

# Introduction to Quantum & Computational Chemistry for Electronically Excited States Lecture 2

**Target:** Computer simulations are employed to study the structure and reactivity of single molecules and molecular systems (**molecule in solution or in a macromolecular cavity**).

**Tools:** We need a series of **software technologies** to describe the **electronic and geometrical structure** of molecules and their time evolution.

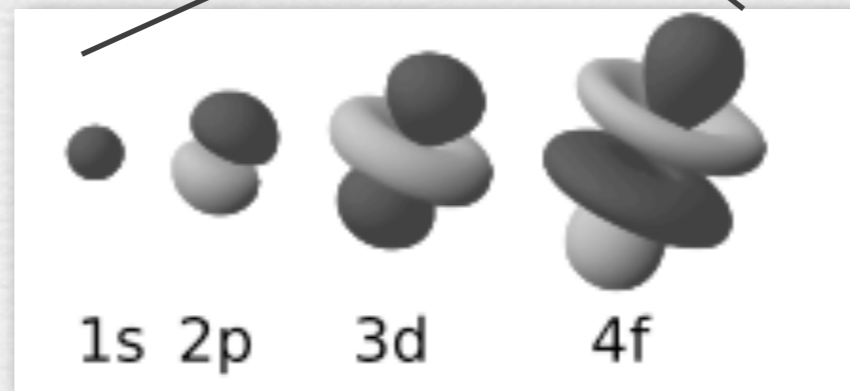
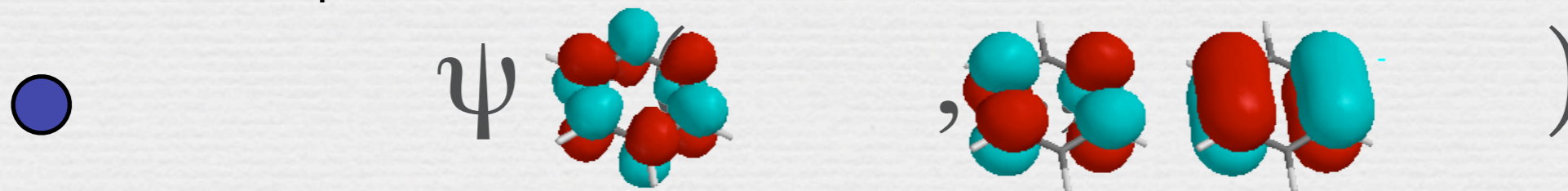
(visit <http://www.lcpp.bgsu.edu>)

# The Electronic Energy: Quantum Chemical Technologies

**Physics:** Total Charge Density (electronic wavefunction)

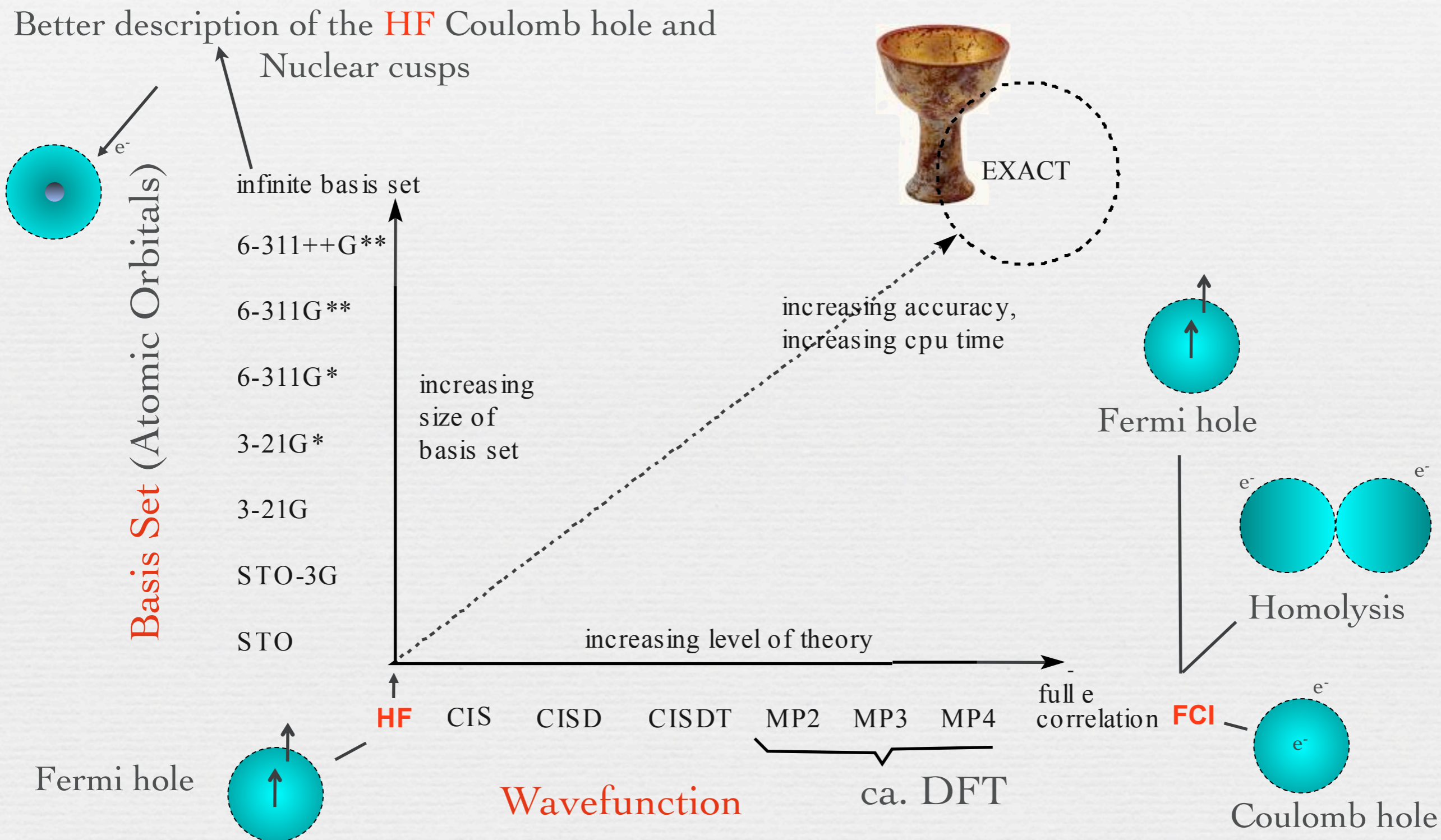
$$\bullet \quad \delta(r) = N \sum_{s1} \dots \sum_{sN} \int dr_1 \dots \int dr_N |\psi(r_1, s_1, r_2, s_2 \dots r_N, s_N)|^2$$

**Technology:** all-electron wavefunction



The “technological” wavefunction is a mathematical expression containing “hydrogen-like orbitals”

# Ab-initio Quantum Chemical Technologies: The Pople Diagram



# How to get a good wavefunction: The Variational Principle

nuclear coord.

