Theoretical Photochemistry WiSe 2018/19

Lecture 10
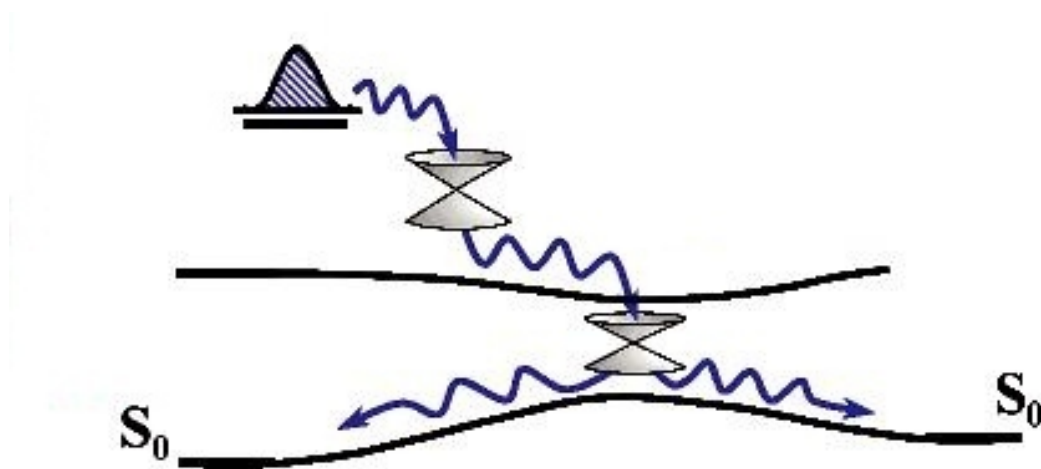
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http://www.theochem.uni-frankfurt.de/teaching/ $\longrightarrow$ Theoretical Photochemistry

Topics

1. **Photophysical Processes**

3. **Wavepackets**

5. **The Franck-Condon picture of electronic transitions**

6. **What do we measure experimentally?**

2. **The Born-Oppenheimer approximation**

4. **Beyond Born-Oppenheimer – non-adiabatic transitions**

7. **Conical intersections**

8. **Some electronic structure & dynamics aspects**

9. **Examples: Ethene, PSBs, PYP**

10. **More on dynamics: trajectories or wavefunctions?**

11. **Wavefunction propagation techniques**

12. **Trajectory surface hopping techniques**

13. **Non-linear optical spectroscopy: calculation of spectroscopic signals**

14. **Extended systems: Excitons, light-harvesting, etc.**

15. **Solvent/environmental effects**

Literature

1. P. W. Atkins and R. Friedman, Molecular Quantum Mechanics, 5th Edition, Oxford University Press (2011).

2. D. Tannor, Introduction to Quantum Mechanics: A Time-Dependent Perspective, University Science Books (2006).

3. M. Klessinger, J. Michl, Excited States and Photochemistry of Organic Molecules, VCH-Wiley (1995).

4. I. N. Levine, Quantum Chemistry, 6th Edition, Pearson International Edition (2009).

5. F. Jensen, Introduction to Computational Chemistry, 2nd Edition, Wiley (2007).

6. C. J. Cramer, Essentials of Computational Chemistry – Theories and Models, 2nd Edition, Wiley (2004).

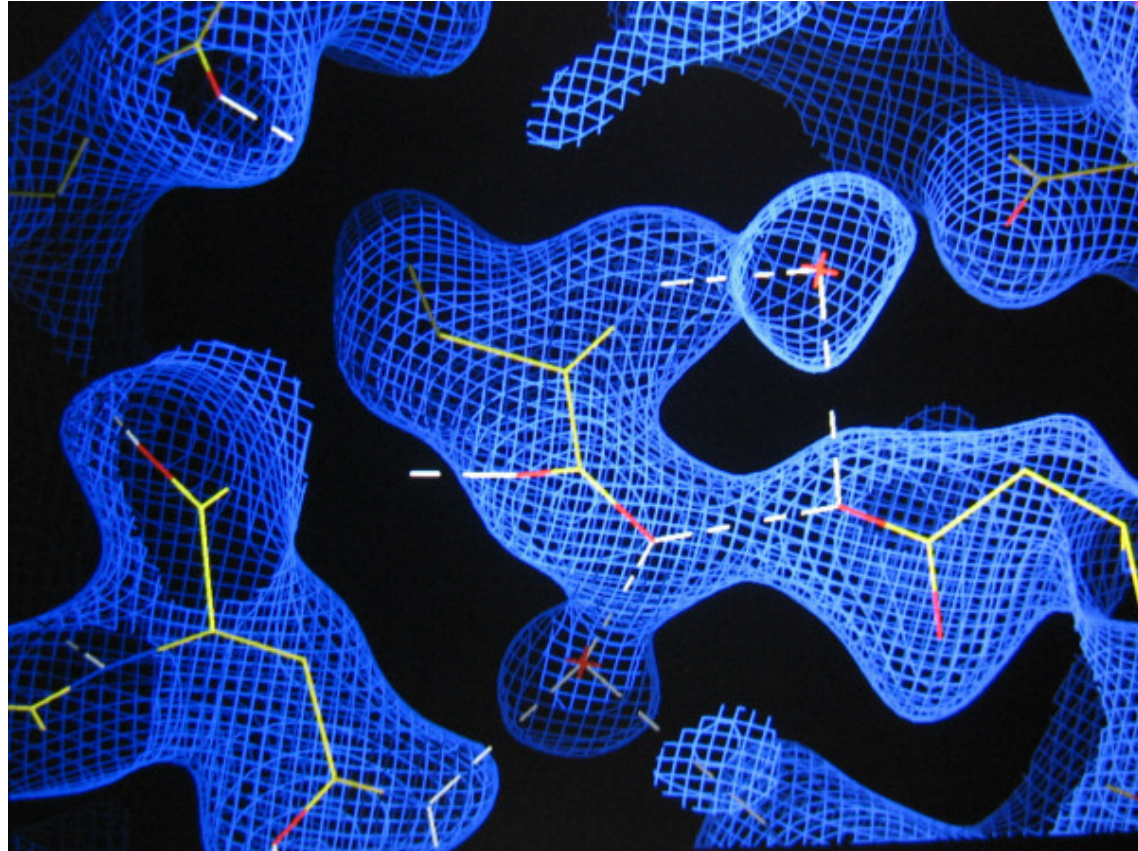# Question: Do we really need the N-electron wavefunction to determine the ground-state energy?

