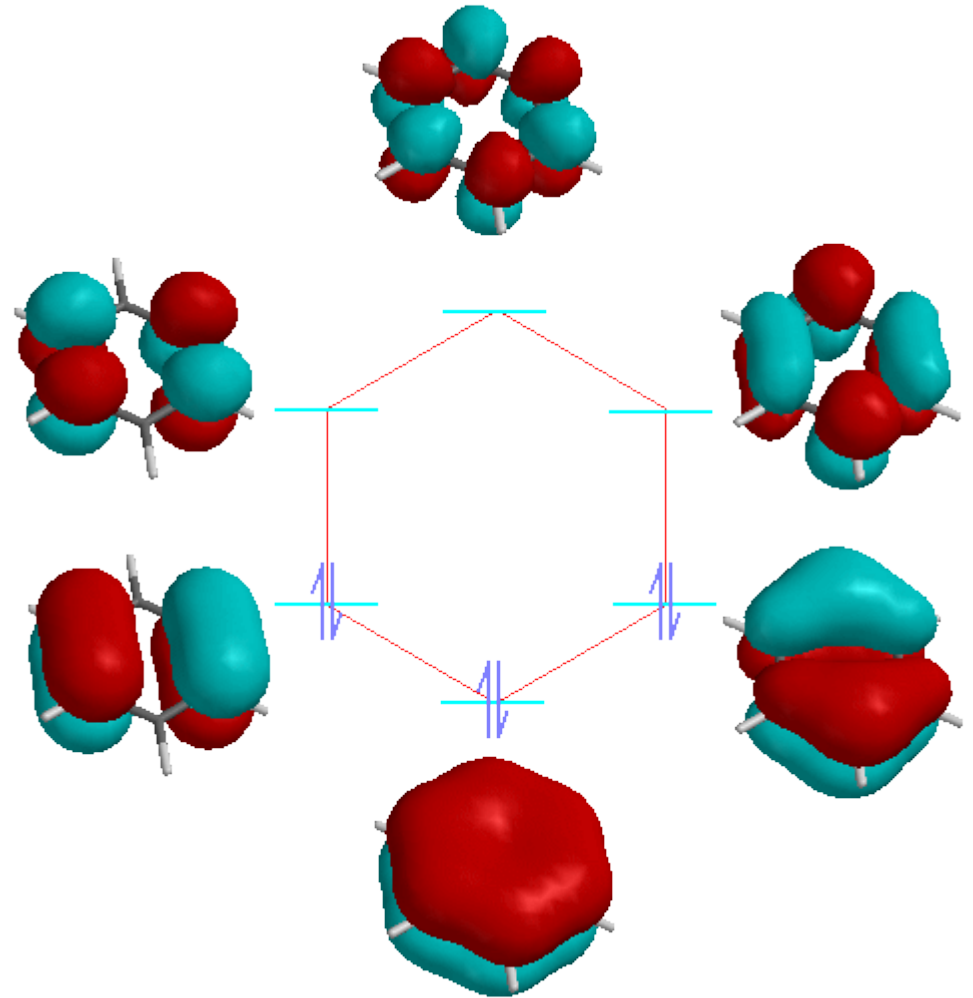
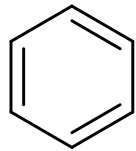
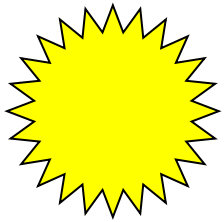




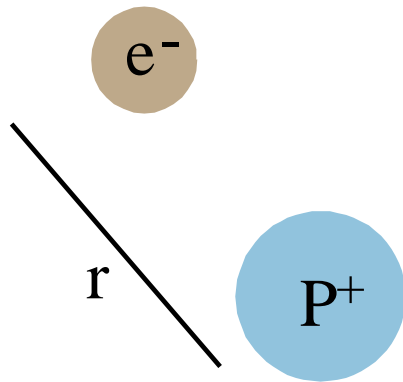
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# Quantum Mechanics & Catalysis

