The Basis Set
-
Introduction

Solving the Schrödinger equation

$$\hat{\mathrm{H}}\Psi = \mathrm{E}\Psi, \text{ with}$$

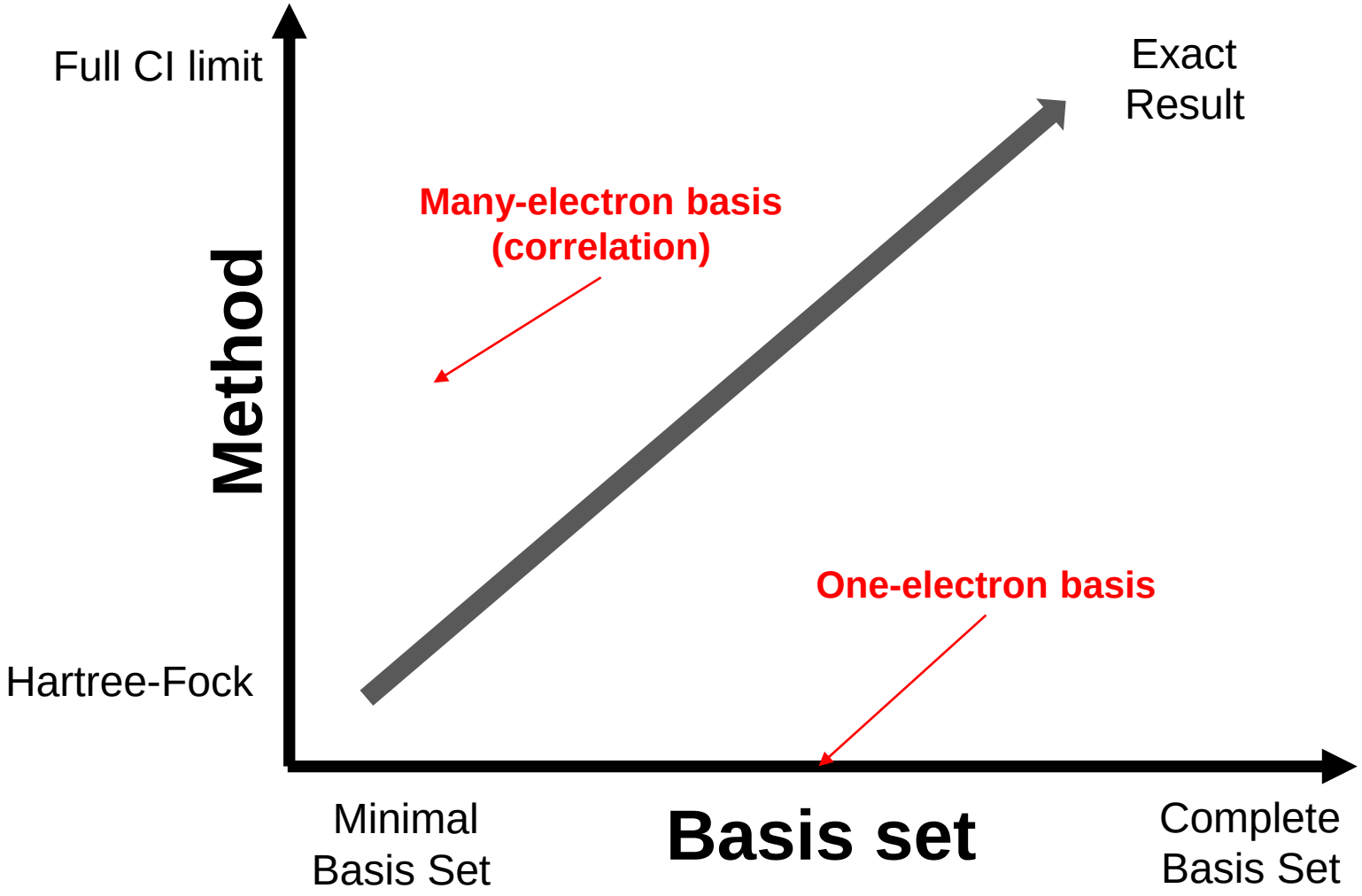
$$\Psi = \Psi(\{R_{Nuc}\}, \{r_{elec}, \sigma_{elec}\})$$

