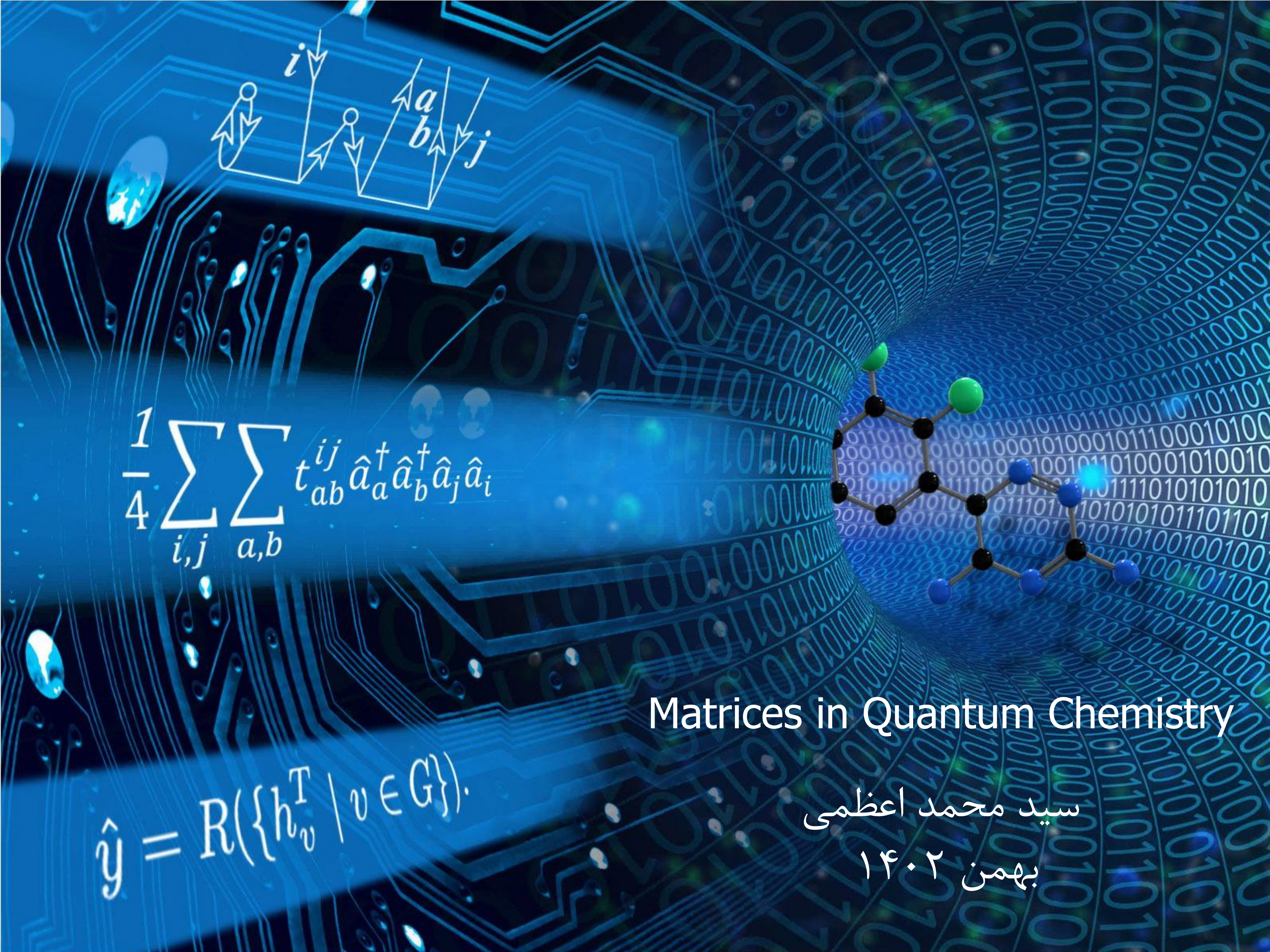