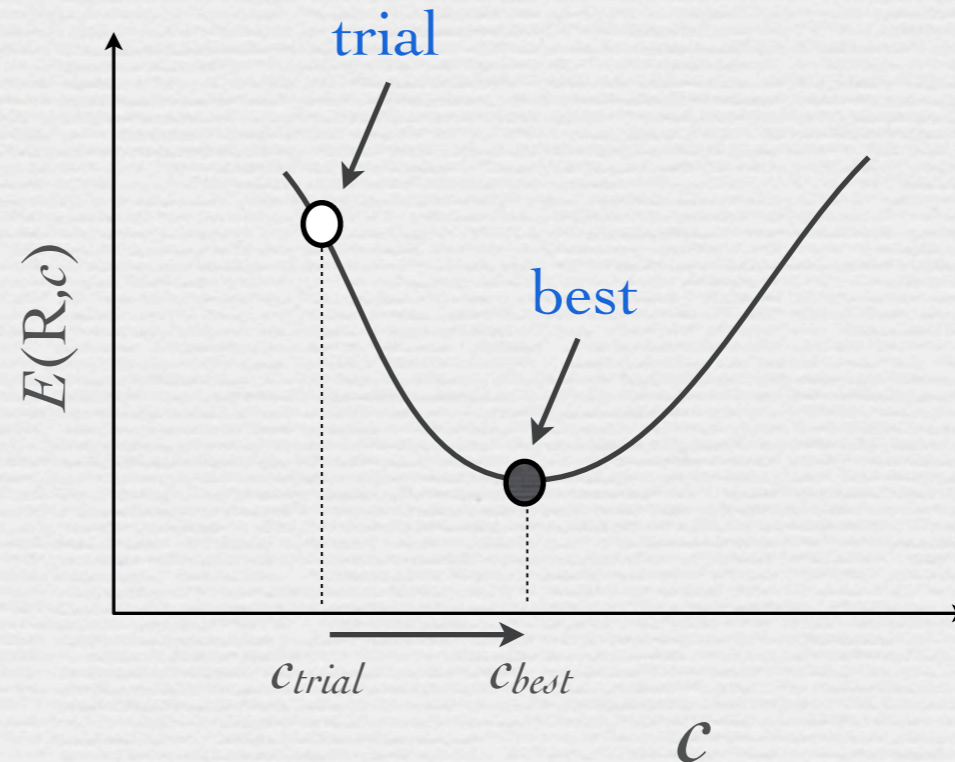
$$E_{el}(R)_{trial} = \frac{\langle \psi_{trial} | H_{el} | \psi_{trial} \rangle}{\langle \psi_{trial} | \psi_{trial} \rangle} \geq E_{el}(R)_{true}$$

Rayleigh ratio

$\Psi(c)_{trial}$        $E_{el}(R,c)_{trial}$   
 ↖                      ↗  
 variational parameters

$$\frac{\partial E_{el}(R,c)_{trial}}{\partial c} = 0$$

$$\frac{\partial^2 E_{el}(R,c)_{trial}}{\partial c^2} > 0$$



# How to get a good wavefunction: The Variational Principle

$$E_{el}(R)_{trial} = \frac{\langle \psi_{trial} | H_{el} | \psi_{trial} \rangle}{\langle \psi_{trial} | \psi_{trial} \rangle} \geq E_{el}(R)_{true} \quad \Rightarrow$$

Basis of the HF and Post-HF Methods:

$$E_{el}(R)_{trial} = \frac{\langle \psi_{trial} | H_{el} | \psi_{trial} \rangle}{\langle \psi_{trial} | \psi_{trial} \rangle} \quad \psi_{trial} = \sum_i c_i \xi_i \quad \leftarrow$$

Orthonormal set

Variational coefficients (variable)

$$E_{el}(R)_{trial} = \frac{\sum_{ij} c_i c_j \langle \xi_i | H_{el} | \xi_j \rangle}{\sum_{ij} c_i c_j \langle \xi_i | \xi_j \rangle}$$

Basis functions (fixed)

(e.g. in the following  $\xi_i$  can be either an atomic orbital or a determinant)

Notice that  $\xi_i$  = any basis function. It can be an atomic orbital, a Slater determinant or a CSF



# How to get a good wavefunction: The Variational Principle

*Matrix elements of the Hamiltonian operator*

*Basis function (a complete set of orthonormal functions)*

*Linear variational coefficients*

$$E_{el}(R)_{trial} = \frac{\sum_{ij} c_i c_j \langle \xi_i | H_{el} | \xi_j \rangle}{\sum_{ij} c_i c_j \langle \xi_i | \xi_j \rangle} = \frac{\sum_{ij} c_i c_j H_{ij}}{\sum_{ij} c_i c_j S_{ij}}$$

# The Variational Principle: the Ritz Method

Linear variational coefficients  
(variable)

if the coefficients are not linear (e.g.  
exponential) the Ritz method cannot be  
applied

$$E_{el}(R)_{trial} = \frac{\sum_{ij} c_i c_j H_{ij}}{\sum_{ij} c_i c_j S_{ij}}$$

matrix representation of the  
Hamiltonian operator

$$E_{el}(R)_{trial} = \frac{c^t H_{el} c}{c^t 1 c}$$

vector of coefficients

The matrix S for a set of orthonormal basis  
functions = the Unit matrix

# The Variational Principle: the Ritz Method (valid for linear variational coeff)

$$E_{el}(R)_{trial} = \frac{c^t H_{el} c}{c^t 1 c}$$



*small and arbitrary variation of c*

$$\delta E_{el}(R)_{trial} = \delta c^t (H_{el} - E_{el} 1) c + c^t (H_{el} - E_{el} 1) \delta c = 0$$



*H<sub>el</sub> is Hermitian, δc arbitrary*

*Secular Equation*  $\longrightarrow (H_{el} - E_{el} 1) c = 0$



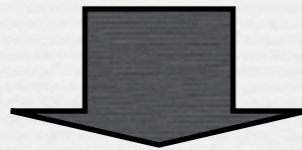
*non-trivial solution only if*

$$\text{Det} |H_{el} - E_{el} 1| = 0$$



# The Variational Principle: the Ritz Method

$$E_{el}(R)_{trial} = \frac{\sum_{ij} c_i c_j H_{ij}}{\sum_{ij} c_i c_j S_{ij}}$$



$$\text{Det} \begin{vmatrix} H_{11} - E_{el}(R)_{trial} & H_{12} & \dots & H_{1n} \\ H_{21} & H_{22} - E_{el}(R)_{trial} & \dots & H_{2n} \\ \dots & \dots & \dots & \dots \\ H_{n1} & H_{n2} & \dots & H_{nn} - E_{el}(R)_{trial} \end{vmatrix} = 0$$




diagonalization  $\longrightarrow$  eigenvectors & eigenvalues

# One way of getting a good wavefunction: The Independent Particle Model

$$H_{el} = -\frac{1}{2} \sum_i^{N_{el}} \nabla_i^2 + \cancel{\sum_i^{N_{el}} \sum_{j < i}^{N_{el}} \frac{1}{|r_i - r_j|}} - \sum_i^{N_{el}} \sum_{j < i}^{N_{nuc}} \frac{Z_j}{|r_i - R_j|}$$

$$H_{el} = -\frac{1}{2} \sum_i^{N_{el}} \nabla_i^2 - \sum_i^{N_{el}} \sum_{j < i}^{N_{nuc}} \frac{Z_j}{|r_i - R_j|} = \sum_i^{N_{el}} h_{el}(r_i)$$

