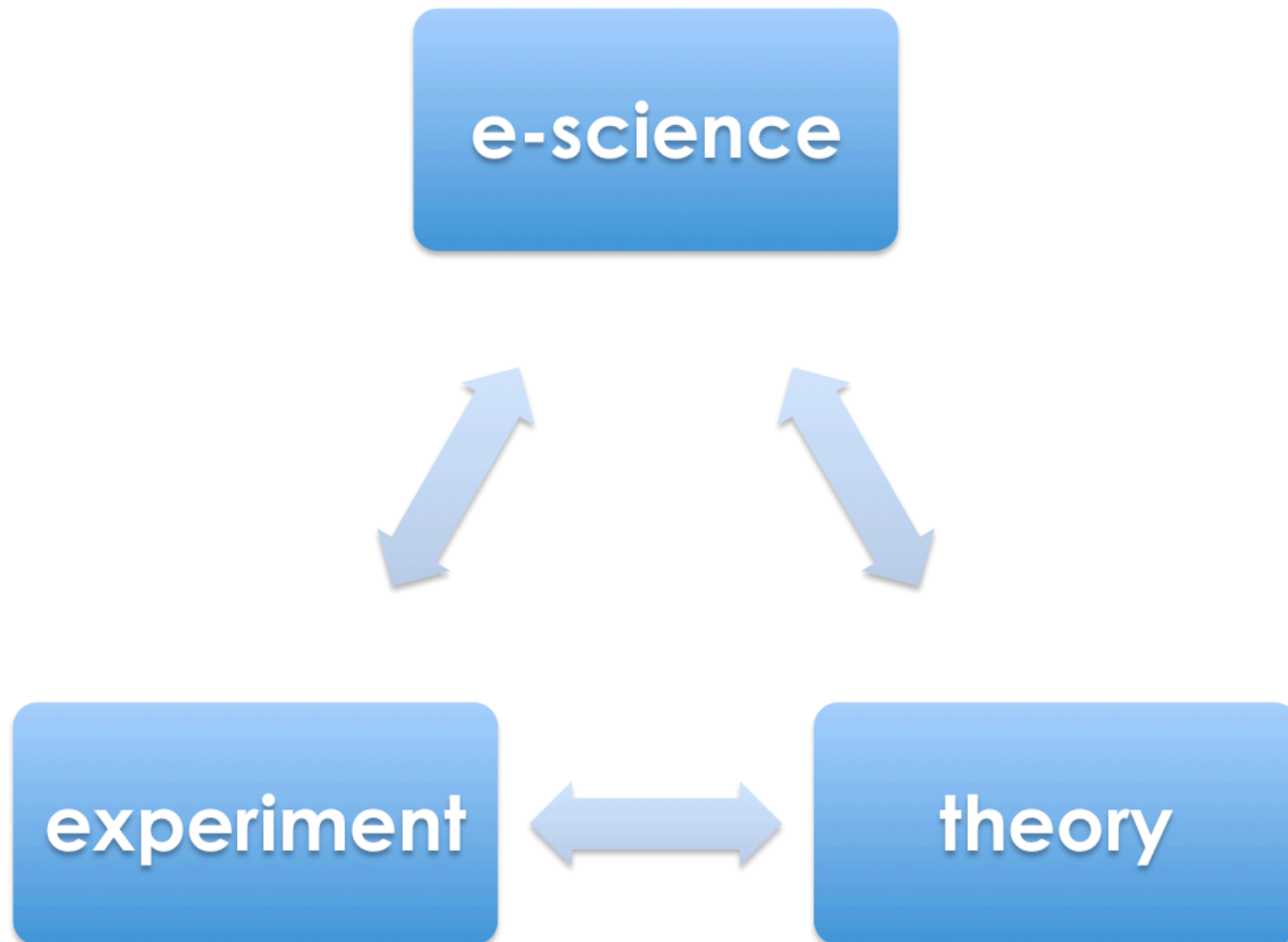
Richard Feynman used functional integrals as the central idea in his sum over the histories formulation of quantum mechanics. This usage implies an integral taken over some function space.

DFT is a typical “e-science”

Use massive computer resources
to solve known but
complicated
equations

(in DFT, we are basically solving the Schrödinger equation
(or Dirac equation))

