



# Basic approximations in quantum chemistry

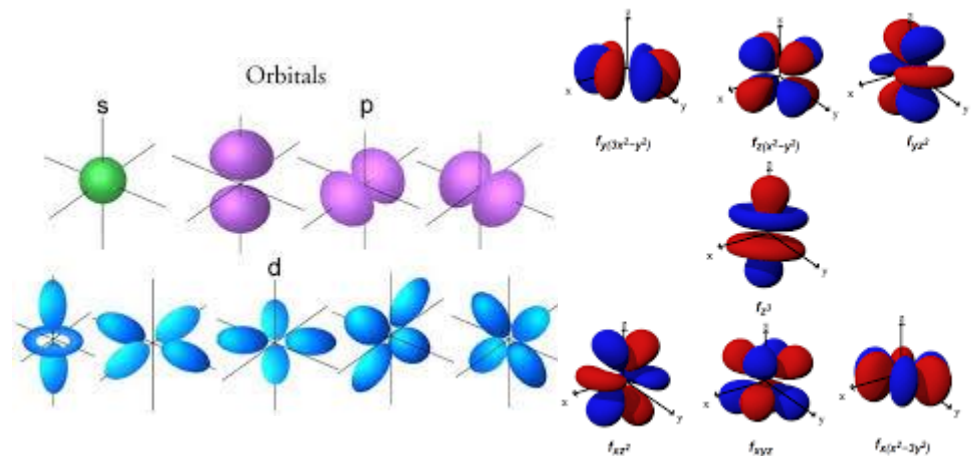
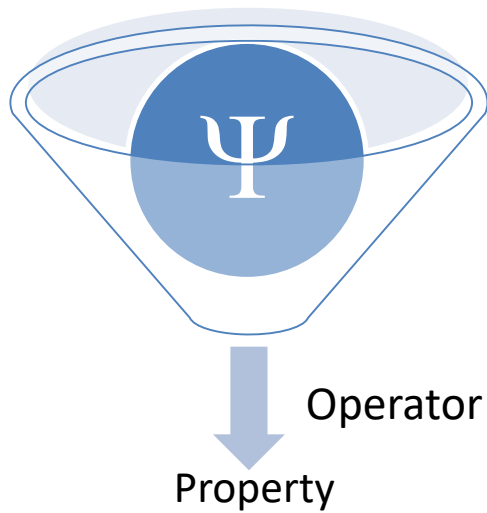
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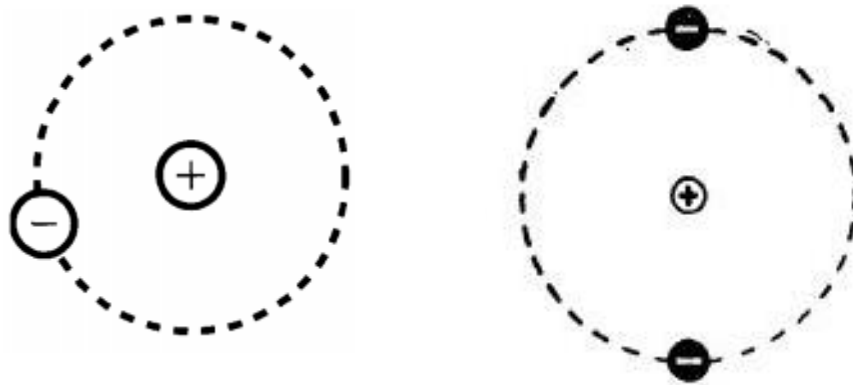
# Ab initio: problems

