



A very short introduction to density functional theory (DFT)

FKA091 - Condensed matter physics

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Overview

- What is density functional theory (DFT) good for?

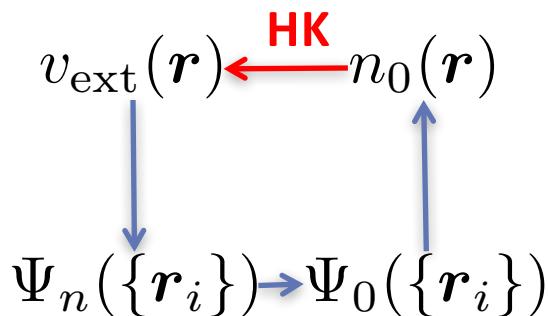
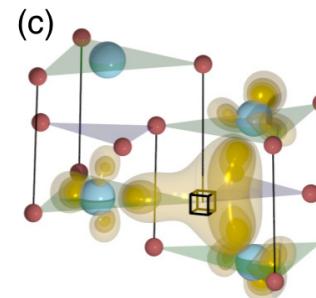
- Basic considerations

- Hohenberg-Kohn theorems

- Kohn-Sham equations and the exchange-correlation functional

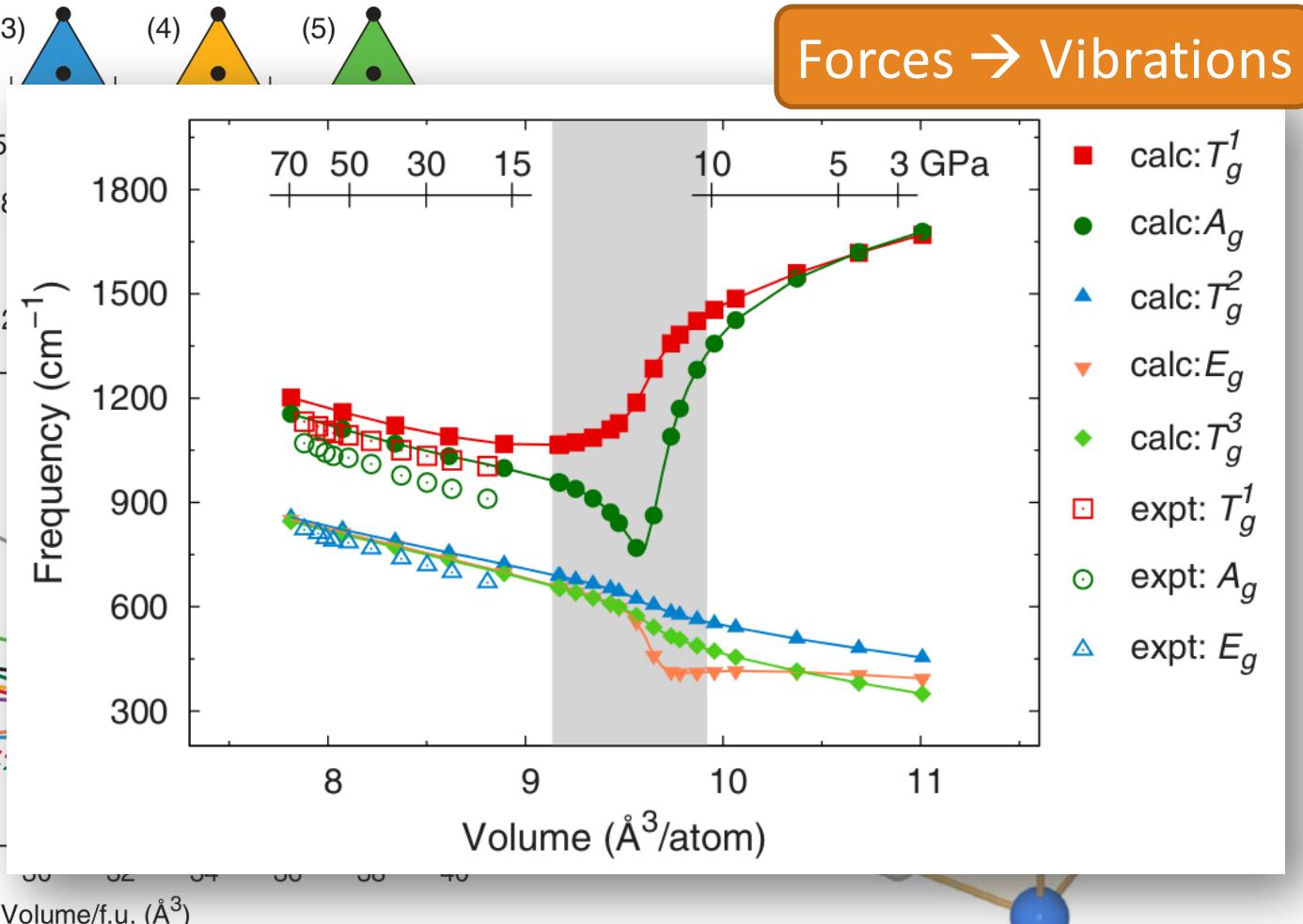
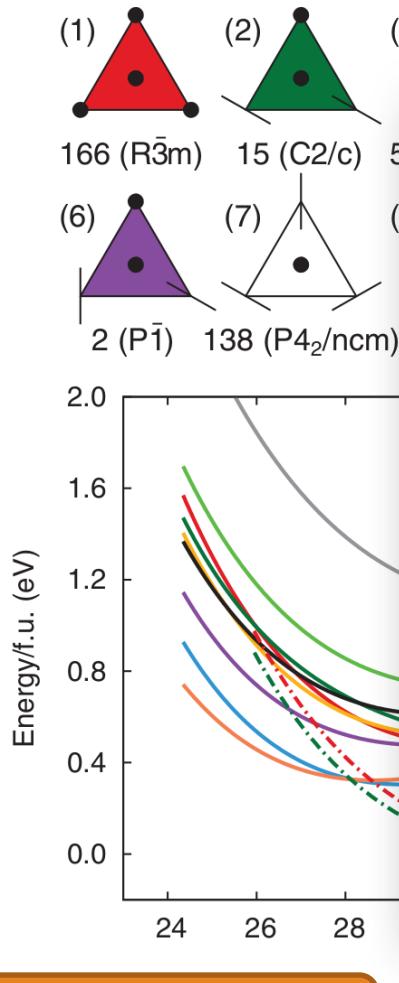
$$\left(-\frac{1}{2} \nabla^2 + v_{\text{ext}}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) \right) \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r})$$