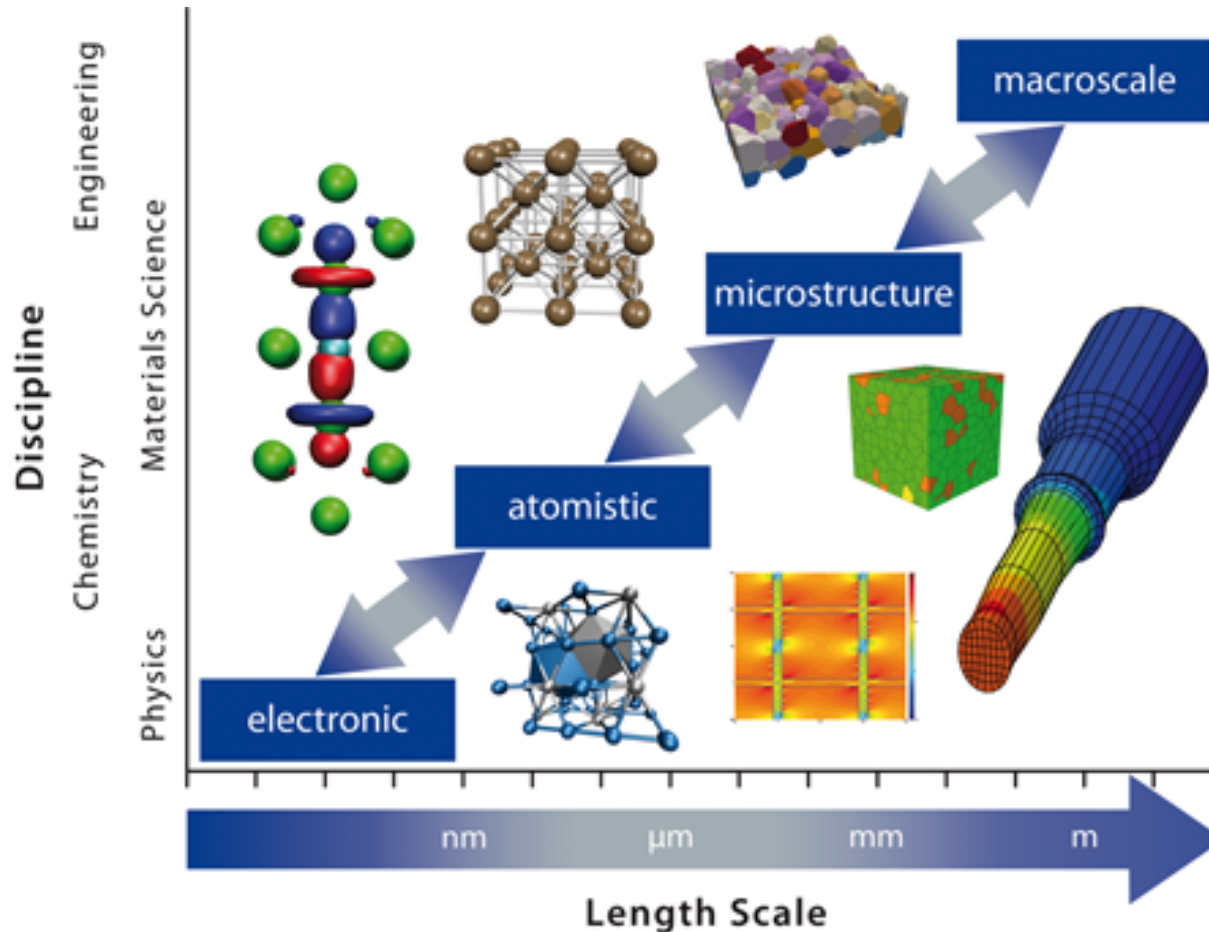
“e-science” is a third distinct
type of science



More examples of properties DFT can predict

- Optical and magnetooptical spectra (also XAS, ARPES, PES, ...)
- If a material is an insulator, semiconductor or metal, and how large the band gap is.
- Magnetic structure (nonmagnetic, ferromagnetic, antiferromagnetic, ferrimagnetic, spin spirals, spin glass)
- Brittleness, chemical stability, magnetic transition temperatures, phase diagrams

DFT is basic for multiscale modeling of materials

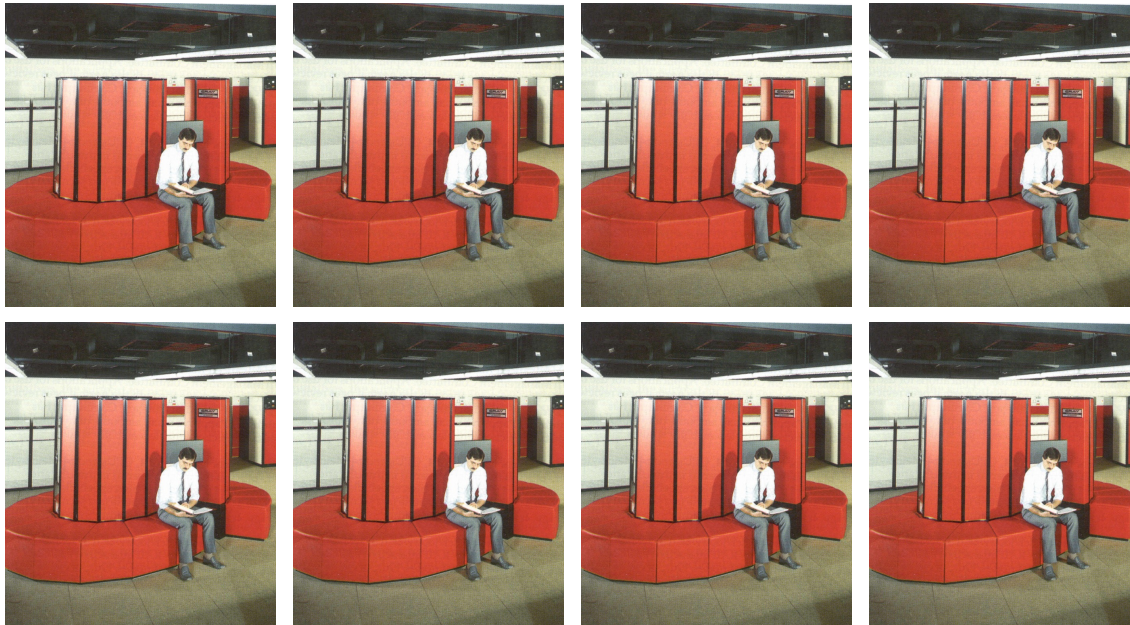
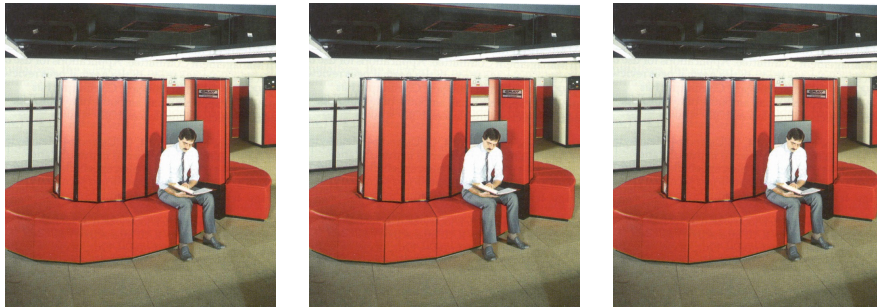