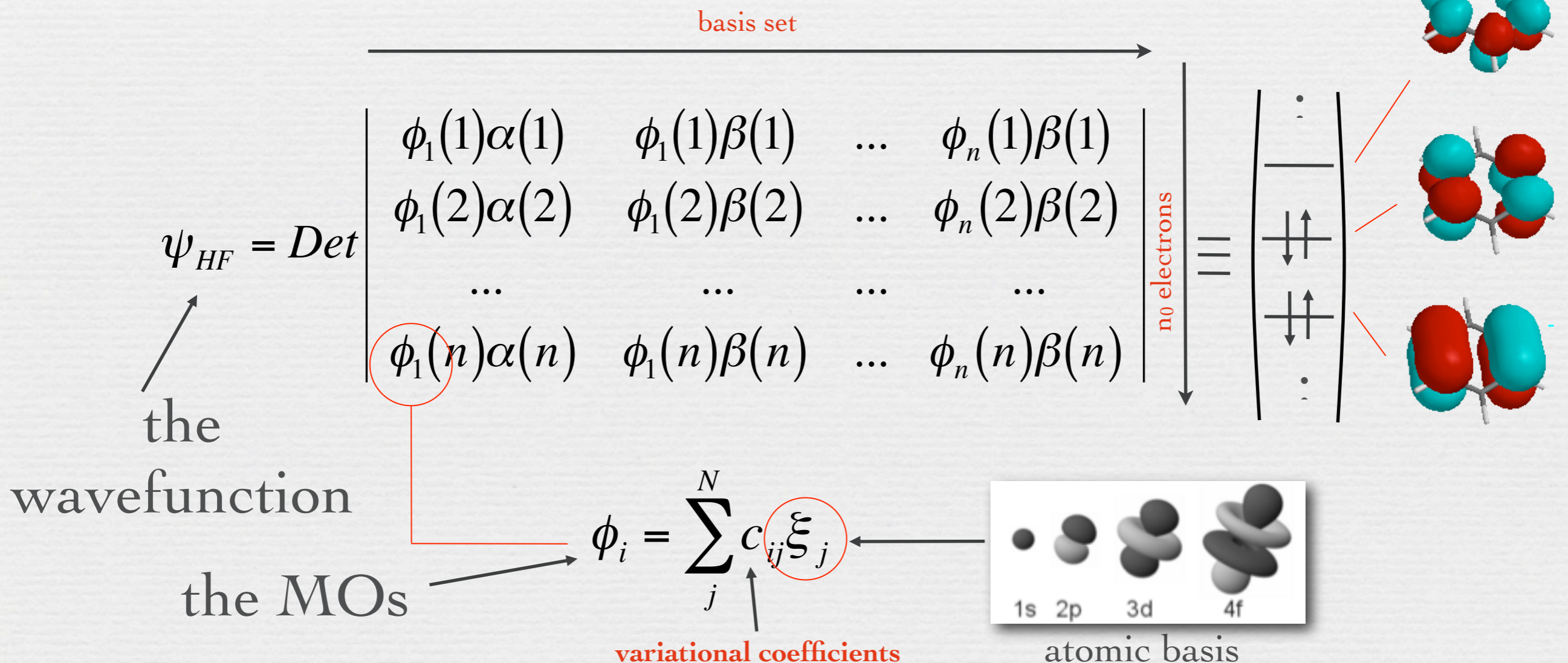
$$h_{el}(r_i) = -\frac{1}{2} \nabla_i^2 - \sum_j^{N_{nuc}} \frac{Z_j}{|r_i - R_j|} \quad \text{Hartree product (no spin functions)}$$


$$\Psi(c)_{trial} = \phi_1(r_1)\phi_2(r_2)\phi_3(r_3)\phi_4(r_4)\dots\phi_N(r_{N_{el}})$$

# Electronic Energy Computation with the Independent Particle Model: HF

The **Fermi hole** is correctly described in Hartree-Fock wavefunction but the **Coulomb hole** and the **Homolysis** are poorly described (> 5% of the electron-electron repulsion is missing).

● Far to large for chemical accuracy



# The Determinant

is a  $n \times n$  matrix

monoelectronic wavefunction  
(molecular orbital)

electronic coordinates

spin wavefunction

spin coordinate

spin-orbital

$\psi_{HF} = \text{Det}$

$$\begin{vmatrix} \phi_1(1)\alpha(1) & \phi_1(1)\beta(1) & \dots & \phi_n(1)\beta(1) \\ \phi_1(2)\alpha(2) & \phi_1(2)\beta(2) & \dots & \phi_n(2)\beta(2) \\ \dots & \dots & \dots & \dots \\ \phi_1(n)\alpha(n) & \phi_1(n)\beta(n) & \dots & \phi_n(n)\beta(n) \end{vmatrix}$$



simplified  
notations

$$\psi_{HF} = \left| \phi(1)_1 \overline{\phi(1)_1} \phi(2)_2 \overline{\phi(2)_2} \dots \phi(n)_n \overline{\phi(n)_n} \right| \quad \text{or} \quad \psi_{HF} = \left| \phi(1)_1 \phi(2)_2 \dots \phi(n)_n \right|$$

# Electronic Energy Computation: HF

Describe the relationship between the variational principle and the Fock equations.



Vladimir Fock

December 22, 1898–December 27, 1974

$$\psi_{HF} = \text{Det} \begin{array}{c} \xrightarrow{\text{basis set}} \\ \left| \begin{array}{cccc} \phi_1(1)\alpha(1) & \phi_1(1)\beta(1) & \dots & \phi_n(1)\beta(1) \\ \phi_1(2)\alpha(2) & \phi_1(2)\beta(2) & \dots & \phi_n(2)\beta(2) \\ \dots & \dots & \dots & \dots \\ \phi_1(n)\alpha(n) & \phi_1(n)\beta(n) & \dots & \phi_n(n)\beta(n) \end{array} \right| \downarrow \text{no electrons} \end{array}$$

$$E_{el}(R)_{HF} = \frac{\langle \psi_{HF} | H_{el} | \psi_{HF} \rangle}{\langle \psi_{HF} | \psi_{HF} \rangle} \geq E_{el}(R)_{true}$$

$\hat{f}$  = Fock operator

$$\hat{f} \phi_k = \epsilon_k \phi_k$$

size of basis set

(one equation for each occupied molecular orbital)

# The Slater-Condon Rules

$$H_{el} = \underbrace{-\frac{1}{2} \sum_i^{N_{el}} \nabla_i^2 - \sum_i^{N_{el}} \sum_{j < i}^{N_{nuc}} \frac{Z_j}{|r_i - R_j|}}_{F \text{ (one-electron)}} + \underbrace{\sum_i^{N_{el}} \sum_{j < i}^{N_{el}} \frac{1}{|r_i - r_j|}}_{G \text{ (two-electrons)}}$$

(i) If two determinants  $| \rangle$  and  $|' \rangle$  are **identical** and **F** and **G** are **one-electron** and **two-electron** additive operators, then:

$$\langle |F + G| \rangle = \sum_i \langle \Phi_i | F | \Phi_i \rangle + \sum_{i > j} [\langle \Phi_i \Phi_j | G | \Phi_i \Phi_j \rangle - \langle \Phi_i \Phi_j | G | \Phi_j \Phi_i \rangle]$$

