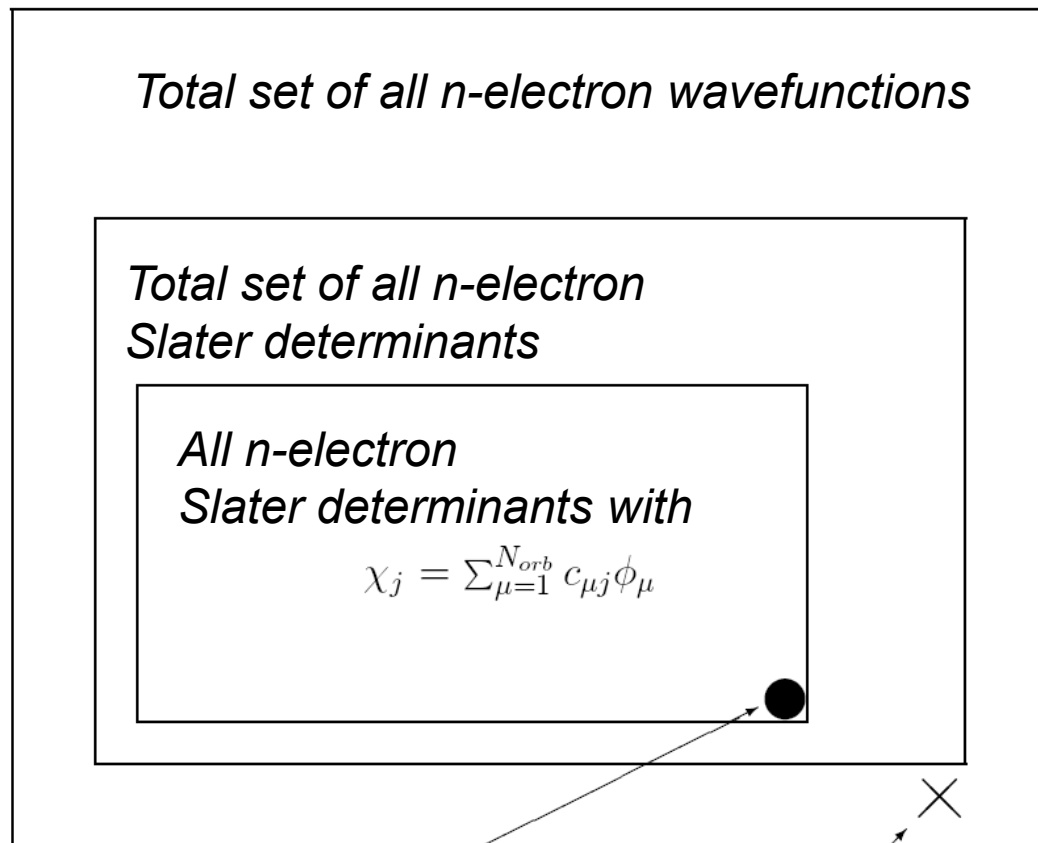


# Principle of Hartree-Fock calculation



*Hartree-Fock (Roothaan-Hall) solution*

*Exact solution for electronic ground state*

# Principle of Hartree-Fock calculation

*Wavefunction*

$$\psi_{j,\alpha}(\mathbf{r}_i, \xi_i) = \chi_j(\mathbf{r}_i)\alpha(\xi_i)$$

or

$$\psi_{j,\beta}(\mathbf{r}_i, \xi_i) = \chi_j(\mathbf{r}_i)\beta(\xi_i)$$

$$\psi_{\text{det}}(\mathbf{r}_1, \xi_1, \mathbf{r}_2, \xi_2, \dots, \mathbf{r}_n, \xi_n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \psi_1(\mathbf{r}_1, \xi_1) & \psi_2(\mathbf{r}_1, \xi_1) & \psi_3(\mathbf{r}_1, \xi_1) & \dots & \psi_n(\mathbf{r}_1, \xi_1) \\ \psi_1(\mathbf{r}_2, \xi_2) & \psi_2(\mathbf{r}_2, \xi_2) & \psi_3(\mathbf{r}_2, \xi_2) & \dots & \psi_n(\mathbf{r}_2, \xi_2) \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \psi_1(\mathbf{r}_n, \xi_n) & \psi_2(\mathbf{r}_n, \xi_n) & \psi_3(\mathbf{r}_n, \xi_n) & \dots & \psi_n(\mathbf{r}_n, \xi_n) \end{vmatrix}$$