Postulate: The ground-state energy can be uniquely derived from the 1-electron density $\rho(r)$, i.e.,

$$E_{\mathrm{GZ}} = E_{\mathrm{GZ}}[\rho(r)]$$

Proof: Hohenberg/Kohn Theorems (1964)

1-electron density

$$\rho^{\mathrm{charge}}(r) = -e\rho(r) = \text{electron density (charge density) in space}$$

Walter Kohn was awarded with the Nobel Prize in Chemistry in 1998 for his development of the density functional theory.

Walter Kohn receiving his Nobel Prize from His Majesty the King at the Stockholm Concert Hall.
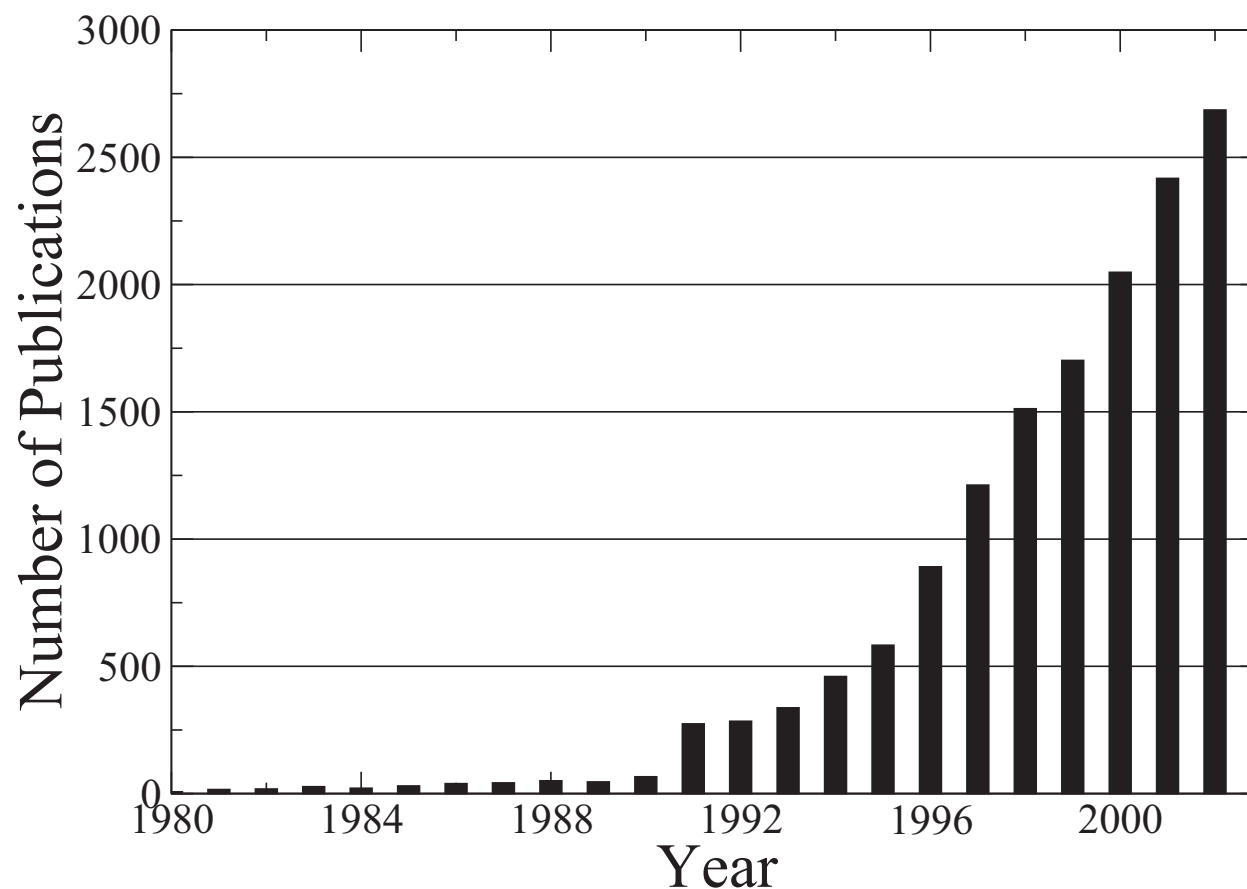

The Nobel Prize medal.

The Density Functional Theory was introduced in two seminal papers in the 60's:

1. Hohenberg-Kohn (1964): ~ 4000 citations

2. Kohn-Sham (1965): ~ 9000 citations

The following figure shows the number of publications where the phrase "density functional theory" appears in the title or abstract (taken from the ISI Web of Science).

Molecular structures: DFT gives the bond lengths of a large set of molecules with a precision of 1-2%. The hybrid functionals have improved the LDA results.

