

Reading Course: Quantum Many-Body Theory
Rensselaer Polytechnic Institute, Spring 2024

**The linear combination of atomic
orbitals ansatz**

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“What we have seen so far”

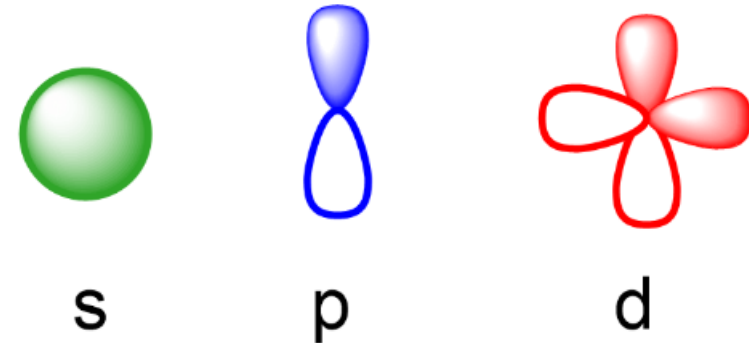
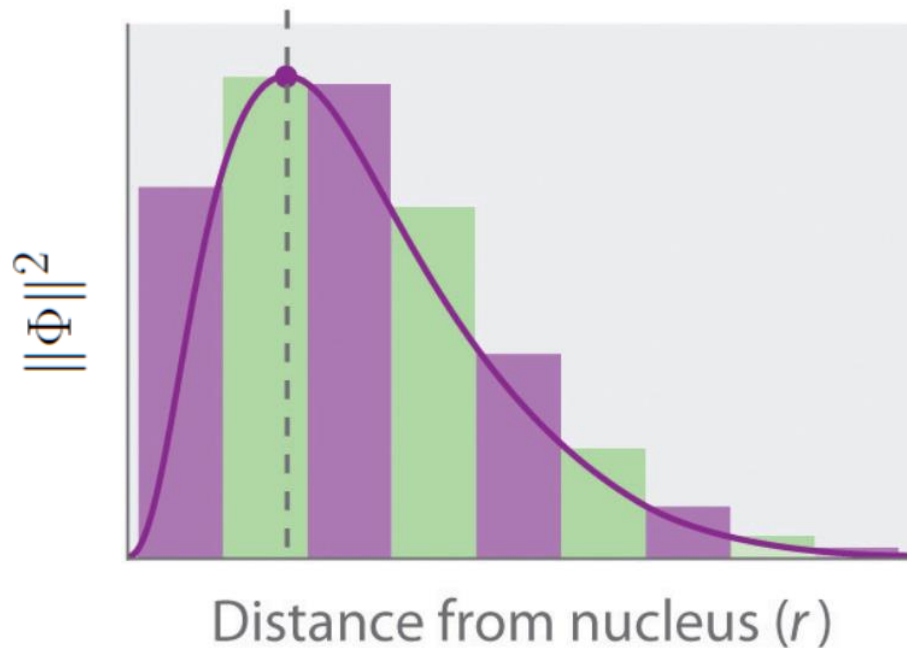
- Overview of the Quantum Many-Body Problem – Instructor
- Quantum mechanics of the hydrogen atom – Tim
- The hydrogen molecule and the Hartree-Fock method – Ben
- Second quantization I – Michael
- Second quantization II - Edie

Content

- AO (“Atomic Orbitals”)
- Connection between hydrogen atom and atomic orbitals
- What about molecules?
 - AO are not a good basis! And why???
 - Change of Basis!
- LCAO (Linear Combination of Atomic orbitals)
- Molecular orbitals

AOs (“Atomic orbitals”)