*Hamiltonian*

$$\widehat{H}_{\text{elec}} = \sum_{i=1}^n \widehat{h}(\mathbf{r}_i, \mathbf{p}_i) + \sum_{i < i'} \widehat{g}(\mathbf{r}_i, \mathbf{r}_{i'}).$$

**Now use variation principle:**

Derive expression for  $\langle \psi_{\text{det}} | \widehat{H}_{\text{elec}} | \psi_{\text{det}} \rangle$

Determine LCAO's  $\chi_j(\mathbf{r}_i) = \sum_{\mu=1}^{N_{\text{orb}}} c_{\mu j} \phi_{\mu}(\mathbf{r}_i)$ . to minimize  $\langle \psi_{\text{det}} | \widehat{H}_{\text{elec}} | \psi_{\text{det}} \rangle$

*Expansion coefficients to be varied*

## Expectation value of Slater determinant

*For closed shells (even number of electrons, each space orbital used twice)*

$$\begin{aligned} & \langle \psi_{\text{det}} | \widehat{H}_{\text{elec}} | \psi_{\text{det}} \rangle \\ &= \sum_{\mu=1}^{N_{\text{orb}}} \sum_{\nu=1}^{N_{\text{orb}}} P_{\mu\nu} \left( H_{\mu\nu}^{\text{core}} + \frac{1}{2} \sum_{\lambda=1}^{N_{\text{orb}}} \sum_{\sigma=1}^{N_{\text{orb}}} P_{\lambda\sigma} \left\{ (\mu\nu | \lambda\sigma) - \frac{1}{2} (\mu\sigma | \lambda\nu) \right\} \right). \end{aligned}$$

$$H_{\mu\nu}^{\text{core}} = \int \phi_{\mu}(\mathbf{r}_1)^* \widehat{h}(\mathbf{r}_1, \mathbf{p}_1) \phi_{\nu}(\mathbf{r}_1) dV_1 \quad \textit{Known completely!}$$

$$(\mu\nu | \lambda\sigma) = \int \int \frac{\phi_{\mu}(\mathbf{r}_1)^* \phi_{\lambda}(\mathbf{r}_2)^* \phi_{\nu}(\mathbf{r}_1) \phi_{\sigma}(\mathbf{r}_2)}{\sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2}} dV_1 dV_2. \quad \textit{Known completely!}$$

Density matrix, closed shells,  
 $n=2m$  electrons, **UNKNOWN**

$$P_{\mu\nu} = 2 \sum_{j=1}^m c_{\mu j}^* c_{\nu j}$$

## Minimize expectation value

*Search for minimum, or at least stationary point with*

$$\frac{\partial \langle \psi_{\text{det}} | \hat{H}_{\text{elec}} | \psi_{\text{det}} \rangle}{\partial c_{\mu j}} = 0,$$

*Additional condition, space orbitals are orthonormal*

$$\int \chi_j(\mathbf{r}_1)^* \chi_k(\mathbf{r}_1) dx_1 dy_1 dz_1 = \delta_{jk}$$

*Corresponding condition for LCAO expansion coefficients*

$$\sum_{\mu=1}^{N_{\text{orb}}} \sum_{\nu=1}^{N_{\text{orb}}} c_{\mu j}^* S_{\mu\nu} c_{\nu k} = \delta_{jk} \quad S_{\mu\nu} = \int \phi_{\mu}(\mathbf{r}_i)^* \phi_{\nu}(\mathbf{r}_i) dx_1 dy_1 dz_1$$

# Roothaan-Hall equations

*Minimization of the expectation values leads to Roothaan-Hall equations*

$$\sum_{\nu=1}^{N_{orb}} (F_{\mu\nu} - \epsilon_j S_{\mu\nu}) c_{\nu j} = 0, \quad \mu = 1, 2, \dots, N_{orb}.$$

$$F_{\mu\nu} = H_{\mu\nu}^{core} + \sum_{\lambda=1}^{N_{orb}} \sum_{\sigma=1}^{N_{orb}} P_{\lambda\sigma} \left\{ (\mu\nu|\lambda\sigma) - \frac{1}{2}(\mu\sigma|\lambda\nu) \right\},$$

$$P_{\mu\nu} = 2 \sum_{j=1}^m c_{\mu j}^* c_{\nu j}$$

$$\{\mathbf{F} - \epsilon_j \mathbf{S}\} \mathbf{c}_j = 0$$

*Formally the Roothaan-Hall equations constitute a matrix eigenvalue problem, but the Fock matrix depends on its own eigenvalues, so non-standard*