Bond lengths for different bonding situations [Å]:

Bond		LDA	BLYP	BP86	Experiment
H-H	R_{H-H}	0.765	0.748	0.752	0.741
H_3C-CH_3	R_{C-C}	1.510	1.542	1.535	1.526
	R_{C-H}	1.101	1.100	1.102	1.088
HC≡CH	R_{C-C}	1.203	1.209	1.210	1.203
	R_{C-H}	1.073	1.068	1.072	1.061

Vibrational frequencies: DFT predicts the vibrational frequencies of a broad range of molecules within 5-10% accuracy.

Vibrational frequencies of a set of 122 molecules: method, rms deviations, proportion outside a 10% error range and listings of problematic cases (taken from Scott and Radom, 1996).

Method	RMS	10%	Problematic cases (deviations larger than 100 cm^{-1})
BP86	41	6	142(H_2), 115(HF), 106(F_2)
B3LYP	34	6	132(HF), 125(F_2), 121(H_2)

N-electron wavefunction vs. 1-electron density

- N-electron wavefunction: $\psi_N(x_1, x_2, \ldots, x_N)$
  where $x_i \equiv (r_i, \omega_i)$, i.e., space and spin coordinates

- N-electron probability distribution:

  $$\rho_N(x_1, x_2, \ldots, x_N) = |\psi_N(x_1, x_2, \ldots, x_N)|^2$$

- 1-electron probability distribution:

  $$\boxed{\rho_1(x_1) = N \int dx_2 \ldots dx_N \, \rho_N(x_1, x_2, \ldots, x_N)}$$

  (normalization such that $\int dx_1 \, \rho_1(x_1) = N$)

- since electrons are indistinguishable:

  $$\rho(x) \equiv \rho_1(x_1)$$

Additional step: integrate out spin

$$\boxed{\rho_1(r_1) = \int d\omega_1 \rho_1(r_1, \omega_1)}$$

$$= N \int d\omega_1 dx_2 \ldots dx_N \, \rho_N(x_1, x_2, \ldots, x_N)$$

$\longrightarrow$ **purely spatial 1-electron density $\rho_1(r_1)$**

(normalization such that $\int dx_1 \, \rho_1(r_1) = N$)

Simple test: HF ground state energy

Can we rewrite the HF ground state energy as a function(al) of the 1-electron density?

$$\langle \psi_N^{\mathrm{HF}} | \hat{H} | \psi_N^{\mathrm{HF}} \rangle = E_{\mathrm{GZ}}[\rho^{\mathrm{HF}}(r)] \qquad \textcolor{red}{\textbf{?!}}$$

N-electron wavefunction vs. 1-electron density: Slater determinants

$$\psi_N(1, 2, \ldots, N) = \left(\frac{1}{N!}\right)^{1/2} |\phi_a(1)\phi_b(2)\ldots\phi_z(N)|$$

1-electron density:

$$\rho(x) = \sum_{m=a}^{z} \phi_m^*(x)\phi_m(x)$$

Sum over all occupied spin orbitals

Can we re-write the HF ground state energy as a function(al) of the 1-electron density?

$$E_{\mathrm{GZ}}[\psi_N^{\mathrm{HF}}] = \langle \psi_N^{\mathrm{HF}} | \hat{H} | \psi_N^{\mathrm{HF}} \rangle$$

$$= \langle T_e \rangle + \langle V_{eN} \rangle + \frac{1}{2}\Big(\langle V_{ee}^J \rangle - \langle V_{ee}^K \rangle \Big)$$

with

$$\langle T_e \rangle = -\sum_{n=1}^{N} \frac{\hbar^2}{2m_e} \langle \phi_n | \boldsymbol{\nabla}^2 | \phi_n \rangle$$

$$\langle V_{eN} \rangle = -\sum_{n=1}^{N} \sum_{k=1}^{K} \frac{Ze^2}{4\pi\epsilon_0} \langle \phi_n | \frac{1}{r_{1k}} | \phi_n \rangle$$

$$\langle V_{ee}^J \rangle = \sum_{n=1}^{N} \sum_{m=1}^{N} \frac{e^2}{4\pi\epsilon_0} \langle \phi_n | J_m | \phi_n \rangle \qquad \langle V_{ee}^K \rangle = \sum_{n=1}^{N} \sum_{m=1}^{N} \frac{e^2}{4\pi\epsilon_0} \langle \phi_n | K_m | \phi_n \rangle$$

NB. Overall energy vs. HF orbital energies

$$
\begin{aligned}
E_{\mathrm{GZ}}[\psi_N^{\mathrm{HF}}] &= \langle \psi_N^{\mathrm{HF}} | \hat{H} | \psi_N^{\mathrm{HF}} \rangle \\[2mm]
&= \langle T_e \rangle + \langle V_{eN} \rangle + \frac{1}{2}\Big(\langle V_{ee}^J \rangle - \langle V_{ee}^K \rangle \Big) \\[2mm]
&= \sum_{n=1}^{N} \epsilon_n - \frac{1}{2}\Big(\langle V_{ee}^J \rangle - \langle V_{ee}^K \rangle \Big)
\end{aligned}
$$

where ϵ_n = orbital energy = eigenvalue of the Fock operator:

$$
\epsilon_n = \langle \phi_n | F_n | \phi_n \rangle = h_n + \sum_{m=1}^{N} \frac{e^2}{4\pi\epsilon_0}\Big(\langle \phi_n | J_m | \phi_n \rangle - \langle \phi_n | K_m | \phi_n \rangle \Big)
$$

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Can we re-write the HF ground state energy as a function(al) of the 1-electron density?