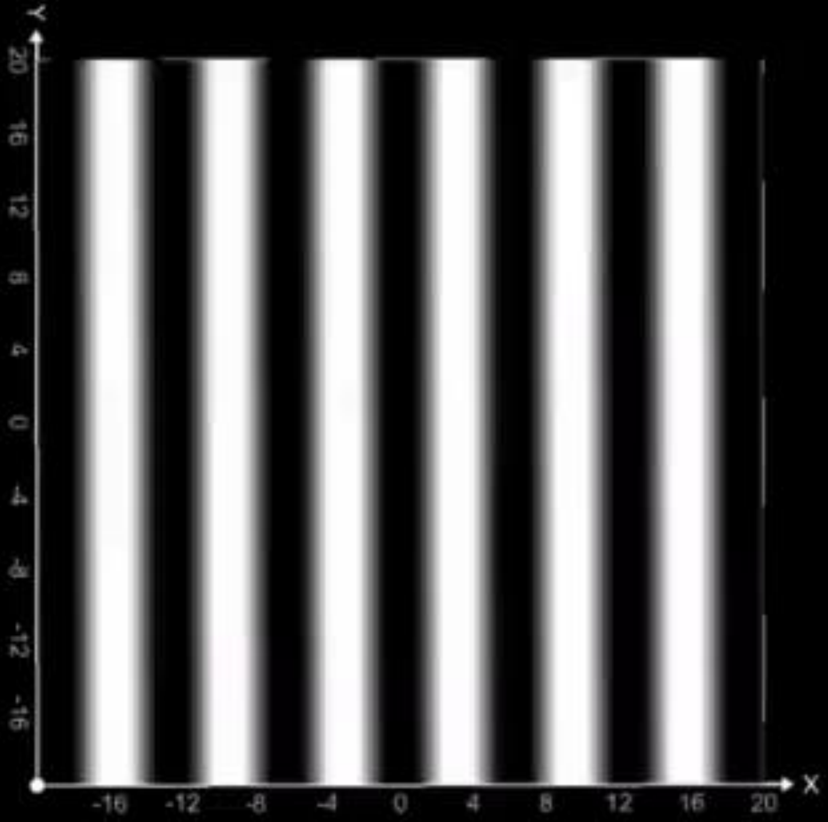