- Shortcomings of DFT

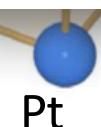


Some possible applications of DFT

Structure prediction and phase stability: Platinum series nitrides

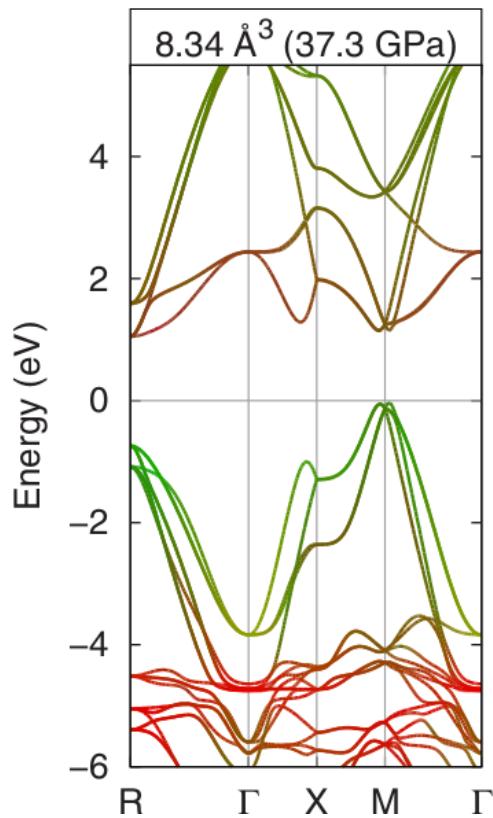


Total energies

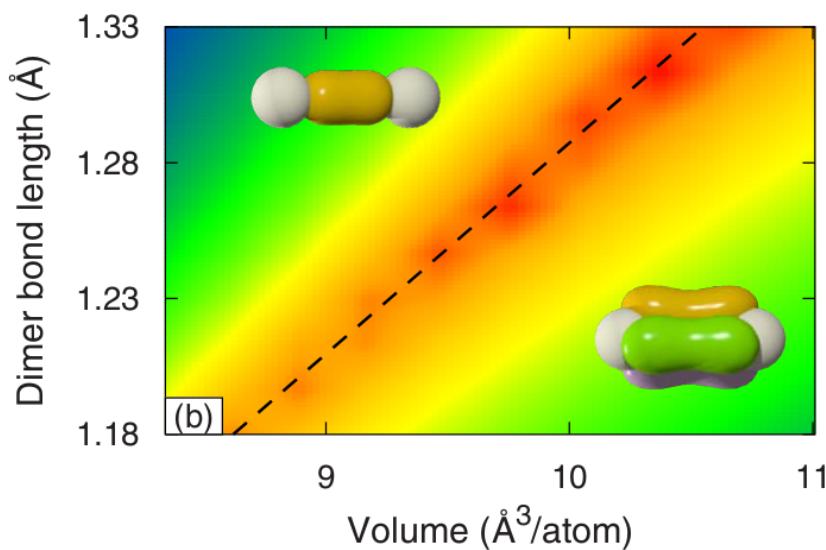


Some possible applications of DFT

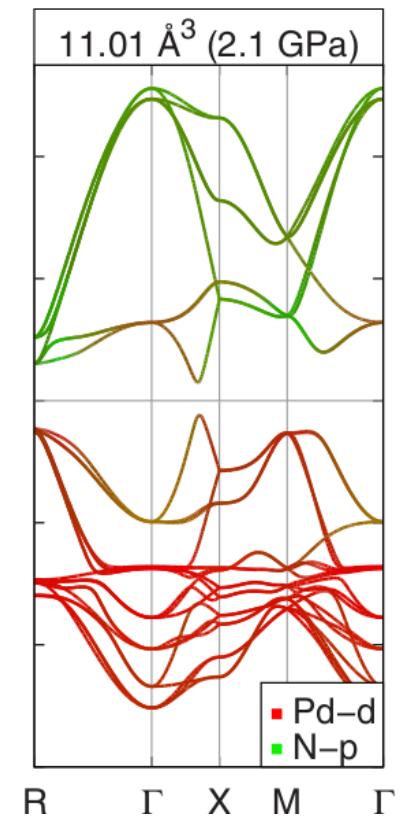
Structure prediction and phase stability: Platinum series nitrides



High pressure
(single bonded nitrogen)



Electronic structure

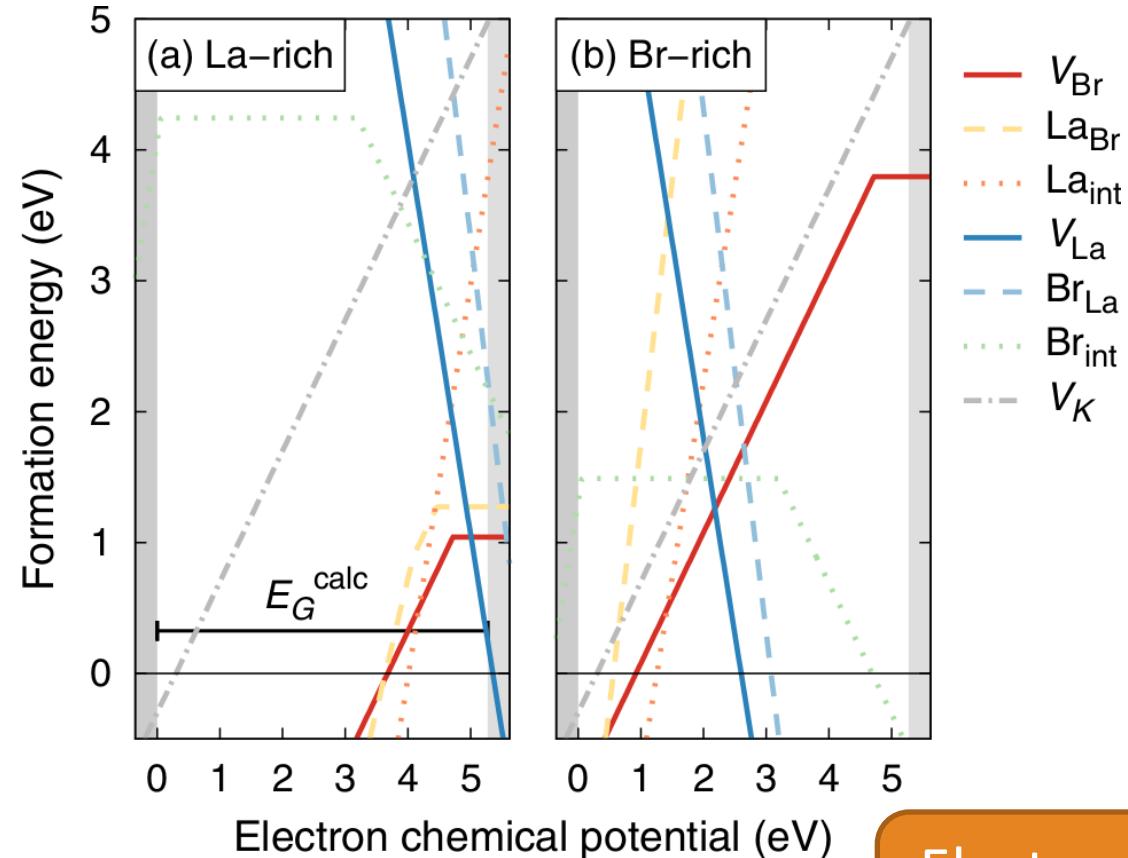


Low pressure
(triple bonded nitrogen)

Some possible applications of DFT

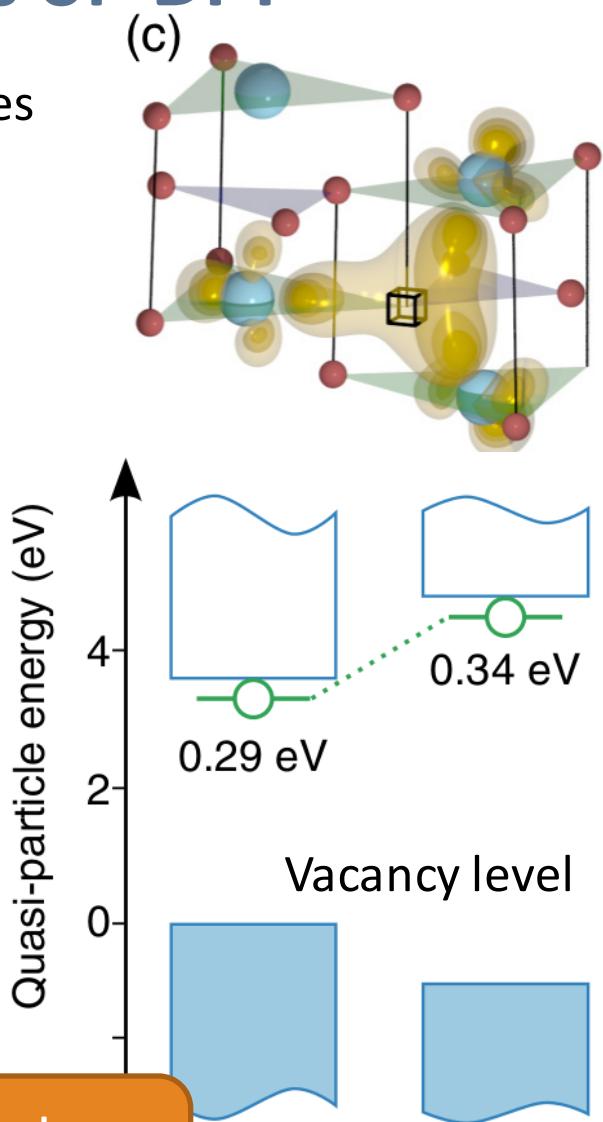
Defects: Thermodynamics, kinetics, electronic properties