Consider individual matrix elements:

- **electron-nuclear interaction:**

$$\langle V_{eN} \rangle = -\sum_n \sum_k \frac{Ze^2}{4\pi\epsilon_0} \langle \phi_n | \frac{1}{r_{1k}} | \phi_n \rangle = -\frac{Ze^2}{4\pi\epsilon_0} \sum_k \int dx_1 \frac{\rho(x_1)}{r_{1k}}$$

- **electron-electron Coulomb interaction:**

$$\langle V_{ee}^J \rangle = \sum_n \sum_m \frac{e^2}{4\pi\epsilon_0} \langle \phi_n | J_m | \phi_n \rangle = \frac{e^2}{4\pi\epsilon_0} \int dx_1 \int dx_2 \frac{\rho(x_1)\rho(x_2)}{r_{12}}$$

HF energy as function of the 1-electron density: exchange interaction and kinetic energy

Consider individual matrix elements:

- **electron-electron exchange interaction:**

$$\langle V_{ee}^K \rangle = \sum_n \sum_m \frac{e^2}{4\pi\epsilon_0} \langle \phi_n | K_m | \phi_n \rangle \neq \frac{e^2}{4\pi\epsilon_0} \int dx_1 \int dx_2 \frac{\hat{P}_{12}\rho(x_1)\rho(x_2)}{r_{12}}$$

- **kinetic energy:**

$$\langle T \rangle = -\sum_n \frac{\hbar^2}{2m_e} \langle \phi_n | \nabla^2 | \phi_n \rangle \neq -\frac{\hbar^2}{2m_e} \int dx_1 \nabla^2 \rho(x_1)$$

Problem: both operators are non-local!

But: Hohenberg-Kohn theorems

- **the ground state energy (and all other ground state properties) can be uniquely derived from the 1-electron density:**

$$\boxed{E_{\mathrm{GZ}} = E_{\mathrm{GZ}}[\rho(x)]}$$

- **the exact ground state density can be determined variationally:**

$$\frac{\delta E_{\mathrm{GZ}}}{\delta \rho(x)} = 0 \qquad E_{\mathrm{test}} \geq E_{\mathrm{exakt}}$$

$\equiv$ **Density Functional Theory (DFT)**

Hohenberg-Kohn theorems

HK theorem 1:

The 1-particle density $\rho(r)$ is **uniquely determined** by the external potential $V_{\mathrm{ext}}(r)$.

(Here, the so-called external potential $V_{\mathrm{ext}}(r)$ corresponds to the electron-nuclear interaction as well as "genuine" external fields, e.g., a laser field)

Hohenberg-Kohn theorems

HK theorem 2:

The ground state energy can be written **uniquely** as a functional of the 1-particle density: $E_{\mathrm{GZ}}[\rho(r)]$.

The **exact** ground state energy is defined by the **minimum** of this functional:

$$\left.\frac{\delta E_{\mathrm{GZ}}}{\delta \rho(r)}\right|_{\rho(r)=\rho_{\mathrm{exakt}}(r)} = 0$$

Hohenberg-Kohn-Theoreme

HK-Theorem 1:

The 1-particle density $\rho(r)$ is uniquely determined by the external potential $V_{\text{ext}}(r)$.

Proof:

Let's assume that two different external potentials $V_{\text{ext}}^{(1)}(r)$ and $V_{\text{ext}}^{(2)}(r)$ generate the same 1-particle density $\rho(r)$.

We further assume that the eigenfunctions are known:

$$H_1\psi_1 = (H_0 + V_{\text{ext}}^{(1)})\psi_1 = E_1\psi_1$$
$$H_2\psi_2 = (H_0 + V_{\text{ext}}^{(2)})\psi_2 = E_2\psi_2.$$

Proof / HK-Theorem 1 – cont'd

From this results:

$$
\begin{aligned}
E_1 = \langle \psi_1 | H_1 | \psi_1 \rangle \quad &< \quad \langle \psi_2 | H_1 | \psi_2 \rangle \\
&= \quad \langle \psi_2 | H_2 | \psi_2 \rangle + \langle \psi_2 | H_1 - H_2 | \psi_2 \rangle \\
&= \quad E_2 + \langle \psi_2 | V_{\text{ext}}^{(1)} - V_{\text{ext}}^{(2)} | \psi_2 \rangle \\
&= \quad E_2 + \int dr\, \rho_2 (V_{\text{ext}}^{(1)} - V_{\text{ext}}^{(2)})
\end{aligned}
$$

At the same time we have (by exchanging indices):

$$
E_2 = \langle \psi_2 | H_2 | \psi_2 \rangle \quad < \quad E_1 + \int dr\, \rho_1 (V_{\text{ext}}^{(2)} - V_{\text{ext}}^{(1)})
$$

Therefore:

$$
E_1 + E_2 < E_1 + E_2 \qquad \qquad \textit{reductio ad absurdum}
$$

What does the functional $E_{\mathrm{GZ}}[\rho]$ look like?

$$E_{\mathrm{GZ}}[\rho] = T[\rho] + V_{eN}[\rho] + V_{ee}^{J}[\rho] + V_{ee}^{XC}[\rho]$$

where

$$V_{eN}[\rho] = -\frac{Ze^2}{4\pi\epsilon_0}\sum_{K}\int dx_1 \frac{\rho(x_1)}{r_{1K}}$$

$$V_{ee}^{J}[\rho] = \frac{e^2}{4\pi\epsilon_0}\int dx_1 \int dx_2 \frac{\rho(x_1)\rho(x_2)}{r_{12}}$$

- **by contrast, $T[\rho]$ and $V_{ee}^{XC}[\rho]$ are unknown to start with!**
- **"XC": exchange (X) plus correlation (C)!**

Thomas-Fermi-Dirac model — Local Density Approximation (LDA)

- **simplest model: Density looks locally like a uniform electron gas**

$$T[\rho] = \frac{3}{10}(3\pi^2)^{2/3} \int dx\, \rho^{5/3}(x) \quad ; \quad V_{ee}^{XC}[\rho] = -\frac{3}{4}(\frac{3}{\pi})^{1/3} \int dx\, \rho^{4/3}(x)$$

- **analytical result, but quite inaccurate for the description of molecules**

Kohn-Sham (KS)-Ansatz

- solution for $T[\rho]$: back to an orbital representation ("Kohn-Sham orbitals")

- solution for $V_{ee}^{XC}[\rho]$: exchange-correlation functional – many variants!