$$\hat{H}\Psi = E\Psi$$

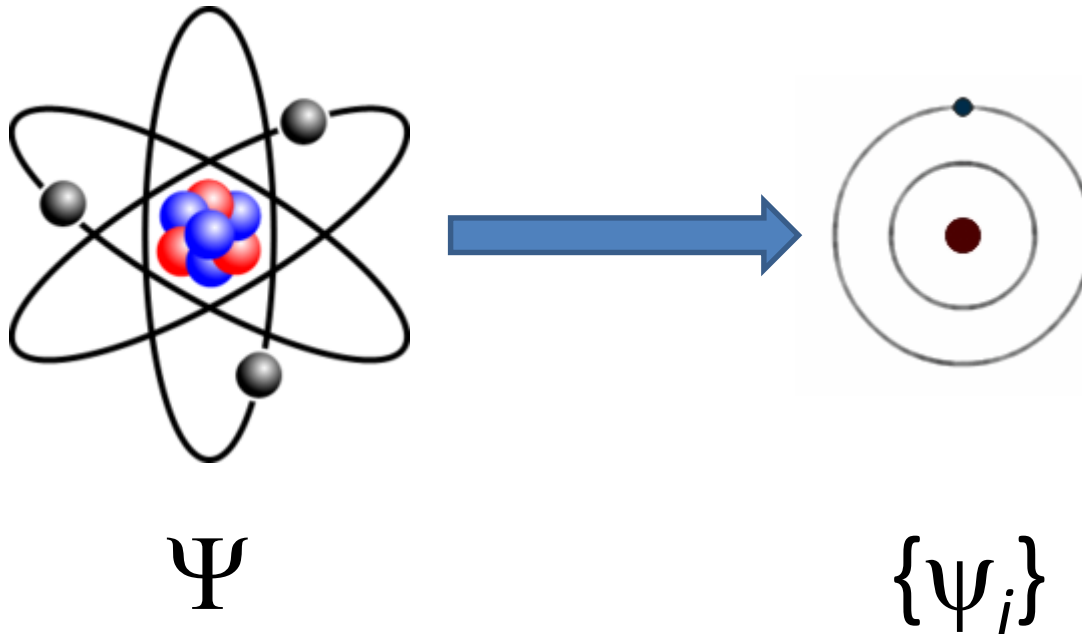
Can be exactly solved only for hydrogen atom and  $\text{H}_2^+$  molecule



Three-body problem



# One electron approximation



**Advantage**: now the task can be solved “exactly” and we can use results of the solution for hydrogen.

**Disadvantage**: we ignore the electron correlation.

# Approximation of basis sets

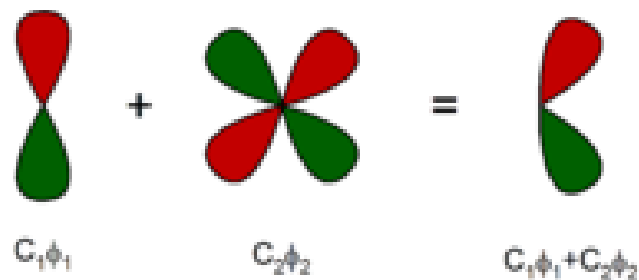
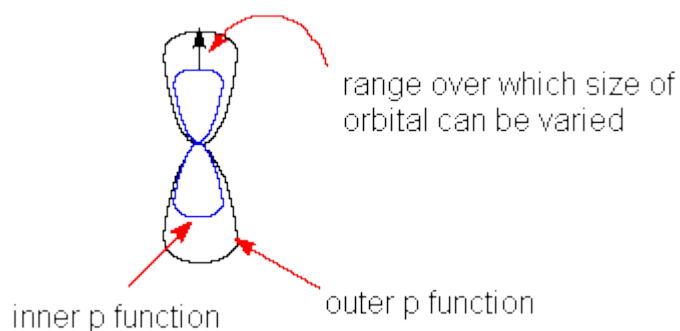
Number of orbitals is infinite – we restrict it.

**Minimal** basis set (OST-nG) – the simplest but the shape of orbitals is fixed.

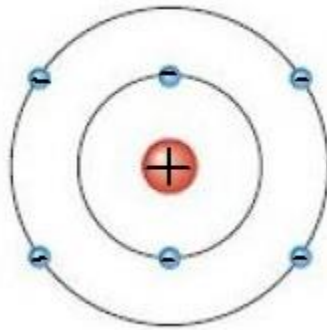
**Split-valence** basis set (X-YZG) – can scale the orbitals.

**Polarized** basis set (X-YZG<sup>\*\*</sup>) – can provide angle distortion of orbitals.

**Diffuse function** basis set (X-YZ++G) – can account for weak interactions.



# Independent electron approximation



$$\Psi \leftarrow \{\psi_i\}$$

$$\Psi = \psi_1 \psi_2 \cdots \psi_n$$

**Disadvantage:** Does not account for Pauli exclusion principle.

# Variation principle

$$\Psi_1 \rightarrow E_1$$

$$\Psi_2 \rightarrow E_2$$

$$E_1 > E_2 > E_{\text{exp}}$$

$\Psi_1$  or  $\Psi_2$ ?

