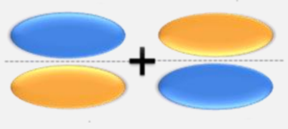
TD4 – Density Functional Theory

Quantum chemistry

Quantum chemistry's bottom-up approach

4. Use WF to get the final electronic WF or density 

3. Use MOs to build electronic wave function (WF) guess 

2. Use AOs to build molecular orbitals (MO) 

1. Define atomic orbital (AO) basis 

Hohenberg-Kohn Density Functional Theory

The electronic energy E is a function of the density function $\rho(\mathbf{r})$, i.e., it is a **functional of the density**, $E[\rho]$

$$E[\rho] = T[\rho] + E_{eN}[\rho] + E_{ee}[\rho]$$

- T is the expected value of the electronic kinetic energy
- E_{eN} is the expected value of the electron-nucleus energy
- E_{ee} is the expected value of the electron-electron energy

Intro to DFT: https://youtu.be/QGyfGCZT110

The E_{eN} term can be exactly written in terms of the density

$$E_{eN}\left[\rho\right]=\sum_{A}\int\frac{Z_A\rho\left(\mathbf{r}\right)}{\left|\mathbf{R}_A-\mathbf{r}\right|}d\mathbf{r}=\int V_{eN}\left(\mathbf{r}\right)\rho\left(\mathbf{r}\right)d\mathbf{r}$$

- the sum runs over all nuclei A with atomic number Z_A. and position $\mathbf{R}_A$

The other two terms $E_{ee}[\rho]$ and $T[\rho]$ are not straightforward to determine.

Kohn-Sham Density Functional Approximation

1. Suppose a fictitious system of **non-interacting electrons**, which generates the **same density as the actual system**.

$$\rho_{NI}(\mathbf{r}) = \sum_{i=1}^{N} |\varphi_i|^2$$
$$= \rho(\mathbf{r})$$

Kohn-Sham Density Functional Approximation

2. Assume that the wavefunction of this **non-interacting system** is a single Slater determinant of orbitals φ_i (Kohn-Sham orbitals)

$$\Phi\left(\mathbf{x}_1,\mathbf{x}_2,\cdots,\mathbf{x}_N\right)=\left(N!\right)^{-1/2}\det\begin{bmatrix}\eta_a\left(\mathbf{x}_1\right) & \eta_b\left(\mathbf{x}_1\right) & \cdots & \eta_K\left(\mathbf{x}_1\right)\\ \eta_a\left(\mathbf{x}_2\right) & \eta_b\left(\mathbf{x}_2\right) & \cdots & \eta_K\left(\mathbf{x}_2\right)\\ \vdots & \vdots & \cdots & \vdots\\ \eta_a\left(\mathbf{x}_N\right) & \eta_b\left(\mathbf{x}_N\right) & \cdots & \eta_K\left(\mathbf{x}_N\right)\end{bmatrix}$$

$$\eta_i\left(\mathbf{x}\right)=\varphi_i\left(\mathbf{r}\right)\sigma_i\left(\omega\right)\qquad \mathbf{x}=\left(r,\omega\right)$$

The kinetic energy of the non-interacting system is

$$T_{NI}\left[\rho\right]=-\frac{1}{2}\sum_{i=1}^{N}\left\langle\varphi_i\left|\nabla^2\right|\varphi_i\right\rangle$$

The Coulomb energy of the electrons is

$$J\left[\rho\right]=-\frac{1}{2}\iint\frac{\rho\left(\mathbf{r}\right)\rho\left(\mathbf{r}'\right)}{\left|\mathbf{r}-\mathbf{r}'\right|}d\mathbf{r}d\mathbf{r}'$$

$$E[n] = \underbrace{T_{NI}[n]}_{OK} + \underbrace{E_{eN}[\rho]}_{OK} + \underset{OK}{J[\rho]} + \underbrace{\left(T[\rho] - T_{NI}[\rho]\right) + \left(E_{ee}[\rho] - J[\rho]\right)}_{?}$$

$$= T_{NI}[\rho] + E_{eN}[\rho] + J[\rho] + E_{xc}[\rho]$$

Everything we don't know goes into the correlation-exchange (*xc*) energy

Kohn-Sham Density Functional Approximation

The Kohn-Sham orbitals are obtained by solving

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{eff}}(\mathbf{r})\right)\varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r})$$

where

$$v_{eff}(\mathbf{r}) = \underbrace{V_{eN}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'}_{\text{Coulomb interactions}} + \underbrace{v_{xc}(\mathbf{r})}_{\text{Everything else!}}$$