Kohn-Sham (KS)-Ansatz

- **construct a Slater determinant for a** *hypothetical non-interacting system* **which has the same density as the real system:**

$$\boxed{\rho(r_1) = N \int d\omega_1 dx_2 \ldots dx_N \, \rho_N^{KS}(x_1, x_2, \ldots, x_N)}$$

$$\rho_N^{KS}(x_1, x_2, \ldots, x_N) = |\psi_N^{KS}(x_1, x_2, \ldots, x_N)|^2$$

$$\psi_N^{KS} = \left(\frac{1}{N!}\right)^{1/2} |\phi_a^{KS}(1)\phi_b^{KS}(2) \ldots \phi_z^{KS}(N)|$$

$$\longrightarrow \rho^{KS}(x) = \sum_{m=a}^{z} \phi_m^{KS*}(x)\phi_m^{KS}(x)$$

$$\longrightarrow \rho^{KS}(r) = \int d\omega_1 \rho^{KS}(x)$$

Kohn-Sham (KS)-Ansatz

- **Since the density is now defined *via Kohn-Sham orbitals* ϕ_m^{KS}, we obtain a variational set-up that's very similar to Hartree-Fock!**

- **effective Hamiltonian:**

$$\left(h_1 + \frac{1}{4\pi\epsilon_0} \int dx_2 \frac{\rho(x_2)}{r_{12}} + V_{XC}(x_1) \right) \phi_m^{KS}(x_1) = \epsilon_m^{KS} \phi_m^{KS}(x_1)$$

- **very similar concept to the Fock operator! Major difference: no exchange integrals, but rather exchange-correlation functional**

Exchange-correlation (XC) functionals

Table 6.1 Perdew classification of exchange–correlation functionals

Level	Name	Variables	Examples
1	Local density	ρ	LDA, LSDA, X_α
2	GGA	$\rho, \nabla\rho$	BLYP, OPTX, OLYP, PW86, PW91, PBE, HCTH
3	Meta-GGA	$\rho, \nabla\rho, \nabla^2\rho$ or τ	BR, B95, VSXC, PKZB, TPSS, τ-HCTH
4	Hyper-GGA	$\rho, \nabla\rho, \nabla^2\rho$ or τ *HF exchange*	H+H, ACM, B3LYP, B3PW91, O3LYP, PBE0, TPSSh, τ-HCTH-hybrid
5	Generalized RPA	$\rho, \nabla\rho, \nabla^2\rho$ or τ *HF exchange* *Virtual orbitals*	OEP2

- **besides the density (ρ), functionals can depend on the gradient of the density ($\nabla\rho$ as well as the second derivative ($\nabla^2\rho$)**

- **functionals can contain an admixture of the Hartree-Fock exchange term ("$HF\ exchange$"): hybrid functionals**

Exchange-correlation (XC) functionals, cont'd

- e.g., Lee-Yang-Parr (LYP):

$$
\begin{aligned}
\varepsilon_c^{LYP} = {} & -4a\frac{\rho_\alpha\rho_\beta}{\rho^2(1+d\rho^{-1/3})} - \\
& ab\omega\left\{\frac{\rho_\alpha\rho_\beta}{18}\left[\begin{array}{l}144(2^{2/3})C_F(\rho_\alpha^{8/3}+\rho_\beta^{8/3})+(47-7\delta)|\nabla\rho|^2 - \\ (45-\delta)\left(|\nabla\rho_\sigma|^2+|\nabla\rho_\beta|^2\right)+2\rho^{-1}(11-\delta)\left(\rho_\sigma|\nabla\rho_\sigma|^2+\rho_\beta|\nabla\rho_\beta|^2\right)\end{array}\right]\right. \\
& \left. +\tfrac{2}{3}\rho^2\left(|\nabla\rho_\sigma|^2+|\nabla\rho_\beta|^2-|\nabla\rho|^2\right)-\left(\rho_\alpha^2|\nabla\rho_\beta|^2+\rho_\beta^2|\nabla\rho_\alpha|^2\right)\right\} \\
\omega = {} & \frac{e^{-c\rho^{-1/3}}}{\rho^{14/3}(1+d\rho^{-1/3})} \\
\delta = {} & c\rho^{-1/3}+\frac{d\rho^{-1/3}}{(1+d\rho^{-1/3})}
\end{aligned}
\tag{6.40}
$$

- the Becke-3-parameter-Lee-Yang-Parr (B3LYP) functional is one of the most successful density functionals

KS-SCF procedure

- **solution by a self-consistent field approach (just like Roothaan-Hall SCF)**

- **DFT methods can scale more advantageously than Hartree-Fock (N_{basis}^3 instead of N_{basis}^4)**

The Self-Consistent Field (SCF) procedure

- The Kohn-Sham operator depends on the molecular orbitals which we seek

- Therefore an iterative procedure needs to be used to find these orbitals

- This procedure is often called a Self-Consistent Field (SCF) calculation

Select initial $\{\psi_i^{(n)}\}$, $n = 0$

Construct Kohn-Sham operator $\hat{h}_{KS}^{(n)} = \hat{h}_{KS}[\{\psi_i^{(n)}\}]$

Solve $\hat{h}_{KS}^{(n)} \psi_i^{(n+1)} = \varepsilon_i^{(n+1)} \psi_i^{(n+1)}$ to obtain $\{\psi_i^{(n+1)}\}$

Are $\{\psi_i^{(n+1)}\}$ same as $\{\psi_i^{(n)}\}$ to within expected tolerance?