Mårten Ahlquist



# Classical Description of Hydrogen Atom



$$E_{potential}(r) = \frac{-e^2}{r}$$

$$E_{kinetic} = \frac{mv^2}{2}$$

# Quantum Mechanics

$$\text{Schrödinger Equation } H\Psi = E\Psi$$

(1925)

$$\underbrace{\left( \frac{-\hbar^2}{2m} \nabla^2 + V(x,y,z) \right)}_{\text{kinetic energy}} \underbrace{\psi(x,y,z)}_{\text{wavefunction describing the system}} = \underbrace{E}_{\text{total energy}} \underbrace{\psi(x,y,z)}_{\text{wavefunction describing the system}}$$

potential energy

# Hydrogen Atom

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) - \frac{l(l+1)}{r^2} R + \frac{2m}{\hbar^2} [E - U(r)] R = 0.$$

$$E = \frac{1}{2} \frac{m_e e^4}{\hbar^2} \frac{1}{n^2} = \frac{1}{2} \frac{1}{n^2}$$

$$\psi = R_{n,l}(r) Y_{lm}(\theta, \varphi)$$

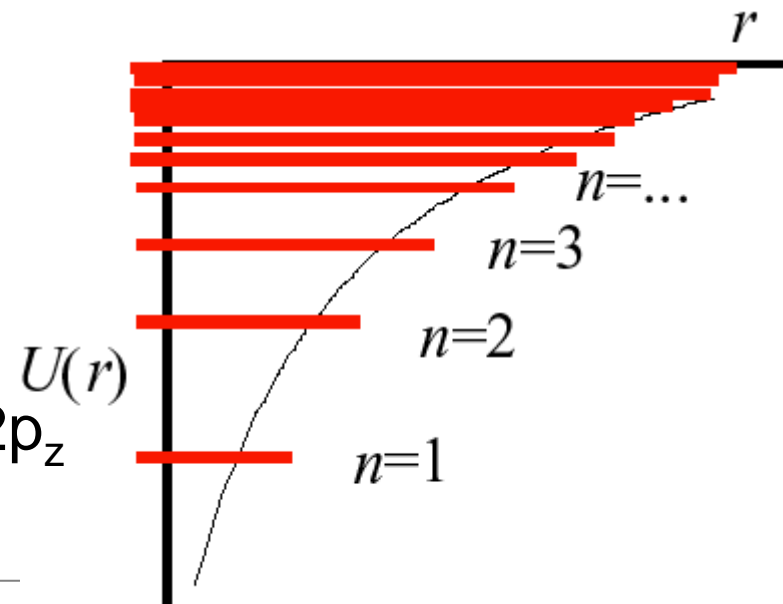
$n = \infty$	$E = 0$ kJ.mol <sup>-1</sup>
$n = 7$	$E = -27$ kJ.mol <sup>-1</sup>
$n = 6$	$E = -37$ kJ.mol <sup>-1</sup>
$n = 5$	$E = -53$ kJ.mol <sup>-1</sup>
$n = 4$	$E = -82$ kJ.mol <sup>-1</sup>
$n = 3$	$E = -146$ kJ.mol <sup>-1</sup>
$n = 2$	$E = -329$ kJ.mol <sup>-1</sup>
$n = 1$	$E = -1316$ kJ.mol <sup>-1</sup>

4s, 4p, 4d, 4f

3s, 3p, 3d

2s, 2p<sub>x</sub>, 2p<sub>y</sub>, 2p<sub>z</sub>

1s



# Hydrogen Wavefunctions

**The Complete Hydrogenlike Atomic Wave Functions for  $n = 1, 2,$  and  $3$ . The Quantity  $Z$  Is the Atomic Number of the Nucleus, and  $\sigma = Zr/a_0$ , Where  $a_0$  is the Bohr Radius.**