All properties can be computed from the Kohn-Sham density

$$\rho_{NI}(\mathbf{r}) = \sum_{i=1}^{N} |\varphi_i|^2$$
$$= \rho(\mathbf{r})$$

Energy, for example

$$E[\rho] = T_{NI}[\rho] + E_{eN}[\rho] + J[\rho] + E_{xc}[\rho]$$

$$E_{xc}[\rho] = \int v_{xc}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r}$$

Exchange-Correlation Functional

$$v_{eff}(\mathbf{r}) = V_{eN}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + v_{xc}(\mathbf{r})$$

?

$$E_{xc}[\rho] = \int v_{xc}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r}$$

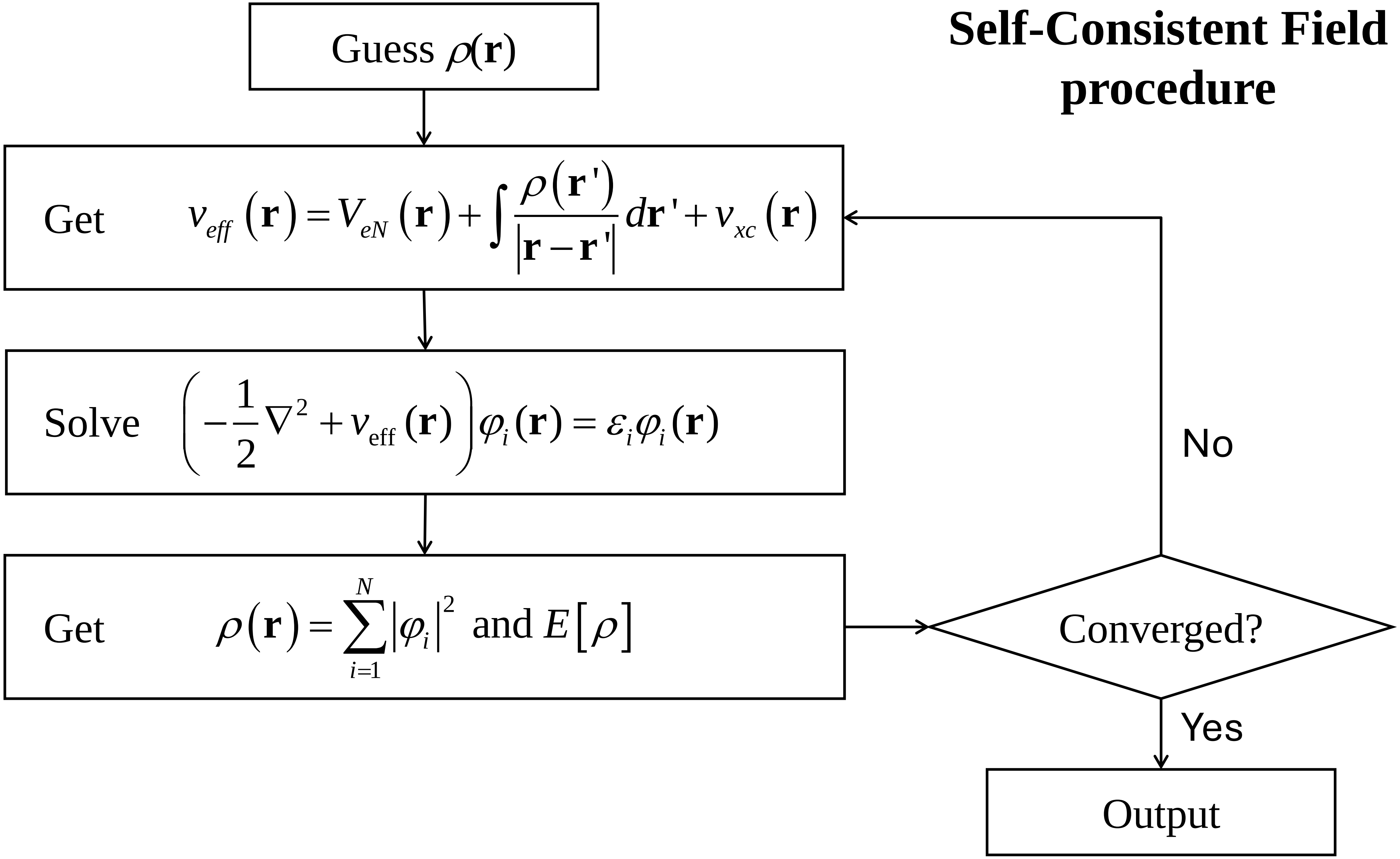
$$E_{xc}[\rho] = E_x[\rho] + E_c[\rho]$$

Example of Exchange Functional

$$E_x^{LDA}[\rho] = -c_x \int \rho^{4/3}(\mathbf{r})\, d\mathbf{r}$$

Check:
https://manual.q-chem.com/5.2/Ch5.S3.SS4.html

Self-Consistent Field procedure



How To Do a DFT Calculation?