Set $\{\psi_i^{(n)}\} \longrightarrow \{\psi_i^{(n+1)}\}$ $n \longrightarrow n + 1$

No

Yes

DFT calculation converged
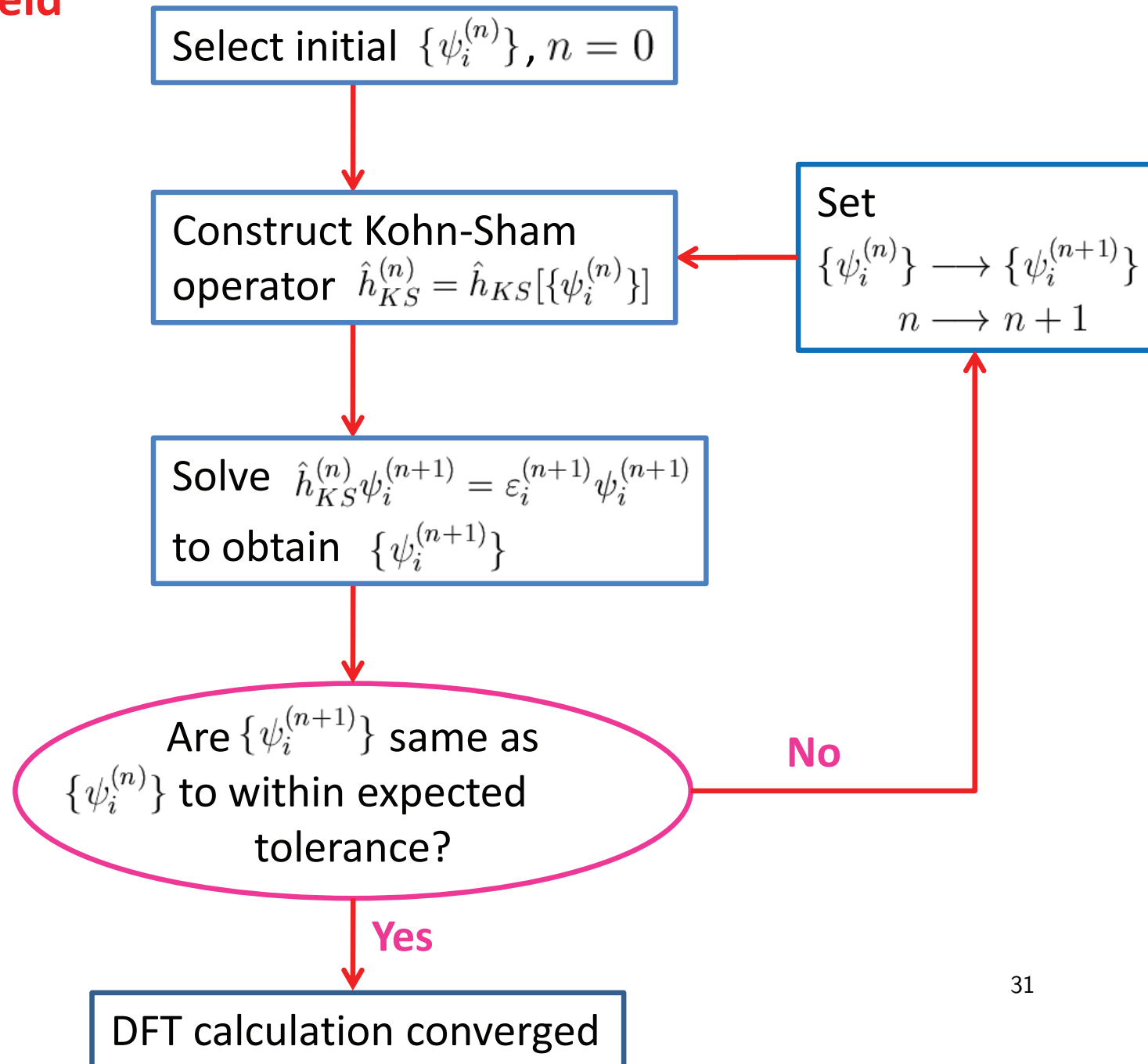
Exact solution of the el. Schrödinger equation

Exact Hamiltonian operator for all electrons together

nucleus of real molecule
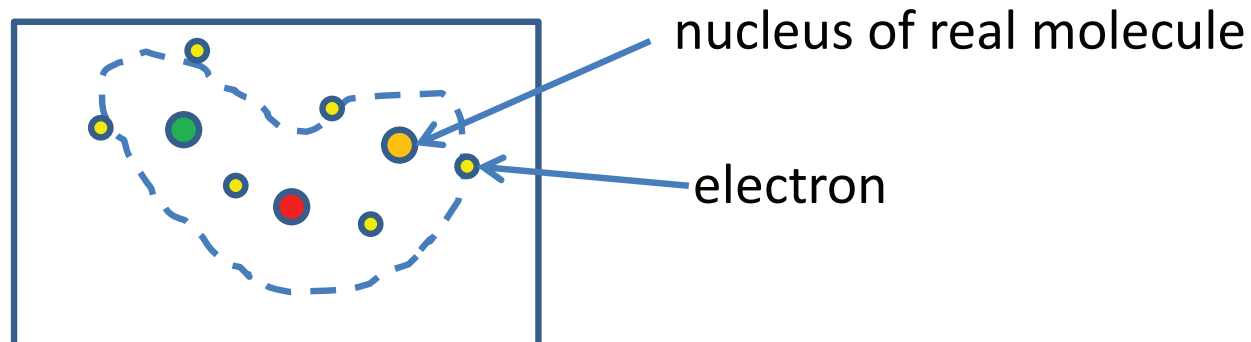
electron

Construct and solve Schrödinger equation to obtain **exact** wavefunction for interacting electrons