Energetics – Which defects and how many



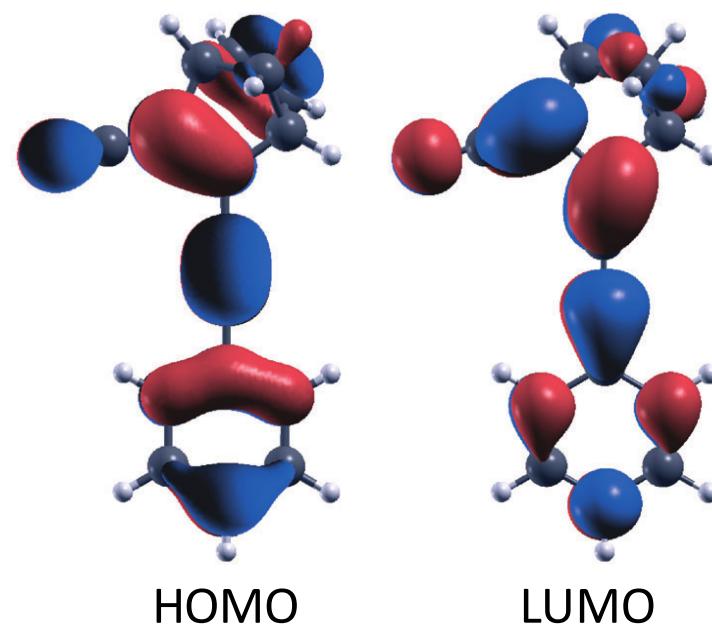
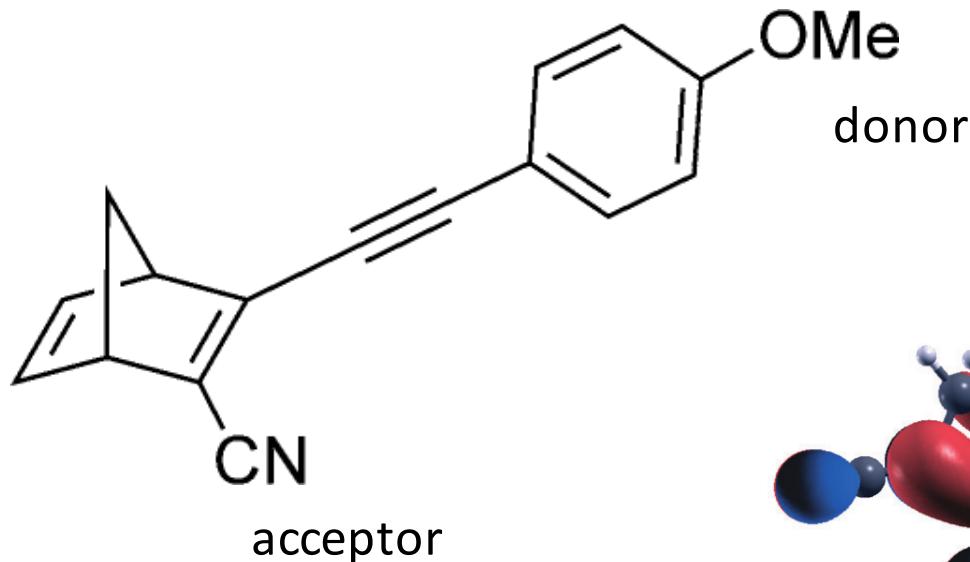
Total energies and forces

Electronic structure
→ optical properties



Some possible applications of DFT

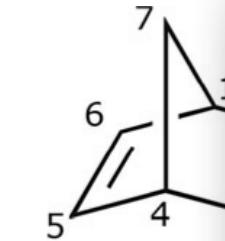
Property prediction and screening: Substituted norbornadienes



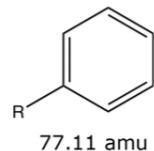
Substitutions affect
position of absorption band
→ can be tuned to solar spectrum

Some possible applications of DFT

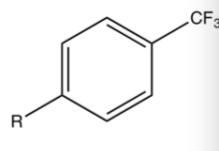
Property prediction and screening: Substituted norbornadienes



D1 C₆H₅•



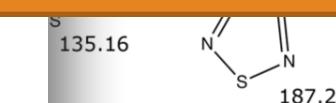
A1 C₇H₄F₃•



(a)

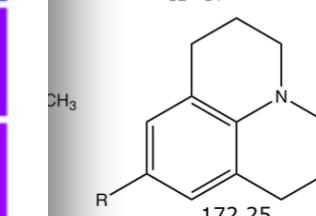
	Acceptor index							
	7	6	5	4	3	2	1	H
7	521 0.10	571 0.07	625 0.06	629 0.06	653 0.07	700 0.07	715 0.07	810 0.06
6	401 0.10	434 0.07	465 0.07	469 0.07	480 0.08	515 0.08	516 0.08	565 0.07
5	393 0.23	418 0.17	432 0.17	422 0.31	456 0.16	457 0.26	465 0.19	458 0.51
4	328 0.20	352 0.15	375 0.17	380 0.16	399 0.17	417 0.21	415 0.19	445 0.18
3	287 0.01	331 0.31	347 0.34	352 0.28	365 0.30	380 0.32	381 0.33	407 0.31
2	320 0.32	343 0.36	356 0.34	375 0.34	377 0.38	360 0.07	375 0.06	402 0.06
1	282 0.14	320 0.22	335 0.22	345 0.22	353 0.22	369 0.22	364 0.22	381 0.22
H	240 0.00	280 0.16						

Balance between computational effort
and accuracy/predictiveness



Donor index

D7 C₁₂H₁₄N•



A7 C₈H₃N₄S•



S 135.16 N=N
N 187.2 S=N

Some possible applications of DFT

- Enables calculation of total energies and forces under very general conditions
 - Structure prediction
 - Thermodynamics and kinetics
- Provides description of electronic structure
 - starting point for e.g., optical properties
- Good balance between accuracy/predictiveness and computational cost
 - Scales N^3 or better (N =number of electrons)
 - Enables calculations with thousands of electrons
- Very well established technique
 - Capabilities and limitations reasonably understood
 - Efficient implementations available

One of the standard computational tools in condensed matter, chemistry, and biochemistry in both academia and industry

FKA091: Density functional theory

Basic considerations

The Schrödinger equation

$$i \frac{\partial}{\partial t} \Phi = \hat{H} \Phi$$

nuclear	R
electronic	r
mixed	

$$\hat{H} = \underbrace{- \sum_n \frac{\hbar^2}{2M} \nabla_n^2}_{\hat{T}_R} - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 + \underbrace{\frac{1}{4\pi\epsilon_0} \frac{1}{2} \sum_{n \neq m} \frac{Z_n Z_m e^2}{|\mathbf{R}_n - \mathbf{R}_m|}}_{\hat{V}_r} + \underbrace{\frac{1}{4\pi\epsilon_0} \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}}_{\hat{V}_r} + \underbrace{- \frac{1}{4\pi\epsilon_0} \sum_{i,n} \frac{Z_n e^2}{|\mathbf{r}_i - \mathbf{R}_n|}}_{\hat{V}_{r,R}}$$

Kinetic terms

Potential terms

The Schrödinger equation

$$i \frac{\partial}{\partial t} \Phi = \hat{H} \Phi \quad \Phi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{R}_1, \mathbf{R}_2, \dots; t)$$

$$\begin{aligned}\hat{H} &= \hat{T}_{\mathbf{r}} + \hat{T}_{\mathbf{R}} + \hat{V}_{\mathbf{r}} + \hat{V}_{\mathbf{r}, \mathbf{R}} + \hat{V}_{\mathbf{R}} \\ &= \hat{T}_{\mathbf{R}} + \hat{V}_{\mathbf{R}} + \hat{T}_{\mathbf{r}} + \hat{V}_{\mathbf{r}} + \hat{V}_{\mathbf{r}, \mathbf{R}} \\ &\quad \text{nuclear} \qquad \text{electronic} \qquad \text{mixed}\end{aligned}$$

Wavefunction is a function of coordinates of all electrons and ions (and depends parametrically on time)

Notational convenience:

$$\begin{aligned}&\Phi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{R}_1, \mathbf{R}_2, \dots; t) \\&= \Phi(\{\mathbf{r}_i\}, \{\mathbf{R}_i\}; t) \\&= \Phi(\mathbf{r}, \mathbf{R}; t)\end{aligned}$$

Density functional theory in a nut shell:
Reduce 3N-dimensional problem
to a 3-dimensional one

Born-Oppenheimer approximation

Expand many body wave function in a complete electronic basis set that depends on positions of both nuclei and electrons

$$\Phi(\mathbf{r}, \mathbf{R}; t) = \sum_n \chi_n(\mathbf{R}; t) \Psi_n(\mathbf{r}, \mathbf{R})$$

Insert wave function ansatz into Schrödinger equation

$$i \frac{\partial}{\partial t} \Phi = \hat{H} \Phi$$

... and project onto the electronic basis: $\Psi_m(\mathbf{r}, \mathbf{R})$

$$i \frac{\partial}{\partial t} \chi_m = \left(\hat{T}_{\mathbf{R}} + \hat{V}_{\mathbf{R}} \right) \chi_m + \sum_n \left[\left\langle \Psi_m(\mathbf{r}, \mathbf{R}) \left| \hat{T}_{\mathbf{r}} + \hat{V}_{\mathbf{r}} + \hat{V}_{\mathbf{R}, \mathbf{r}} \right| \Psi_n(\mathbf{r}, \mathbf{R}) \right\rangle + \hat{V}_{mn} \right] \chi_n$$

$$\hat{V}_{mn} = -\frac{\hbar^2}{M_k} \langle \Psi_m(\mathbf{r}, \mathbf{R}) | \nabla_{\mathbf{R}_k} | \Psi_n(\mathbf{r}, \mathbf{R}) \rangle \cdot \nabla_{\mathbf{R}_k} + \frac{-\hbar^2}{2M_k} \langle \Psi_m(\mathbf{r}, \mathbf{R}) | \nabla_{\mathbf{R}_k}^2 | \Psi_n(\mathbf{r}, \mathbf{R}) \rangle$$

