

# Self-consistent field calculations: Hartree-Fock method

## General case:

N electrons with coordinates  $r_j$ ,  $j = 1, \dots, N$  and M fixed nuclei with coordinates  $R_K$ ,  $K = 1, \dots, M$

Many-electron Schrödinger equation: 
$$H\Psi(r_1, \dots, r_N) = E\Psi(r_1, \dots, r_N) \quad (1)$$

with the total hamitonian: 
$$H = \sum_{j=1}^N H(j) + H_{ww} \quad (2)$$

$$H(r_j) \equiv H(j) = -\frac{\hbar^2}{2m_0} \Delta_j + V(r_j) \text{ and } V(r_j) = \sum_K \left( -\frac{Z_K e^2}{4\pi\epsilon_0 |R_K - r_j|} \right) \quad (3)$$

$$H_{ww} = \frac{1}{2} \sum_{j \neq l} \frac{e^2}{4\pi\epsilon_0 |r_j - r_l|} \quad (4)$$

## The wavefunction:

The j electron that occupies the molecular orbital q is characterized by:

$$\chi_k(j) = \psi_q(r_j) s_m(j) \quad \text{where} \quad \begin{aligned} k &= (q, m) \\ s_{1/2} &= \alpha \\ s_{-1/2} &= \beta \end{aligned} \quad (5)$$



# Self-consistent field calculations

Term (b): Coulomb interaction energy

$$V_{kk',kk'} = \left\langle \iint \chi_k^*(1)\chi_{k'}^*(2) \frac{e^2}{4\pi\epsilon_0|r_1-r_2|} \chi_k(1)\chi_{k'}(2) dV_1 dV_2 \right\rangle \quad (10)$$

$$V_{kk',kk'} \equiv V_{qq',qq'} (s_m(1)s_m(1)) (s_{m'}(2)s_{m'}(2)) \xrightarrow{\langle s_m s_m \rangle = 1} V_{qq',qq'}$$

where

$$V_{qq',qq'} = \int \psi_q^*(r_1)\psi_{q'}^*(r_2) \frac{e^2}{4\pi\epsilon_0|r_1-r_2|} \psi_q(r_1)\psi_{q'}(r_2) dV_1 dV_2 \quad (11)$$

Term (c): Coulomb exchange interaction

$$V_{kk',k'k} = \left\langle \iint \chi_k^*(1)\chi_{k'}^*(2) \frac{e^2}{4\pi\epsilon_0|r_1-r_2|} \chi_{k'}(1)\chi_k(2) dV_1 dV_2 \right\rangle \quad (12)$$

$$V_{kk',k'k} = V_{qq',q'q} (s_m(1)s_{m'}(1)) (s_m(2)s_{m'}(2)) \xleftrightarrow{\text{only if } m=m'} V_{qq',q'q}$$

where

$$V_{qq',q'q} = \int \psi_q^*(r_1)\psi_{q'}^*(r_2) \frac{e^2}{4\pi\epsilon_0|r_1-r_2|} \psi_{q'}(r_1)\psi_q(r_2) dV_1 dV_2$$

# Hartree-Fock Method for a Closed Shell

Closed shell with N electrons: N/2 electrons have spin up, N/2 electrons have spin down .

$$\bar{E} = \sum_k H_{k,k} + \frac{1}{2} \sum_{k,k'} (V_{kk',kk'} - V_{kk',k'k}) \quad (8)$$

becomes: 
$$\bar{E} = 2 \sum_q^{N/2} H_{qq} + \sum_{qq'}^{N/2} (2V_{qq',qq'} - V_{qq',q'q}) \quad (12)$$

requirements: 
$$\langle \Psi^* | H_{\text{ges}} | \Psi \rangle = \text{Min!} \quad (13)$$

## HF approximation:

one electron moves in the potential that is a spherical average due to the other electrons and the nuclei of the molecule.

$$\int \psi_q^* \psi_q dV = 1, \quad q = 1, \dots, N \quad \longrightarrow \quad \langle \Psi^* | \Psi \rangle = 1 \quad (14)$$

# Hartree-Fock Method for a Closed Shell

One electron  $\Psi_q(1)$  moves into the averaged potential due to the other electr. and nuclei.