Powerful computers made
the DFT method useful

Cray supercomputer, 1970s



1 iPhone = 11 Cray



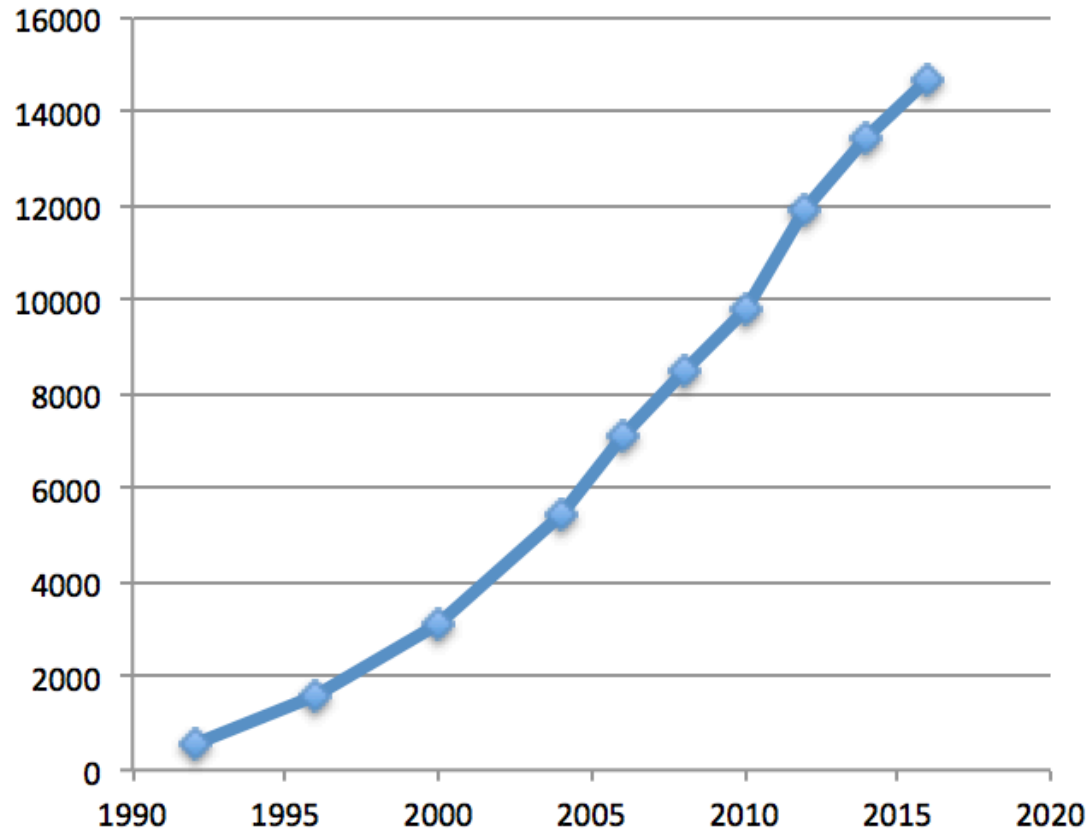
Cray Titan (2012)



≈ one
million



"Density functional" publications



It's very easy to start using a standard DFT code. At PDC, many codes are installed