Kolos W., Wolniewicz L. 1964  
Calculation of H<sub>2</sub> molecule

# Perturbation theory

We consider the main interactions in the system and ignore weaker interactions. Having an exact solution for this approximation we then consider the weaker interaction as a 'perturbation' of the system and obtain an improved solution.

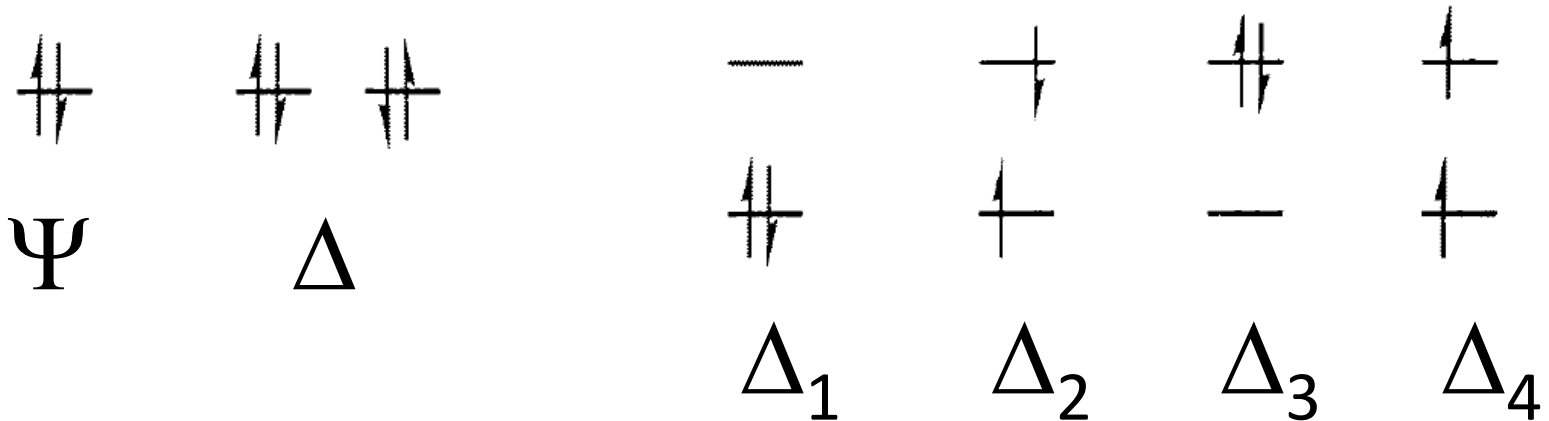
Examples: electron-electron interactions  
electron-nucleus interactions  
Van der Waals interactions

# Configuration interaction

$$\Psi \leftarrow \{\psi_i\}$$

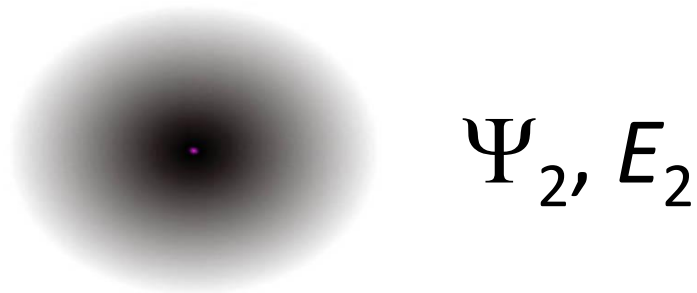
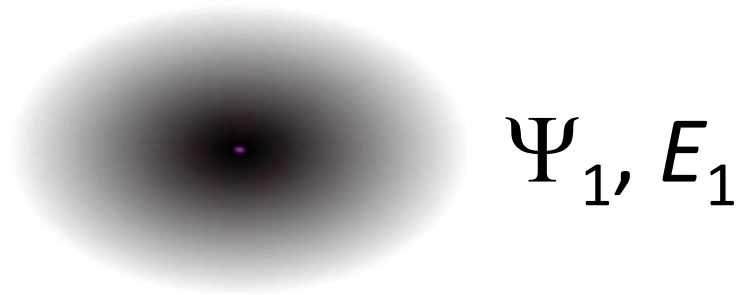
$$\Psi = \psi_1 \psi_2 \cdots \psi_n$$