Several Approximations required

- **Accuracy of Method (Hamilton)**
- **Flexibility of Wave Function (Basis Set, k-grid)**
- *Other Numerical Settings (Integrals, etc.)*
- Geometry (Approximate System)

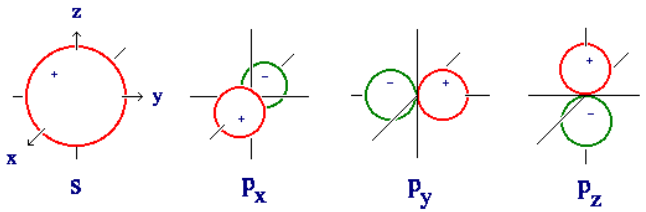
Accurate Solutions ⟷ **Compromise** ⟷ **Computational Demand**

Solving the Schrödinger equation accurately

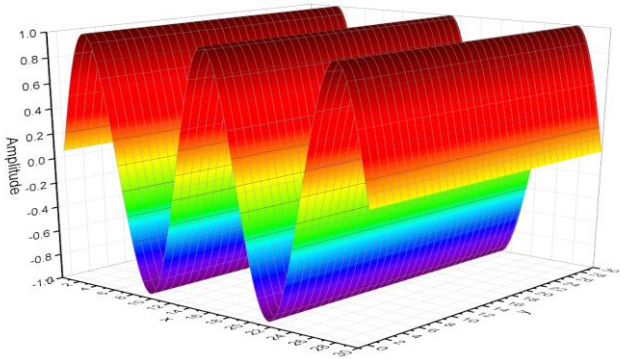


Basis set types

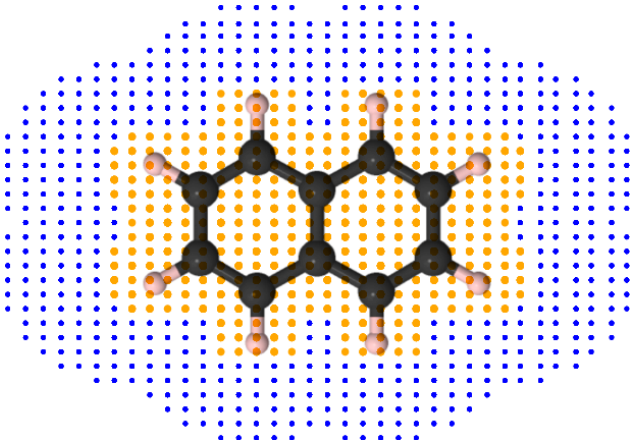
- **Linear Combination of Atomic Orbtials (LCAO)**