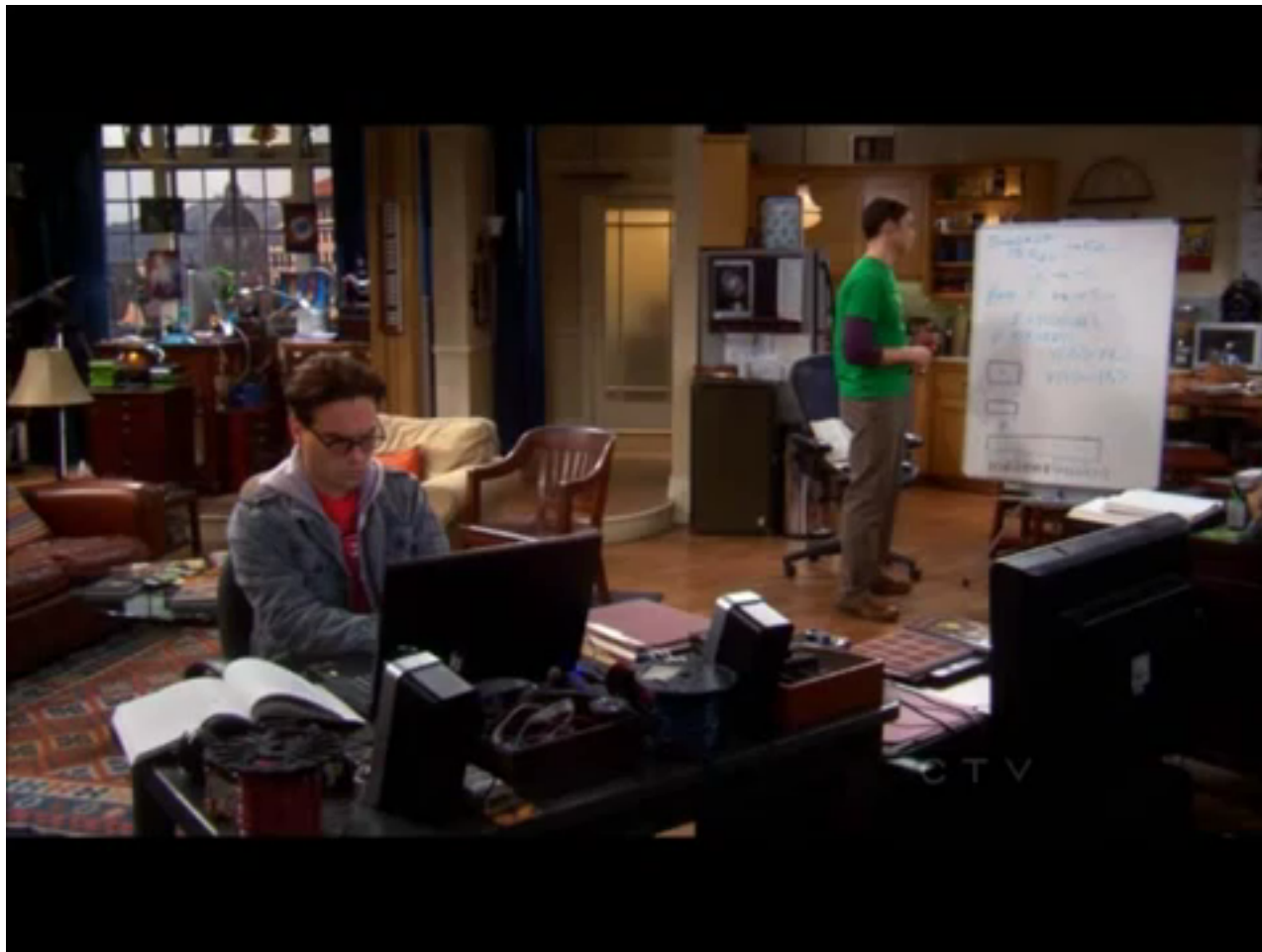
Chemistry

Program	System	Available versions
<i>ABINIT</i>	Beskow	<i>7.10.5, 7.10.2</i>
<i>ase</i>	Beskow	<i>3.10.0, 3.8.1</i>
	Tegner	<i>3.10.0</i>
<i>cp2k</i>	Beskow	<i>3.0-libxc-plumed, 3.0, 2.6.2, 2.5.1</i>
<i>Dalton</i>	Beskow	<i>2013.4</i>
<i>DIRAC</i>	Beskow	<i>14.0</i>
<i>gamess</i>	Beskow	<i>2013-05-01-R1, 2012-05-01-R1</i>
<i>Gaussian</i>	Tegner	<i>g09.D01</i>
<i>gpaw</i>	Beskow	<i>1.0.0, 0.10.0</i>
<i>libxc</i>	Beskow	<i>2.0.1</i>
<i>NWChem</i>	Beskow	<i>6.5</i>
<i>Quantum-ESPRESSO</i>	Beskow	<i>6.0, 5.2.1+west-1.0.2, 5.1.1</i>
<i>siesta</i>	Beskow	<i>trunk-462, 3.2-pl-5</i>
<i>VASP</i>	Beskow	<i>5.4.1.patched, 5.3.5-vtst3.1, 5.3.5-31Mar14</i>
	Tegner	<i>5.4.1, 5.3.5</i>
<i>Yambo</i>	Beskow	<i>4.0.2</i>

End of commercial.

Time for nitty-gritty mathematics.