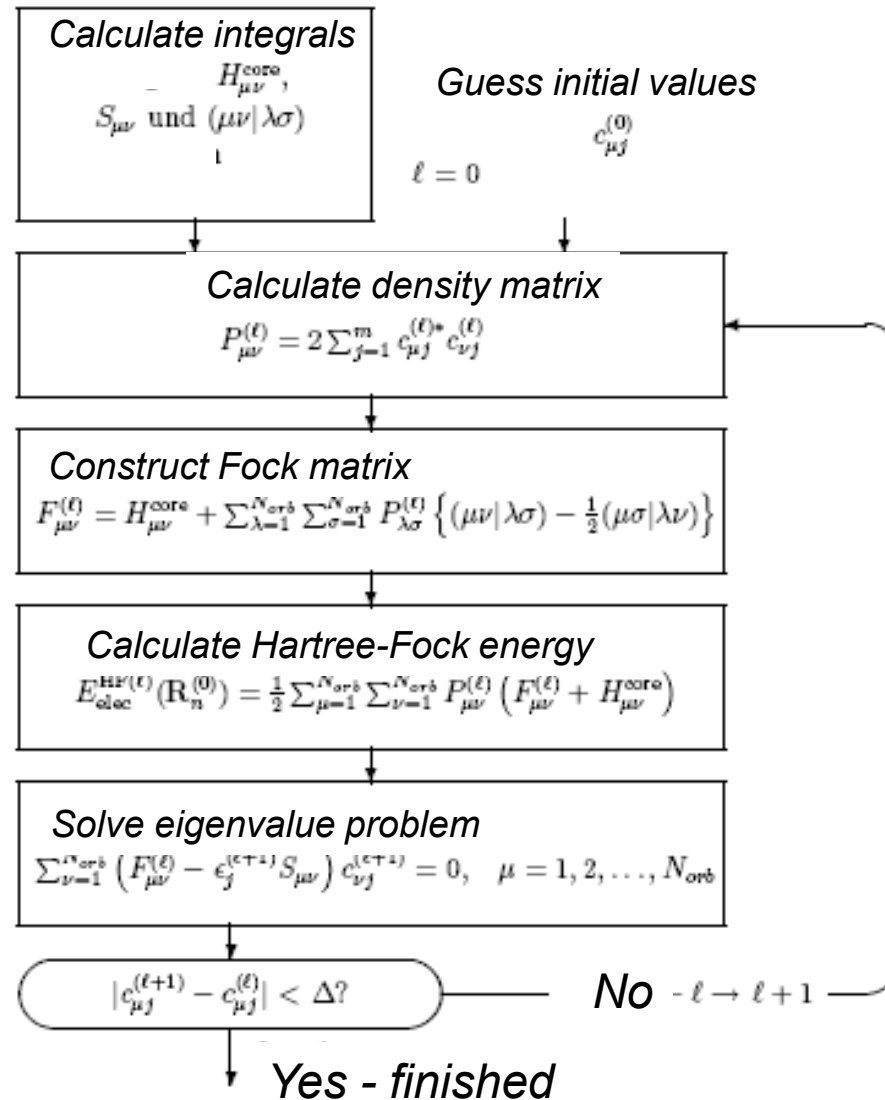
## Roothaan-Hall equations

We solve the Roothaan-Hall equations *iteratively*

$$\{\mathbf{F} - \epsilon_j \mathbf{S}\} \mathbf{c}_j = 0$$

$$F_{\mu\nu} = H_{\mu\nu}^{\text{core}} + \sum_{\lambda=1}^{N_{\text{orb}}} \sum_{\sigma=1}^{N_{\text{orb}}} P_{\lambda\sigma} \left\{ (\mu\nu|\lambda\sigma) - \frac{1}{2}(\mu\sigma|\lambda\nu) \right\},$$

# Roothaan-Hall equations



# MOLPRO input

```
***,h2 potential
basis=6-31g**
! -----
i=0
do rhh=0.65,0.80,0.01,ang
! -----
geometry={H1;
H2 H1 rhh
}
! -----
hf
i=i+1
rval(i)=rhh
escf(i)=energy
enddo
{table,rval,escf
head,r,scf
save,h2.tab
title,Results for H2, basis $basis
}
---
```

!Title  
!Use Pople basis set

!closed-shell scf

!save the table in file h2.tab  
!title for table



# MOLPRO output

Molecular orbitals read from record 2100.2 Type=RHF/CANONICAL (state 1.1)