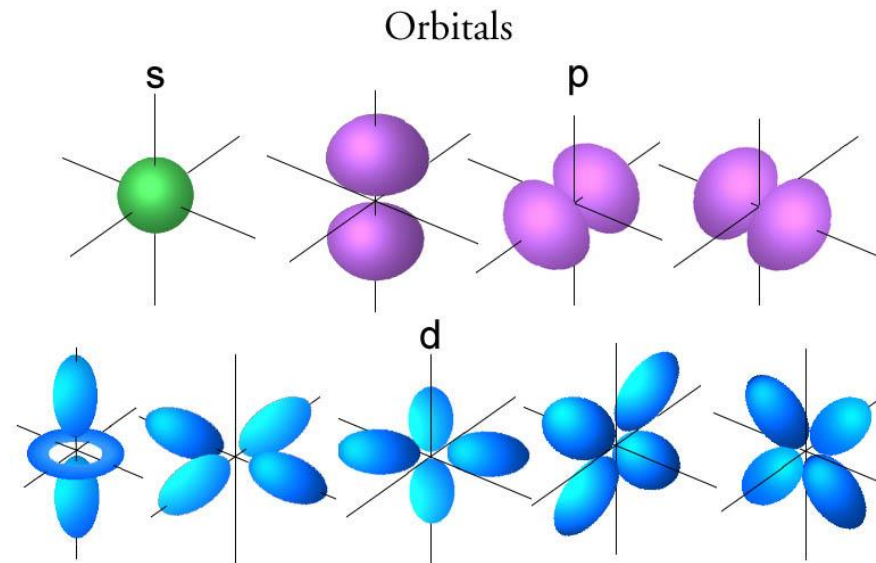
- AOs... What are they?
 - Spatial region where we are likely to find an electron
 - Orbitals are mathematically derived regions of space with different *probabilities* of having an electron.



S P D...

- Energy levels and sub levels
- Quantum numbers
- How to identify a quantum number?
- Electron configuration
Ex:- Phosphorus

Principal energy level, n	Number of Sublevels	Type of sublevel and number of orbitals	Maximum number of electrons
1	1	1s (1 orbital)	2
2	2	2s (1 orbital), 2p (3 orbitals)	8
3	3	3s (1 orbital), 3p (3 orbitals), 3d (5 orbitals)	18
4	4	4s (1 orbital), 4p (3 orbitals), 4d (5 orbitals), 4f (7 orbitals)	32
5	5	5s (1 orbital), 5p (3 orbitals) 5d (5 orbitals), 5f (7 orbitals) 5g (9 orbitals)	50



AOs (“Spatial and Spin Orbitals”)

- Spatial Orbitals... What are they?
 - A spatial orbital is a function of the position vector $r \in \mathbb{R}^3$ describing the spatial probability distribution of locating an electron.
- Spin Orbitals... What are they?
 - Spin up spin down

Spatial orbitals - $\Phi(r)$

Spin up - $\alpha(\omega)$ and spin down - $\beta(\omega)$

AOs are well studied

- Basis set exchange
 - A web portal that provides advanced browsing and download capabilities, facilities for contributing basis set data, and an environment that incorporates tools to foster development and interaction of communities.

The screenshot shows the Basis Set Exchange website. The header includes the logo and navigation links: Download, GitHub, Feedback, About, Help, and Request a Basis set. The main content area is divided into several sections:

- Orbital basis:** A dropdown menu set to "All Electron" and a list of basis sets. The selected basis set is "cc-pCVDZ".
- Total found: 309 basis sets:** A periodic table where elements are color-coded to represent different basis sets. A "Select All" button and a "Reset Selection" button are present.
- References for selected basis:** A section with a "Plain Text" dropdown and a "Get References" button.
- Download basis set:** A section with a "Format" dropdown set to "NWChem" and a "Get Basis Set" button, with an "Advanced" link next to it.