Exact electron density
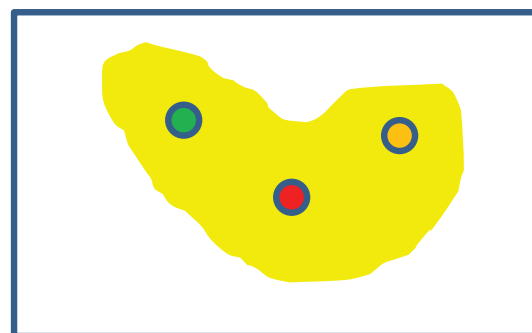
Hartree-Fock solution

Hamiltonian operator for one electron moving in an "average" potential caused by the rest of the electrons

nucleus of real molecule
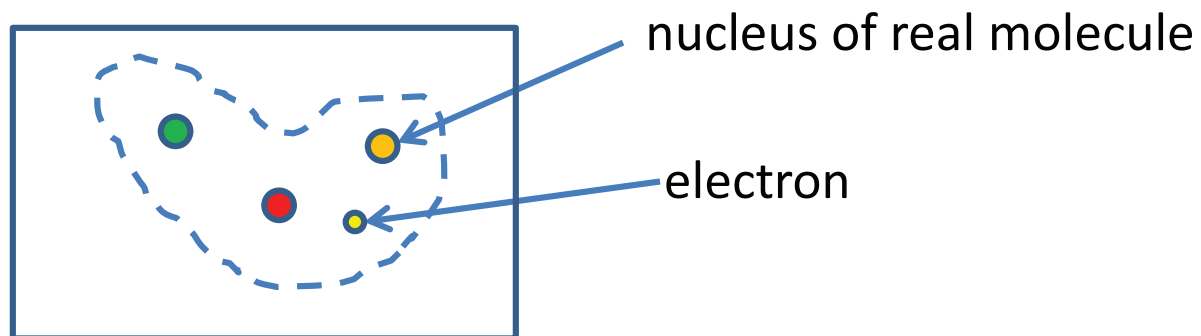
electron

Construct and solve Schrödinger equation for one electron. Combine many one-electron wavefunctions (molecular orbitals) to obtain **approximate** wavefunction for all electrons

Approximate electron density
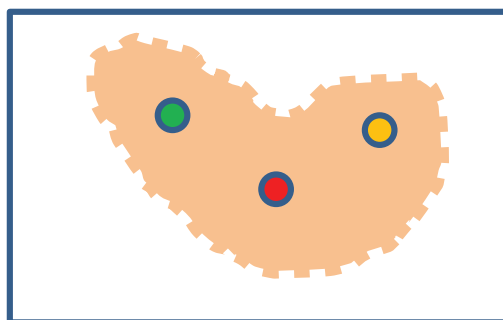
KS-DFT

Hamiltonian operator for one electron moving in an "average" potential caused by a special **fictitious** system of electrons

nucleus of "fictitious" molecule
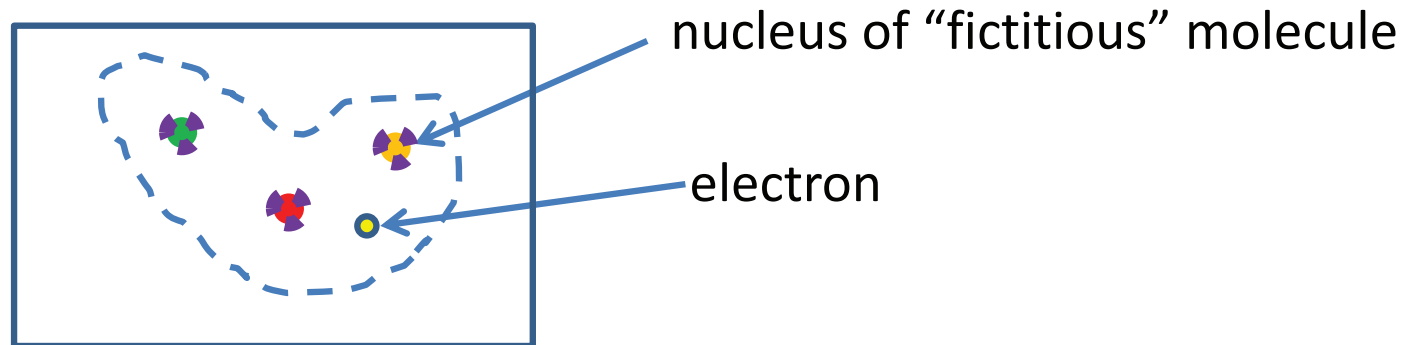
electron

