Plane-wave density functional theory in GPAW

Matej Huš

Department of Catalysis and
Chemical Reaction Engineering

MODERN QUANTUM MECHANICS

- Quantum mechanics encompasses the wave-particle duality.
- Particles do not travel along definite paths but are distributed through space like a wave.
- This is represented by the **wavefunction**, which is the central quantity.
- It contains all the information that can be accessed experimentally. <u>The WF is not itself measurable</u>.
- It depends on the coordinates of every particle.
- It is represented by the Greek letter ‘psi’ Ψ.

SCHRÖDINGER EQUATION

- The wavefunction is the solution of the Schrödinger equation.
- It can be applied to all systems: electrons, atoms, molecules …
- Time-dependent Schrödinger equation:

$$\boxed{i\hbar \frac{\partial \Phi(\mathbf{x},t)}{\partial t} = \hat{H}\Phi(\mathbf{x},t)}$$

Hamiltonian operator Wavefunction

- When the potential energy does not change with time:

$$\boxed{\hat{H}\Psi(\mathbf{x}) = E\Psi(\mathbf{x})}$$

- There exists an operator for each experimentally observable property (energy, position, momentum). Hamiltonian is the energy operator. The expectation value:

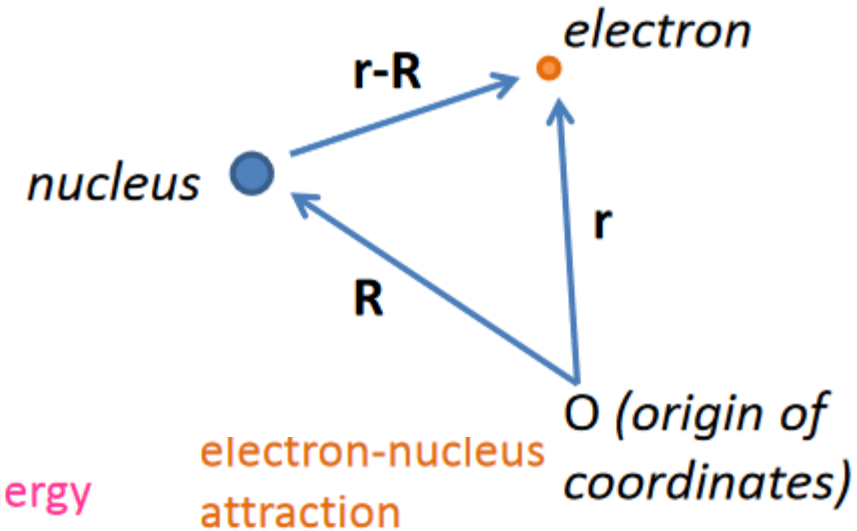
$$\hat{H} = \hat{T} + \hat{V}$$

$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} \Psi^*(x)\, \hat{x}\, \Psi(x) dx}{\int_{-\infty}^{\infty} \Psi^*(x) \Psi(x) dx}$$

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$$

HAMILTONIAN FOR HYDROGEN ATOM

- We are solving the many-body (time-independent) Schrödinger equation.
- This is a hard problem. Analytically can be solved for one-electron systems only.



nuclear kinetic energy

electronic kinetic energy

electron-nucleus attraction

$$\hat{H} = -\frac{\hbar^2}{2M}\left(\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2}\right) - \frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{|\mathbf{r}-\mathbf{R}|}$$

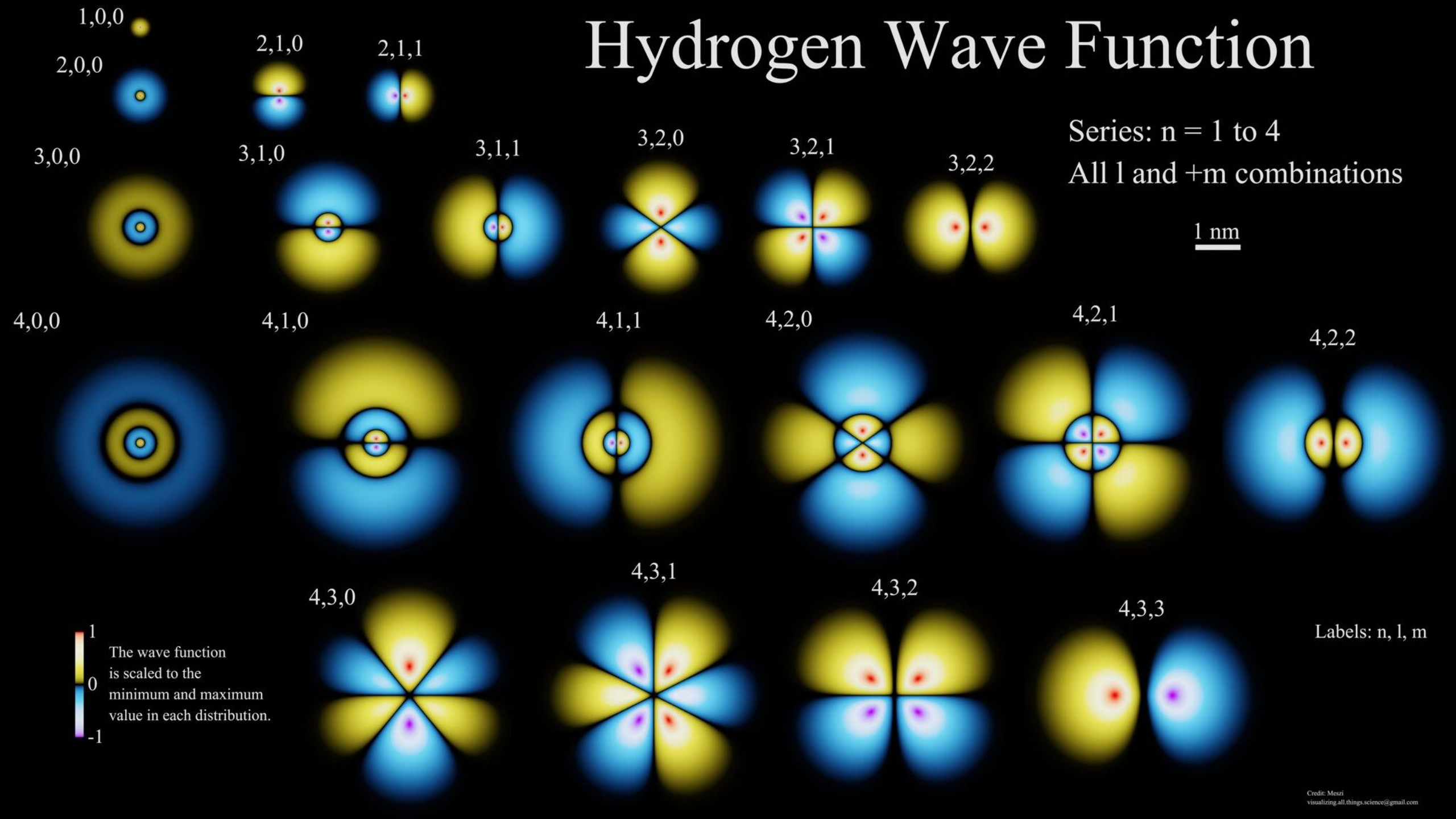
Born-Oppenheimer approximation

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_{N_{\text{electrons}}})$$

$$\hat{H} = -\frac{\hbar^2}{2M}\nabla^2_{\mathbf{R}} - \frac{\hbar^2}{2m}\nabla^2_{\mathbf{r}} - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{|\mathbf{r}-\mathbf{R}|}$$