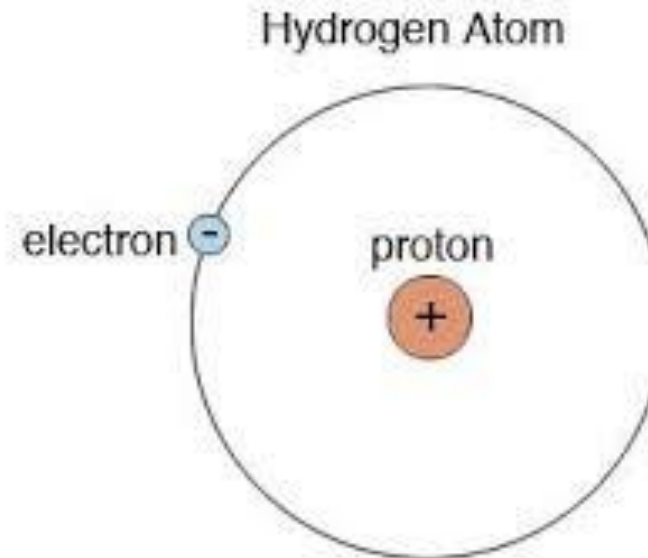
AOs are well studied

- How to use?
 - Ex:
 - Basis set: 6-31++G* (John Pople)
 - Molecule: H₂O
 - 6, 31, *, ++ stands for...

```
#-----  
# Basis Set Exchange  
# Version v0.9.1  
# https://www.basissetexchange.org  
#-----  
#   Basis set: 6-31++G*  
# Description: 6-31G + diffuse functions on all atoms, polarization on  
#               heavy atoms  
#   Role: orbital  
#   Version: 1 (Data from Gaussian 09/GAMESS)  
#-----  
  
BASIS "ao basis" CARTESIAN PRINT  
#BASIS SET: (5s) -> [3s]  
H   S  
    0.1873113696E+02      0.3349460434E-01  
    0.2825394365E+01      0.2347269535E+00  
    0.6401216923E+00      0.8137573261E+00  
H   S  
    0.1612777588E+00      1.0000000  
H   S  
    0.3600000000E-01      0.1000000000E+01  
#BASIS SET: (11s,5p,1d) -> [4s,3p,1d]  
O   S  
    0.5484671660E+04      0.1831074430E-02  
    0.8252349460E+03      0.1395017220E-01  
    0.1880469580E+03      0.6844507810E-01  
    0.5296450000E+02      0.2327143360E+00  
    0.1689757040E+02      0.4701928980E+00  
    0.5799635340E+01      0.3585208530E+00  
O   SP  
    0.1553961625E+02      -0.1107775495E+00      0.7087426823E-01  
    0.3599933586E+01      -0.1480262627E+00      0.3397528391E+00  
    0.1013761750E+01      0.1130767015E+01      0.7271585773E+00  
O   SP  
    0.2700058226E+00      0.1000000000E+01      0.1000000000E+01  
O   SP  
    0.8450000000E-01      0.1000000000E+01      0.1000000000E+01  
O   D  
    0.8000000000E+00      1.0000000  
END
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Hydrogen atom and AOs

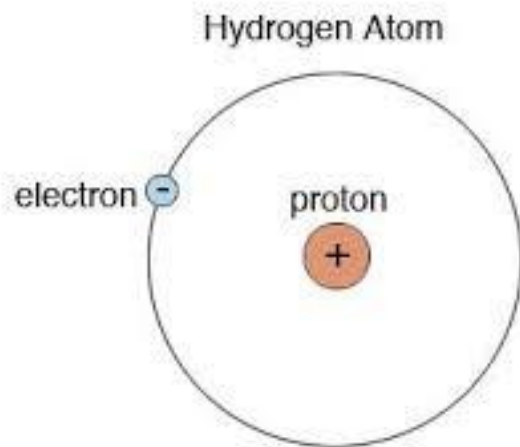