Matrices in Quantum Chemistry

سید محمد اعظمی

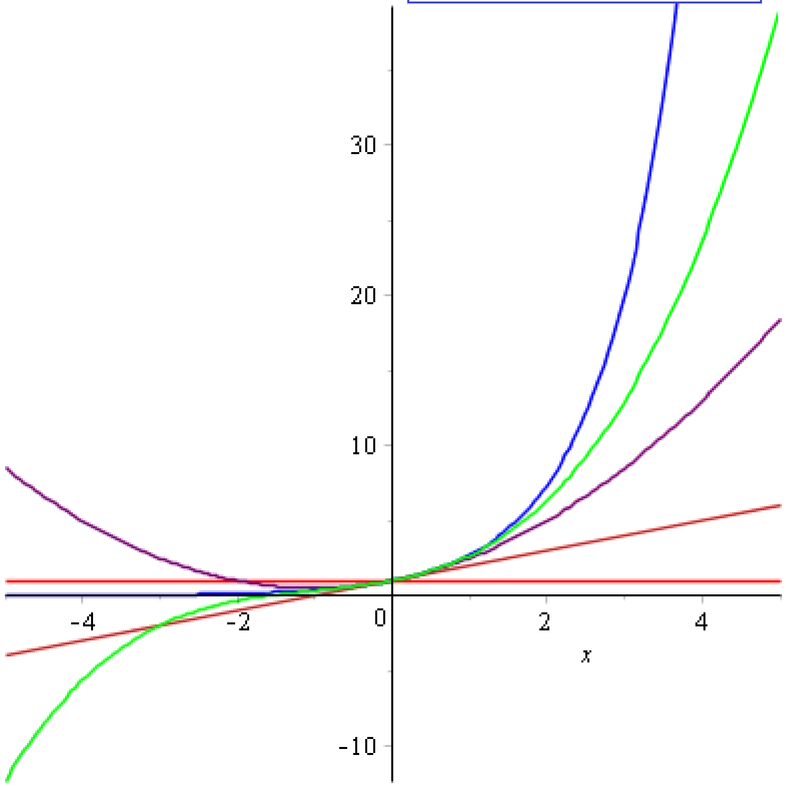
بهمن ۱۴۰۲

$$z = \cos x$$



$y = e^x$ is in blue

$y = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!}$ is in green

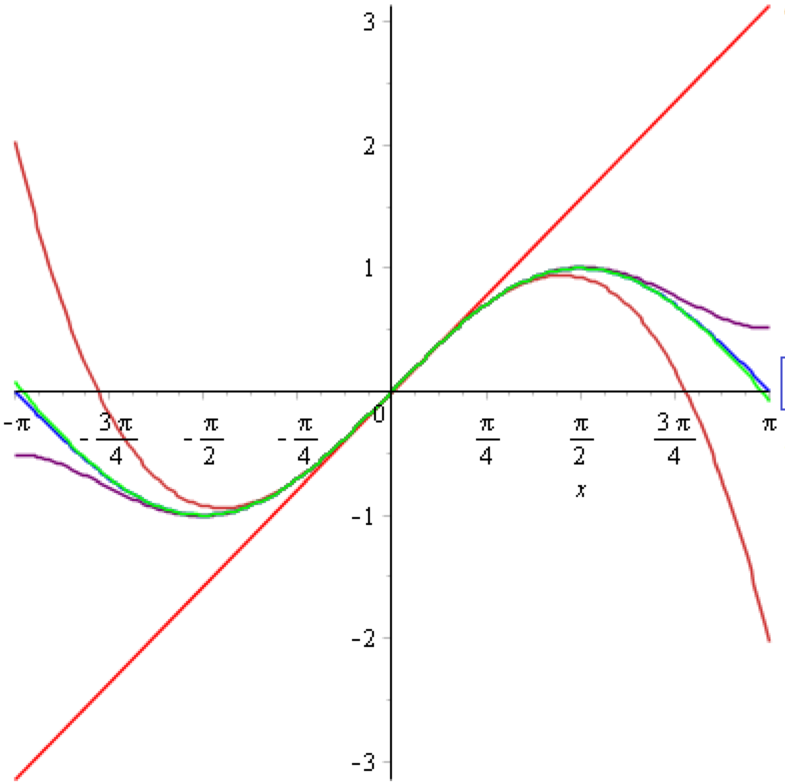


$y = 1 + x + \frac{x^2}{2!}$ is in purple

$y = 1 + x$ is in orange

$y = 1$ is in red

$$e^x \equiv 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \ldots + \frac{x^k}{k!} + \ldots$$