Construct and solve Schrödinger equation for one electron. Combine one-electron wavefunctions (molecular orbitals) to obtain **approximate wavefunction** for all electrons
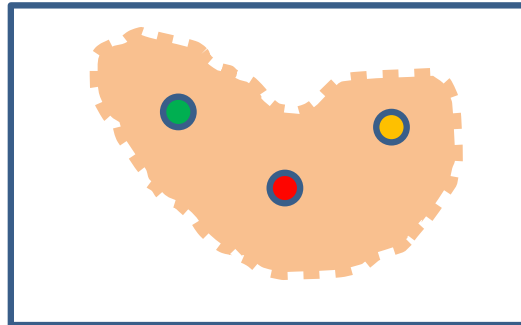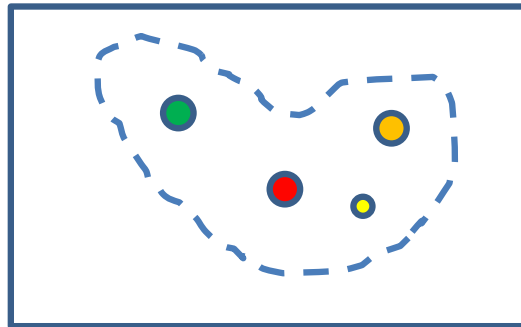
Exact electron density
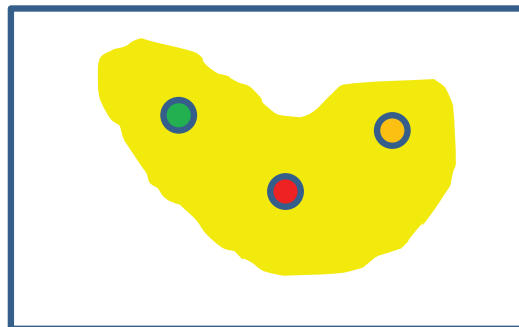
- Interacting electrons
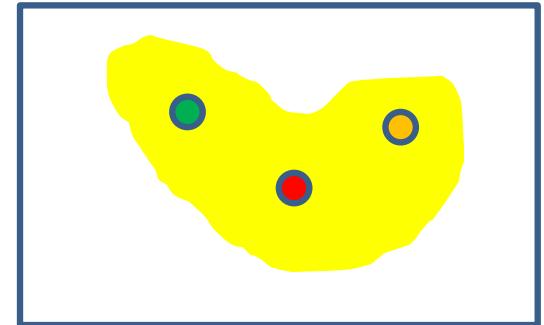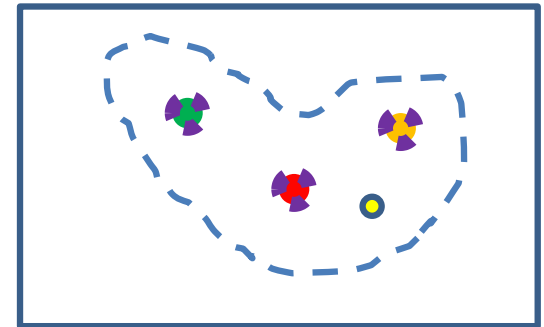- Exact Hamiltonian for real molecule
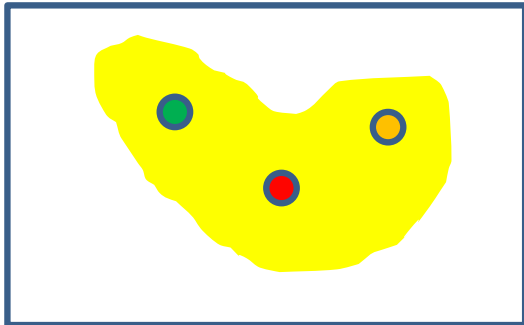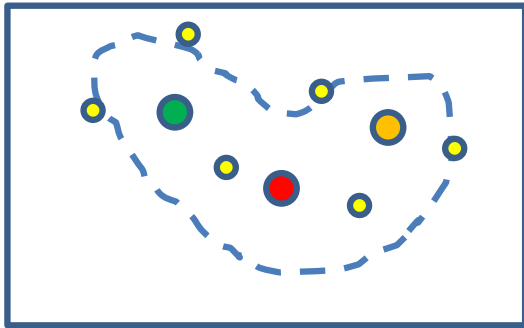
- Non-Interacting electrons
- Approximate Hamiltonian for real molecule

- Kohn-Sham non-interacting electrons
- Approximate Hamiltonian for fictitious molecule

Density of interacting electrons (=exact density)

Density of non-interacting electrons (=approximate density)

Density of fictitious system of non-interacting electrons (= exact density of interacting electrons)

DFT – Pro's & Con's

Advantages:

- variational equations
- obtain electron correlations with the effort of Hartree-Fock
- good performance for bond energies and molecular geometries
- more efficient than Hartree-Fock, with the same accuracy

Disadvantages:

- "trial & error" with a large number of functionals
- no systematic way to increase accuracy
- only suitable for ground state

TD-DFT for excited states

Time dependent Kohn-Sham Equations:

$$\left(-\frac{1}{2}\nabla^2 + v_s(\mathbf{r}, t)\right)\phi_i(\mathbf{r}, t) = i\frac{\partial}{\partial t}\phi_i(\mathbf{r}, t)$$

with the effective potential

$$v_s(\mathbf{r}, t) = v_{\text{ext}}(\mathbf{r}, t) + v_J(\mathbf{r}, t) + v_{\text{xc}}(\mathbf{r}, t)$$

where $v_{\text{xc}}(\mathbf{r}, t) = v_{\text{xc}}[\rho(\mathbf{r}, t)]$ **= exchange correlation functional**

time-dependent density: $\rho(\mathbf{r}, t) = \sum_{i=1}^{N} |\phi_i(\mathbf{r}, t)|^2$

- **however, TD-DFT uses a perturbative Linear Response (LR) version of the above equations!**
- **problems: many approximate functionals, charge transfer described incorrectly ($\longrightarrow$ long-range corrections . . .)**