- For the hydrogen atom, the cusp in the radial probability plot occurs at $r = 0.529 \text{ \AA}$ (52.9 pm), which is exactly the radius calculated by Bohr for the $n = 1$ orbit.
 - ❖ Thus the *most probable radius* obtained from quantum mechanics is identical to the radius calculated by classical mechanics.



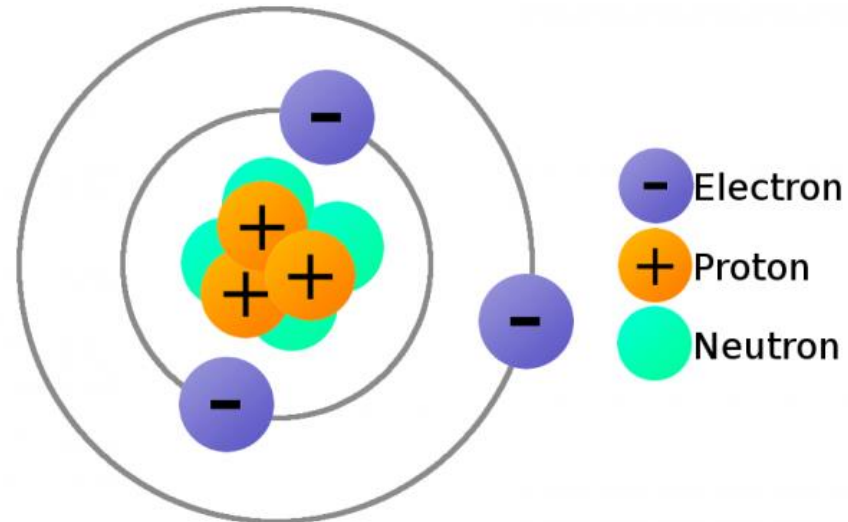
Single electron functions

- All of the atomic orbitals describe “single electron functions”
 - That is: it is a function of $\mathbb{R}^3 \times \{\pm\frac{1}{2}\}$

For H_2

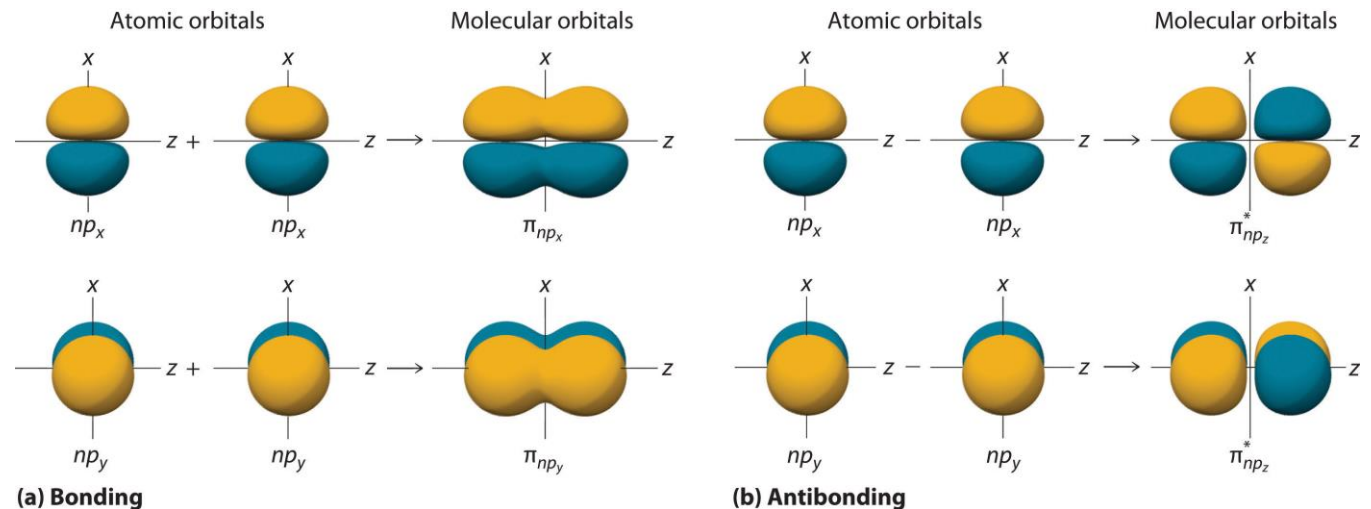
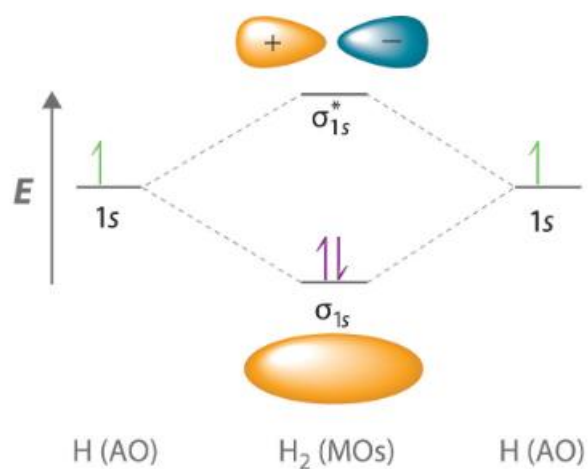


For any atom (Ex: Li)



MOs (“Molecular orbitals”)

- MOs... What are they?
 - a mathematical function describing the location and wave-like behavior of an electron in a molecule.
- Difference to AOs
 - atomic orbitals represent electron density in space associated with a particular atom. Molecular orbitals are associated with the entire molecule, meaning the electron density is delocalized (spread out) over more than one atom.



Still a single electron function

- From the given set of AOs we can obtain MOs as single electron functions

$$\{\Phi_i\}_{i=1}^k \rightarrow \{\chi_i\}_{i=1}^k$$

- Our Approach (Ansatz): **LCAO**

$$\chi_i(x) = \sum_{j=1}^k C_{ij} \Phi_j(x), x \in \mathbb{R}^3 \times \{\pm \frac{1}{2}\}$$

HF optimizes C_{ij} 's such that certain conditions are fulfilled

Can you guess???

Linear combination

- For two hydrogen atoms...
 - One electron each – 1s
- We have 1S atomic orbitals
 - Let $\Phi_1 = 1S(\text{atom 1}), \Phi_2 = 1s(\text{atom 2})$
- Then

$$\chi_1(x) = C_1\Phi_1(x) + C_2\Phi_2(x), x \in \mathbb{R}^3 \times \{\pm\frac{1}{2}\}$$

Linear combination of 1s and 1s. Still a single electron function