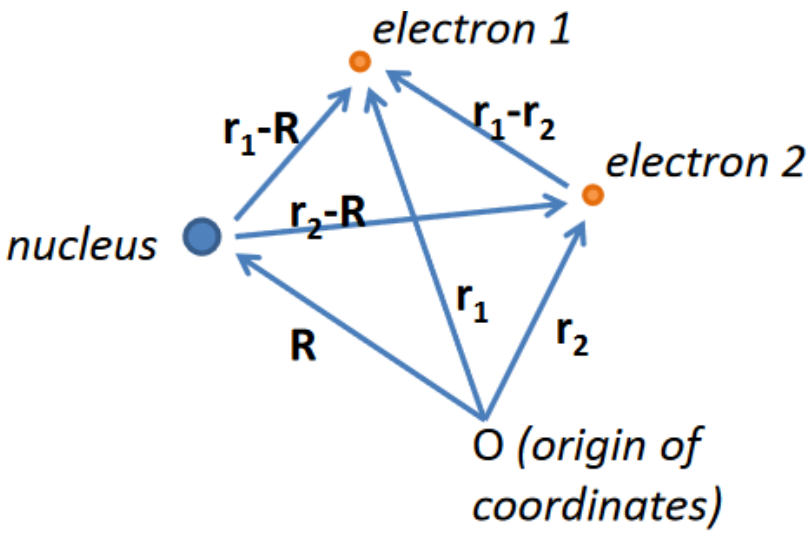
$$\varphi(p, \theta_p, \varphi_p) = \sqrt{\frac{2}{\pi}\frac{(n-\ell-1)!}{(n+\ell)!}}\, n^2 2^{2\ell+2}\ell!\,\frac{n^\ell p^\ell}{(n^2p^2+1)^{\ell+2}}\, C^{\ell+1}_{n-\ell-1}\left(\frac{n^2p^2-1}{n^2p^2+1}\right) Y^m_\ell(\theta_p, \varphi_p),$$

Hydrogen Wave Function



HAMILTONIAN FOR HELIUM ATOM

- Cannot be done analytically because it has two electrons!
- We can do it computationally, but it is exhausting: 8 electrons in a 6x6x6 grid require 10^{10} GB.



B.O.

$$\hat{H} = -\cancel{\frac{1}{2M}\nabla^2_{\mathbf{R}}} - \frac{1}{2}\nabla^2_{\mathbf{r_1}} - \frac{1}{2}\nabla^2_{\mathbf{r_2}} - \frac{2}{|\mathbf{r_1} - \mathbf{R}|} - \frac{2}{|\mathbf{r_2} - \mathbf{R}|} + \frac{1}{|\mathbf{r_1} - \mathbf{r_2}|}$$

kinetic energy of nucleus	kinetic energy of electron 1	kinetic energy of electron 2	attraction of electron 1 by nucleus	attraction of electron 2 by nucleus	repulsion between electrons 1 and 2

HAMILTONIAN FOR WATER MOLECULE

$$\hat{H}_{\mathrm{H_2O}} = \underbrace{-\cancel{\frac{1}{2M_{\mathrm{O}}}}\nabla^2_{\mathbf{R}_{\mathrm{O}}}}_{\text{Kinetic energy of O}} \overset{\text{B.O.}}{} \underbrace{-\cancel{\frac{1}{2M_{\mathrm{H1}}}}\nabla^2_{\mathbf{R}_{\mathrm{H1}}}}_{\text{Kinetic energy of H1}} \overset{\text{B.O.}}{} \underbrace{-\cancel{\frac{1}{2M_{\mathrm{H2}}}}\nabla^2_{\mathbf{R}_{\mathrm{H2}}}}_{\text{Kinetic energy of H2}} \overset{\text{B.O.}}{} \underbrace{-\sum_{i=1}^{10}\frac{1}{2}\nabla^2_{\mathbf{r}_i}}_{\text{Kinetic energy of electron } i}$$

$$\underbrace{-\sum_{i=1}^{10}\frac{8}{|\mathbf{r}_i-\mathbf{R}_{\mathrm{O}}|}}_{\text{Electron attraction to O}} \underbrace{-\sum_{i=1}^{10}\frac{1}{|\mathbf{r}_i-\mathbf{R}_{\mathrm{H1}}|}}_{\text{Electron attraction to H1}} \underbrace{-\sum_{i=1}^{10}\frac{1}{|\mathbf{r}_i-\mathbf{R}_{\mathrm{H2}}|}}_{\text{Electron attraction to H2}}$$

$$\underbrace{+\sum_{i=1}^{10}\sum_{j=i+1}^{10}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}}_{\text{Electron-electron repulsion}} \underbrace{+\sum_{I=1}^{3}\sum_{J=I+1}^{3}\frac{Z_I Z_J}{|\mathbf{R}_I-\mathbf{R}_J|}}_{\text{nucleus-nucleus repulsion}}$$

E.g. Assume
$Z_1 = Z_O$
$Z_2 = Z_{H1}$
$Z_3 = Z_{H2}$

- A complicated expression.
- Quickly becomes intractable.
- We need an easier way to write down Hamiltonians.
- We develop a general, compact expression for any molecule.

ELECTRONIC WAVEFUNCTION

- Solutions of the electronic Schrödinger equation are **wavefunctions**
- They must be:
  - Finite
  - Continuous
  - Single-valued
  - Antisymmetric
- They account for the indistinguishability of electrons.
- Their square is a probability distribution

ELECTRONIC DENSITY

- The wavefunction is a function of 4 N_{el} variables.

$$\Psi(\mathbf{r}_1, \omega_1, \mathbf{r}_2, \omega_2, \ldots, \mathbf{r}_{N_{el}}, \omega_{N_{el}}) = \Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_{N_{el}})$$

- The electronic density is a function of 3 variables and can be experimentally observed.