- **Plane Waves**

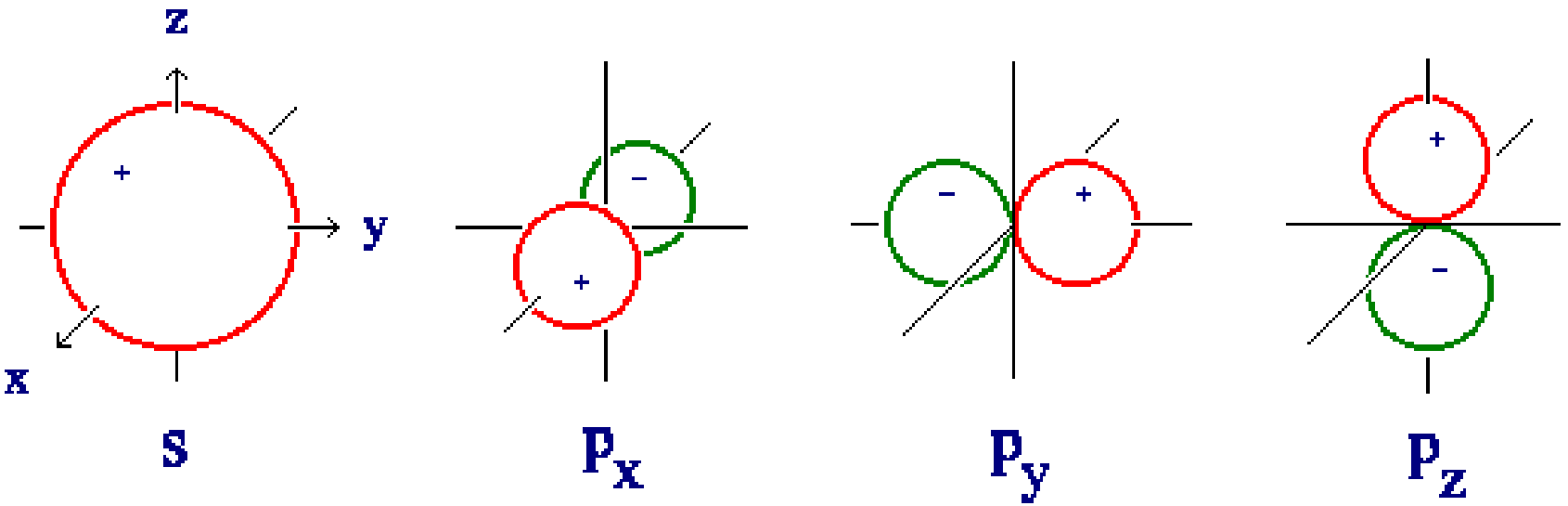


- **Grid-based (orbital free)**



The Basis Set

$$\psi_{MO} = \sum_i c_i \phi_i$$ Linear Combination of Functions



The Basis Set

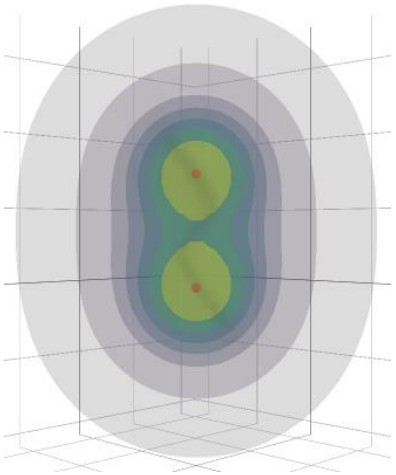
$$\psi_{MO} = \sum_i c_i \phi_i$$ Linear Combination of Functions

Intuitive Solution: One basis function per electron, e.g.