Linear combination

- For two Carbon atoms...
 - 6 electrons each – 1s, 2s, 2p
- We have 1S, 2S and 2P atomic orbitals
 - Let $\Phi_1 = 1S, \Phi_2 = 2s, \Phi_3 = 2P$
- Then

$$\chi_2(x) = C_2\Phi_2(x) + C_3\Phi_3(x), x \in \mathcal{R}^3 \times \{\pm\frac{1}{2}\}$$

Linear combination of 2s and 2p. Still a single electron function

Objective

- Obtain the minimized the Hartree-Fock energy
- For N electrons...

$$\min_{\chi_i} \mathcal{E}_{HF}(\{\chi_{i=1}^N\}) = \min_{C_{ij}} \hat{\mathcal{E}}_{HF}\{C_{ij}\}$$

where, $\{i = 1, \dots, N\}$ and $\{j = 1, \dots, k\}$

Ansatz with AOs

For a given molecule, we have a set of basis functions

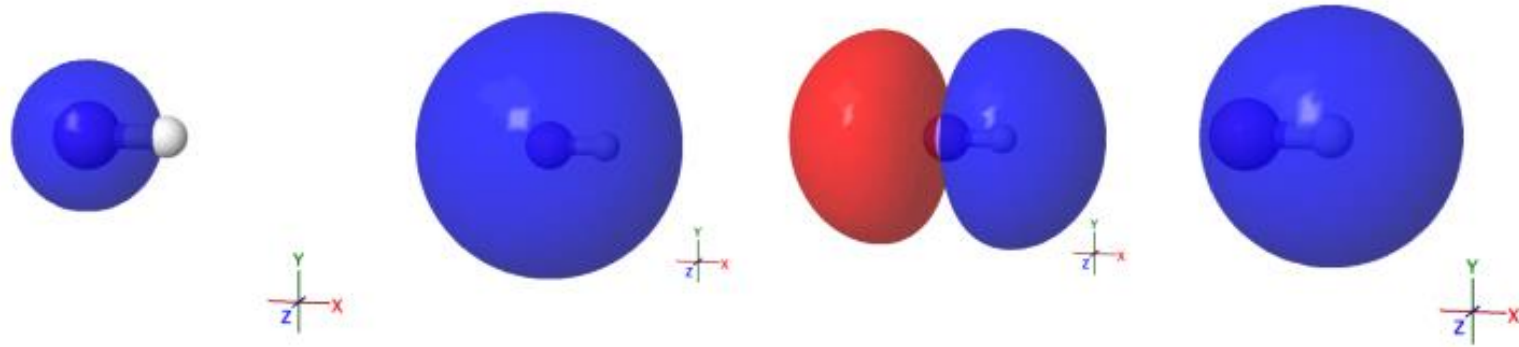
$$\{\phi_1, \dots, \phi_K \mid \phi_i \in L^2(X) \text{ and } \langle \phi_i, \phi_j \rangle_x = \delta_{i,j}\}$$

where

$$\langle \phi_i, \phi_j \rangle_x = \int_X \phi_i^*(x) \phi_j(x) dx = \sum_{\sigma \in \{\pm 1/2\}} \int_{\mathbb{R}^3} \phi_i^*(r, \sigma) \phi_j(r, \sigma) dr$$

Graphical representation

For a given molecule, we have a set of basis functions



Continue...

For a given molecule, we have a set of basis functions

$$\{\phi_1, \dots, \phi_K\}$$

We can build N -particle functions (Slater determinants)

$$\Phi[i_1, \dots, i_N] = \frac{1}{\sqrt{N!}} \phi_{i_1} \wedge \dots \wedge \phi_{i_N}$$

that form a basis for our numerics.

Are they “any good”? Does

$$\langle \Phi[i_1, \dots, i_N], H\Phi[i_1, \dots, i_N] \rangle$$

mean anything?

Minimize the Hartree-Fock energy (End goal)

- The best single Slater determinant that approximates E_0
- For N electrons...

$$\min_{|\Psi\rangle \in \mathcal{M}} \langle \Psi | \mathcal{H} | \Psi \rangle = E_0$$