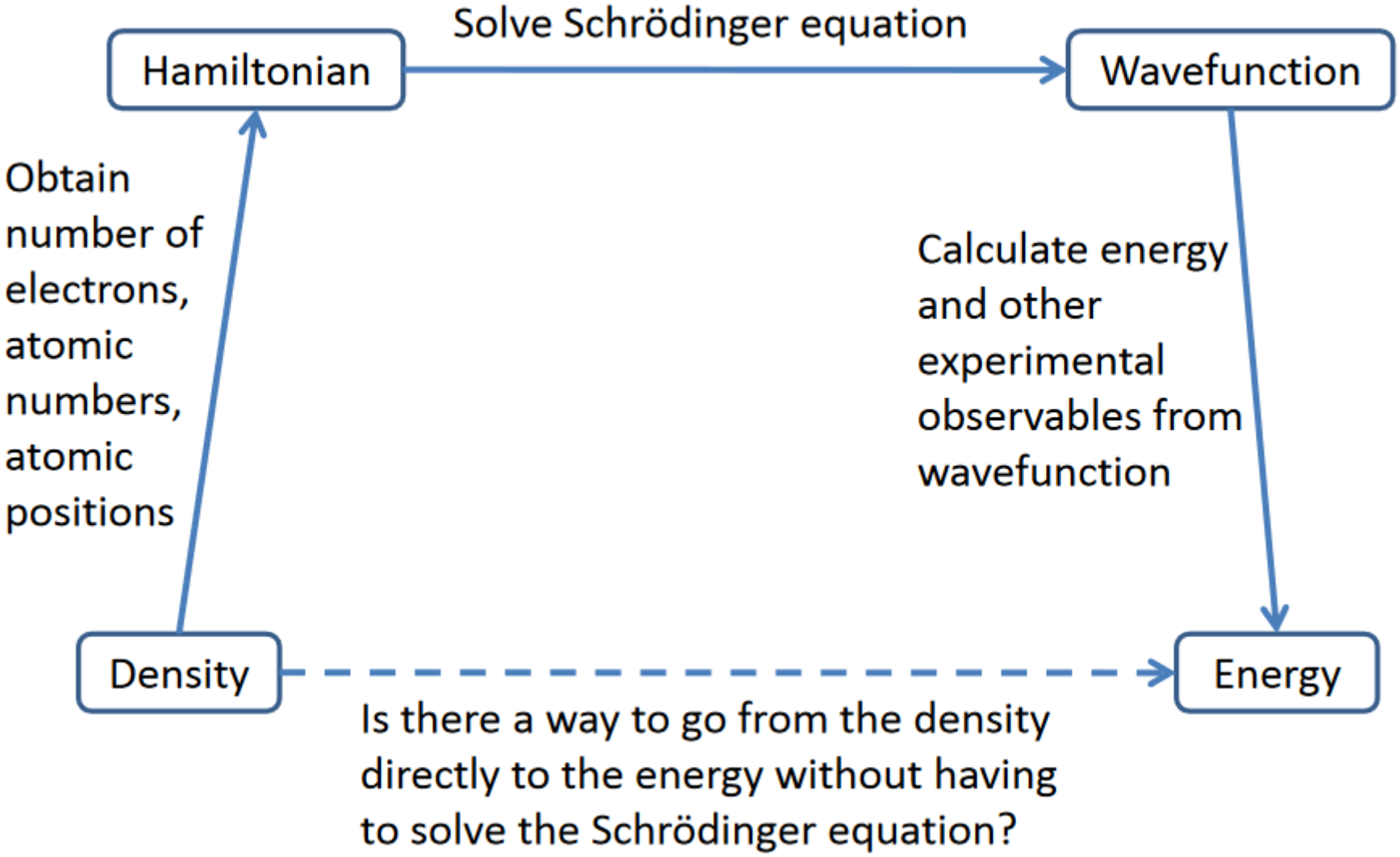
$$n(\mathbf{r}) = N_{el} \int \cdots \int \Psi^*(\mathbf{r}, \omega_1, \mathbf{r}_2, \omega_2, \cdots, \mathbf{r}_{N_{el}}, \omega_{N_{el}}) \Psi(\mathbf{r}, \omega_1, \mathbf{r}_2, \omega_2, \cdots, \mathbf{r}_{N_{el}}, \omega_{N_{el}}) \; d\omega_1 d\mathbf{r}_2 \omega_2 \ldots d\mathbf{r}_{N_{el}} d\omega_{N_{el}}$$

- The electronic density tells us about the positions of the nuclei, atomic numbers and the total number of electrons.

$$N_{el} = \int n(\mathbf{r}) d\mathbf{r}$$

- How do we get the energy? Unfortunately, in the Schrödinger equation the wavefunction is required.

ELECTRONIC DENSITY



DENSITY FUNCTIONAL THEORY

- Can we solve for the electronic density instead of the wavefunction?
- Hohenberg and Kohn in 1965 laid the foundation for **density functional theory**.
- What is a functional? A "function of function"

$$f(x) = x^2$$

$$g(x, y) = \cos(x) + e^{-3\sqrt{x^2+y^2}}$$

$$F[f] = \int_{-\infty}^{\infty} f^3(x)dx$$

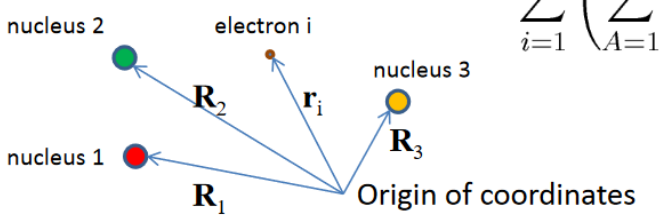
$$H[g] = \int_2^3 \int_{-10}^4 \left(\frac{\partial^2 g(x, y)}{\partial x^2} - 2.3\, g(x, y) \right) dxdy$$

DENSITY FUNCTIONAL THEORY

- Hamiltonian for the electrons is:

$$\hat{H}_{\text{el}} = \sum_{i=1}^{N_{el}} -\frac{1}{2}\nabla_i^2 + \sum_{i=1}^{N_{el}} \sum_{j=i+1}^{N_{el}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^{N_{el}} \sum_{A=1}^{N_{at}} \frac{-Z_A}{|\mathbf{r}_i - \mathbf{R}_A|}$$

$$\sum_{i=1}^{N_{\text{el}}} \left(\sum_{A=1}^{N_{\text{at}}} \frac{-Z_A}{|\mathbf{r}_i - \mathbf{R}_A|} \right) = \sum_{i=1}^{N_{\text{el}}} V_{\text{ext}}(\mathbf{r}_i)$$

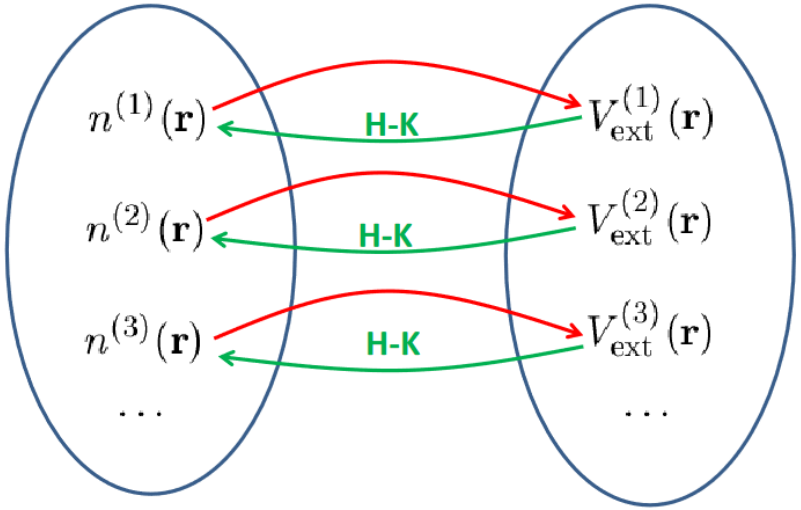


- The operator is Hermitian:

$$E_{\text{exact}} = \frac{\int \Psi^*_{\text{exact}} \hat{H} \Psi_{\text{exact}}\, dx}{\int \Psi^*_{\text{exact}} \Psi_{\text{exact}}\, dx} \leq \frac{\int \Psi^*_{\text{approx}} \hat{H} \Psi_{\text{approx}}\, dx}{\int \Psi^*_{\text{approx}} \Psi_{\text{approx}}\, dx} = E_{\text{approx}}$$