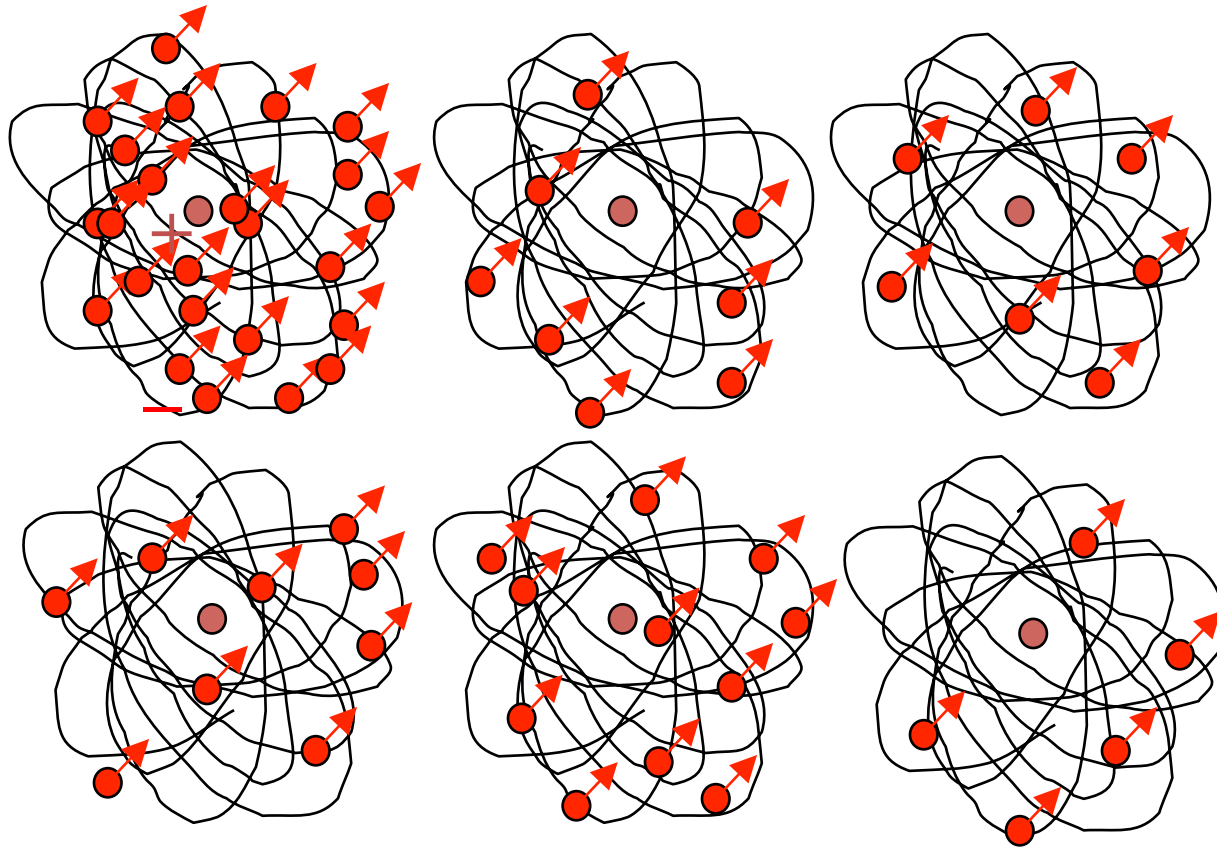
Quantum Mechanics!



But first, mentimeter question 2:

What does "density" in density functional theory refer to?

Many electrons interact in a solid or molecule



electrons with mass m , charge e
nuclei with mass M , charge Z

In quantum mechanics, the Hamiltonian is the operator corresponding to the total energy of the system in most of the cases. It is usually denoted by H , also \hat{H} or \hat{H} . Its spectrum is the set of possible outcomes when one measures the total energy of a system.

Hamiltonian for many-atom system

Kinetic energy of the nuclei

Electrostatic nucleus-nucleus interaction

Kinetic energy of the electrons

$$\mathcal{H} = -\frac{\hbar^2}{2} \sum_I \frac{\nabla_I^2}{M_I} + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{4\pi\epsilon_0 |\mathbf{R}_I - \mathbf{R}_J|} - \frac{\hbar^2}{2m} \sum_i \nabla_i^2$$
$$+ \frac{1}{2} \sum_{i \neq j} \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,I} \frac{Z_I e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{R}_I|},$$

Electrostatic electron-electron interaction

Electrostatic nucleus-electron interaction

The Hamiltonian H is input to the Schrödinger equation $H\psi = E\psi$.
We obtain a partial differential equations that are exceedingly complex.

Born-Oppenheimer approximation:

the assumption that the motion of atomic nuclei and electrons in a molecule can be separated. Time scales!

$$\mathcal{H} = -\frac{\hbar^2}{2} \sum_I \frac{\nabla_I^2}{M_I} + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{4\pi\epsilon_0 |\mathbf{R}_I - \mathbf{R}_J|} - \frac{\hbar^2}{2m} \sum_i \nabla_i^2 \\ + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,I} \frac{Z_I e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{R}_I|},$$

simplifies to

$$\mathcal{H} = -\frac{1}{2} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,I} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} = T + W + V_{\text{ext}}.$$

Unit system?