$$\Psi = \Delta \text{ (Slater determinant)}$$



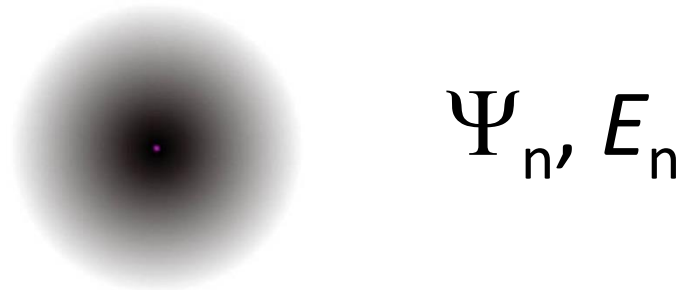


# Hartree-Fock self-consistent field



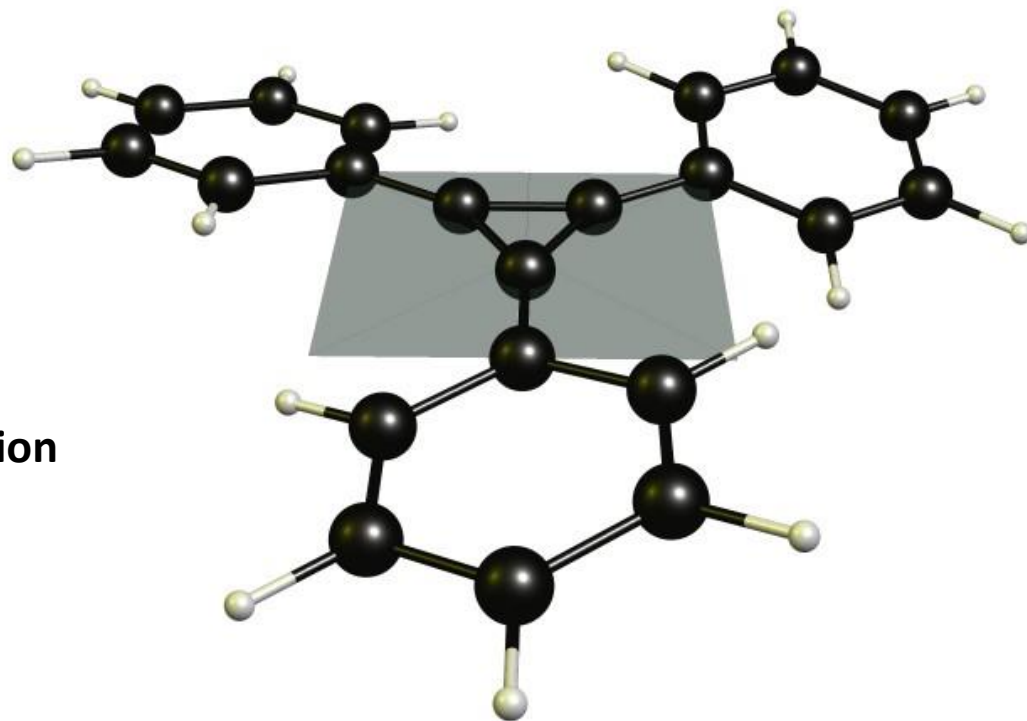
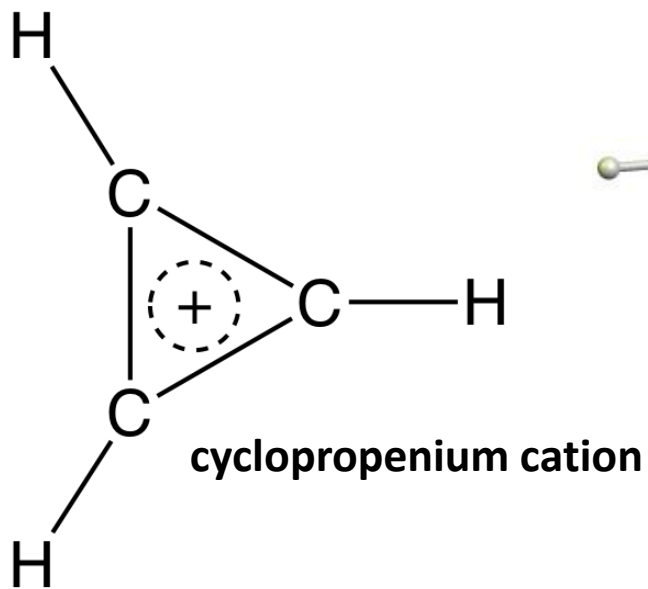
⋮