$$H(1)\psi_q(1) + 2 \sum_{q'} \int |\psi_{q'}(2)|^2 \frac{e^2}{4\pi\epsilon_0 r_{12}} dV_2 \psi_q(1) - \sum_{q'} \int \psi_{q'}^*(2) \psi_q(2) \frac{e^2}{4\pi\epsilon_0 r_{12}} dV_2 \psi_{q'}(1) = \epsilon_q \psi_q(1)$$



$$H^{\text{eff}} \Psi_q(1) = \epsilon_q \Psi_q(1) \quad \text{Hartree-Fock equation} \quad (15)$$

hamiltonian of the electron  $\Psi_q(1)$  in the field of the fixed atomic nuclei



Coulomb interaction energy of electr. 1 with the field of charge densities

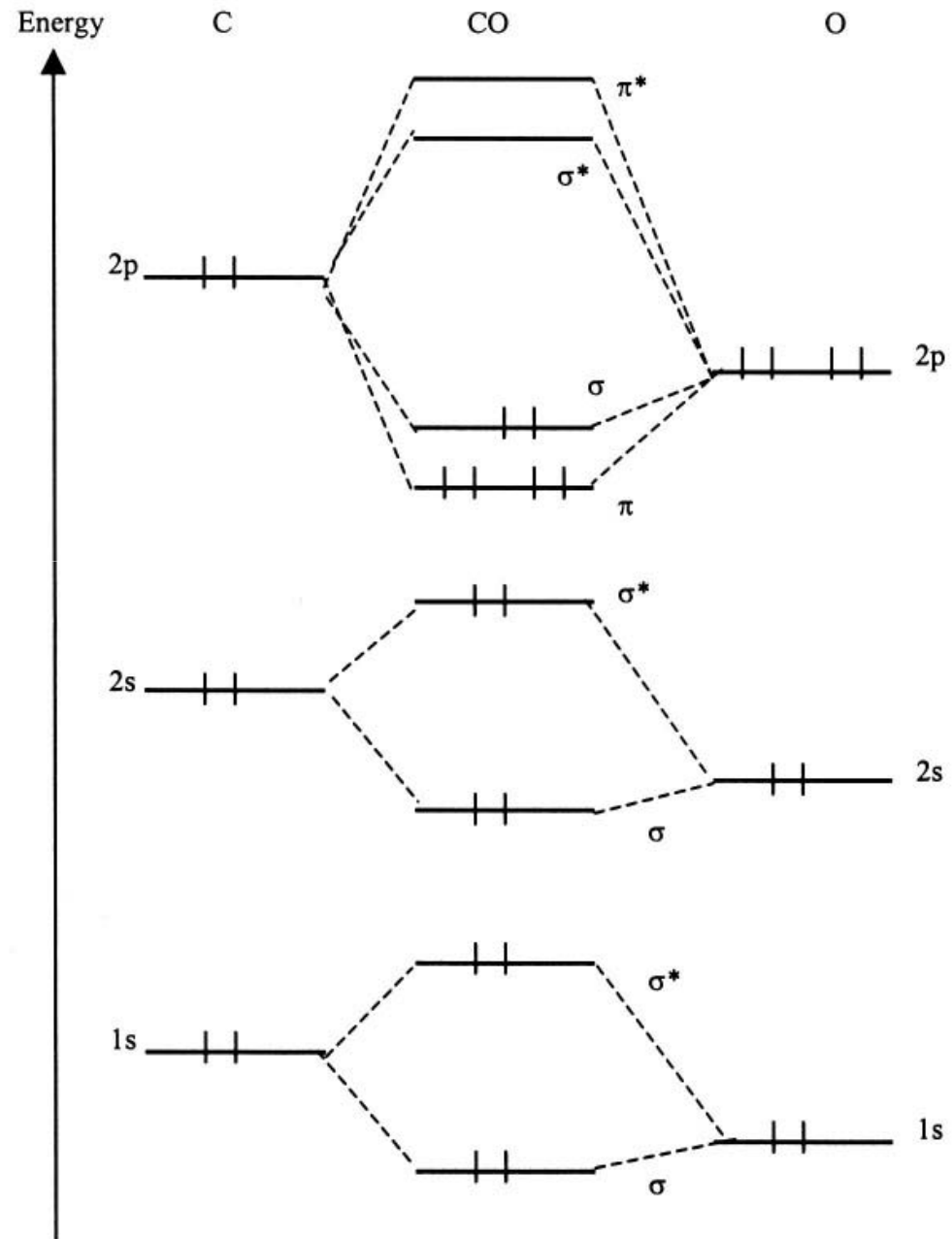
$$e |\psi_{q'}(2)|^2$$



Coulomb interaction energy of electr. 1 with the exchange density of electr. 2.