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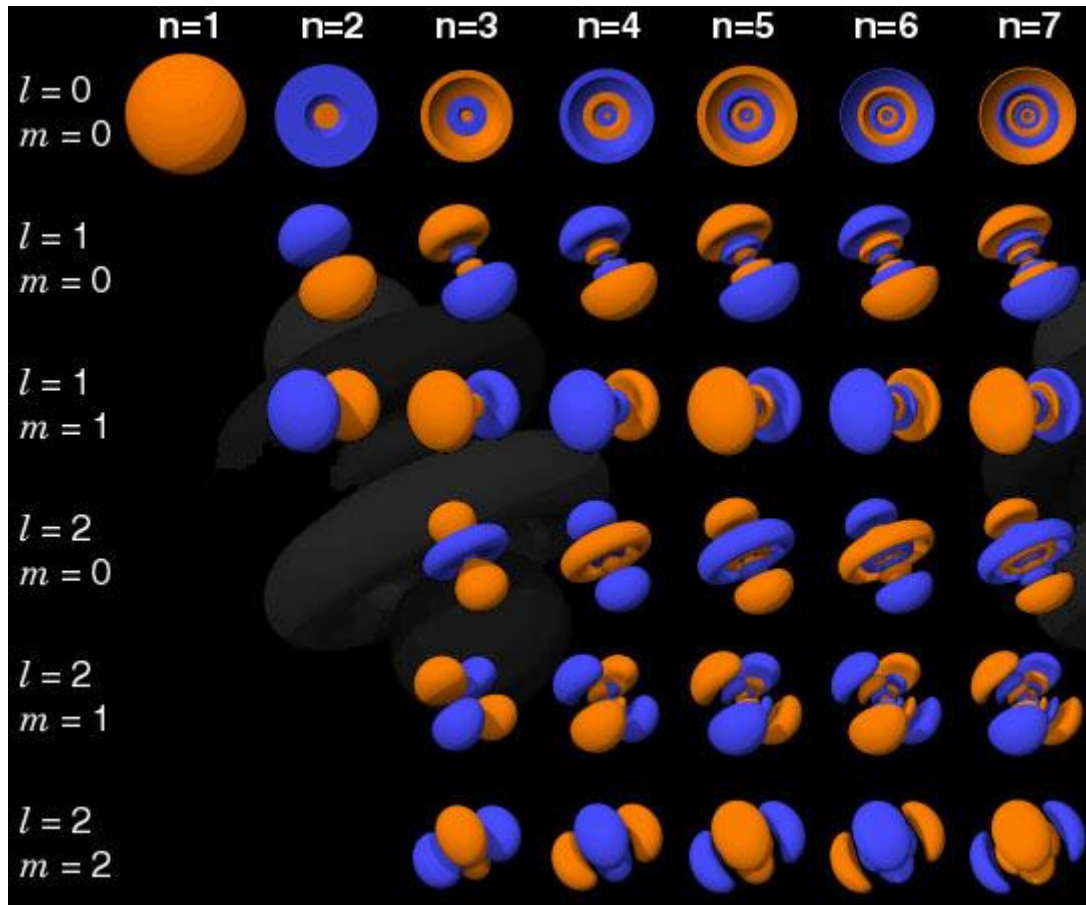
$$n = 1; l = 0, m = 0 \quad \psi_{100} = \frac{1}{\sqrt{\pi}} \left( \frac{Z}{a_0} \right)^{3/2} e^{-\sigma}$$

$$n = 2; l = 0, m = 0 \quad \psi_{200} = \frac{1}{\sqrt{32\pi}} \left( \frac{Z}{a_0} \right)^{3/2} (2 - \sigma) e^{-\sigma/2}$$

$$l = 1, m = 0 \quad \psi_{210} = \frac{1}{\sqrt{32\pi}} \left( \frac{Z}{a_0} \right)^{3/2} \sigma e^{-\sigma/2} \cos \theta$$

$$l = 1, m = \pm 1 \quad \psi_{21\pm 1} = \frac{1}{\sqrt{64\pi}} \left( \frac{Z}{a_0} \right)^{3/2} \sigma e^{-\sigma/2} \sin \theta e^{\pm i\phi}$$

# Hydrogen Orbitals



# Hamiltonian for a Molecule

## Born-Oppenheimer Approximation

$$\hat{H} = \sum_i^{\text{electrons}} \frac{-\hbar^2}{2m_e} \nabla_i^2 + \sum_A^{\text{nuclei}} \frac{-\hbar^2}{2m_A} \nabla_A^2 + \sum_i^{\text{electrons}} \sum_A^{\text{nuclei}} \frac{-e^2 Z_A}{r_{iA}} + \sum_{i>j}^{\text{electrons}} \frac{e^2}{r_{ij}} + \sum_{A>B}^{\text{nuclei}} \frac{e^2 Z_A Z_B}{r_{AB}}$$

- kinetic energy of the electrons
- kinetic energy of the nuclei
- electrostatic interaction between the electrons and the nuclei
- electrostatic interaction between the electrons
- electrostatic interaction between the nuclei

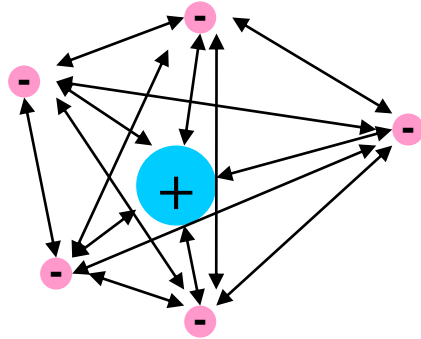
# Hartree-Fock

- assume that a many electron wavefunction can be written as a product of one electron functions

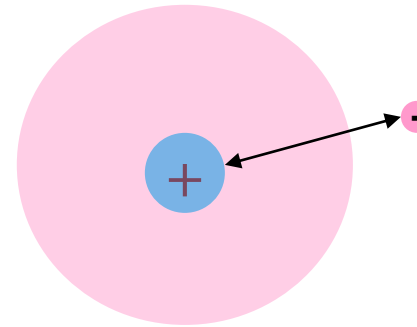
$$\Psi(r_1, r_2, r_3, \dots) = \phi(r_1)\phi(r_2)\phi(r_3)\dots$$

- if we use the variational energy, solving the many electron Schrödinger equation is reduced to solving a series of one electron Schrödinger equations
  - each electron interacts with the average distribution of the other electrons
-

# Hartree-Fock



Many-electron system  
All electron-electron repulsion  
is included explicitly.