Hartree atomic units:

$$\hbar = m_e = e = 4\pi\epsilon_0 = 1$$

Born-Oppenheimer approximation

- Assumes that the movement of the electrons can be treated independently from the movement of the atomic nuclei.
- The nuclei of the atoms move much more slowly than the electrons
- The electrons reach their ground state before the nuclear potential changes
- "Stationary" nuclei surrounded by electron cloud.

Is the Born-Oppenheimer approximation always valid?

Even with the Born-Oppenheimer approximation, the Hamiltonian is still very complicated:

$$\mathcal{H} = -\frac{1}{2} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,I} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} = T + W + V_{\text{ext}}.$$

electron kinetic
energy(operator)

electron-electron
interaction

“external potential” =
electron-nucleus
interaction

A smart approach is to focus on the total energy $E =$ expectation value of Hamiltonian

$$E = \langle \Psi | \mathcal{H} | \Psi \rangle = T + W + \int d^3r V_{\text{ext}}(\mathbf{r})n(\mathbf{r}) ,$$

kinetic energy
of the electrons



electron-electron interaction

interaction with the
“external potential”

Mentimeter question 3:

What is a Hamiltonian?

Some earlier attempts to solve the many-electron problem

The Hamiltonian is the sum of the kinetic energies of all the particles, plus the potential energy of the particles associated with the system. For different situations or number of particles, the Hamiltonian is different since it includes the sum of kinetic energies of the particles, and the potential energy function corresponding to the situation.

- Free electron model
- Hartree approach
- Thomas-Fermi model
- Hartree-Fock
- Empirical tight-binding models
- ...

Free electron model (FEM)

- Ideal gas of noninteracting fermions
- same thing as Drude-Sommerfeld model
- Works pretty well for "free-electron metals" like aluminium and silver.
- How can this possibly work?

Thomas-Fermi(-Dirac) model

$$E_{\text{TF}}[n] = C_1 \int d^3r n(\mathbf{r})^{5/3}$$

kinetic energy

$$+ \int d^3r V_{\text{ext}}(\mathbf{r}) n(\mathbf{r})$$

interaction with nuclei

$$+ C_2 \int d^3r n(\mathbf{r})^{4/3}$$

exchange

$$+ \frac{1}{2} \int d^3r d^3r' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

Hartree term

Thomas-Fermi model

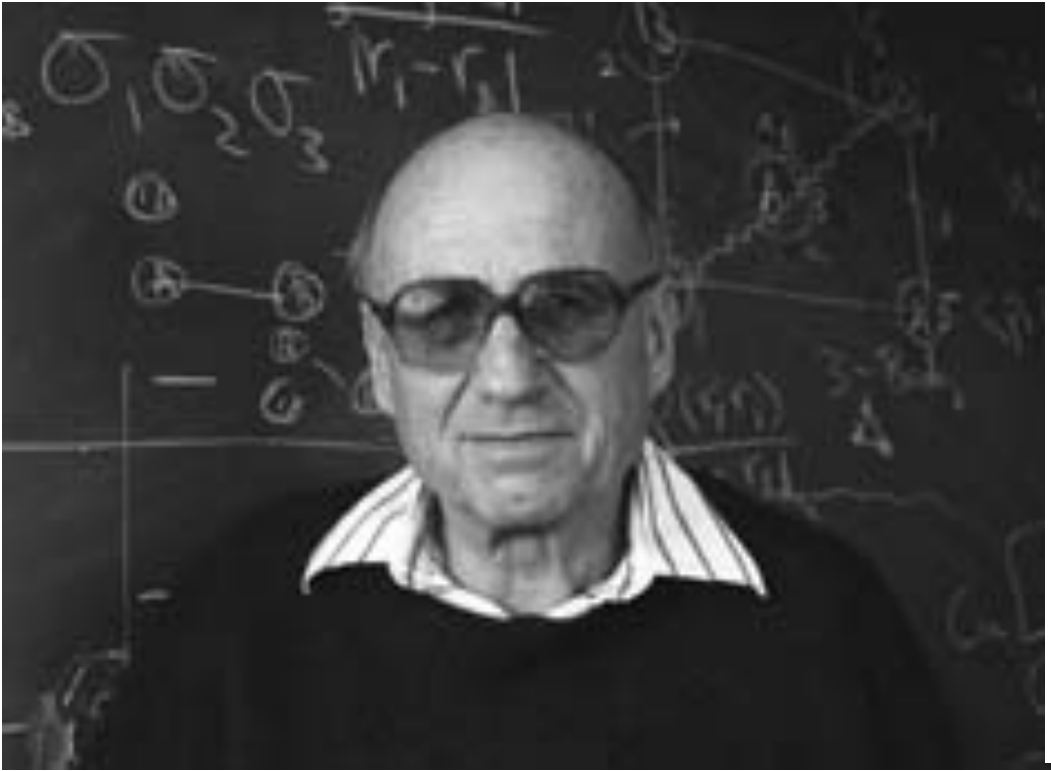
- First serious attempt to formulate the many-electron problem in terms of the electronic density (instead of the wave function).
- Critical sources of error: **the kinetic energy** and also the lack of exchange energy and electron-electron correlation energy.
- Fails to describe molecular bonding (shown in 1962)
- ... so this approach never became very popular.