Molecular orbital dump at record 2100.2

ITERATION	DDIFF	GRAD	ENERGY	2-EL.EN.	DIPOLE MOMENTS			DIIS
1	0.000D+00	0.000D+00	-1.12842012	1.274837	0.000000	0.000000	0.000000	0
2	0.000D+00	0.147D-02	-1.12843442	1.272059	0.000000	0.000000	0.000000	1
3	0.134D-02	0.224D-03	-1.12843474	1.271594	0.000000	0.000000	0.000000	2
4	0.236D-03	0.581D-05	-1.12843474	1.271596	0.000000	0.000000	0.000000	3
5	0.140D-05	0.525D-08	-1.12843474	1.271596	0.000000	0.000000	0.000000	0

Final occupancy: 1 0 0 0 0 0 0

!RHF STATE 1.1 ENERGY -1.128434741894

Nuclear energy 0.66147156

One-electron energy -2.42570452

Two-electron energy 0.63579821

Virial quotient -1.05262513

!RHF STATE 1.1 DIPOLE MOMENT 0.00000000 0.00000000 0.00000000

Dipole moment /Debye 0.00000000 0.00000000 0.00000000

# MOLPRO input

```
***,h2 potential
basis=6-31g**
! -----
i=0
do rhh=0.65,0.80,0.01,ang
! -----
geometry={H1;
H2 H1 rhh
}
! -----
hf
i=i+1
rval(i)=rhh
escf(i)=energy
enddo
{table,rval,escf
head,r,scf
save,h2.tab
title,Results for H2, basis $basis
}
---
```

!Title  
!Use Pople basis set

!closed-shell scf

!save the table in file h2.tab  
!title for table

# LCAO: The basis set consists of atomic orbitals

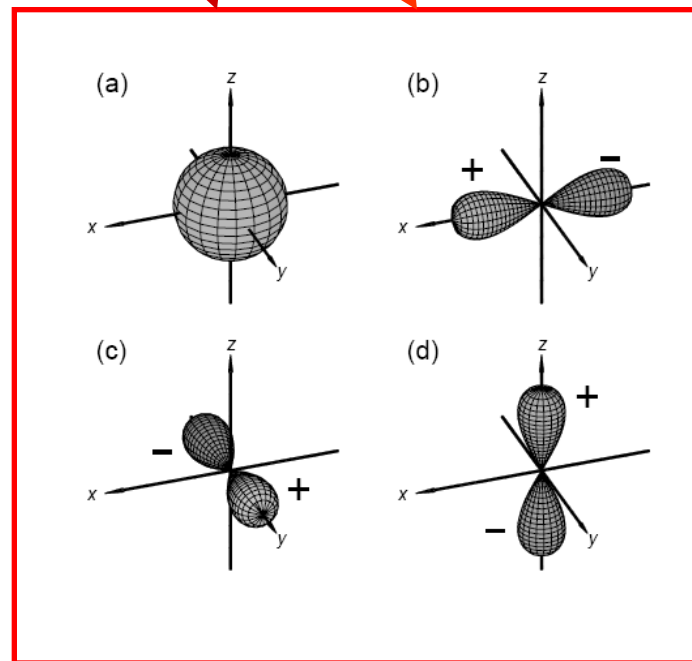
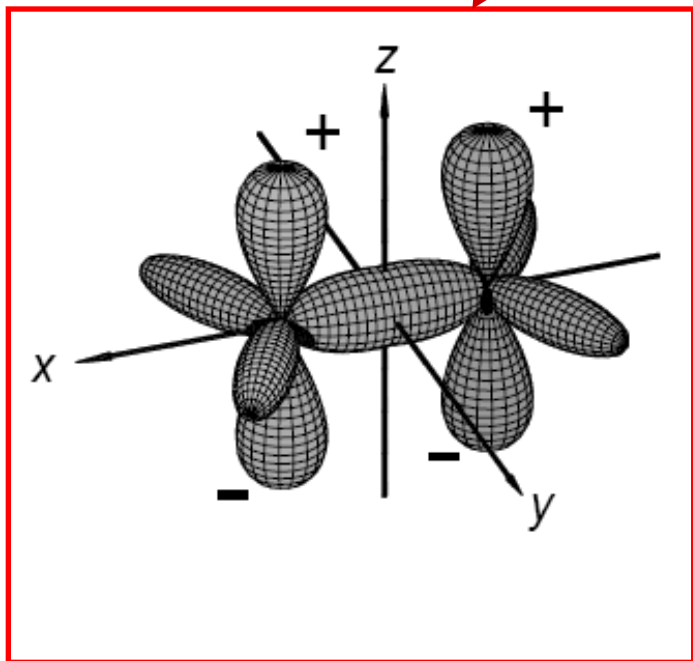
Molecular orbitals  
(MO's)