One-electron system  
with remaining electrons  
represented by an average  
charge density.  
**Mean field approach**

# Hartree-Fock

- take the Hartree-Fock wavefunction

$$\Psi = |\phi_1 \phi_2 \cdots \phi_n|$$

- put it into the variational energy expression

$$E_{\text{var}} = \frac{\int \Psi^* \hat{H} \Psi d\tau}{\int \Psi^* \Psi d\tau}$$

- minimize the energy with respect to changes in the orbitals

$$\partial E_{\text{var}} / \partial \phi_i = 0$$

- yields the Fock equation

$$\hat{\mathbf{F}} \phi_i = \varepsilon_i \phi_i$$

---

# Hartee-Fock

$$\hat{\mathbf{F}} = \hat{\mathbf{T}} + \hat{\mathbf{V}}_{NE} + \hat{\mathbf{J}} - \hat{\mathbf{K}}$$

- Coulomb operator (electron-electron repulsion)

$$\hat{\mathbf{J}}\phi_i = \left\{ \sum_j^{\text{electrons}} \int \phi_j \frac{e^2}{r_{ij}} \phi_j d\tau \right\} \phi_i$$

- exchange operator (purely quantum mechanical - arises from the fact that the wavefunction must switch sign when you exchange to electrons)

$$\hat{\mathbf{K}}\phi_i = \left\{ \sum_j^{\text{electrons}} \int \phi_j \frac{e^2}{r_{ij}} \phi_i d\tau \right\} \phi_j$$

---

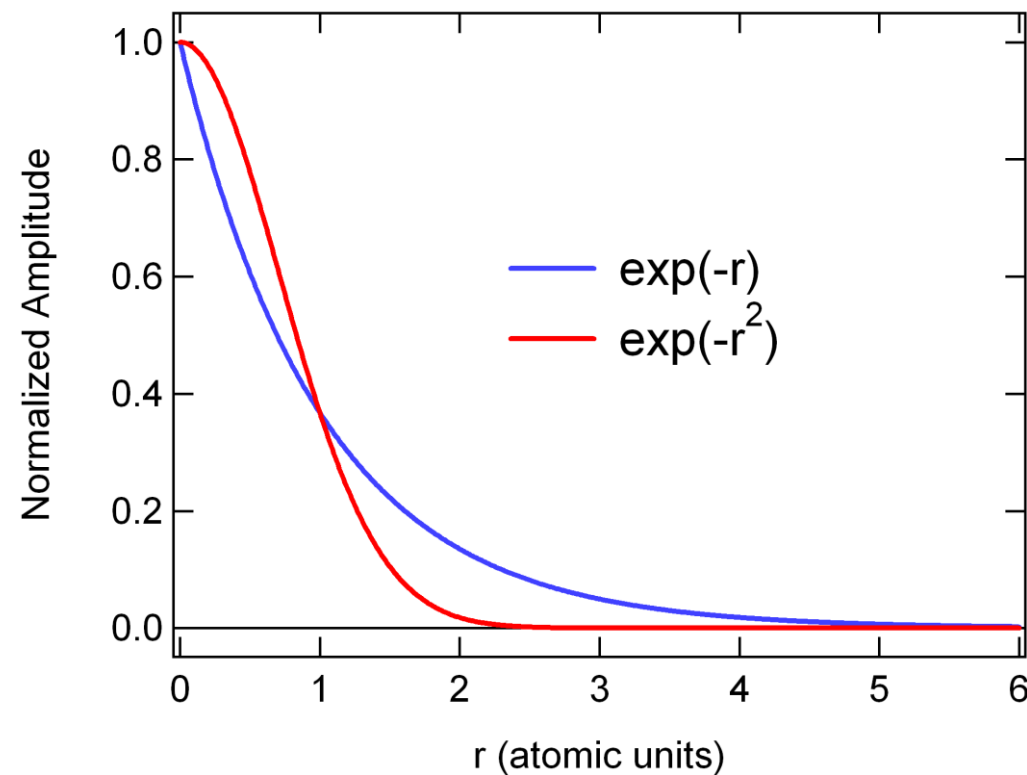
# Basis Functions

$$\phi = \sum_{\mu} c_{\mu} \chi_{\mu}$$

- $\chi$ 's are called basis functions
  - usually centered on atoms
  - can be more general and more flexible than atomic orbitals
  - larger number of well chosen basis functions yields more accurate approximations to the molecular orbitals
-