1. Choose a program
2. Define nuclear geometry **R**
3. Define the number of electrons N
4. Define the spin multiplicity
5. Choose a basis set
6. Choose an E_{xc} functional
7. Choose the properties you want

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Cluster

- Orca
- Gamess
- Turbomole ($)
- Gaussian ($)
- …

Crystal

- VASP ($)
- CP2K
- Quantum expresso
- …

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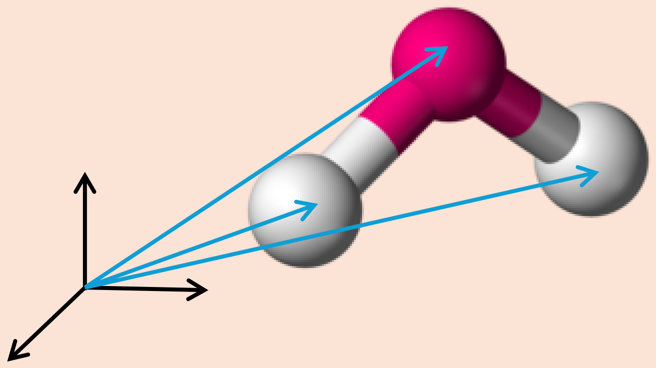
$$\mathbf{R} = \left(x_1, y_1, z_1, x_2, y_2, z_2, \cdots, x_{Nat}, y_{Nat}, z_{Nat}\right)$$



- ChemSketch
- Avogadro
- ChemDraw ($)
- …

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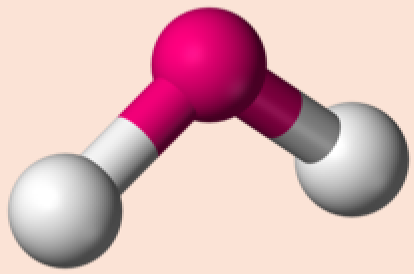

H_2O: 8 + 1 + 1 = 10 electrons
H_2O^+: 8 + 1 + 1 - 1 = 9 electrons
H_2O^-: 9 + 1 + 1 + 1 = 11 electrons

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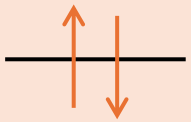
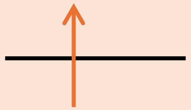
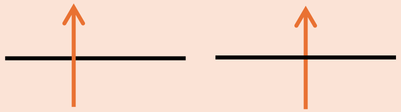
Configuration	**S**	**M = 2S+1**	
	0	1	Singlet
	1/2	2	Doublet
	1	3	Triplet
	…	…	…

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Cluster
- Gaussians

Crystal
- Plane waves

Every program has built-in basis sets to choose

https://www.basissetexchange.org

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It depends on molecular:

- type
- size
- properties

Check a recent benchmark paper or a recent research paper in your field

How To Do a DFT Calculation?

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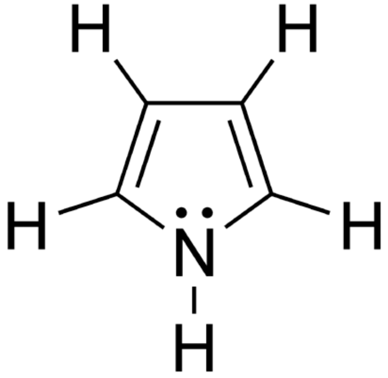
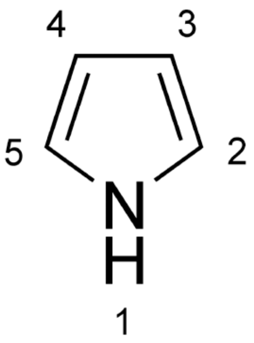
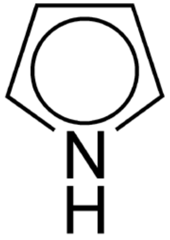
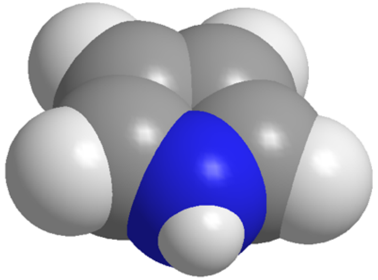
7. Choose the properties you want

- Geometry optimization
- IR and normal modes
- Electronic energy, dipoles, etc
- Reaction pathways
- Electronic excitation
- …

Do It Yourself

Use **GAMESS software** to study the **singlet** ground state properties of **pyrrole**.

Use:

- 6-31G* **basis set**
- B3LYP **functional**

Let's go to
https://chemcompute.org

Log in with your AMU email account.

You can use GAMESS there without installing it in your computer.