HOHENBERG-KOHN THEOREMS

- Let us use **electron density** as the basic quantity, *n*.
- **All properties** of the system are determined by **the ground state density.**
- Each property is **a functional** of the ground state.
- A universal functional exists (shown by H-K). It is unfortunately not known.
- The ground state density minimizes the total energy functional (2nd H-K)



$$E_{\text{el}} = \int \Psi^* \left(\sum_{i=1}^{N_{\text{el}}} \frac{-1}{2} \nabla_i^2 \right) \Psi \, d\mathbf{X} + \int \Psi^* \left(\sum_{i=1}^{N_{\text{el}}} \sum_{j=i+1}^{N_{\text{el}}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right) \Psi \, d\mathbf{X} + \int \Psi^* \left(\sum_{i=1}^{N_{\text{el}}} V_{\text{ext}}(\mathbf{r}_i) \right) \Psi \, d\mathbf{X}$$

$$= \boxed{F_{HK}[n]} + \boxed{\int V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) \, d\mathbf{r}} = E_{\text{el}}[n]$$

ELECTRONIC ENERGY

- We can separate the electronic energy in the following contributions.

$$E_{\mathrm{el}} = \int \Psi^* \left(\sum_{i=1}^{N_{\mathrm{el}}} \frac{-1}{2} \nabla_i^2 \right) \Psi \, d\mathbf{X} + \int \Psi^* \left(\sum_{i=1}^{N_{\mathrm{el}}} \sum_{j=i+1}^{N_{\mathrm{el}}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right) \Psi \, d\mathbf{X} + \int \Psi^* \left(\sum_{i=1}^{N_{\mathrm{el}}} V_{\mathrm{ext}}(\mathbf{r}_i) \right) \Psi \, d\mathbf{X}$$

$$E_{\mathrm{el}} = E_{\mathrm{kin}} + E_{\mathrm{Coul}} + E_{\mathrm{x}} + E_{\mathrm{c}} + E_{\mathrm{ext}}$$

$$\frac{1}{2} \int \int \frac{n(\mathbf{r})\, n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r} d\mathbf{r}' \qquad \int V_{\mathrm{ext}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r}$$

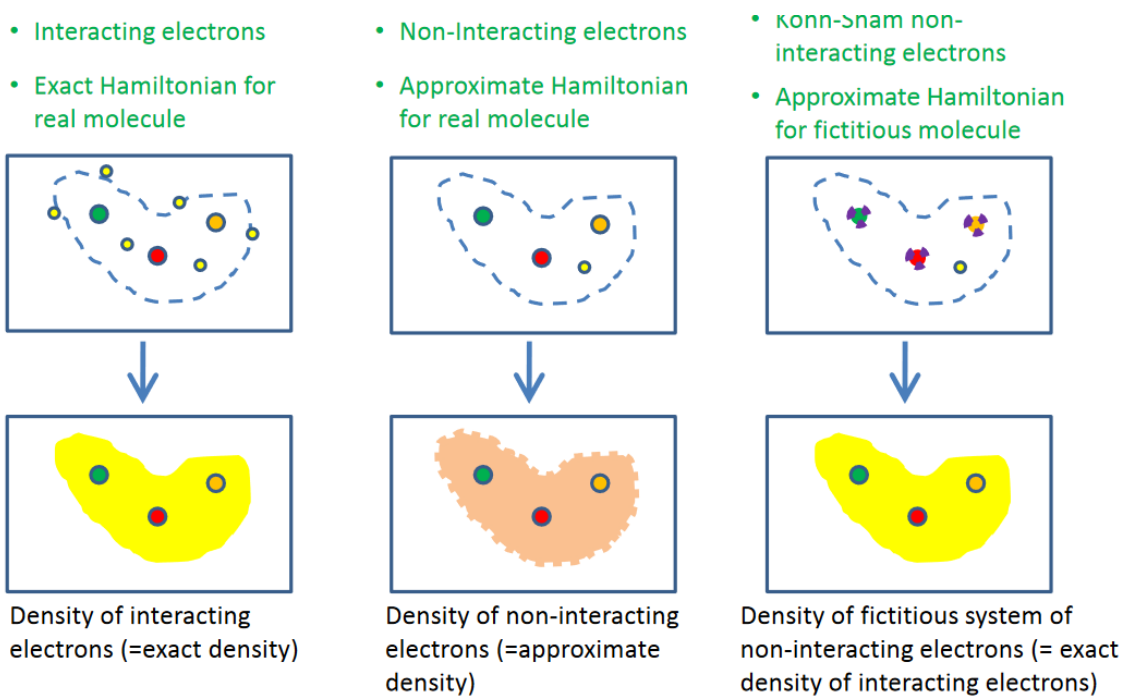
Where:
- kin: kinetic energy
- Coul: Coulomb energy
- x: exchange energy
- c: correlation energy
- ext: external potential energy

- Similarly, the H-K functional can be split into a sum functionals (we assume).

$$F_{\mathrm{HK}}[n] = E_{\mathrm{kin}}[n] + E_{\mathrm{Coul}}[n] + E_{\mathrm{x}}[n] + E_{\mathrm{c}}[n]$$

KOHN-SHAM EQUATIONS

- Doing ‘pure’ DFT is in principle possible.
- In practice, it is not very accurate because we lack good approximation for the kinetic energy functional
- Kohn and Sham proposed an alternative approach
- Let’s work with a system of non-interacting electrons.
- The wavefunction will be different **but** a fictitious non-interacting system is constructed with the **same** electronic density as the interacting system.
- We do not need to find a universal H-K functional. We just need a functional of the fictitious system.
- The expression of the kinetic energy is now known *exactly*.