# Gaussian Basis Functions

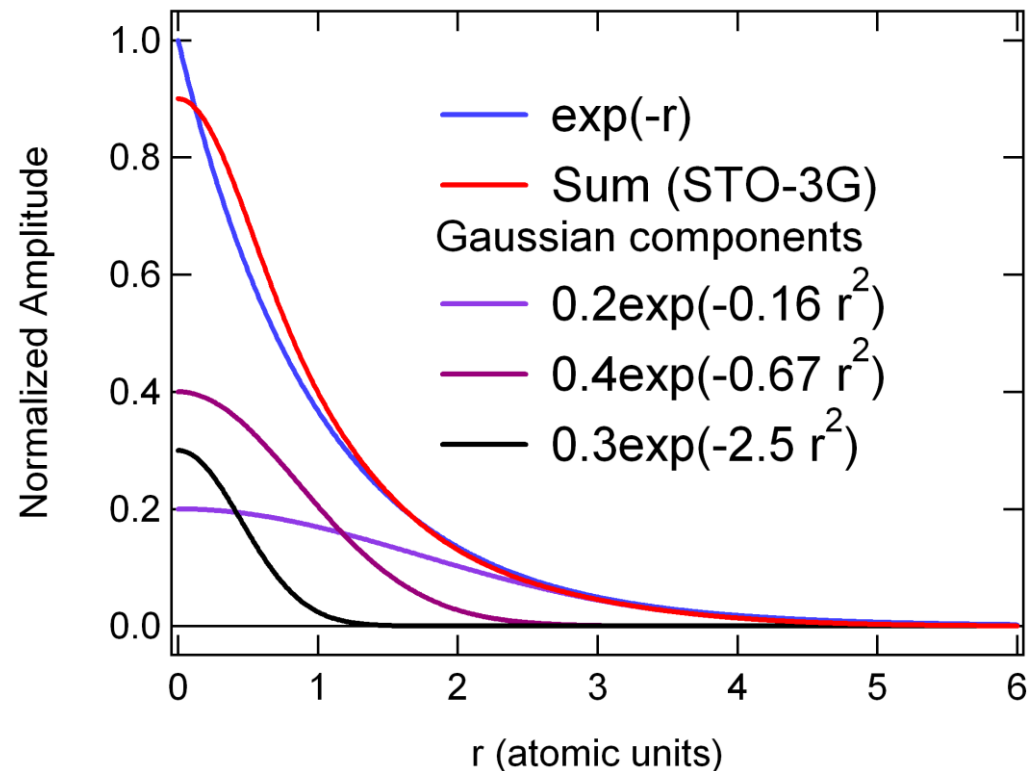
GTOs are mathematically easy to work with, but the shape of a Gaussian is not that similar to that of an exponential.



# Gaussian Basis Functions

Therefore, linear combinations of Gaussians are used to imitate the shape of an exponential. Shown is a representation of the 3-Gaussian model of a STO.

$$\chi_{\mu} = D_{\mu a} e^{-\zeta_a r} + D_{\mu b} e^{-\zeta_b r}$$



# Pople Basis Sets

$$\chi_{\mu} = D_{\mu a} e^{-\zeta_a r} + D_{\mu b} e^{-\zeta_b r}$$

- K-LMN++G\*\*

- 3-21G

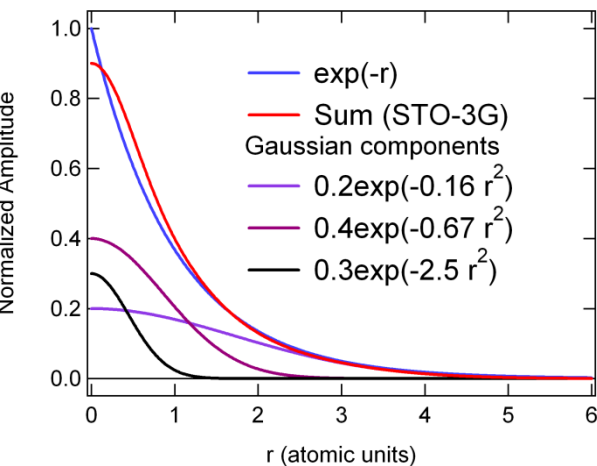
3 Contracted gaussian functions for core electrons.  
2 Uncontracted gaussian functions for valence electrons where one is formed from 2 contracted functions, and one is formed from a single gaussian function.