(ii) If  $| \rangle$  and  $|' \rangle$  differ by a single spin-orbital ( $\Phi_p \neq \Phi'_p$ ),

$$\langle |F + G|' \rangle = \langle \Phi_p | F | \Phi'_p \rangle + \sum_j [\langle \Phi_p \Phi_j | G | \Phi'_p \Phi_j \rangle - \langle \Phi_p \Phi_j | G | \Phi_j \Phi'_p \rangle]$$

(iii) If  $| \rangle$  and  $|' \rangle$  differ by two ( $\Phi_p \neq \Phi'_p$  and  $\Phi_q \neq \Phi'_q$ ),

$$\langle |F + G|' \rangle = \langle \Phi_p \Phi_q | G | \Phi'_p \Phi'_q \rangle - \langle \Phi_p \Phi_q | G | \Phi'_q \Phi'_p \rangle$$

(iv) If  $| \rangle$  and  $|' \rangle$  differ by three or more spin orbitals, then

$$\langle |F + G|' \rangle = 0$$

(v) For the identity operator  $I$ ,  $\langle |I|' \rangle = 0$  if  $| \rangle$  and  $|' \rangle$  differ by one or more spin-orbitals.

# Electronic Energy Computation: HF

How does one find a good  $V_{MF}$ ? One way is the **single determinant trial function**  $\psi = |\phi_1 \phi_2 \phi_3 \dots \phi_n|$ , and write down  $\langle \psi | H_{el} | \psi \rangle$  using the **Slater-Condon rules**

$$\langle \psi | H_{el} | \psi \rangle = \sum_{k=occ.} \langle \phi_k | T_e + V_{e,n} | \phi_k \rangle + 1/2 \sum_{k,j=occ.}$$

$$[\langle \phi_k(1) \phi_j(2) | e^2/r_{1,2} | \phi_k(1) \phi_j(2) \rangle - \langle \phi_k(1) \phi_j(2) | e^2/r_{1,2} | \phi_j(1) \phi_k(2) \rangle]$$

and observe that Coulomb ( $J_{k,j}$ ) and exchange ( $K_{k,j}$ ) integrals among **occupied** orbitals arise.

If one minimizes this energy with respect to the  $\phi_j$ 's coefficients (c), with the constraint that

$$\langle \phi_J | \phi_K \rangle = \delta_{J,K}$$

one obtains the HF system of equations:

$$\mathbf{f} \phi_J = \varepsilon_J \phi_J = [T_e + V_{e,n}] \phi_J + \sum_k [\langle \phi_k(1) | e^2/r_{1,2} | \phi_k(1) \rangle \phi_J(2) - \langle \phi_k(1) | e^2/r_{1,2} | \phi_J(1) \rangle \phi_k(2)]$$

therefore  $\mathbf{f}$  contains the  **$J_k(1) = \langle \phi_k(1) | e^2/r_{1,2} | \phi_k(1) \rangle$**  and  **$K_k(1) = \langle \phi_k(1) | e^2/r_{1,2} | \phi_J(1) \rangle$**  **integral operators.**

# Electronic Energy Computation: HF

*A physical picture of Coulomb and Exchange interactions:*

$$J_{1,2} = \int |\phi_1(\mathbf{r})|^2 \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} |\phi_2(\mathbf{r}')|^2 d\mathbf{r} d\mathbf{r}' = \int J_1(\mathbf{r}) |\phi_2(\mathbf{r}')|^2 d\mathbf{r}' = \int |\phi_1(\mathbf{r})|^2 J_2(\mathbf{r}') d\mathbf{r}$$

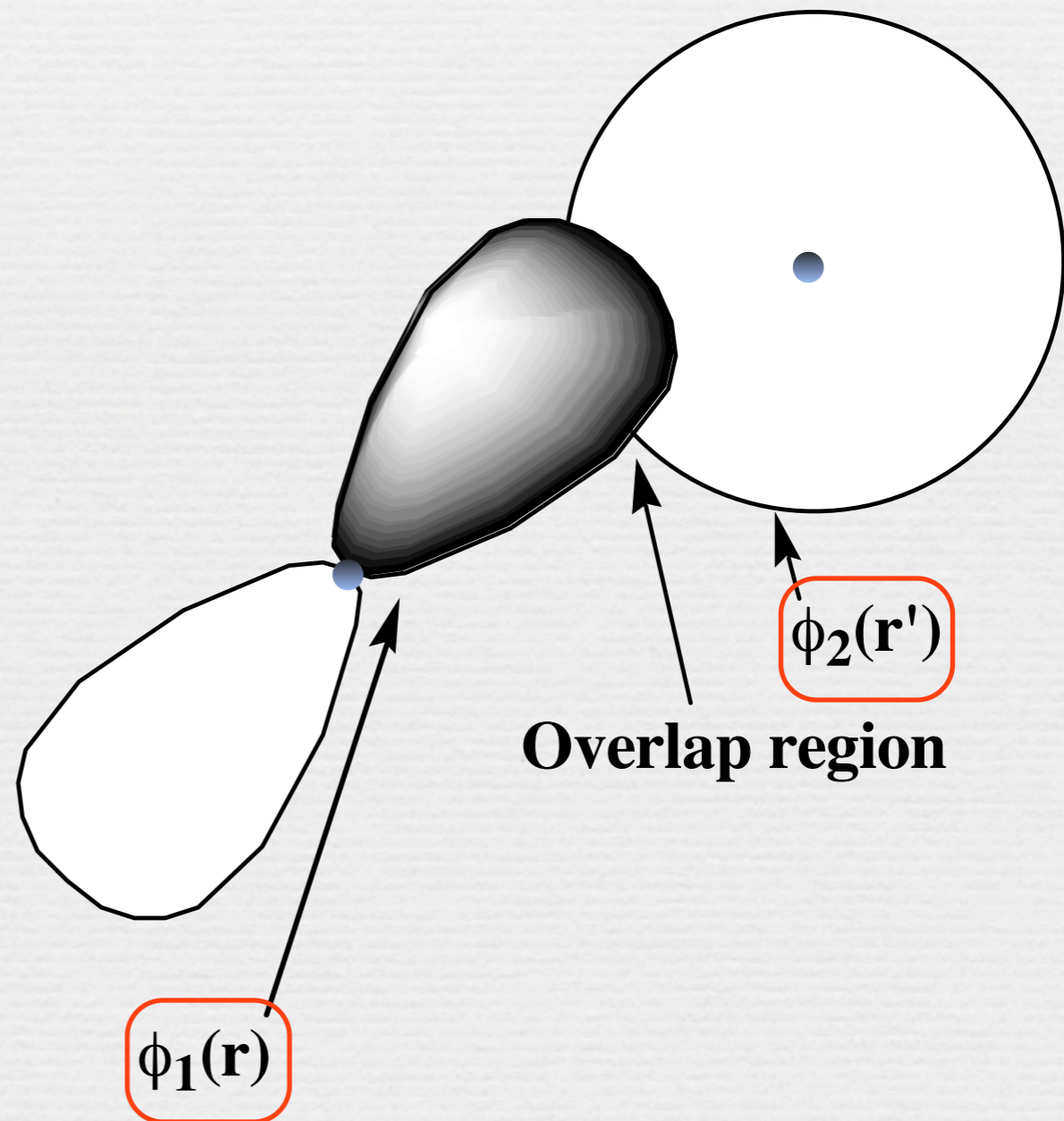
$$J_k = \int \frac{|\phi_k(\mathbf{r})|^2}{r-r'} d\mathbf{r}$$

Coulomb operator  
operates on  $\Phi_j(\mathbf{r})$

$$K_{1,2} = \int \phi_1(\mathbf{r}) \phi_2(\mathbf{r}') \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \phi_2(\mathbf{r}) \phi_1(\mathbf{r}') d\mathbf{r} d\mathbf{r}'$$

$$K_k = \int \frac{|\phi_j(\mathbf{r})\phi_k(\mathbf{r}')|}{r-r'} d\mathbf{r}$$

Exchange operator  
operates on  $\Phi_j(\mathbf{r})$  and  $\Phi_k(\mathbf{r})$





# Electronic Energy Computation: HF

$$H = T_e + V_{e,n} + V_{e,e}$$

So, one can define  $V_{MF}$  in terms of the J and K interactions. This is the **Hartree-Fock** definition of  $V_{MF}$ .