\hat{V}_{mn} depends on derivatives of electronic states with respect to nuclear positions and velocities

Born-Oppenheimer approximation

$$\epsilon_m(\mathbf{R}) = \sum_n \langle \Psi_m(\mathbf{r}; \mathbf{R}) | \hat{T}_{\mathbf{r}} + \hat{V}_{\mathbf{r}} + \hat{V}_{\mathbf{R}, \mathbf{r}} | \Psi_n(\mathbf{r}; \mathbf{R}) \rangle$$

Rearrange terms

$$i \frac{\partial}{\partial t} \chi_m(\mathbf{R}; t) = [\hat{T}_{\mathbf{R}} + \hat{V}_{\mathbf{R}} + \epsilon_m(\mathbf{R})] \chi_m(\mathbf{R}; t) + \sum_n V_{mn} \chi_n(\mathbf{R}; t)$$

... and choose a representation (the so-called **adiabatic representation**),
in which electronic wave function depends only parametrically
on the nuclear positions, i.e. $\Psi_m(\mathbf{r}, \mathbf{R}) \rightarrow \Psi_m(\mathbf{r}; \mathbf{R})$

Born-Oppenheimer approximation = neglect of cross terms

Born-Oppenheimer approximation

The Born-Oppenheimer approximation enables separation into two separate problems

1. **The electron-structure problem:** Regard the nuclei as fixed in space and solve for the electronic degrees of freedom.

$$\hat{H}_e \Psi_m(\mathbf{r}; \mathbf{R}) = \epsilon_m(\mathbf{R}) \Psi_m(\mathbf{r}; \mathbf{R})$$

$$\hat{H}_e = \underbrace{-\sum_i \frac{1}{2} \nabla_i^2}_{\hat{T}_r} + \underbrace{\frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}}_{\hat{V}_r} - \underbrace{\sum_{i,n} \frac{Z_n}{|\mathbf{r}_i - \mathbf{R}_n|}}_{\hat{V}_{\mathbf{r}; \mathbf{R}}}$$

2. **The nuclear problem:** Solve for the nuclear degrees of freedom using the derived potential energy surface (PES).

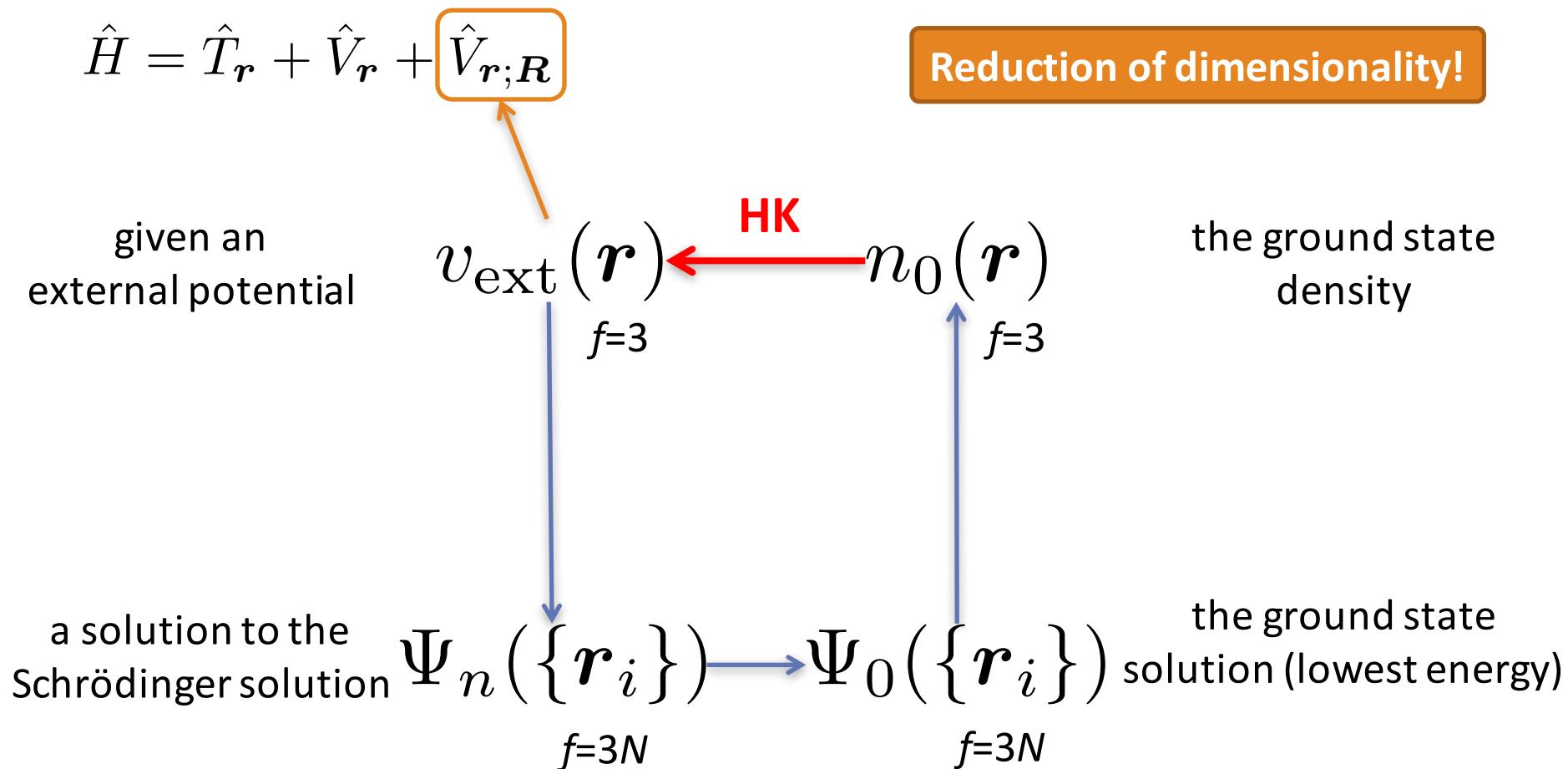
$$i \frac{\partial}{\partial t} \chi_m(\mathbf{R}; t) = [\hat{T}_{\mathbf{R}} + \hat{V}_{\mathbf{R}} + \epsilon_m(\mathbf{R})] \chi_m(\mathbf{R}; t)$$

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The Hohenberg-Kohn theorems

Schematic of Hohenberg-Kohn theorems

Hohenberg and Kohn, 1964 (**HK**):
a density functional theory as an exact theory of many-body systems



Hohenberg-Kohn theorem #1

Theorem #1

- For any electronic system in an external potential $v_{\text{ext}}(\mathbf{r})$ said potential is determined uniquely, save for a constant, by the ground state density $n_0(\mathbf{r})$

Corollary #1

- Since the Hamiltonian is thus fully determined, it follows that the many-body wave functions for all states (ground and excited) are determined.
- Thus all properties of the system are completely determined given only the ground state density.