Exact electronic Hamiltonian

$$\hat{H}_{\mathrm{el}} = \sum_{i=1}^{N_{\mathrm{el}}} -\frac{1}{2}\nabla_i^2 + \sum_{i=1}^{N_{\mathrm{el}}}\left(\sum_{A=1}^{N_{at}} \frac{-Z_A}{|\mathbf{r}_i - \mathbf{R}_A|}\right) + \sum_{i=1}^{N_{\mathrm{el}}}\sum_{j=i+1}^{N_{\mathrm{el}}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$= \sum_{i=1}^{N_{\mathrm{el}}} -\frac{1}{2}\nabla_i^2 + \sum_{i=1}^{N_{\mathrm{el}}} V_{\mathrm{ext}}(\mathbf{r}_i) + \sum_{i=1}^{N_{\mathrm{el}}}\sum_{j=i+1}^{N_{\mathrm{el}}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Fictitious

$$\hat{H}_{\mathrm{eff}} = \sum_{i=1}^{N_{\mathrm{el}}} -\frac{1}{2}\nabla_i^2 + \sum_{i=1}^{N_{\mathrm{el}}} V_{\mathrm{ext}}(\mathbf{r}_i) + \sum_{i=1}^{N_{\mathrm{el}}} V_{\mathrm{av}}(\mathbf{r}_i)$$

KOHN-SHAM EQUATIONS

$$E[n] = E_{\mathrm{kin,KS}}[n] + (E_{\mathrm{kin}}[n] - E_{\mathrm{kin,KS}}[n]) + E_{\mathrm{Coul}}[n] + E_{\mathrm{xc}}[n] + E_{\mathrm{ext}}[n]$$

- Kohn-Sham approach is *exact*.
- Single-particle equations are used instead of the many-body wavefunction.
- What we don't know is crammed into the exchange correlation
- Note: Eigenvalues and eigenvectors of the KS system **have no physical meaning**.
- The electron density and the energy **do**.

Orbital-free approach

" Find approximation for $F_{HK}[n]$ "

↓

Compute density $n_0(\mathbf{r})$ by minimising $E[n]=F_{HK}[n]+E_{ext}[n]$

↓

Compute energy $E[n_0]$

Kohn-Sham approach

" Find a $V_{eff}(\mathbf{r})=V_{KS}(\mathbf{r})$ such that $n_{KS}(\mathbf{r}) = n_0(\mathbf{r})$ "

↓

Solve for the wavefunction (Slater determinant) of the non-interacting electrons (i.e. find the molecular orbitals)

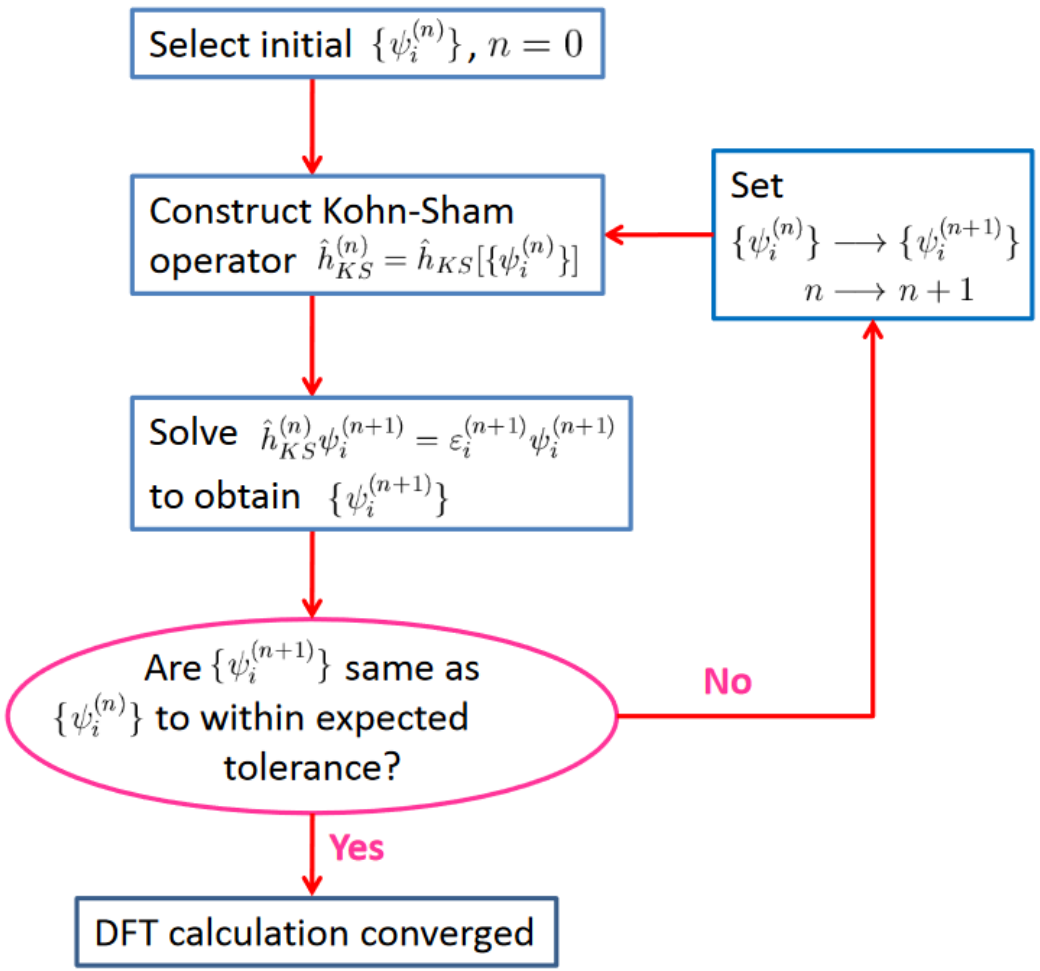
↓

Build the density $n_0(\mathbf{r})$ from the molecular orbitals

↓

Compute energy $E[n_0]$

SELF-CONSISTENT FIELD PROCEDURE




```
Unit cell:
                periodic      x           y           z       points   spacing
  1. axis:        yes    10.210622    0.000000    0.000000     48      0.1842
  2. axis:        yes     5.105311    8.842658    0.000000     48      0.1842
  3. axis:        no      0.000000    0.000000   18.252703     90      0.2028

  Lengths:  10.210622  10.210622  18.252703
  Angles:   90.000000  90.000000  60.000000

Effective grid spacing dv^(1/3) = 0.1996

                        log10-error:    total        iterations:
                time    wfs    density  energy       poisson
iter:    1   12:56:20                  -349.959972
iter:    2   12:56:52  -1.58   -1.17   -320.920088
iter:    3   12:57:22  -1.12   -1.24   -294.229872
iter:    4   12:57:53  -1.34   -1.43   -297.578625
iter:    5   12:58:27  -2.00   -1.50   -285.406400
iter:    6   12:59:01  -2.29   -1.70   -282.490025
iter:    7   12:59:32  -2.12   -1.84   -282.491436
iter:    8   13:00:01  -2.99   -1.90   -281.668936
iter:    9   13:00:30  -2.73   -2.06   -281.214343
iter:   10   13:00:59  -2.50   -2.27   -280.967638
iter:   11   13:01:25  -3.41   -2.35   -280.818154
iter:   12   13:01:56  -3.89   -2.55   -280.833332
iter:   13   13:02:22  -3.44   -2.58   -280.748721
iter:   14   13:02:48  -4.42   -2.83   -280.734465
iter:   15   13:03:15  -4.87   -2.95   -280.729745
iter:   16   13:03:45  -4.21   -3.07   -280.727703
iter:   17   13:04:20  -5.31   -3.44   -280.724003
iter:   18   13:04:54  -5.18   -3.49   -280.721088
```

SOFTWARE: GPAW

- Density-functional theory and time-dependent DFT
- Uses the projector augmented wave method
- Supports various basis sets.
- Is massively parallelized
- Open-sourced under GPL
- Supports a wide range of XC functionals

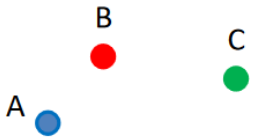
What it can do?