It has the characteristic that

$$E^{HF} = \langle \psi | H^{HF} | \psi \rangle \geq E^{true}$$

if  $H^{HF}$  is defined as

$$H^{HF} = T_e + V_{e,n} + (J-K).$$

In this case,

$$H - H^{HF} = V_{e,e} - (J-K).$$

Notice that it is by making a mean-field model that our (chemists') concepts of orbitals  $\phi_J$  and of electronic configurations (e.g.,  $1s \alpha 1s \beta 2s \alpha 2s \beta 2p_1 \alpha$ ) arise.

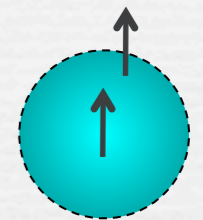
# Electronic Energy Computation: HF

How to compute the molecular orbitals efficiently ?

There are N MOs

$$f \phi_k = \varepsilon_k \phi_k$$

Occupied MOs



Fermi hole

Fock operator (for each  $k$  orbital)

Exchange

$$f = -\frac{1}{2} \nabla_k^2 - \sum_i^M \frac{Z_i}{r_{ki}} + \sum_j^N (2J_j(k) - K_j(k))$$

total number of nuclei

total number of occupied MOs

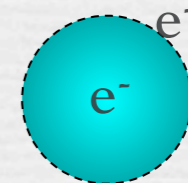
electron in orbital  $k$  interacting with electron in orbital  $i$

Coulomb

average

$$J_i(k) = \int \int \phi_i \phi_i \frac{1}{r_{12}} \phi_k \phi_k dr_1 dr_2$$

$$K_i(k) = \int \int \phi_i \phi_k \frac{1}{r_{12}} \phi_i \phi_k dr_1 dr_2$$



# Electronic Energy Computation: HF

matrix elements of the Fock operator

● Secular equations:

$$f_{\mu\nu} = \langle \xi_{\mu} | f | \xi_{\nu} \rangle \quad S_{\mu\nu} = \langle \xi_{\mu} | \xi_{\nu} \rangle$$

$$\sum_{\mu} (f_{\mu\nu} - \varepsilon S_{\mu\nu}) c_{\mu} = 0$$

The number of orbitals

- equal the number of basis functions ("atomic" orbitals).

atomic orbitals

$$\begin{array}{l} \vdots \\ \varepsilon_i, \quad \phi_i = c_{i,0}\xi_0 + c_{i,1}\xi_1 + \dots + c_{i,\mu}\xi_{\mu} + \dots \\ \vdots \\ \varepsilon_1, \quad \phi_1 = c_{1,0}\xi_0 + c_{1,1}\xi_1 + \dots + c_{1,\mu}\xi_{\mu} + \dots \\ \vdots \\ \varepsilon_0, \quad \phi_0 = c_{0,0}\xi_0 + c_{0,1}\xi_1 + \dots + c_{0,\mu}\xi_{\mu} + \dots \end{array}$$

Basis functions

Molecular orbitals coefficients (eigenvectors)

Molecular orbital energies (eigenvalues)

# Electronic Energy Computation: HF

- Orbital energies: kinetic energy of the electron + the energy resulting from the averaged interaction of the electron with the other  $2N-1$  electrons.

$$E_{el}(R) = \sum_{k=1}^N [2\varepsilon_k - \sum_{j=1}^N (2J_{kj} - K_{kj})]$$

total number of orbitals

- Electron density —  $\rho = \sum_k |\phi_k|^2$

Orbitals: linear combinations of atomic orbitals with  $c_{ik}$  being the variational coefficients.