- + means diffuse functions on all atoms except hydrogen

++ means diffuse functions on all atoms

Important for Anions, Hydrogen Bonds, Polarization

- \* polarization functions on all atoms but H
- \*\* polarization functions on all atoms



# Pople Basis Sets

$$\chi_{\mu} = D_{\mu a} e^{-\zeta_a r} + D_{\mu b} e^{-\zeta_b r}$$

- K-LMN++G\*\*

- 3-21G

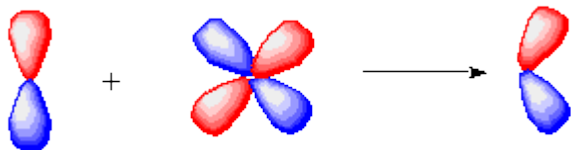
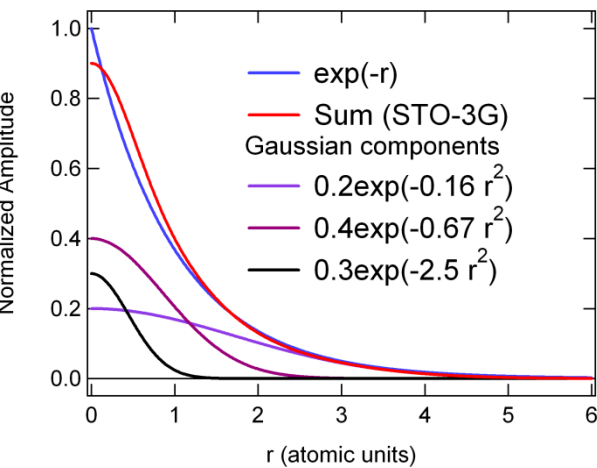
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Important for Anions, Hydrogen Bonds, Polarization

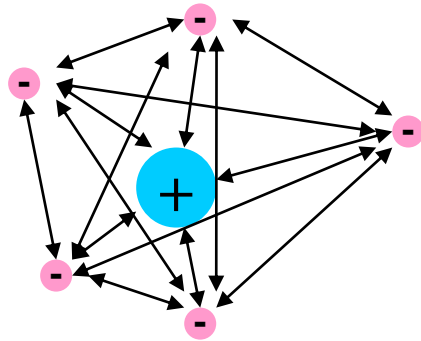
- \* polarization functions on all atoms but H
- \*\* polarization functions on all atoms



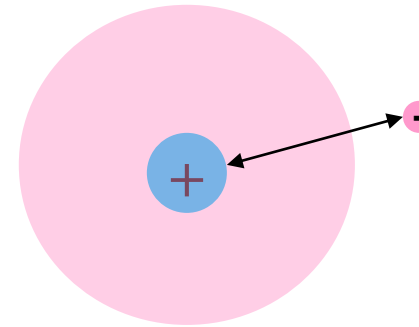
# People Basis Sets

- 6-31G\*
  - 6-311++G\*\*
  - 4-21G\*
-

# Electron Correlation



Many-electron system  
All electron-electron repulsion  
is included explicitly.



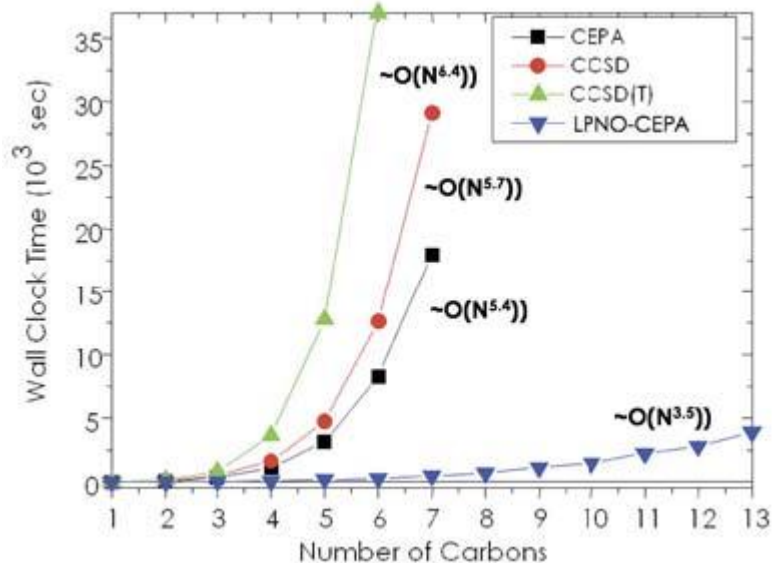
One-electron system  
with remaining electrons  
represented by an average  
charge density.  
**Mean field approach**