$$\chi_j(\mathbf{r}_i)$$

$$= \sum_{\mu=1}^{N_{orb}}$$

$$c_{\mu j} \phi_{\mu}(\mathbf{r}_i).$$

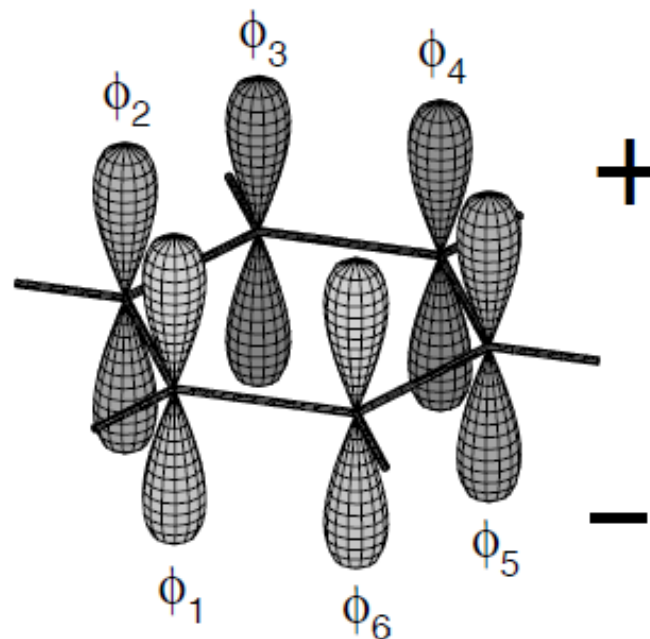
Atomic orbitals  
(AO's), 1s, 2s, 2p



## Basis sets (I)

In **LCAO-MO** computations basis functions are employed which are centered at the corresponding atomic nuclei.

For example,  $p_z$  orbitals in benzene:



The obvious choice of AO basis functions are the orbitals of the hydrogen atom. We call them Slater-type orbitals here.

- **Slater-type orbitals (STO)**

$$\phi_{\mu} = N_{nl} r^{n-1} e^{-\zeta r} Y_l^m(\theta, \varphi)$$

Good quality (exact for the H atom, qualitatively correct asymptotic behavior for  $r \rightarrow 0$  and  $r \rightarrow \infty$ ), however inefficient when computing integrals (especially three-center and four-center two-electron integrals).

## Basis sets (II)

- Gauss-type orbitals (GTO)

$$\phi_{\mu} = N_{\mu} x^l y^m z^n e^{-\alpha_{\mu} r^2}$$

Quality less high than for STOs, but very efficient computation of integrals (reason: the product of two GTOs is a new GTO so that all two-electron integrals are solvable as two-center integrals). GTO's can be expressed in terms of spherical harmonics.

**Result:** *Ab initio* LCAO-MO calculations typically make use of GTO basis functions.

### Fit of GTOs to STOs:

STOs may be simulated by a linear combination of several GTOs.

Example: energy of the H atom (au)

1 STO	1 GTO	2 GTO	3 GTO	...	6 GTO
-0.5	-0.424	-0.482	-0.495		-0.4998

## Basis sets (III)

Contracted GTOs:

$$\phi_{\mu} = x^l y^m z^n \sum_k d_{\mu k} e^{-\alpha_{\mu k} r^2}$$

Construction of basis sets: derivation of optimal contraction coefficients  $d_{\mu k}$  and exponents  $\alpha_{\mu k}$ , e.g. by fitting to STOs or by variational calculations in atoms.

## Basis sets (IV)

The quality of *ab initio* LCAO-MO results depends on the size of the employed basis.

**Minimum basis:** one basis function per atomic orbital;

e.g. for C: 5 basis functions ( $1s$ ,  $2s$ ,  $2p_x$ ,  $2p_y$ ,  $2p_z$ ).

**Double-zeta (DZ) basis:** two basis functions per atomic orbital to describe radial anisotropies;

e.g. for C: 10 basis functions.

**Triple-zeta (TZ) basis:** three basis functions per atomic orbital to increase the radial flexibility further;

e.g. for C: 15 basis functions.

## Basis sets (V)

**Polarization functions:** additional basis functions with higher angular quantum number ( $l$ ) to take into account the angular polarization; e.g. for C: d and perhaps also f basis functions.

**Diffuse functions:** additional basis functions with low exponents allowing to describe electron density at large distances from the atomic nucleus; e.g. important for anions.

**Note:** The employed basis sets must be **balanced**. The choice of suitable basis sets is a matter of experience and is done **empirically**.

**Hartree-Fock limit:** the best result obtainable with a Hartree-Fock variational calculation (converged with respect to enlargement of the basis set).