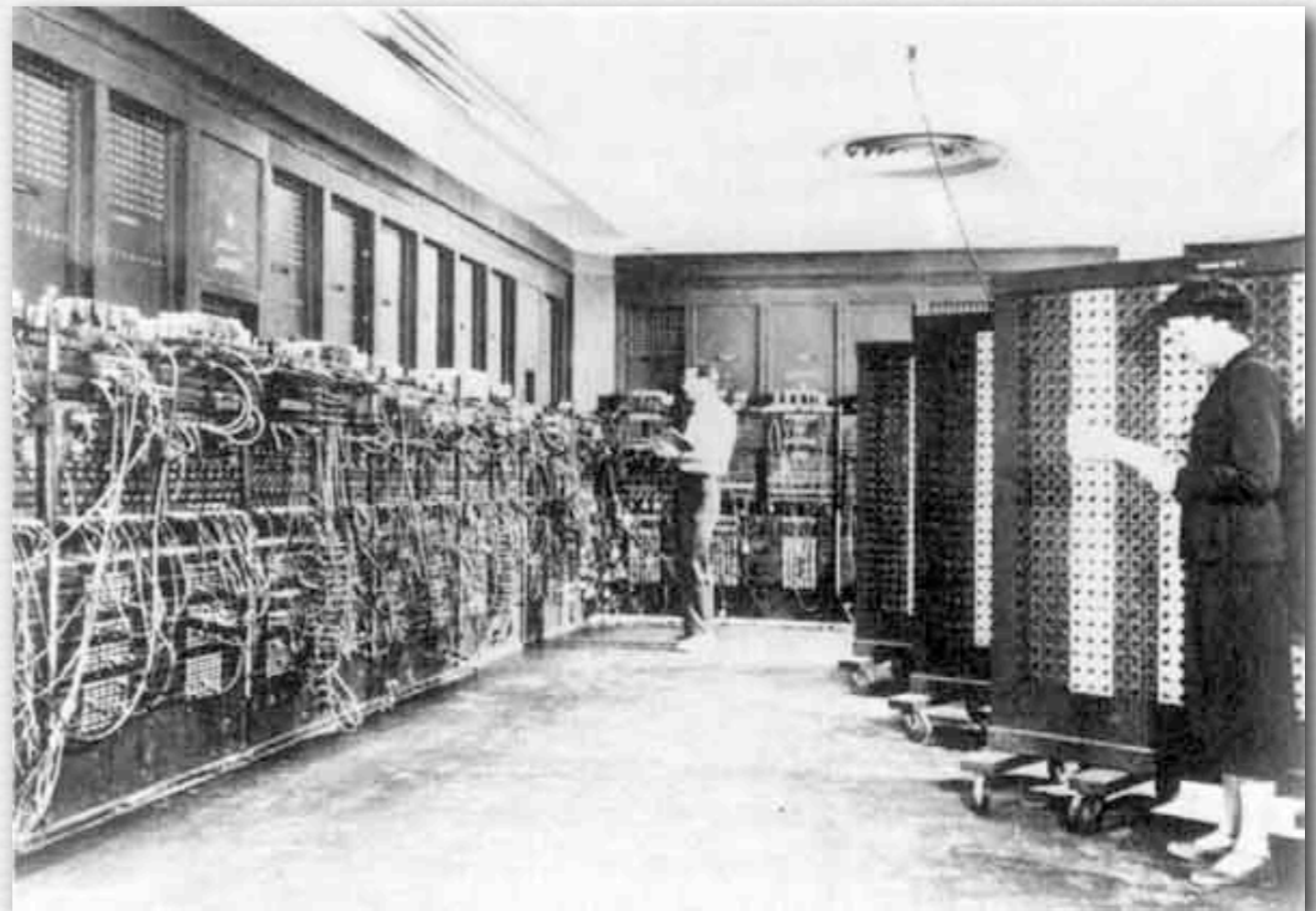
# Electronic Energy Computation: HF

ENIAC, short for Electronic Numerical Integrator and Computer



Douglas Hartree

27 March 1897 – 12 February 1958



# Hardware Technologies

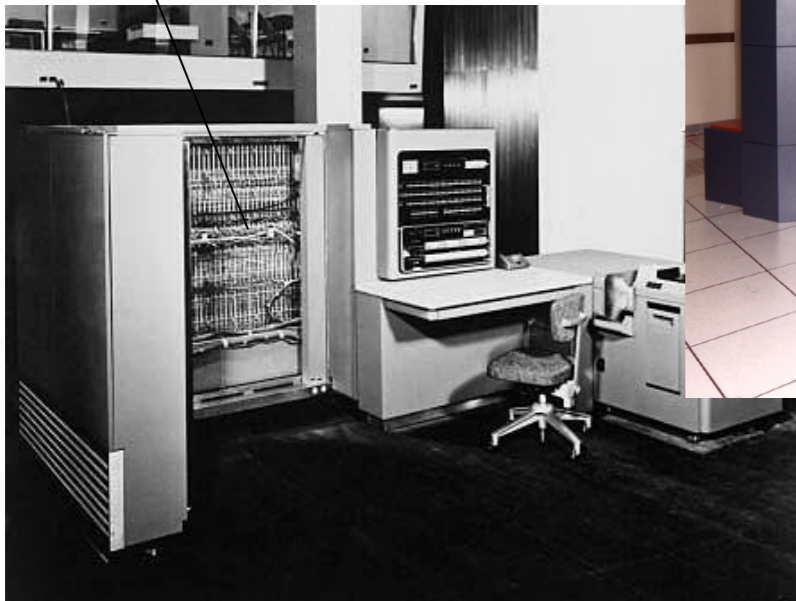
MIPS

(Millions of Operation/Sec)

FLOPS

(Floating Point Operation/Sec)

R. Mulliken



CRAY Y-MP C90, 16 CPUs **1 gigaflop** each



Dual-core Intel Xeon Woodcrest 64 CPUs  
**30 gigaflop** each, 2006



IBM RoadRunner, **1 petaflops** (6,912 AMD Opteron 2210 + 12,960 IBM Power XCell), November, 2008.

Present speed

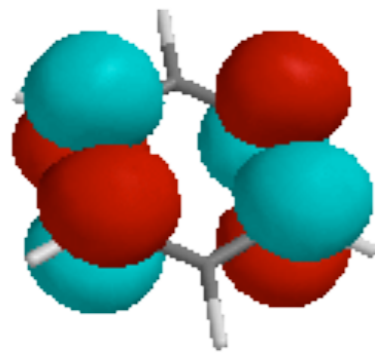
LCPP@BGSU

PostDoc in London

IBM 701 was formally announced on May 21, 1952. It could perform more than 16,000 addition or subtraction operations a second.

# "Atomic" Basis (Basis Sets)

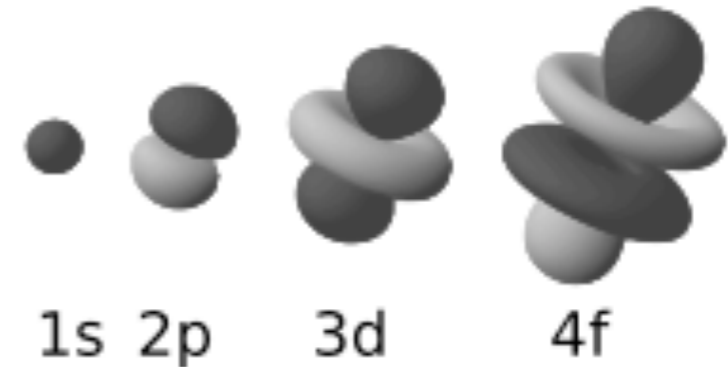
- $\xi_i$  must form a  $\approx$  complete set of orthonormal functions



HOMO (benzene)

$$\phi_i = \sum_j c_{ij} \xi_j$$

↑  
variational coefficients



Hydrogen-like orbitals

n	principal quantum number → shell	$n \geq 1$
l	angular momentum → sub-shell	$0 \leq l \leq n-1$
$m_l$	projection of l → energy shift	$-l \leq m_l \leq l$

# "Atomic" Basis (Basis Sets)

- $\xi_i$  must form a  $\approx$  complete set of orthonormal functions

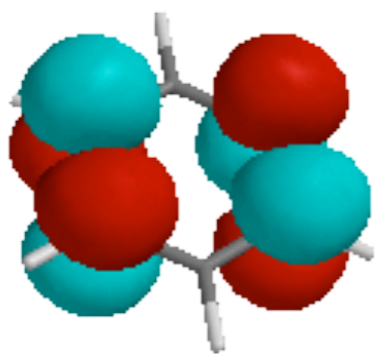
one-center  
two-centers  
three-centers  
four-centers

$$J_{kj} = \left\langle \phi_k(1)\phi_j(2) \left| \frac{1}{|r_1 - r_2|} \right| \phi_k(1)\phi_j(2) \right\rangle \Rightarrow \sum_{\alpha\beta\gamma\delta}^{M_{basis}} c_{\alpha k} c_{\gamma j} c_{\beta k} c_{\delta j} \left\langle \xi_{\alpha}(1)\xi_{\gamma}(2) \left| \frac{1}{|r_1 - r_2|} \right| \xi_{\beta}(1)\xi_{\delta}(2) \right\rangle$$

Coulomb

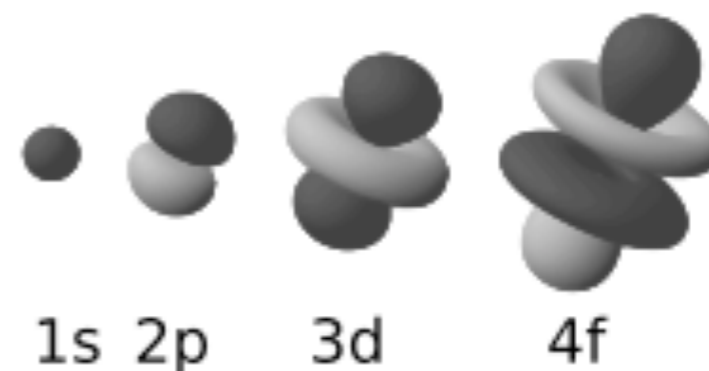
atomic integrals ! no variational coefficients  
(disk storage or direct)

variational coefficients



HOMO (benzene)