where,

$$\mathcal{M} = \{ \Psi \in \mathcal{H}^N \mid \Psi = \frac{1}{\sqrt{N!}} \chi_1 \wedge \dots \wedge \chi_N, \chi_i = \sum_{j=1}^k C_{ij} \Phi_j, \langle \chi_i, \chi_l \rangle = \delta_{ij} \}$$

And note that this set is determined by $\{C_{ij}\}$

Hartree-Fock energy via AOs

$$\begin{aligned}\mathcal{E}_{\text{HF}}(\{\phi_i\}_{i=1}^N) &= \sum_{i=1}^N \int_{\mathcal{X}} \frac{1}{2} |\nabla_r \phi_i(x)|^2 + V_{\text{ext}}(r) |\phi_i(x)| dx \\ &\quad + \frac{1}{2} \sum_{i,j} \int_{\mathcal{X} \times \mathcal{X}} \frac{|\phi_i(x)|^2 |\phi_j(x')|^2}{\|r - r'\|} dx dx' \\ &\quad - \frac{1}{2} \sum_{i,j} \int_{\mathcal{X} \times \mathcal{X}} \frac{\phi_i^*(x) \phi_j^*(x') \phi_j(x) \phi_i(x')}{\|r - r'\|} dx dx' \\ &= \sum_{i=1}^N \langle i || i \rangle - \frac{1}{2} \sum_{i,j} \langle ij || ij \rangle - \langle ij || ji \rangle\end{aligned}$$

Question: Can we find $\{\xi_i\}_{i=1}^N$ that minimize \mathcal{E}_{HF} ?

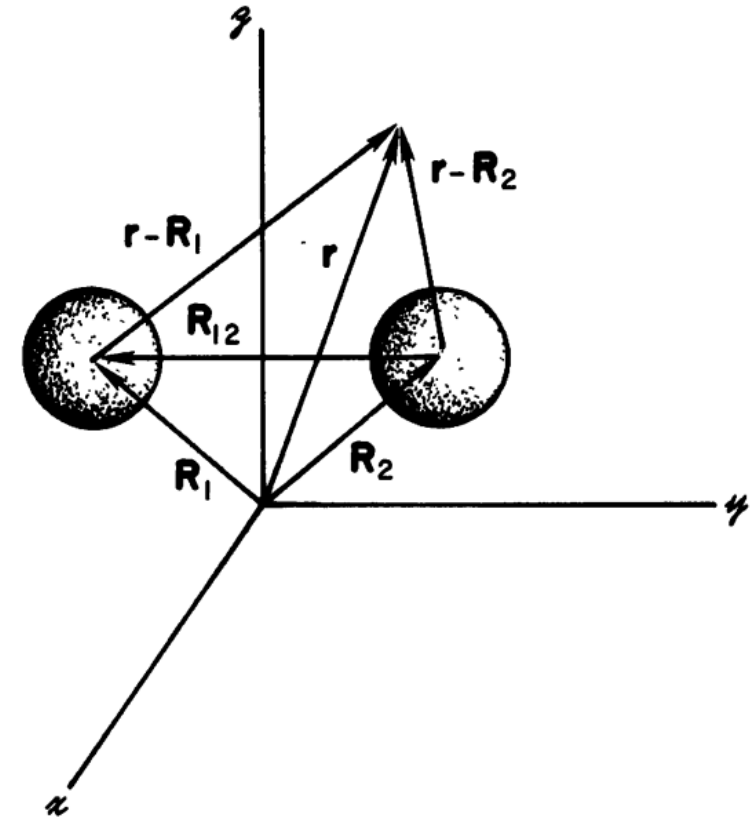
$$E_{\text{HF}} := \min_{\{\phi_i\}_{i=1}^N, \langle \phi_i, \phi_j \rangle = \delta_{i,j}} \mathcal{E}_{\text{HF}}(\{\phi_i\}_{i=1}^N)$$

Why???

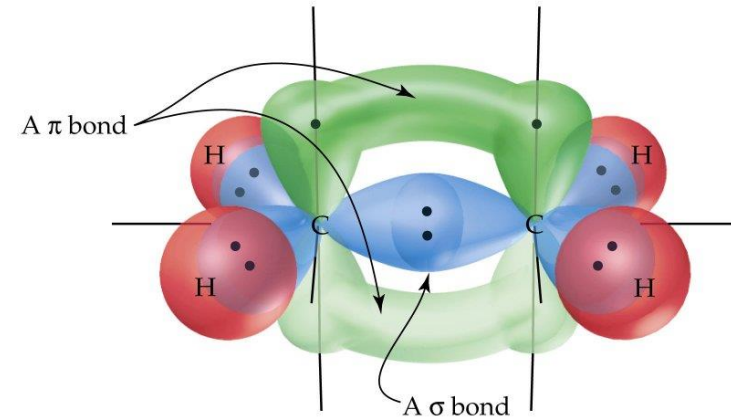
- For the present, we need not be concerned with the particular form of the 1S orbital. The two atomic orbitals can be assumed to be normalized, but they will not be orthogonal.

- They will overlap, such that overlap integral is

$$S_{12} = \int d\mathbf{r} \phi_1^*(\mathbf{r})\phi_2(\mathbf{r})$$



Why???



- The overlap will depend on the distance $R_{12} = |R_1 - R_2|$, such that $S_{12} = 1$ when $R_{12} = 0$ and $S_{12} = 0$ when R_{12} goes to infinity.