H: 1s

C: 1s, 2s, $2p_x$, $2p_y$, $2p_z$

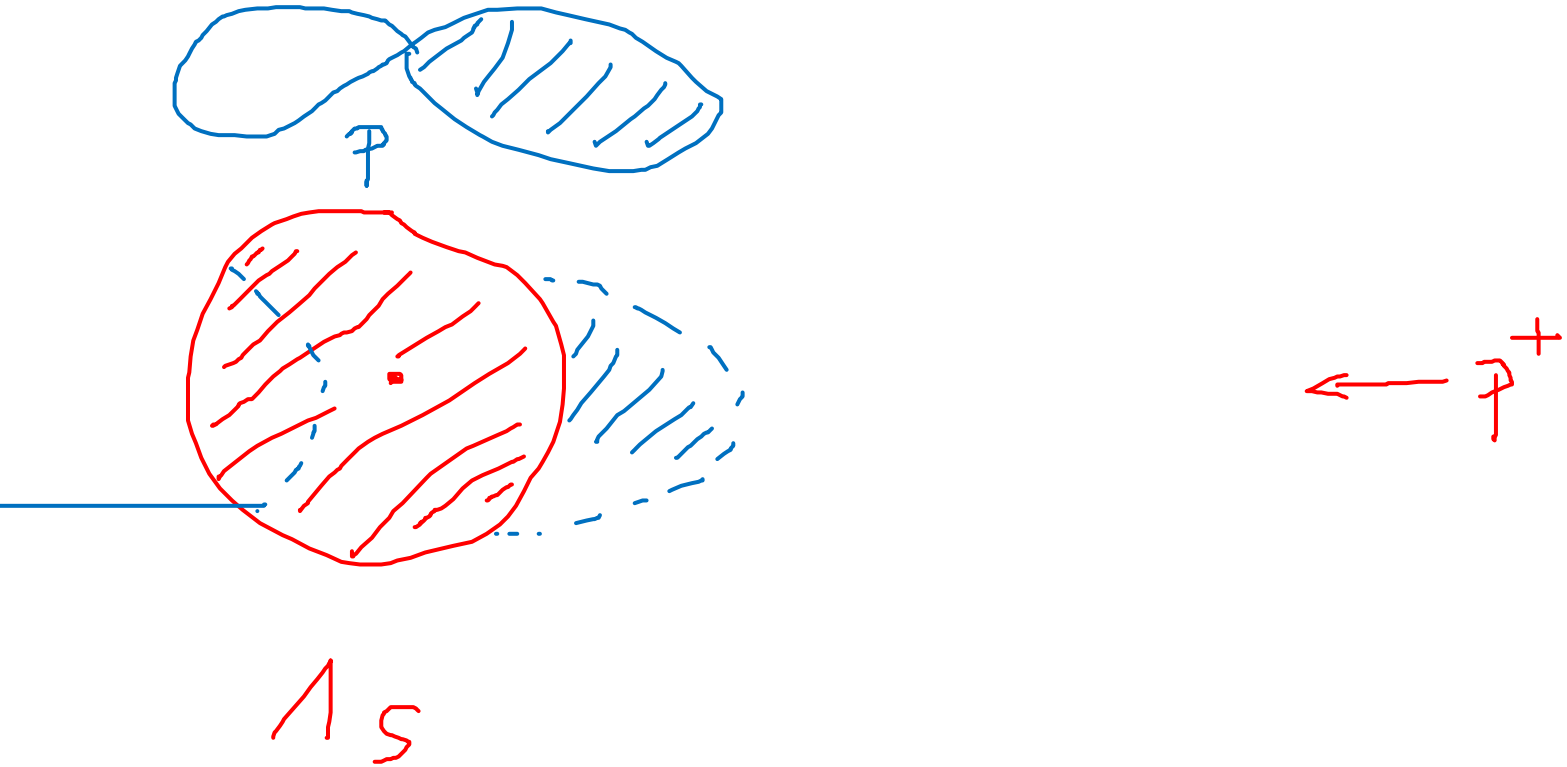
K: 1s, 2s, 2p, 3s, 3p, 3d



„Minimal Basis Set“

Why is the Minimal Basis not Enough?

Consider H atom + proton:

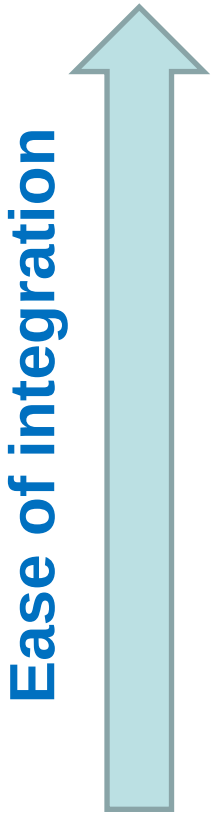


The Basis Set

Desired Properties:

- **Suited for the problem**
- **Efficiency (few basis functions / high accuracy)**
- **Easy to evaluate**
- **Systematic, encompasses full Hilbert-Space**
- **Linear independent**
- **Well-defined hierarchy (extrapolation)**
- **Universal across different methods and for different properties**

Basis functions versus ease of integration



Wavelets &

Plane Wave Basis Sets (PW)

- **Pseudopotentials**
- **Projector Augmented Waves**
- **Muffin-Tin Potentials**

Atom-Centered Basis Functions (LCAO)

- **Gaussian Type Orbitals (GTOs)**
- **Numerically Tabulated Orbitals**
- **Correlated Basis Sets**

Time-Deciding Factors in the SCF

Integral Evaluation:

Scales as $\mathcal{O}(N_{Basis})^2$

Prefactor depends on basis function type

Matrix Diagonalization:

Scales formally, as $\mathcal{O}(N_{Basis})^3$

Formally independent of basis function type

Reduced by sparse matrix algebra, etc.

Number of steps:

Scales as $\mathcal{O}(\sqrt{N_{Basis}})$

Communication