- Total energies and forces, structural optimization, magnetic moments
- Analysis of electronic structure (band structure, density of states)
- Excited state properties (TD-DFT, GW, Bethe-Salpeter)
- X-ray spectra, STM images …

ATOMIC ORBITALS VS. PLANE WAVES

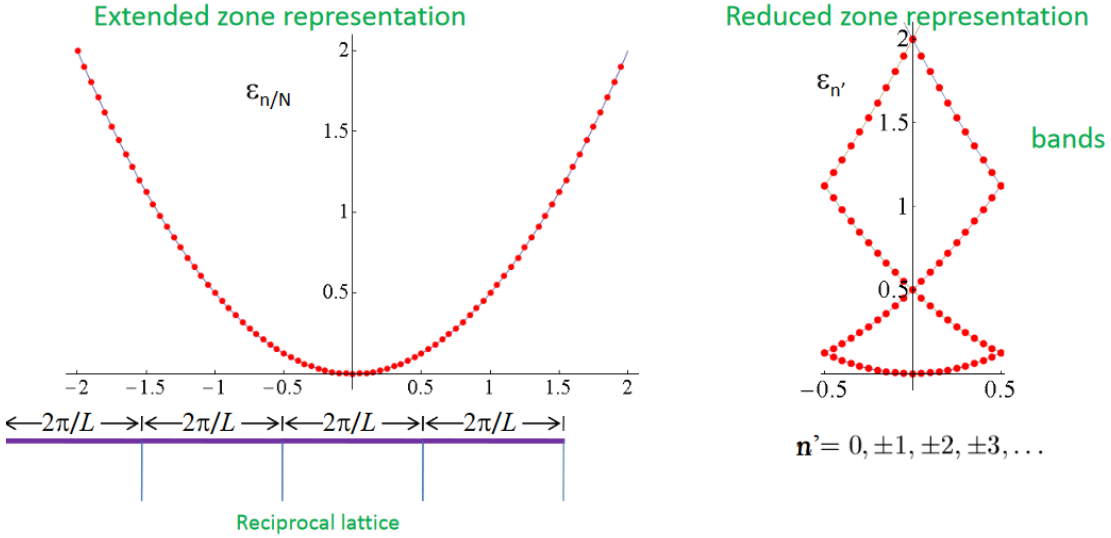
- Linear combination of atomic orbitals (LCAO) as a compact basis set.
- AOs are obtained from a free atom in a confining potential well.
- Difficult to improve accuracy in a systematic way.

Example:



$$\psi(\mathbf{r}) = \underbrace{c_1\chi_1(\mathbf{r})+c_2\chi_2(\mathbf{r})}_{\text{AOs on atom A}}+\underbrace{c_3\chi_3(\mathbf{r})+c_4\chi_4(\mathbf{r})+c_5\chi_5(\mathbf{r})}_{\text{AOs on atom B}}+\underbrace{c_6\chi_6(\mathbf{r})+c_7\chi_7(\mathbf{r})}_{\text{AOs on atom C}}+\ldots$$

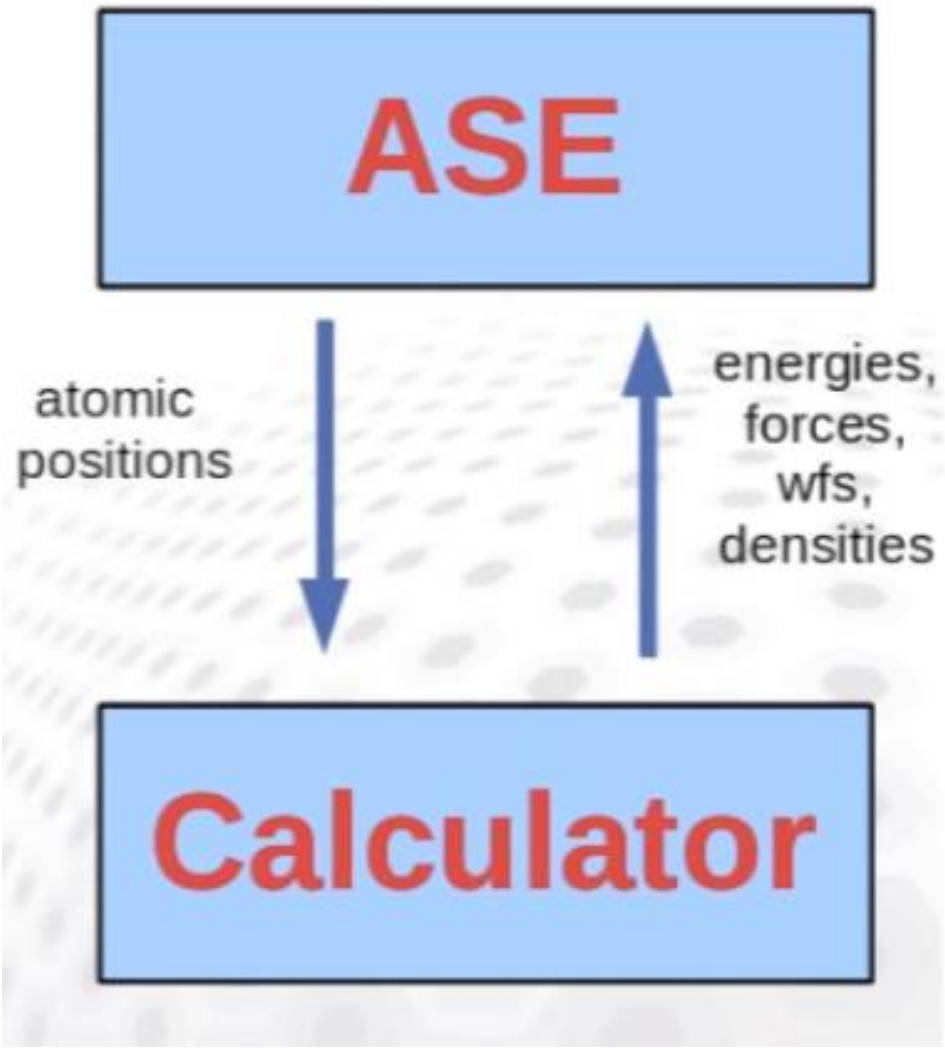
- Functions that are periodic with respect to the unit cell can be written as a sum of plane waves.
- Only periodic structures (but we can cheat with vacuum).
- Improving accuracy is easy.