# Electron Correlation

- Let electrons occupy excited virtual orbitals

$$\Psi = a_0 \Psi_{HF} + \sum_i^{occ. \text{ vir.}} \sum_r a_i^r \Psi_i^r + \sum_{i,j}^{occ. \text{ vir.}} \sum_{r,s} a_{ij}^{rs} \Psi_{ij}^{rs} + \dots$$

- This is in principle exact but very expensive



level of theory	scaling
DFT	$N^3$
Hartree Fock	$N^4$
MP2	$N^5$
CCSD	$N^6$
CCSD(T)	$N^7$
CCSDTQ	$N^{10}$

# Density Functional Theory DFT

## The Hohenberg-Kohn Theorems

The first Hohenberg-Kohn theorem asserts that the density of any system determines all *ground-state* properties of the system, that is,  $E = E[\rho]$ , where  $\rho$  is the ground-state density of the system.

The second H-K theorem shows that there exists a **variational principle** for the above energy density functional  $E[\rho]$ . Namely, if  $\rho'$  is not the ground state density of the above system, then  $E[\rho'] > E[\rho]$ .

---

# DFT

The wave function  $\phi$  of an N-electron system includes  $3N$  variables, while the density,  $\rho$  no matter how large the system is, has only three variables  $x$ ,  $y$ , and  $z$ . Moving from  $E[\phi]$  to  $E[\rho]$  in computational chemistry significantly reduces the computational effort needed to understand electronic properties of atoms, molecules, and solids.

- H-K Theorem says nothing about the form of the functional
  - Electron density is seldom known
-

# Kohn-Sham Approach

Treat the electrons as  $N$  fictitious non-interacting particles moving in an effective potential.

$|\phi_i\rangle \equiv$  *independent particle wavefunction*

*density.*  $\rho_{KS} = \sum_{i=1}^N |\phi_i|^2$

*kinetic energy.*  $T_{KS} = -\frac{1}{2} \sum_{i=1}^N \langle \phi_i | \nabla^2 | \phi_i \rangle$

The Kohn-Sham assumption is that the K-S density  $\rho_{KS}$  is equal to the true density.

Kohn-Sham energy partitioning:

$$E[\rho] = T[\rho] + E_{\text{ext}}[\rho] + E_{\text{Coul}}[\rho] + E_{\text{xc}}[\rho]$$

---

- Total electronic energy can be partitioned

$$E = E_T + E_{NE} + E_J + E_X + E_C$$

$E_T$  = kinetic energy of the electrons

$E_{NE}$  = Coulomb attraction energy between electrons  
and nuclei

$E_J$  = Coulomb repulsion energy between electrons

$E_X$  = Exchange energy, a correction for the self-repulsions of electrons

$E_C$  = Correlation energy between the motions of electrons with different spins

- $E_T$ ,  $E_{NE}$ , &  $E_J$  are largest contributors to  $E$
  - $E_X > E_C$
-



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## Becke (1993): B3LYP, 3 fitted parameters

$$F^{B3LYP} = A \cdot F_x^{HF} + (1-A) \cdot F_x^{Slater} + B \cdot F_x^{Becke} + C \cdot F_c^{LYP} + (1-C) \cdot F_c^{VWN}$$

