Basis Sets and Methods

Schrödinger Equation

$$H_e \Psi_e = E_e \Psi_e$$

- Derive He
- Find Ψ_e
  - GUESS!
  - use hydrogenic orbitals
  - =functions of same form as H orbitals

Hydrogenic Atomic Orbitals

$$R_{1s} = 2\left(\frac{Z}{a}\right)^{\frac{3}{2}} e^{-\frac{Zr}{a}}$$

$$R_{2s} = \frac{1}{\sqrt{2}}\left(\frac{Z}{a}\right)^{\frac{3}{2}}\left(1-\frac{Zr}{2a}\right)e^{-\frac{Zr}{2a}} \qquad R_{2p} = \frac{1}{2\sqrt{6}}\left(\frac{Z}{a}\right)^{\frac{5}{2}} re^{-\frac{Zr}{2a}}$$

$$R_{3s} = \frac{1}{3\sqrt{3}}\left(\frac{Z}{a}\right)^{\frac{3}{2}}\left(1-\frac{2Zr}{3a}+\frac{2Z^2r^2}{27a^3}\right)e^{-\frac{Zr}{3a}}$$

$$R_{3p} = \frac{8}{27\sqrt{6}}\left(\frac{Z}{a}\right)^{\frac{3}{2}}\left(\frac{Zr}{a}-\frac{Z^2r^2}{6a^2}\right)e^{-\frac{Zr}{3a}} \qquad R_{3d} = \frac{4}{81\sqrt{30}}\left(\frac{Z}{a}\right)^{\frac{7}{2}} r^2 e^{-\frac{Zr}{3a}}$$

Hydrogenic Atomic Orbitals

coefficient

exponent

polynomial

$$R_{1s} = 2\left(\frac{Z}{a}\right)^{\frac{3}{2}} e^{-\frac{Zr}{a}}$$

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exponent

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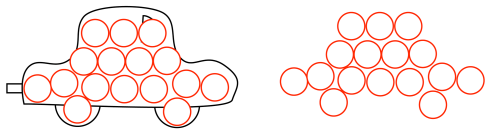
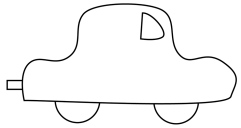
Basis Functions

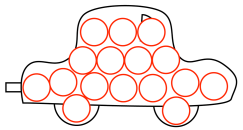
1 basis function

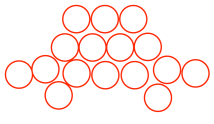


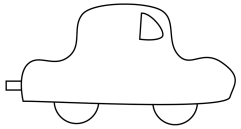


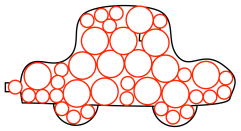
Basis Functions

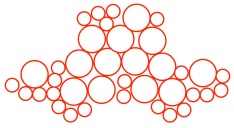
2 basis functions





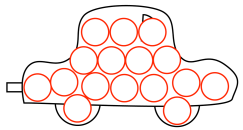


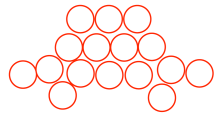


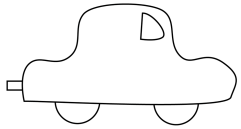


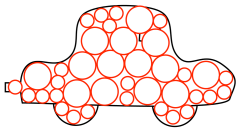
Basis Functions

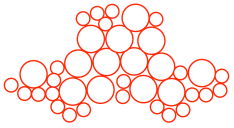
3 basis functions

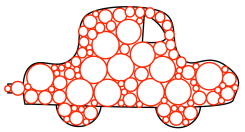


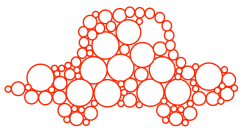












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- Derive He
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  - =functions used together to describe a more complex function
  - use gaussian functions

Basis Sets

- gaussian function

$$N r^l e^{-\zeta r_a^2} Y(\theta,\phi)$$

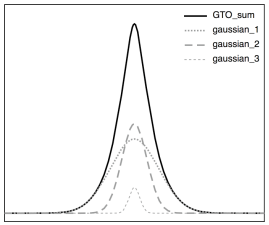
coefficient

exponent

polynomial

- linear combination of 3 gaussians

$$STO-3G = c_1 g(\alpha_1) + c_2 g(\alpha_2) + c_3 g(\alpha_3)$$



Basis Sets

- Basis set hierarchy
  - STO-3G
  - 3-21G
  - 4-31G
  - 6-31G
  - 6-311G

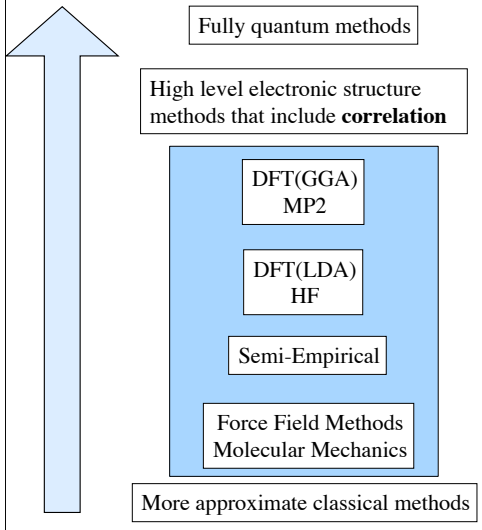
start here

medium level basis set: publishable

finish here

- Much much more out there!

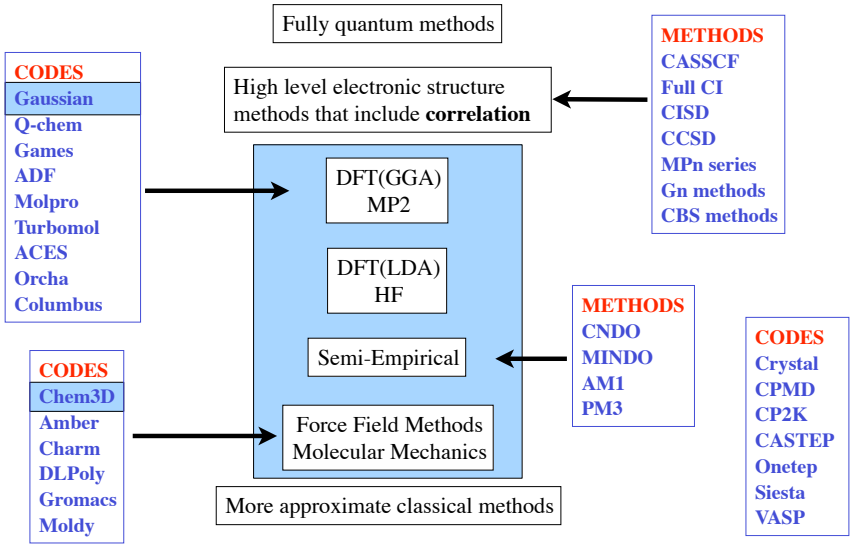
Methods!



- increasing complex ways of describing H

$$H_e \Psi_e = E_e \Psi_e$$

Methods!



Comments

- **Rubbish In Rubbish Out**
- **Understand what you are doing**
  - if you don't understand ASK!!!
- **The computer is not always right**
  - reporting numbers!
  - bond distances and angles
  - convert energy to kJ/mol
- **Human error is the source of most errors**
  - read the error message in the program
  - don't just repeat the process => a waste of time
  - understand where the error comes from: **think**
  - ASK!!! don't waste **your** time.
- **Explore, experiment, try your own simulations!**