⋮



# Quantum mechanics vs. quantum chemistry

R. Feynman, Quantum mechanics



triphenylcyclopropenium cation

# Born-Oppenheimer approximation

- The system of nuclei is static from the electron point of view
- No exchange by movement energy between electrons and nuclei
- Nuclei and electrons move independently
- Vibronic interactions are absent

**Hellmann-Feynman theorem** → Force acting to the nuclei is a sum of the force acting from all other nuclei and from the electron system

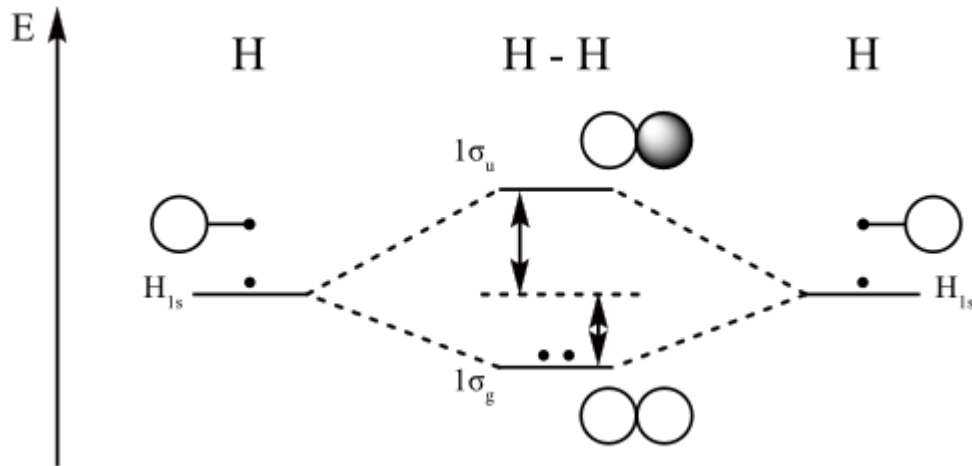
## Adiabatic approximation

Vibronic interactions are small – they are a perturbation

When is it incorrect?

**Jahn-Teller theorem** any **nonlinear** molecule with a spatially degenerate electronic ground state will undergo a geometrical distortion that removes that degeneracy.

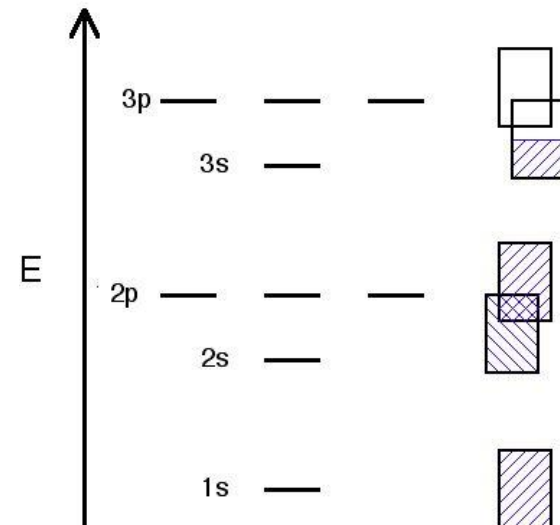
# MO LCAO approximation



- Atoms are preserved in molecules
- The molecule is divided into regions belonging to a particular atom

**Electronic band structure**

example: Na



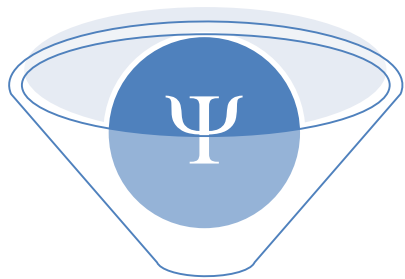
Ab initio



DFT

*It follows...*

# Summary



↓  $\hat{H}$   
 $E$

$\Psi$

$$\Psi \leftarrow \{\psi_i\}$$

$$\Psi = \psi_1 \psi_2 \dots \psi_n$$

$$\Psi = \Delta$$

$$\Psi = c_1 \Delta_1 + c_2 \Delta_2 + \dots + c_n \Delta_n$$

Atom

$\hat{H}$

$$\hat{H} = \hat{H}^0 + V$$

$$\phi_i = c_1 \phi_1 + c_2 \phi_2 + \dots + c_n \phi_n$$

$$\Delta \leftarrow \{\phi_i\}$$

$$\Psi = c_1 \Delta_1 + c_2 \Delta_2 + \dots + c_n \Delta_n$$

Molecule

HF SCF



$\Psi, E, \phi_i, \varepsilon_i$