Photoshop
for Photographers

ASE + GPAW

- ASE is a Python package for
  - Building structures
  - Structure optimization and molecular dynamics
  - Analysis and visualization
- ASE uses external code: in our case GPAW (supports a lot of codes)
- Input files will be Python scripts
- We run the calculations by calling these scripts.
- For simple calculations, you can do it locally. Otherwise, **scp** to the supercomputer.
- It has a graphical interface for visualization.
- We can also use external visualization programs (Avogadro, VESTA, VMD …)



GENERAL INSTRUCTIONS

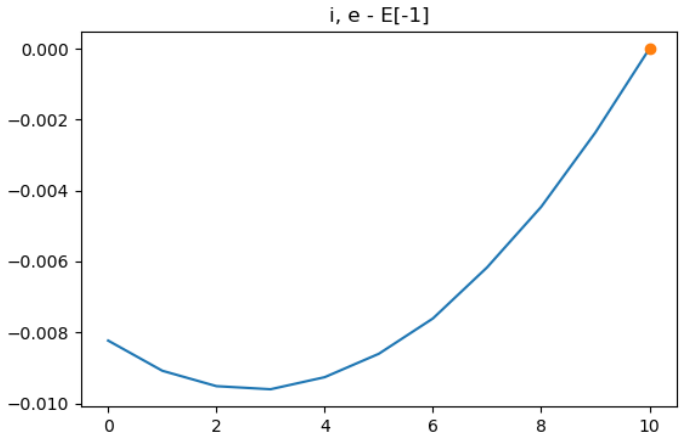
- The exercises are in the directory **`/home/kemijski/d13/Ex0X`** `(~/d13/Ex0X)`, N = 1, 3, 4, 5, 6, 7
- In every directory, there is a Python script that executes the calculation.
- You run it as: `gpaw python <scriptname.py>`
- The file 'submit.sh' is needed if you wish to execute the script on the supercomputer.
- You need to scp the files to and from the supercomputer (see the tutorial).
- The pre-calculated results are in folders `/home/kemijski/d13/Ex0X/`**`reference`**
- Data is visualized by `ase gui <filename>`

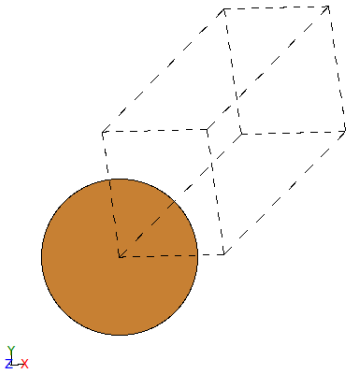
```
(base) kemijski@KICLIENT:~/d13$ ll
total 140
drwxrwxr-x  9 kemijski kemijski  4096 Oct 15 09:23 ./
drwxr-xr-x 40 kemijski kemijski  4096 Oct 15 09:47 ../
-rw-rw-r--  1 kemijski kemijski 90279 Oct 13 12:27 DFT.docx
drwxrwxr-x  3 kemijski kemijski  4096 Oct 15 09:24 Ex01/
drwxrwxr-x  3 kemijski kemijski  4096 Oct 15 09:22 Ex03/
drwxrwxr-x  3 kemijski kemijski  4096 Oct 15 09:22 Ex04/
drwxrwxr-x  3 kemijski kemijski  4096 Oct 15 09:22 Ex05/
drwxrwxr-x  3 kemijski kemijski  4096 Oct 15 09:22 Ex06/
drwxrwxr-x  3 kemijski kemijski  4096 Oct 15 09:22 Ex07/
drwxrwxr-x  3 kemijski kemijski  4096 Oct 15 09:22 opt/
-rw-rw-r--  1 kemijski kemijski  9054 Oct 12 08:29 results.xlsx
(base) kemijski@KICLIENT:~/d13$
```

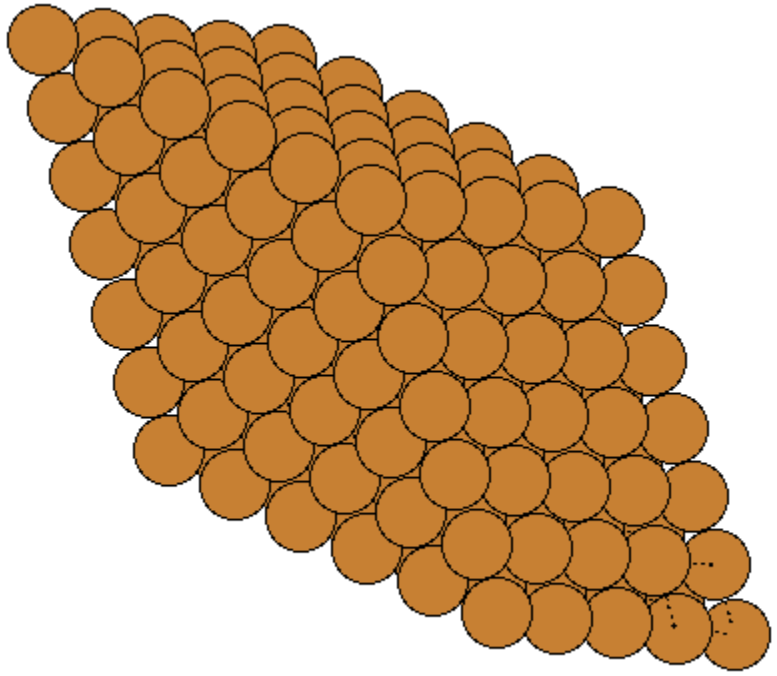
EXERCISE 1

- We will calculate the unit cell of copper.
- We start from a reasonable (experimental) initial approximation and calculate the energy for different unit cell parameters (expanding the crystal).
- The minimum in energy corresponds to the equilibrium lattice constant.
- We will calculate the bulk modulus from these data.

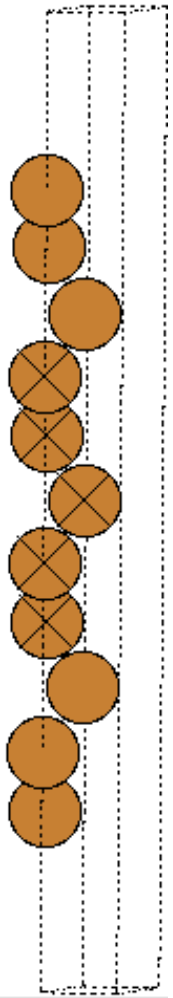
$$B = -V\frac{\partial p}{\partial V} \text{ and } p = -\frac{\partial E(V)}{\partial V}, \text{ so } B = V\frac{\partial^2 E(V)}{\partial V^2}.$$