Hohenberg-Kohn theorem #1 – Proof

Let $v_{\text{ext}}(\mathbf{r})$ be the external potential of a system, with associated ground state density $n(\mathbf{r})$, the total number of particles N , Hamiltonian H , and the ground state wave function ψ and ground state energy E .

$$v_{\text{ext}} : H, n(\mathbf{r}), \psi, E, N$$

Similarly consider a second system of N particles where $v_{\text{ext}} \neq v'_{\text{ext}} + C$ and hence $\psi \neq \psi'$

$$v'_{\text{ext}} : H', n'(\mathbf{r}), \psi', E', N$$

Then by the variational principle

$$E = \langle \psi | H | \psi \rangle < \langle \psi' | H | \psi' \rangle = \langle \psi' | H' | \psi' \rangle + \int [v_{\text{ext}}(\mathbf{r}) - v'_{\text{ext}}(\mathbf{r})] n'(\mathbf{r}) d\mathbf{r}$$

$$\begin{array}{c} \uparrow \\ = \end{array}$$

$$E' + \int [v_{\text{ext}}(\mathbf{r}) - v'_{\text{ext}}(\mathbf{r})] n'(\mathbf{r}) d\mathbf{r}$$

$$H = \hat{T}_{\mathbf{r}} + V_{\mathbf{r}} + \int v_{\text{ext}}(\mathbf{R}) n'(\mathbf{r})$$

$$H' = \hat{T}_{\mathbf{r}} + V_{\mathbf{r}} + \int v'_{\text{ext}}(\mathbf{R}) n'(\mathbf{r})$$

Hohenberg-Kohn theorem #1 – Proof

Thus

$$E < E' + \int [v_{\text{ext}}(\mathbf{r}) - v'_{\text{ext}}(\mathbf{r})] n'(\mathbf{r}) d\mathbf{r}$$

... and conversely

$$E' < E + \int [v'_{\text{ext}}(\mathbf{r}) - v_{\text{ext}}(\mathbf{r})] n(\mathbf{r}) d\mathbf{r}$$

Adding the inequalities gives

$$E + E' < E + E' + \int [v_{\text{ext}}(\mathbf{r}) - v'_{\text{ext}}(\mathbf{r})] [n'(\mathbf{r}) - n(\mathbf{r})] d\mathbf{r}$$

$n'(\mathbf{r}) \equiv n(\mathbf{r})$ is excluded as this would result in $0 < 0$

Thus any potential $v_{\text{ext}}(\mathbf{r})$ except $v_{\text{ext}}(\mathbf{r}) + C$
leads to $n'(\mathbf{r}) \neq n(\mathbf{r})$

Q.E.D.

Hohenberg-Kohn theorem #2

Theorem #2

- A universal functional of the energy $E[n]$ can be defined in terms of the density $n(\mathbf{r})$, which is valid for any external potential $v_{\text{ext}}(\mathbf{r})$. For any particular $v_{\text{ext}}(\mathbf{r})$ the **exact ground state** of the system is determined by the **global minimum value of this functional**.

Corollary #2

- Said functional alone is sufficient to determine the ground state energy and density.
- Excited states have to be determined by other means.
- DFT is a ground state theory

Thus by means of minimization, the ground-state electron density can be found as

$$E_0[n] = \min_{\Psi \rightarrow \tilde{n}} \langle \Psi | \hat{H} | \Psi \rangle = \min_{\Psi \rightarrow \tilde{n}}, \min_{\tilde{n} \in N} E[n]$$

Hohenberg-Kohn theorem #2

For convenience separate the energy functional into

- and a universal part (independent on N, mass and charge of nuclei, etc)
- a system dependent part, i.e. depends on $v_{\text{ext}}(\mathbf{r})$

Energy functional:

$$E[n(\mathbf{r})] = \boxed{\underset{\text{universal}}{F[n(\mathbf{r})]} + \int \underset{\text{system dependent}}{v_{\text{ext}}(\mathbf{r})n(\mathbf{r})d\mathbf{r}}$$

The universal functional contains the individual contributions of
kinetic energy, classical Coulomb interaction, and
the non-classical self-interaction correction

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

Some remarks

- The HK theorems can be generalized to include spin (not magnetic fields)
- ... reformulate the many-body problem in terms of the density **but do not actually solve it**
- **The HK functional is *a priori* unknown!**
There is no direct link from the density to e.g., the kinetic energy.
- HK-DFT is in principle exact (no approximations) but impractical
→ In practice one uses the **Kohn-Sham approach**

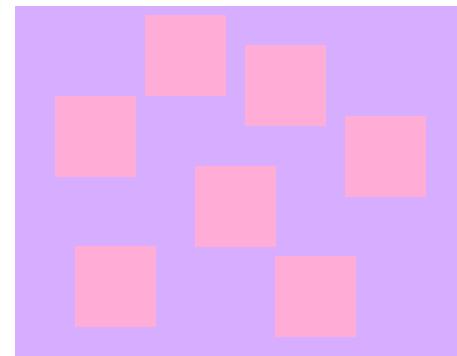
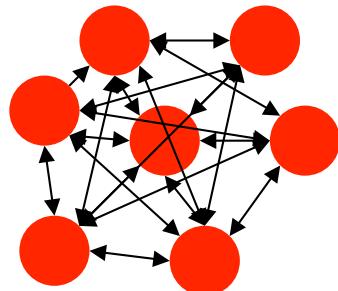
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The Kohn-Sham equations

The Kohn-Sham ansatz

- Replace the original many-body problem with an auxiliary system of non-interacting particles.

Interacting electrons
+ real potential



Non-interacting
auxiliary
particles in an
effective potential

Walter Kohn Lu Jue Sham



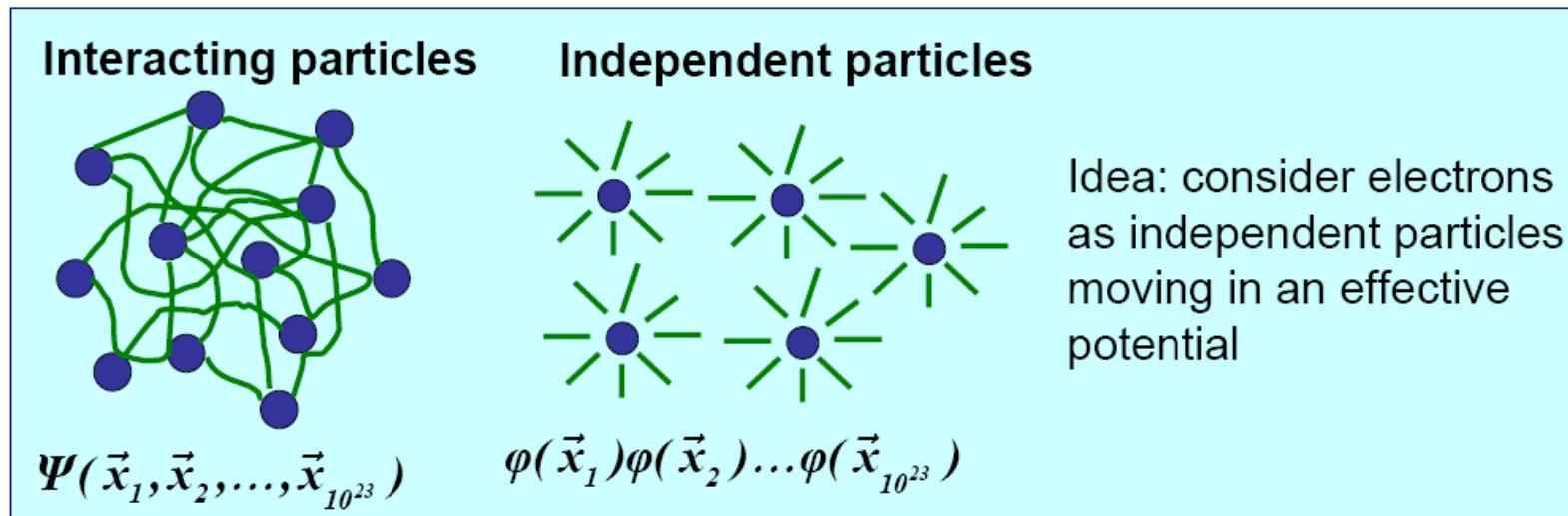
1998 (chemistry)

Assumption:

Ground state density of **interacting system** is equal to that of some **non-interacting system** that is exactly soluble, with all the difficult parts (exchange and correlation) included in some **approximate functional of the density**.

Independent particles approximations

- Hartree ansatz $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)\dots\psi_N(\mathbf{r}_N)$
- Fock: does not satisfy anti-symmetry requirement (fermions)
→ need to take Slater determinant



D. R. Hartree

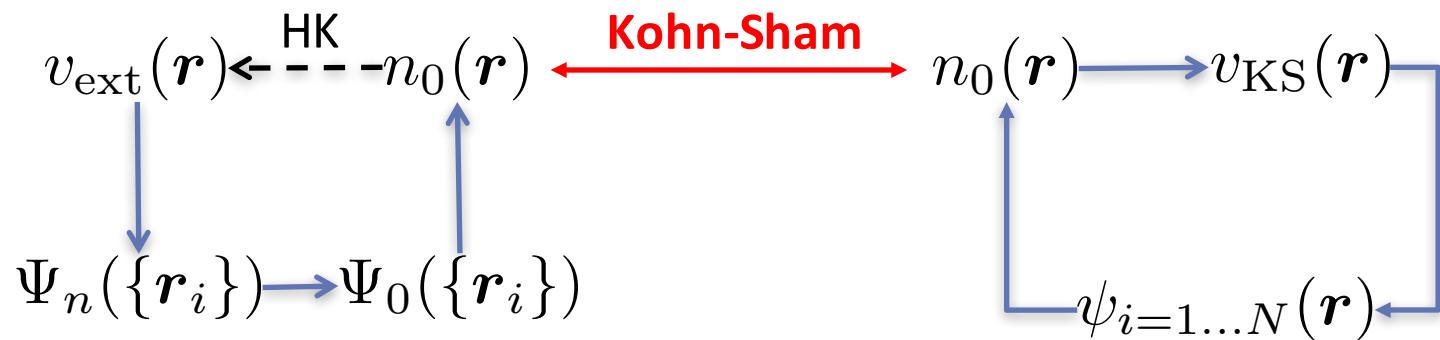
V. A. Fock



Erhart, I.