- From the two localized atomic orbitals Φ_1 and Φ_2 one can form, by linear combination, two delocalized molecular orbitals.
- One atomic orbital is said to be orthogonal to another atomic orbital if there is no interaction between the electrons in one orbital with the electrons (wavefunction) in the other orthogonal orbital.

Hartree-Fock energy via MOs

Substituting the LCAO into \mathcal{E}_{HF} yields

$$\begin{aligned}\mathcal{E}_{\text{HF}}(C) &= \sum_{i=1}^N \frac{1}{2} \sum_{j,k=1}^K C_{i,j}^* C_{i,k} \langle \nabla \phi_j, \nabla \phi_k \rangle \\ &\quad - \sum_{i=1}^N \sum_{j,k=1}^K C_{i,j}^* C_{i,k} \langle \phi_j, V_{\text{ext}} \phi_k \rangle \\ &\quad + \frac{1}{2} \sum_{i_1=1}^N \sum_{j_1,k_1=1}^K C_{i_1,j_1}^* C_{i_1,k_1} \sum_{i_2=1}^N \sum_{j_2,k_2=1}^K C_{i_2,j_2}^* C_{i_2,k_2} \langle \langle j_1 k_1 || j_2 k_2 \rangle \rangle \\ &\quad - \frac{1}{2} \sum_{i_1=1}^N \sum_{j_1,k_1=1}^K C_{i_1,j_1}^* C_{i_1,k_1} \sum_{i_2=1}^N \sum_{j_2,k_2=1}^K C_{i_2,j_2}^* C_{i_2,k_2} \langle \langle j_1 j_2 || k_1 k_2 \rangle \rangle\end{aligned}$$

Continue...

$$\chi_i(x) = \sum_{j=1}^k C_{ij} \Phi_j(x), x \in \mathbb{R}^3 \times \{\pm \frac{1}{2}\}$$

$$E_0 = \min_{|\Psi\rangle \in \mathcal{M}} \langle \Psi | \mathcal{H} | \Psi \rangle$$

Here to obtain this minimum energy we will require

$$\delta_{il} = \langle \chi_i, \chi_l \rangle = \sum_{j,m} C_{j,i}^* \langle \Phi_j, \Phi_m \rangle C_{m,l} = C^* S C$$

With $S_{ij} = \langle \Phi_i, \Phi_j \rangle$

Continue...

$$\rightarrow C_* = \arg \min_{C \in C(k)} \langle \chi_{i_1} \wedge \dots \wedge \chi_{i_N} | \mathcal{H} | \chi_{i_1} \wedge \dots \wedge \chi_{i_N} \rangle$$

Where C is unitary!!!

END

Thank you!!!

Questions???