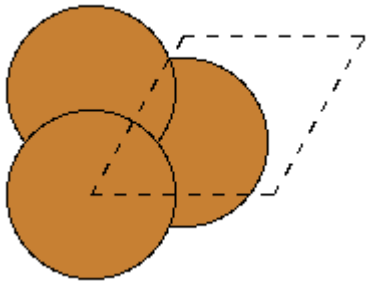
EXERCISE 3

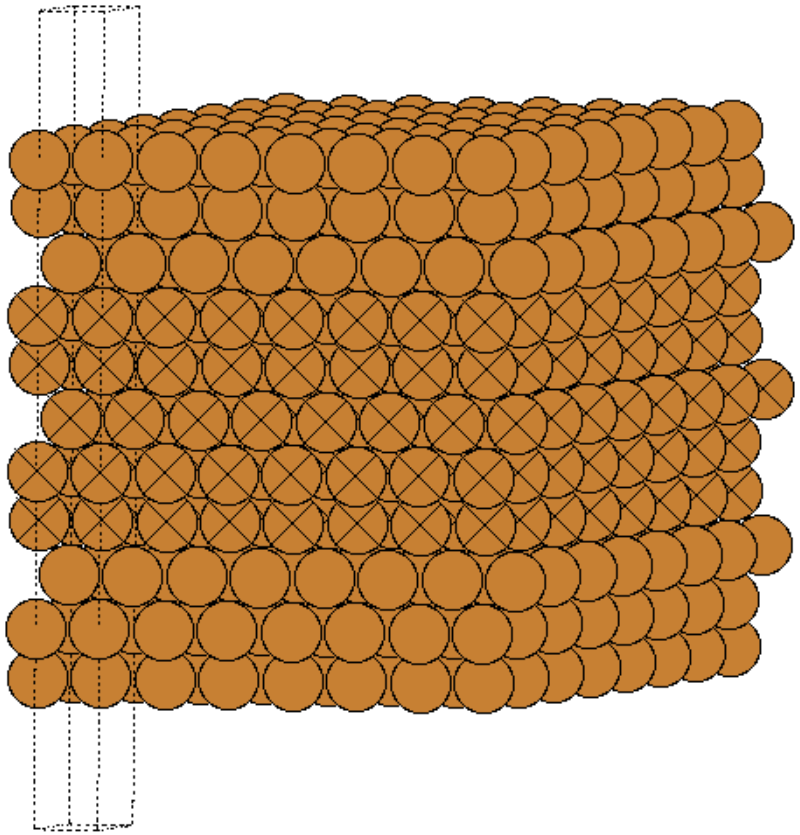


- We will calculate the energy of the Cu(111) slab.
- It consists of 11 layers, middle ones are fixed in their bulk positions.
- The atoms in this slab have a larger energy than in bulk. This is the surface energy.

$$\gamma = \frac{E_{slab} - nE_{bulk}}{2A}$$

- How would you calculate *A* (area)? Why is there a factor 2?



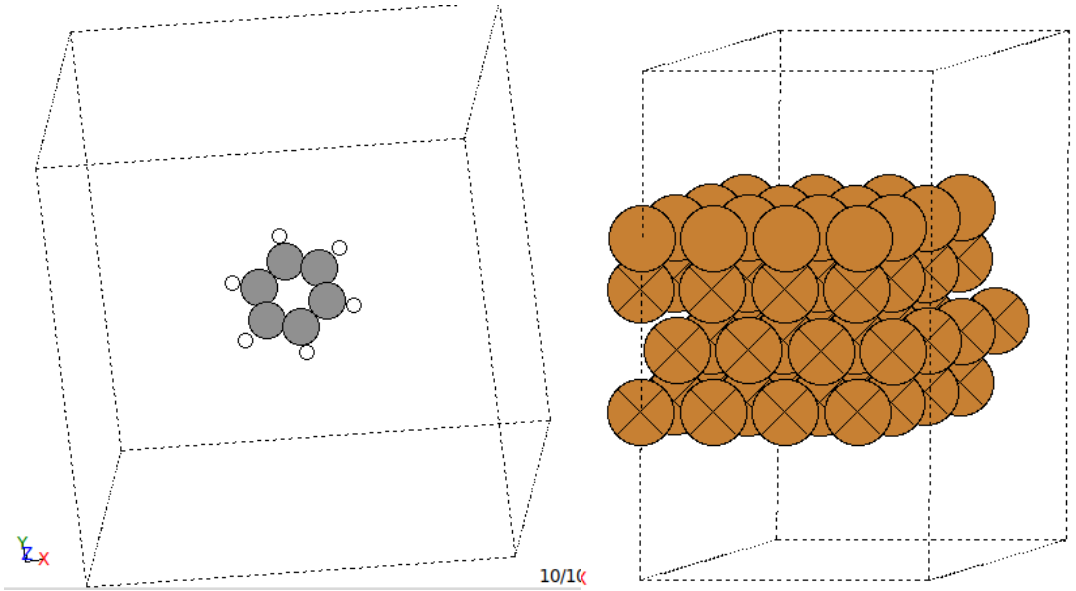


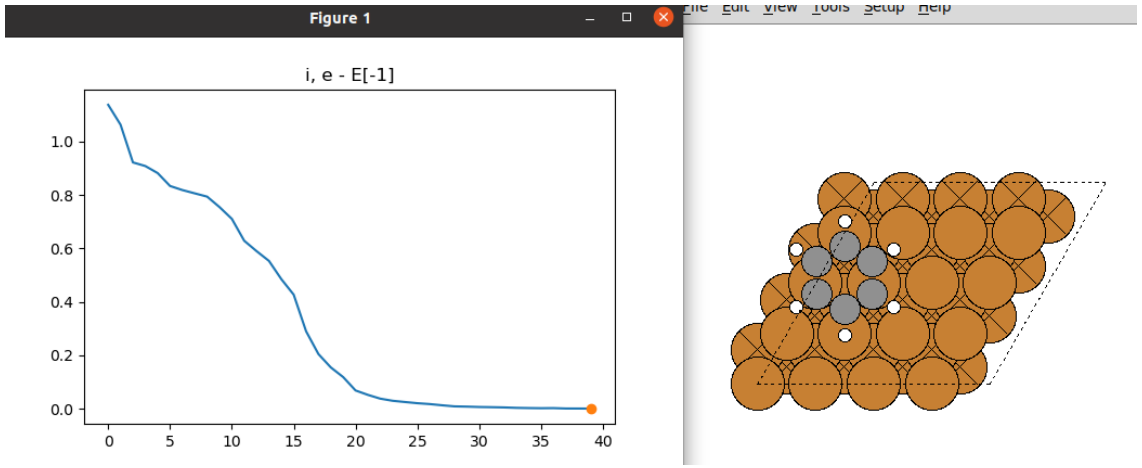
EXERCISES 4-6

- We will optimize the structure and calculate the energy of a 4x4x4 slab of Cu(111) in Exercise 4.
- We will optimize a benzene molecule in vacuum and calculate its energy in Exercise 5.
- We will optimize the benzene molecule on the slab and calculate its energy in Exercise 6.
- From this, we will get the adsorption energy.

$$E_{ads} - E_{surf} - E_{gas}$$

- The calculations are rather slow. You might want to look at the pre-computed results.





EXERCISE 7

Done by: `structures.py`

- We will construct a 3x3x4 Cu(111) slab with an adatom on the fcc site and optimize it.
- Then, we will move the adatom to the adjacent fcc site and optimize.

Done by: `neb.py`

- Then, we will use the nudged elastic band method to follow this ‘reaction’ and identify the saddle (transition state) and activation barrier for Cu-hopping.
- Activation barrier is the difference in energy between the saddle point and initial state.