$y = x$ is in red

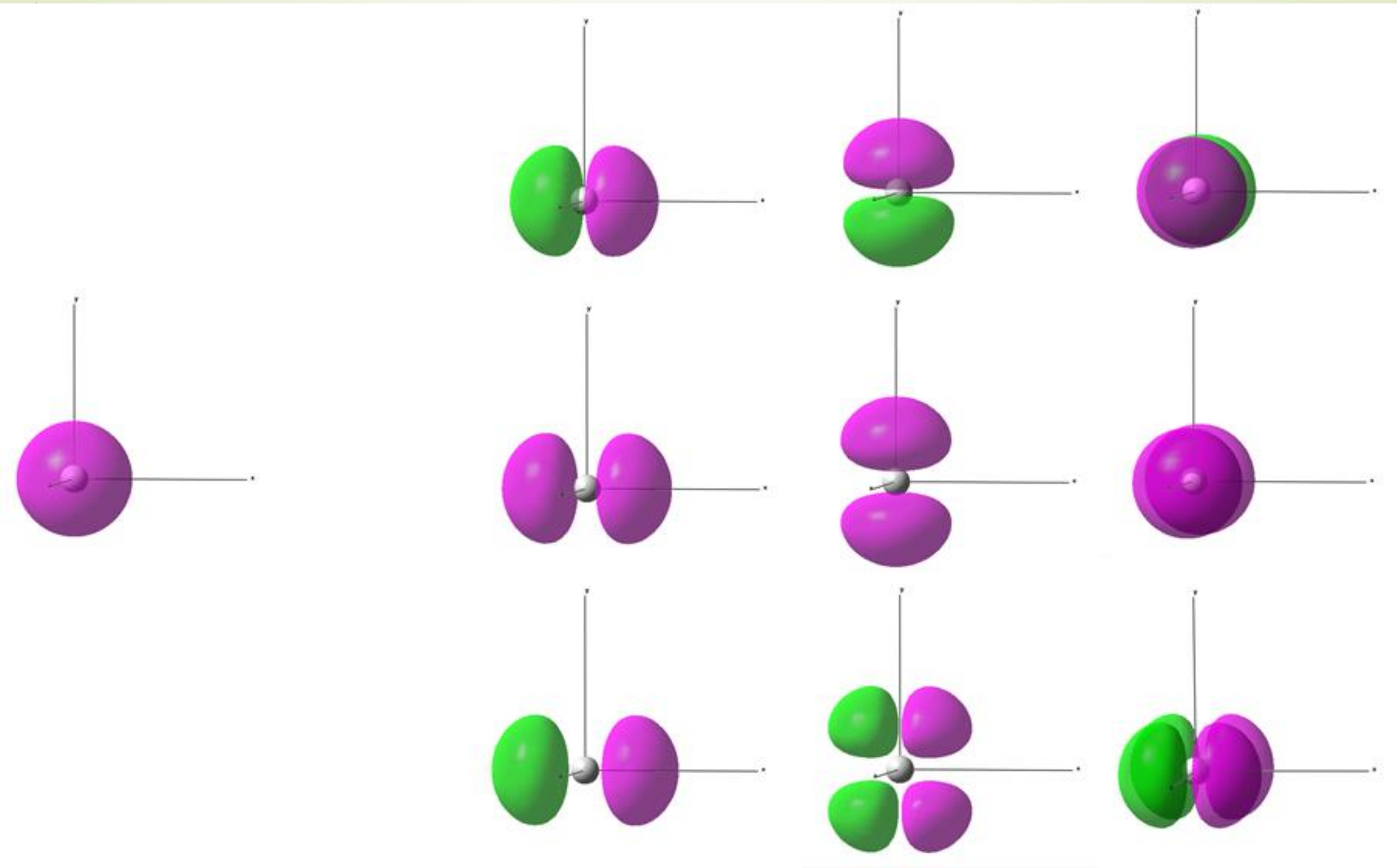
$y = x - \frac{x^3}{3!} + \frac{x^5}{5!}$ is in purple

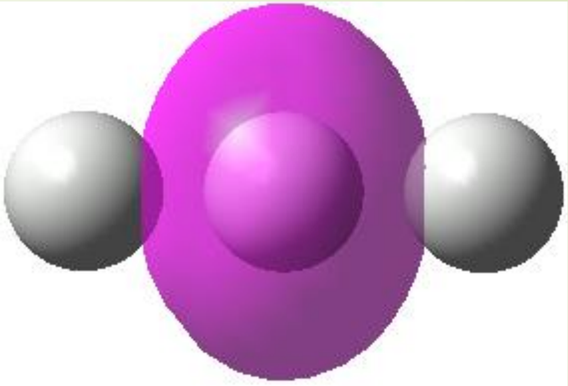
$\boxed{y = \sin x \text{ is in blue}}$

$y = x - \frac{x^3}{3!} + \frac{x^5}{5!} - \frac{x^7}{7!}$ is in green

$y = x - \frac{x^3}{3!}$ is in orange

$$\sin x \equiv x - \frac{x^3}{3!} + \frac{x^5}{5!} - \frac{x^7}{7!} + \ldots + \frac{(-1)^k x^{2k+1}}{(2k+1)!} + \ldots$$





What is this orbital?