Kohn-Sham ansatz

- In principle, the solution of the independent KS problem determines all properties of the full many-body system.



The auxiliary Hamiltonian contains the **usual kinetic energy term** and a **local effective potential** acting on the electrons

The Kohn-Sham energy functional

- In KS decomposition the total energy of a many electron system in an external potential is

$$E[n] = T_0[n(\mathbf{r})] + \int d\mathbf{r} n(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) + E_H[n(\mathbf{r})] + E_{xc}(\mathbf{r})$$

Hohenberg-Kohn theorem #2

For convenience separate the energy functional into

- and a universal part (independent on N, mass and charge of nuclei, etc)
- a system dependent part, i.e. depends on $v_{\text{ext}}(\mathbf{r})$

Energy functional:

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The universal functional contains the individual contributions of
kinetic energy, classical Coulomb interaction, and
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$$F[n(\mathbf{r})] = \boxed{T[n(\mathbf{r})]} + \boxed{\frac{1}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'} + \boxed{E_{xc}^{\text{true}}}$$

The Kohn-Sham energy functional

- In KS decomposition the total energy of a many electron system in an external potential is

$$E[n] = T_0[n(\mathbf{r})] + \int d\mathbf{r} n(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) + E_H[n(\mathbf{r})] + E_{xc}(\mathbf{r})$$

“0” → non-interacting particles

kinetic external potential class. Coul. self-int.

$$n(\mathbf{r}) = \sum_i^{\text{occ}} |\psi_i(\mathbf{r})|^2$$

electron density

$$v_{\text{ext}} = - \sum_n \frac{Z_n}{\mathbf{r} - \mathbf{R}_I}$$

potential from the nuclei

$$E_H[n] = \frac{1}{2} \int \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

classical Coulomb energy

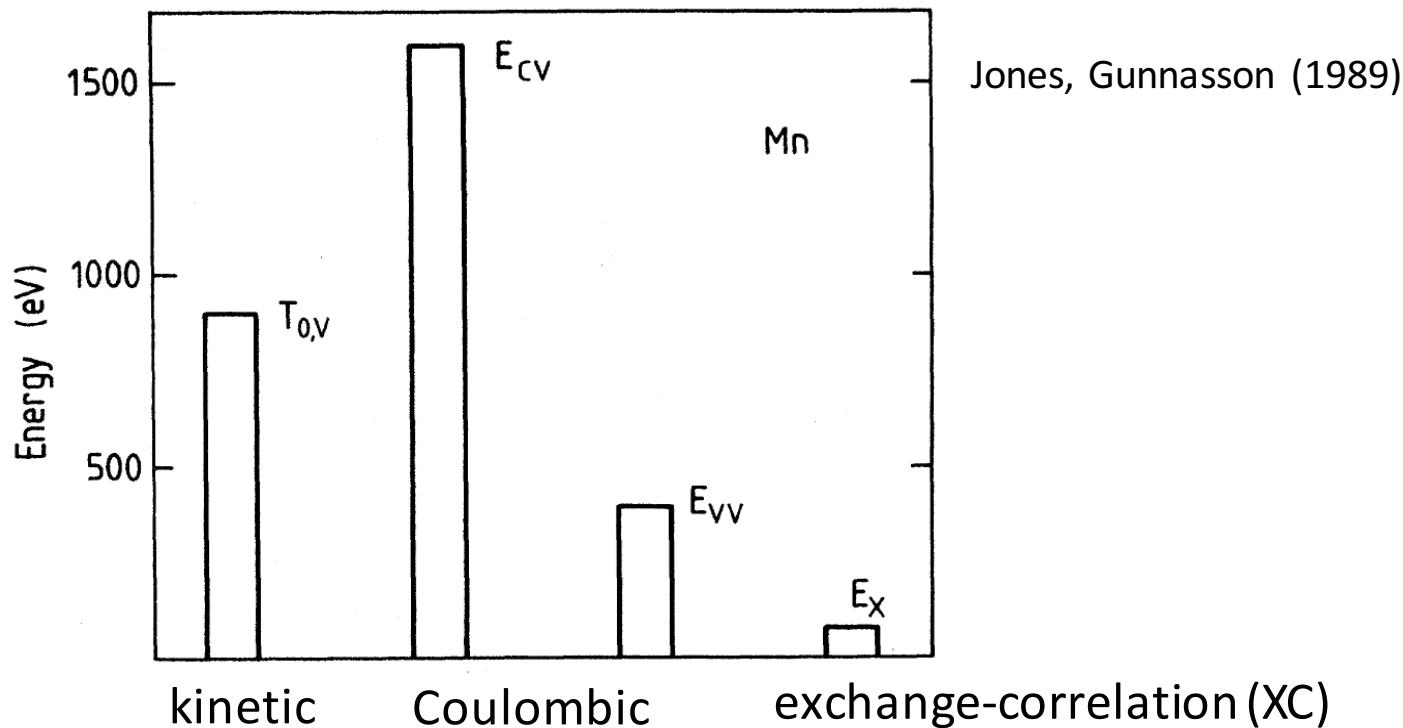
$$E_{xc}[n] = \int d\mathbf{r} n(\mathbf{r}) \varepsilon_{xc}[n(\mathbf{r})]$$

exchange and correlation

N.B.: Here, we use atomic units.

Kohn-Sham functional

- The KS decomposition separates contributions that are (in principle) possible to compute from contributions that are much more complicated.



XC is on an absolute scale a minor contribution to the total energy.
It is crucial that the kinetic energy is evaluated to a high accuracy
(this is not done in Thomas-Fermi theory).

Kohn-Sham one-electron orbitals

- The one-electron orbitals (KS orbitals) are solutions to the KS equation (**one-particle equation!!**)

$$\left(-\frac{1}{2} \nabla^2 + v_{\text{ext}}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) \right) \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r})$$

↑
KS orbital
↑
KS eigenenergy

- It is tempting to treat these states as proper electronic (quasi) particle states; but beware, this are **fictitious states**
- Nonetheless band structures often useful; although **band gap underestimation** is common

DFT in practice: The exchange-correlation functional

$$E_{xc}[n] = \int d\mathbf{r} n(\mathbf{r}) \varepsilon_{xc}[n(\mathbf{r})]$$
$$v_{xc} = \frac{\delta \epsilon_{xc}}{\delta n}$$

potential

Local density approximation (LDA)