Can we do better?

Yes.

Density functional theory, as
developed by Walter Kohn and
coworkers.

Difficult problem!



1998

Walter Kohn

Hohenberg-Kohn theorems

- Uniqueness
- Variational principle
- Universality

"Uniqueness"

- All properties of the system are known if we know the ground state electron density $n(\mathbf{r})$.
- The ground state expectation value of any observable is a unique functional of the exact ground state density $n(\mathbf{r})$.
- The point is that we need to know only the charge density, not the wave function.
- *Examples of observables?*

"Variational principle"

- The correct ground state density can be found by finding the global minimum of $E[n]$.
- This statement provides us a scheme how to find the ground state charge density. Simply try all possible densities and choose the one that gives the lowest energy.
- Is this a scheme one can use in practice? If so, how?

"Universality", but first...

- ... we need to take a closer look at the concept "external potential":

$$E = \langle \Psi | \mathcal{H} | \Psi \rangle = T + W + \int d^3r V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) ,$$

$$\mathcal{H} = -\frac{1}{2} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,I} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} = T + W + V_{\text{ext}} .$$

"External potential" concept

- The potential from the atomic nuclei + core electrons. This is the potential that the bonding electrons "feel".
- Physical systems with the same number of electrons but different external potentials have different charge densities $n(\mathbf{r})$ in their ground states.
- Example: N_2 molecule vs C_2H_2 molecule.

"Universality"

$$E = \langle \Psi | \mathcal{H} | \Psi \rangle = T + W + \int d^3r V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) ,$$

$$E[n] = F[n] + \int d^3r V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) .$$

- The functional $F[n]$ is universal in the sense that it does not depend on $V_{\text{ext}}(\mathbf{r})$.
- $F[n]$ is a unique expression, the same for all systems.

We rewrite the total energy slightly

$$E[n] = F[n] + \int d^3r V_{\text{ext}}(\mathbf{r})n(\mathbf{r})$$

$$F[n] = T_{\text{S}}[n] + \frac{1}{2} \int d^3r d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{\text{XC}}[n]$$

“kinetic energy”

Hartree term

Exchange-
correlation term
= the mysterious
remainder

Remaining unknowns

First problem: $E_{xc}[n]$

- Solution: e.g. quantum Monte Carlo simulations of the homogeneous electron gas.
- Result: LDA Barth-Hedin, LDA Vosko-Wilk-Nusair, GGA Perdew-Wang 91, GGA Perdew-Becke-Einzerhof, ... and many many more! The stupidity term

Second problem: the kinetic energy functional $T_s[n]$

- Solution: Map onto system of noninteracting particles.
- Result: Kohn-Sham equations.

$T[n]$ versus $T_s[n]$

- $T[n]$ = kinetic energy of the interacting electron system
- $T_s[n]$ = kinetic energy of a hypothetical noninteraction electron systems with the same electron density.

Kohn-Sham equations

- Find stationary point ("Variational principle") for the interacting system

$$\delta E[n] = 0$$

$$\mu = \frac{\delta E[n]}{\delta n(\mathbf{r})} = V_{\text{ext}} + \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta T_S[n]}{\delta n(\mathbf{r})} + \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})},$$

Same exercise for the
noninteracting particle
Schrödinger equation

$$E[n] = T_S[n] + \int d^3r V_{\text{eff}}(\mathbf{r})n(\mathbf{r})$$

$$\mu = \frac{\delta E[n]}{\delta n(\mathbf{r})} = \frac{\delta T_S[n]}{\delta n(\mathbf{r})} + V_{\text{eff}}.$$

Now, compare:

$$\mu = \frac{\delta E[n]}{\delta n(\mathbf{r})} = V_{\text{ext}} + \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta T_{\text{S}}[n]}{\delta n(\mathbf{r})} + \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})},$$

$$\mu = \frac{\delta E[n]}{\delta n(\mathbf{r})} = \frac{\delta T_{\text{S}}[n]}{\delta n(\mathbf{r})} + V_{\text{eff}}.$$

Our effective potential must be

$$V_{\text{eff}} = V_{\text{ext}} + \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})}.$$

- Why can we compare the independent particle model with the full model in this way? (which HK theorem applies?)

We finally arrive at the Kohn-Sham equations:

$$\mathcal{H}_{\text{eff}}(\mathbf{r})\psi_i(\mathbf{r}) = \left[-\frac{1}{2}\nabla^2 + V_{\text{eff}}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}).$$

$$n(\mathbf{r}) = \sum_{i=1}^N |\psi_i(\mathbf{r})|^2$$

Now, the kinetic energy term
can be calculated

$$T_S = \sum_{i=1}^N \langle \psi_i | -\frac{1}{2} \nabla^2 | \psi_i \rangle = \sum_{i=1}^N \epsilon_i - \int d^3r V_{\text{eff}}(\mathbf{r}) n(\mathbf{r}),$$

Where is the rest of the kinetic energy?