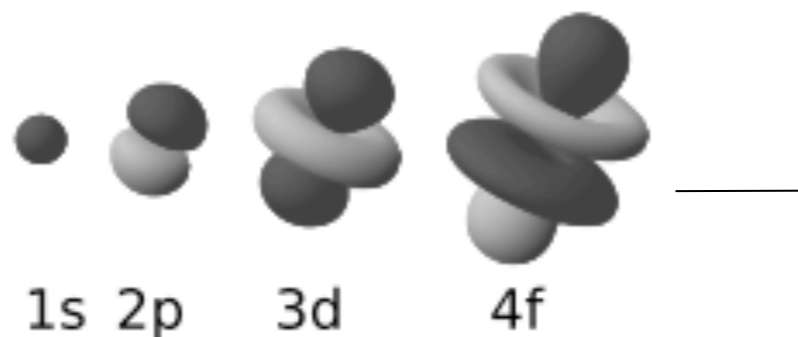
$$\phi_i = \sum_j c_{ij} \xi_j$$





# "Atomic" Basis (Basis Sets)

three-centers  
four-centers  
Integrals  
are very time-consuming to compute  
with the STO radial part



Shape  
(spherical harmonics):

$$Y_{l,m_l}(\theta, \varphi)$$

Hydrogen-like orbitals  $\longrightarrow$  Slater Type Orbitals (STO):

$$\xi_{\zeta, n, l, m_l}(r, \theta, \varphi) = N Y_{l, m_l}(\theta, \varphi) r^{n-1} e^{-\zeta r}$$

$$\zeta = \frac{Z - s}{n}$$

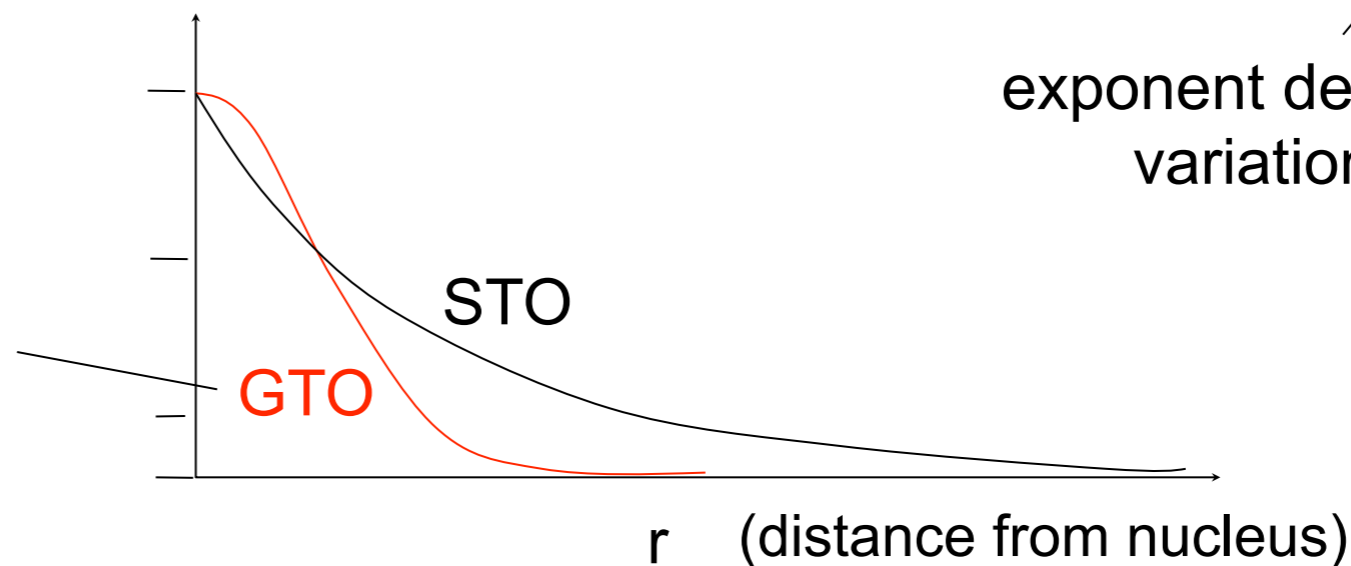
screening constant

No radial nodes

radial behavior (critical)

exponent determined  
variationally

Integrals ( $J_{kj}$  and  $K_{kj}$ )  
are fast to compute  
but not accurate



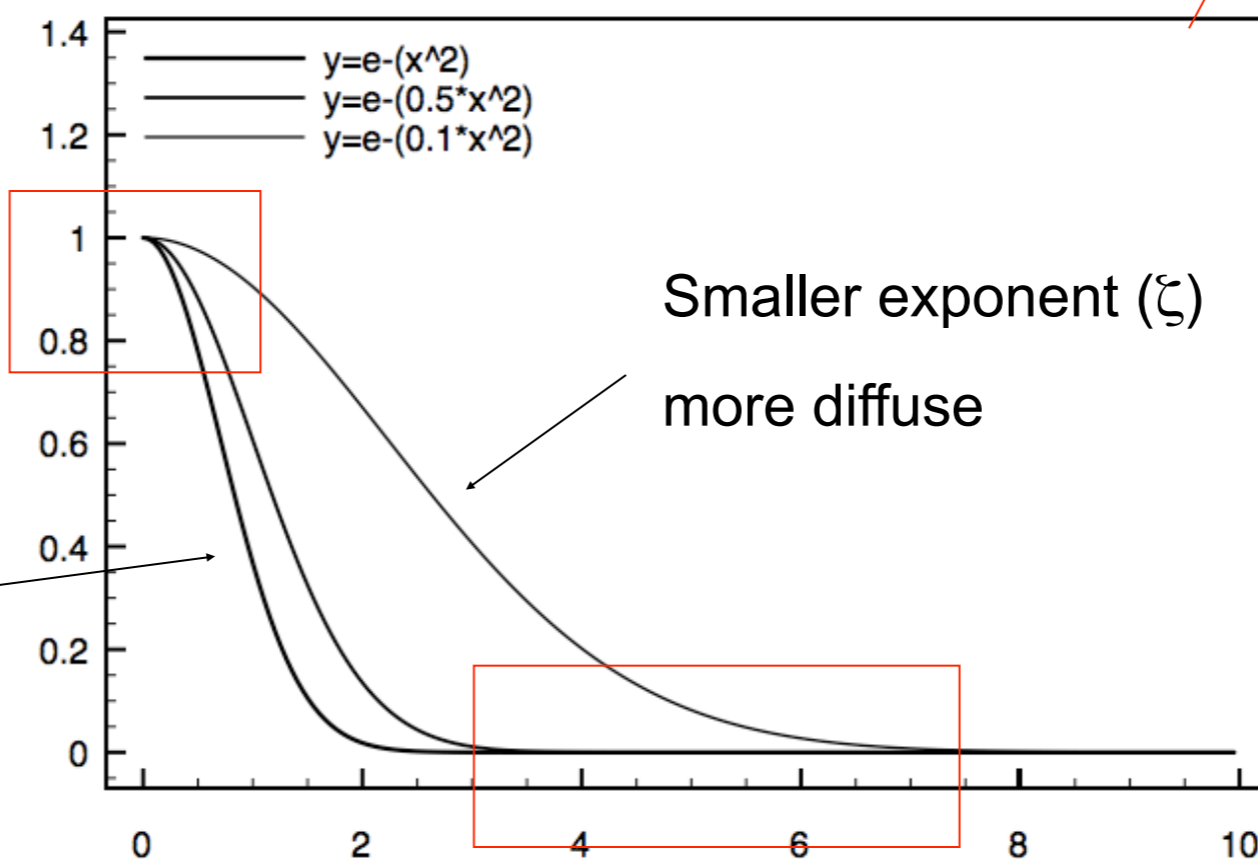
# "Atomic" Basis (Basis Sets)