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

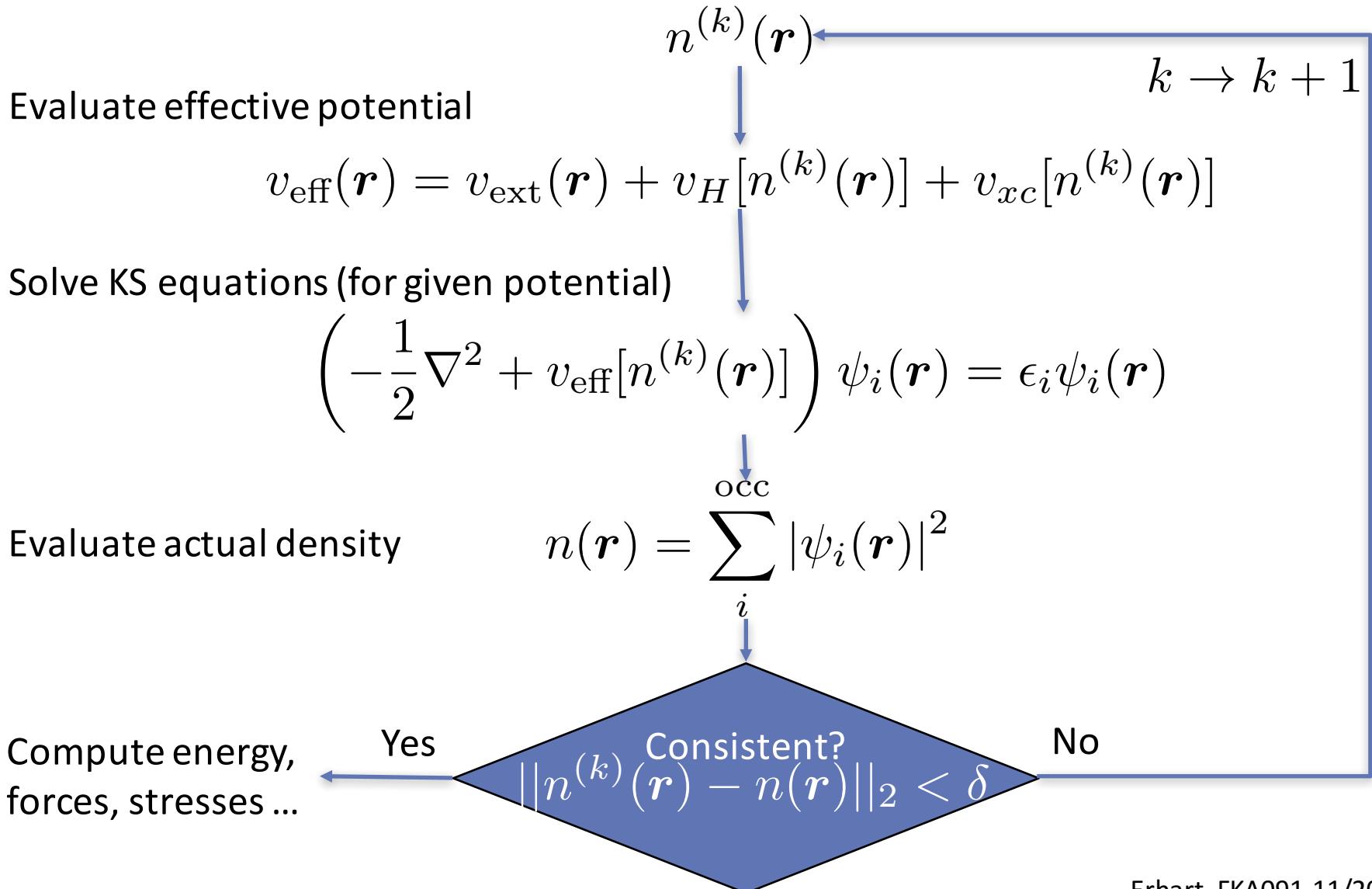
where $\varepsilon_{xc}^{\text{HEG}}(n)$ is the exchange-correlation energy of a homogeneous electron gas of density n

Generalized gradient approximations (GGA; semi-local functionals)

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

DFT in practice: The self-consistency loop

Initial guess (usually superposition of atomic densities for $k=1$)



Implementation aspects

Fully relativistic
Semi-relativistic
Non-relativistic

$$\left(-\frac{1}{2} \nabla^2 + v_{\text{ext}}(\mathbf{r}) + v_{Hxc}(\mathbf{r}) \right) \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r})$$

All-electron full potential
All-electron muffin-tin
All-electron PAW
Pseudopotential

Beyond DFT

GW (quasi-particles)
EXX (exact exchange)
sX-LDA
Time dependent DFT
LDA+U

Beyond DFT ←
Generalized Gradient Approximation (GGA)
Local Density Approximation (LDA)

Atomic orbitals

Gaussians(GTO)
Slater type (STO)

PLAPW
s

In practice

- a lot of numerics related to basis sets, treatment of core/valence electrons, exchange-correlation, solving differential equations, finding eigen values etc.
- Actual production DFT codes contain tens to hundreds of thousands of lines of code

Kohn-Sham one-electron orbitals

- The one-electron orbitals (KS orbitals) are solutions to the KS equation (**one-particle equation!!**)

$$\left(-\frac{1}{2} \nabla^2 + v_{\text{ext}}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) \right) \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r})$$

KS orbital

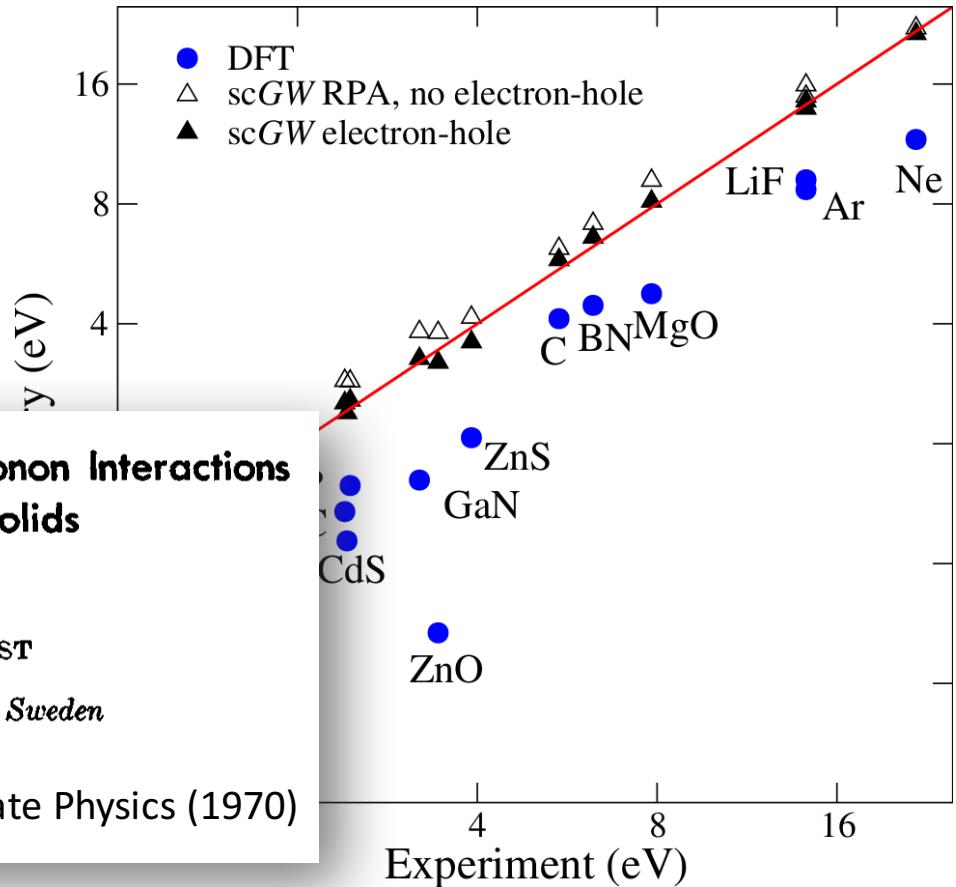
↑

KS eigenenergy

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Kohn-Sham one-electron orbitals

- Band gap underestimation



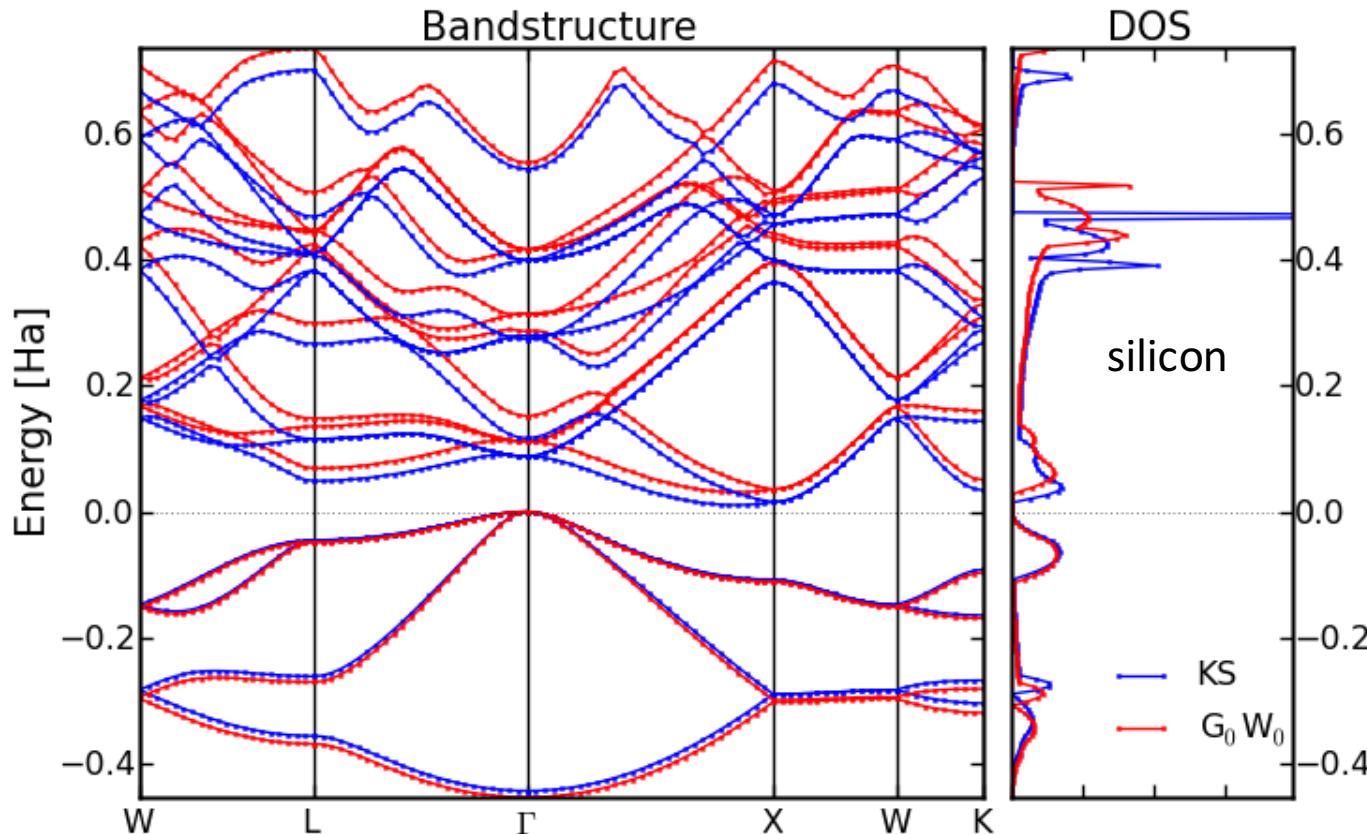
GW is a many body perturbation technique