Final expression for total energy

$$E = \sum_{i=1}^N \epsilon_i - \frac{1}{2} \int d^3r d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \int d^3r V_{\text{xc}}[n]n(\mathbf{r}) + E_{\text{xc}}[n] .$$

Mentimeter question 4:

Why do we need the Kohn-Sham equations?

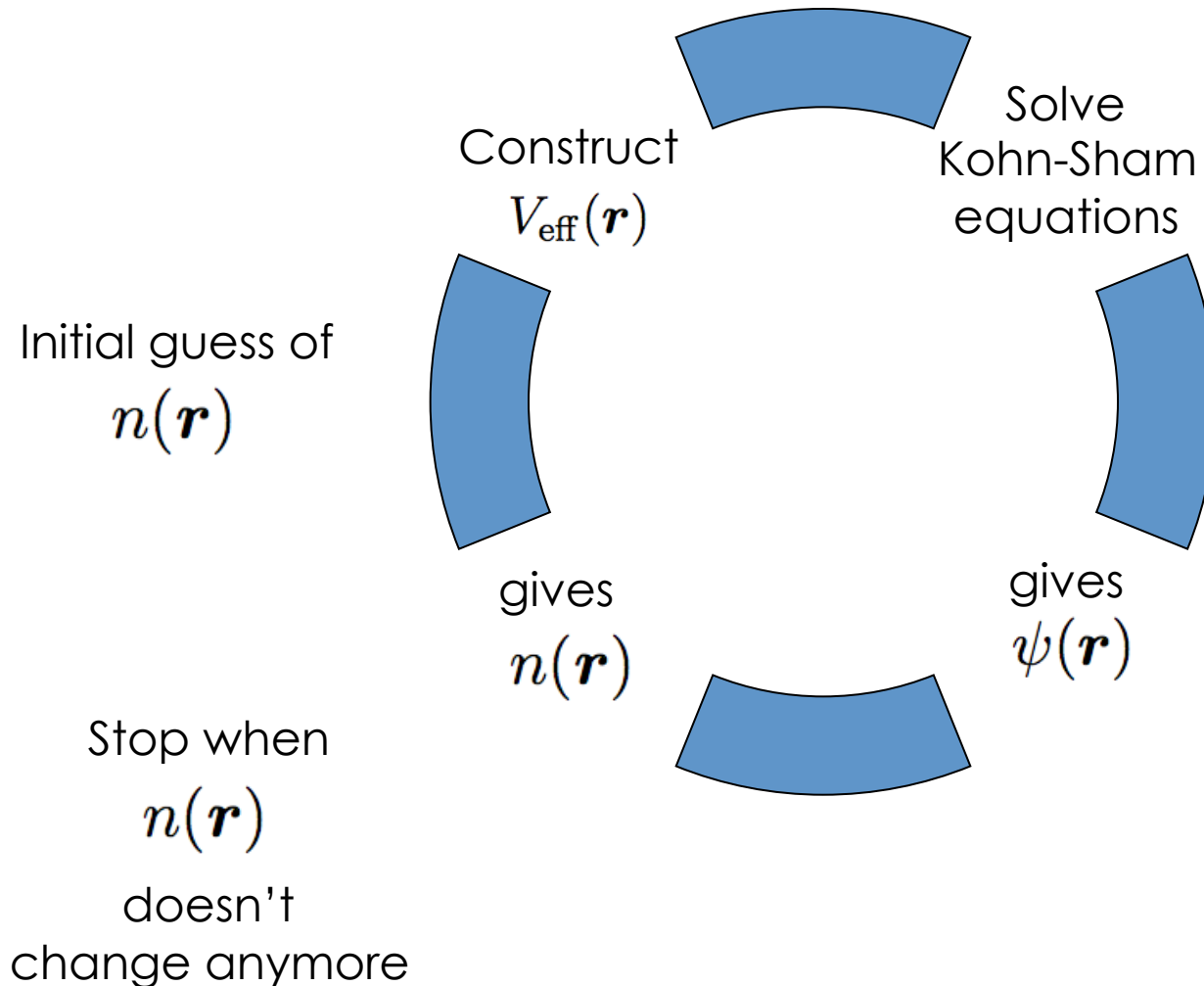
Observation

- The effective potential depends on the solution we want to find!
- How are we then supposed to be able at all to solve the problem?

Answer

- We make a first guess of the charge density,
- use it to calculate the effective potential (so that we have a Kohn-Sham equation to solve).
- Solving the Kohn-Sham equations gives a new charge density,
- which we use to construct a new effective potential,
- with which we can calculate a new charge density
- ...

“Iterate to self-consistency”



Summary of basic main points:

- DFT is a method for calculating materials properties.
- DFT is based on quantum mechanics and is a "first principles" methods, i.e. no parameters taken from experiments are needed in the calculations.
- The basic variable is the electron density (also called the charge density).

*Project task: write DFT
program for the helium atom
(in, e.g., Matlab)*

Project

- Helium has 2 electrons = simplest possible system to try out.
- Step 1: go from the charge density to the effective potential
- Step 2: go from the effective potential to the single-particle wave functions to the charge density
- Step 3: put it all together and iteration to self-consistency

Thanks for listening!