$$e \psi_{q'}^*(2) \psi_q(2)$$

# Closed Shell: CO Molecule



Bond order:  $(10-4)/2 = 3$

# Basis sets

1. Atomic (H) orbitals:  $\varphi_{n,l,m_l}(r, \theta, \varphi) = R_{n,l}(r) Y_{l,m_l}(\vartheta, \varphi)$

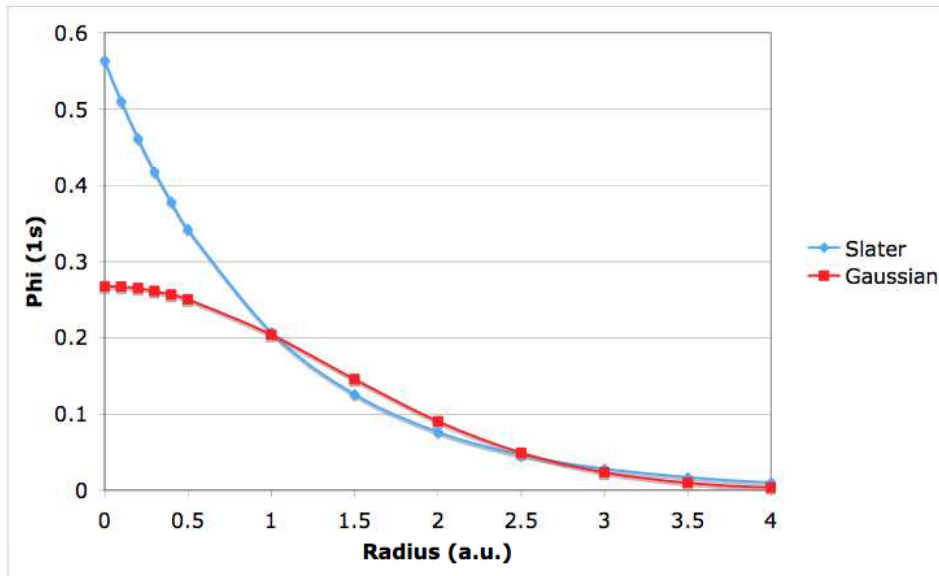
2. Slater-type orbitals (STO):  $\chi_{\zeta,n,l,m}(r, \theta, \varphi) = N Y_{l,m}(\theta, \varphi) r^{n-1} e^{-\zeta r}$

$s = \text{shielding constant}$ ,  $N = \text{radial normalization constant}$

The effective nuclear charge:  $\zeta = (Z-s)/n$

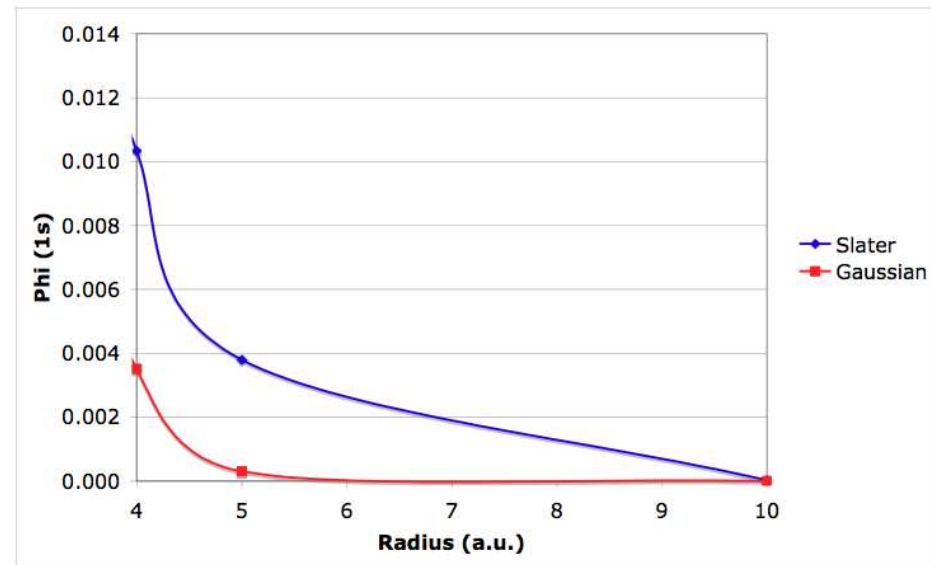
3. Gaussian type orbitals (GTO):  $\chi_{\zeta,n,l,m}(r, \theta, \varphi) = N Y_{l,m}(\theta, \varphi) r^{2n-2-l} e^{-\zeta r^2}$

# STO versus GTO



Short Radius

Long Radius





# Gaussian type orbitals