G : Green's function

W : Screened Coulomb interaction

Kohn-Sham one-electron orbitals

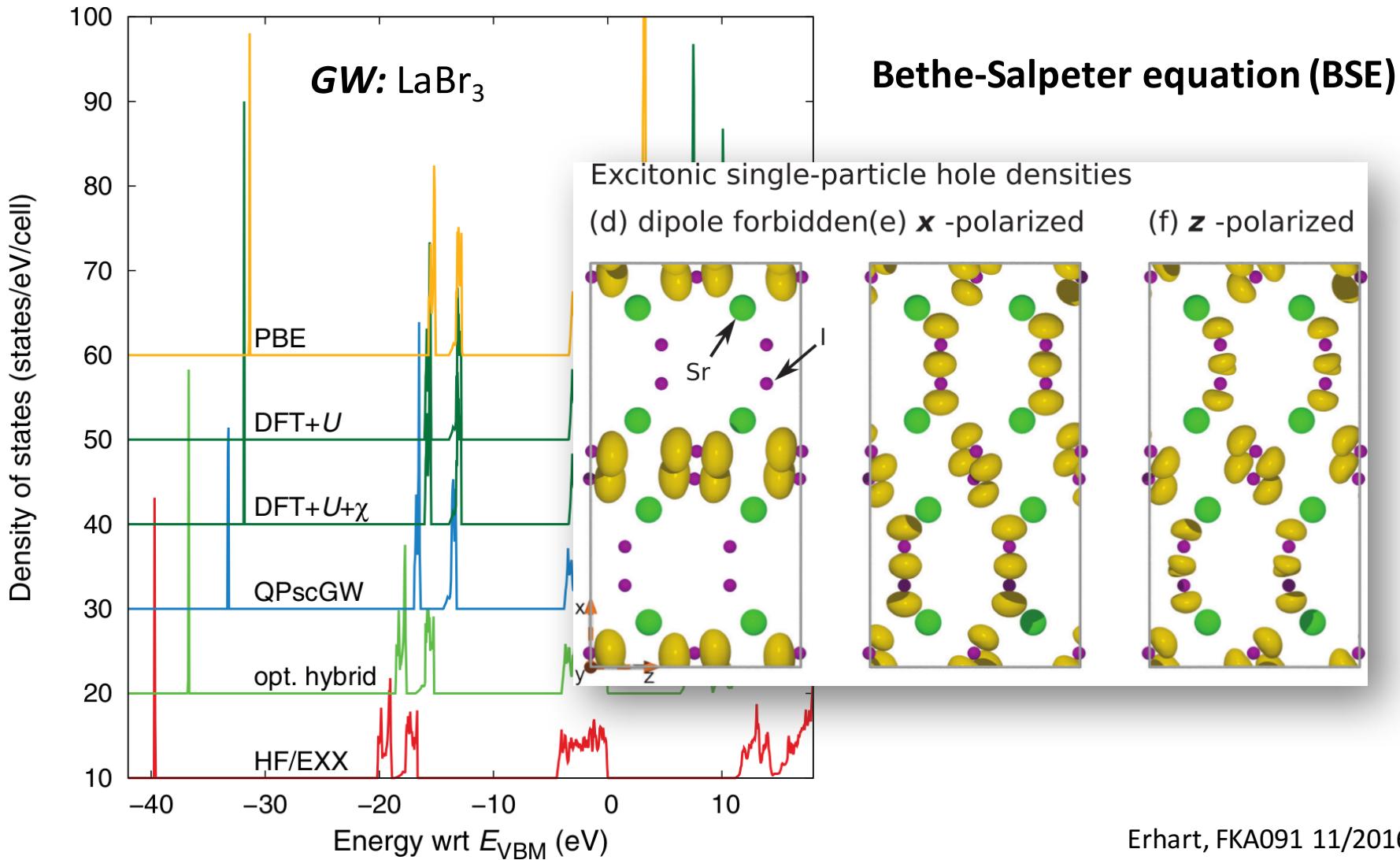
- Band structures



- Dispersion usually very good

Beyond DFT

- DFT represents a very starting point for many-body perturbation theory



Take away messages

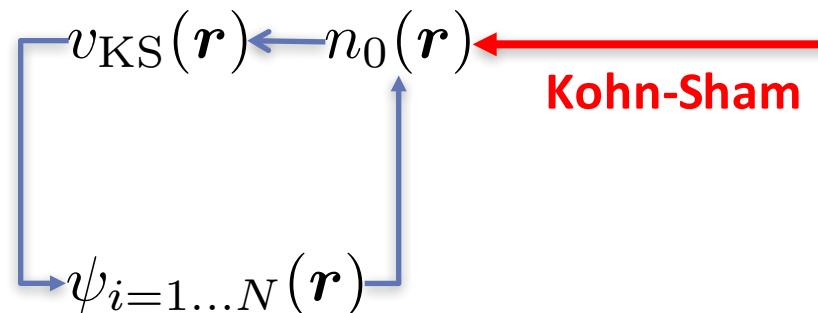
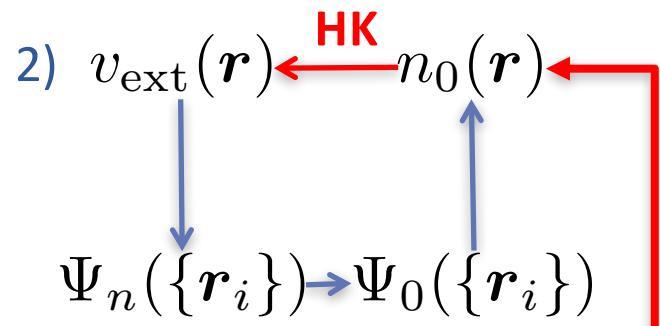
- Hohenberg-Kohn theorems

- 1) All properties determined by density
- 2) A functional can be defined the minimum of which yields the ground state

- Kohn-Sham equations

- Replace fully interacting system with set of fictitious effective single-particle problems
- The magic happens in the exchange-correlation functional
- Can be solved iteratively

$$1) \quad n(\mathbf{r}) \xleftrightarrow{\Psi(\{\mathbf{r}\})} f=3 \qquad f=3N$$



DFT yields total energies, forces, and electronic structure
→ excellent starting point for many-body perturbation theory techniques (GW, BSE, also TD-DFT)

Take away messages

Density functional theory (DFT)

- ... yields **total energies, forces, and electronic structure** and therefore allows computing e.g.,
 - Structural relaxation and phase stability
 - Energy differences (input for thermodynamics, kinetics ...)
 - Phonon dispersions (mechanical stability)
 - Property prediction and screening
 - Band structures (a bit more complicated, see above)
- ... provides a reasonable balance between
computational efficiency and accuracy
(thousands of electrons, hundreds of atoms)
- ... has **limitations** e.g., with respect to
 - Band gaps and optical properties (excitonic effects)
 - Strongly correlated systems