## Gaussian Type Orbitals (GTO):

$$\xi_{\zeta, n, l, m_l}(r, \theta, \varphi) = N Y_{l, m_l}(\theta, \varphi) r^{2n-2-l} e^{-\zeta r^2}$$

Radial nodes

Larger exponent ( $\zeta$ )  
less diffuse



# "Atomic" Basis (Basis Sets)



John Edward Lennard-Jones (Cambridge, UK)  
1894-1954



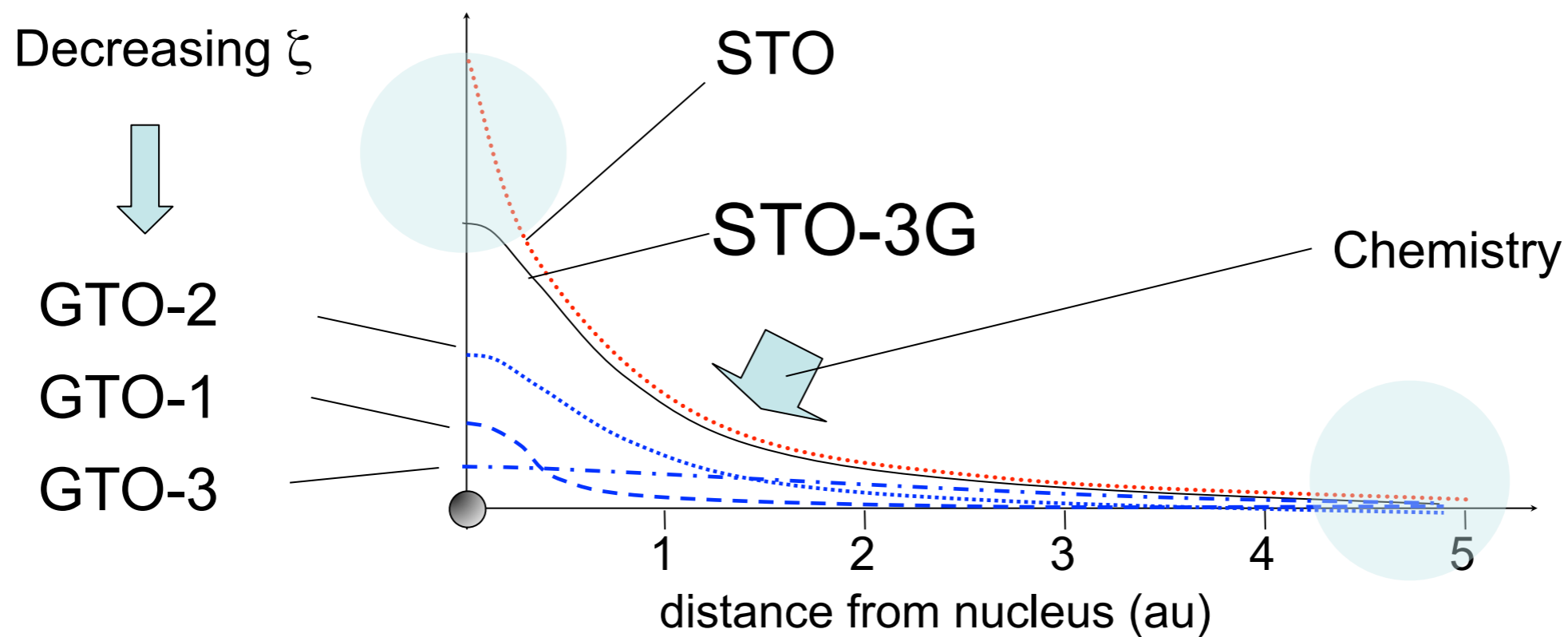
Samuel Francis Boys  
was born in 1911, he died in 1972.

S.F. Boys, G.B. Cook, C.M. Reeves and I.  
Shavvitt,

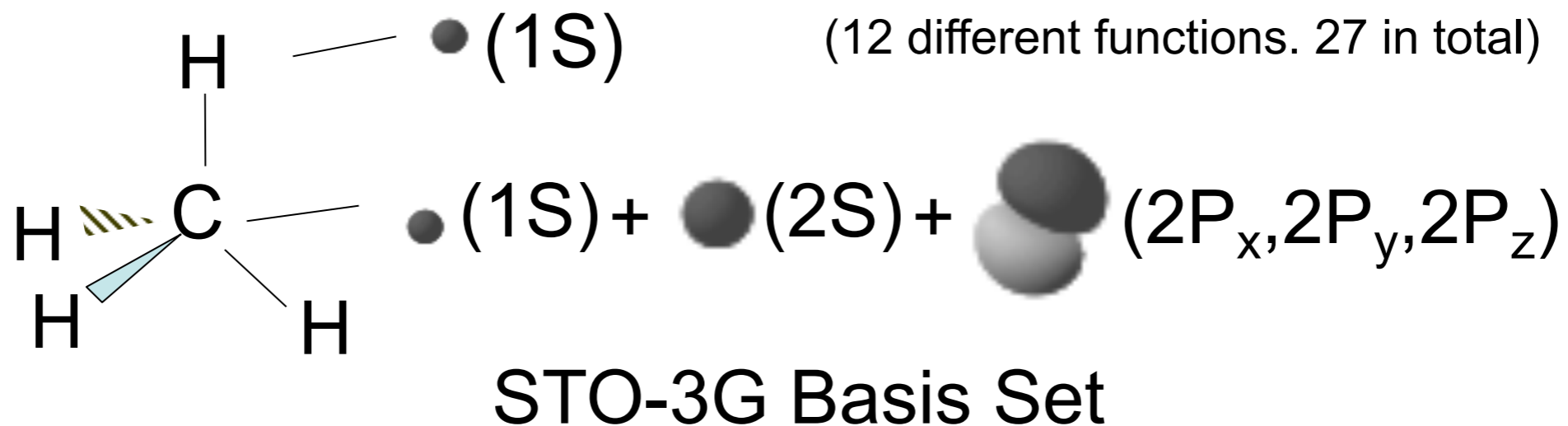
Automatic fundamental calculations of molecular  
structure.

*Nature* 178, 1207 (1958).

# "Atomic" Basis (Basis Sets)



● **Minimal Basis:** enough functions to accommodate all the electrons



**End  
Lecture 2**