### Benchmark tests of 1 - 2 row molecules:

**Energies: 2.2 kcal/mol**

**Distances: 0.013 Å**

**Angles: 0.62°**

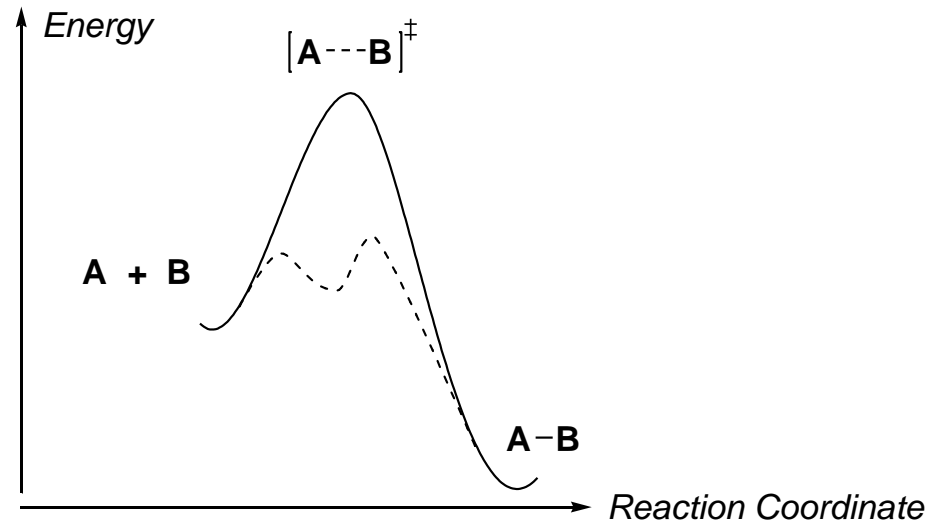
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# Catalysis

## Catalysis

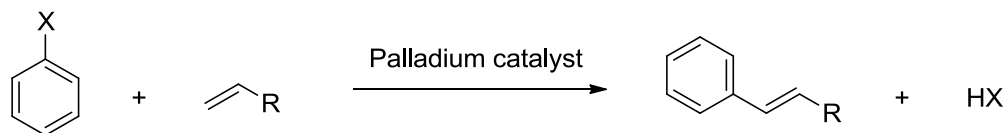


*Catalyst – Facilitates a reaction. Not consumed.*

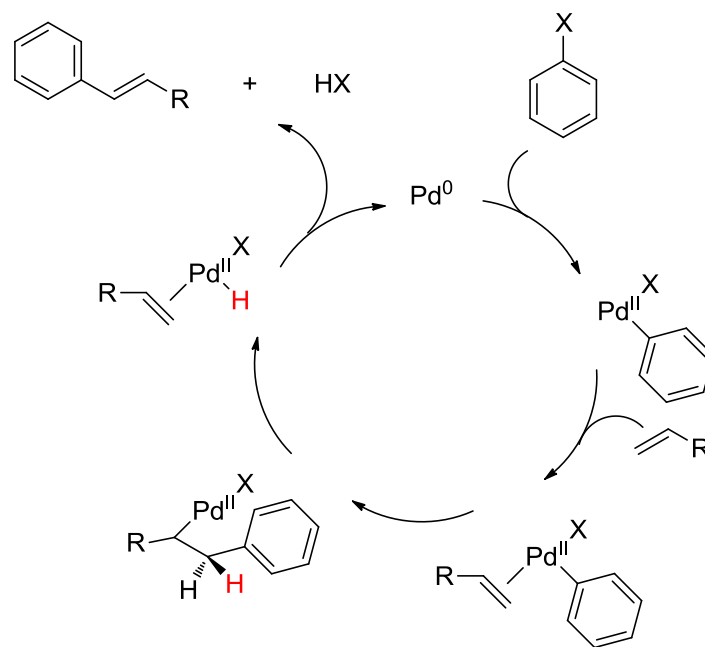


# Modeling of Catalysis

## Nobel Prize Chemistry 2010 – Heck Reaction

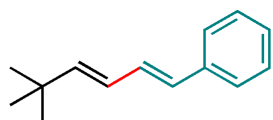
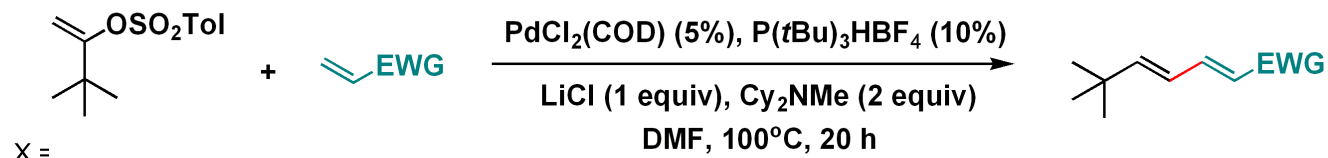


X = Cl, Br, I, OTs, OTf

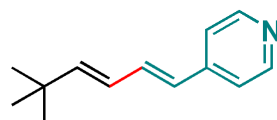


# Modeling of Catalysis

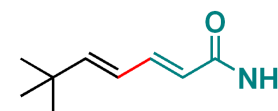
## Heck reaction with a 1,2-migration



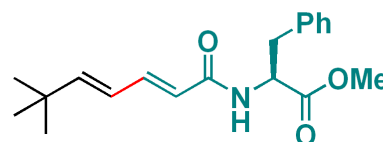
79%



93%



72%



80%

Hansen, Skrydstrup

# Modeling of Catalysis