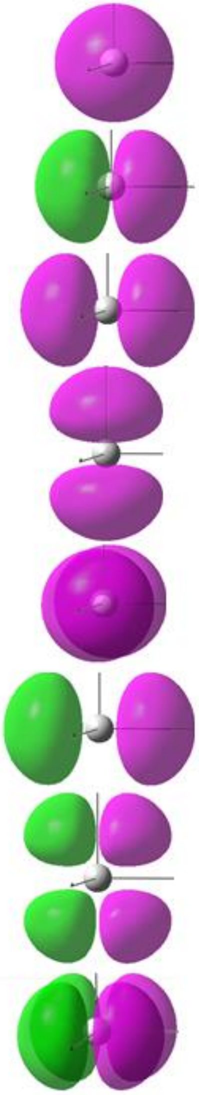
1s ?
Deformed 1s ?

Which atom(s) this orbital belongs to?

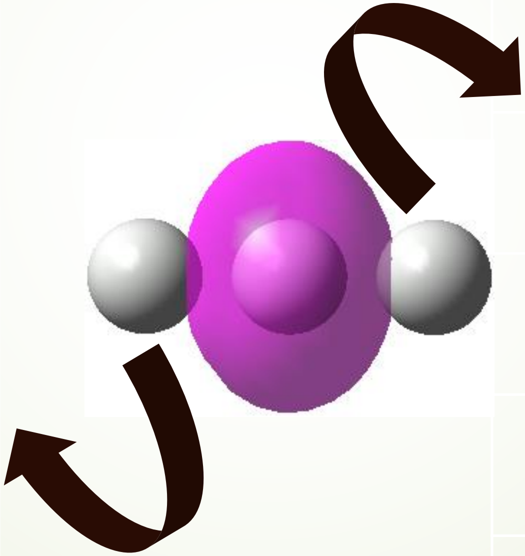
Left?
Middle?
Right?
All?

No orbital for the middle atom at all !!

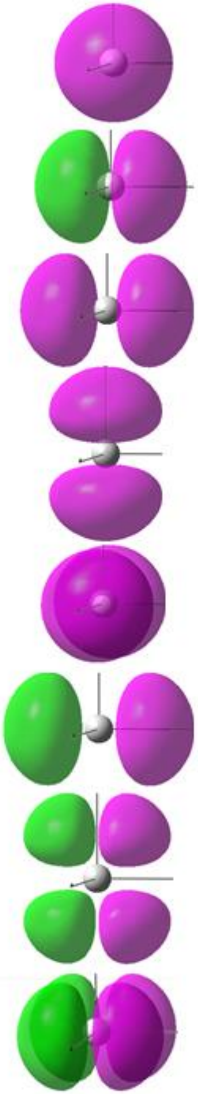
Left atom



0.23	s
0.35	p x
0.33	d xx
0.02	d yy
0.02	d zz
0.26	f xxx
0.04	f xzz
0.04	f yzz



Right atom



0.23	s
- 0.35	p x
0.33	d xx
0.02	d yy
0.02	d zz
- 0.26	f xxx
- 0.04	f xzz
- 0.04	f yzz

A closer look

Can we remove those extra green area? YES!

Can we construct a true spherical orbital? YES!

Linear vector space

Two-dimensional Cartesian vector:

$$\vec{A} = A_x \vec{i} + A_y \vec{j} = (\vec{i} \quad \vec{j}) \begin{pmatrix} A_x \\ A_y \end{pmatrix}$$

Two-dimensional molecular orbital:

$$\psi = c_1 \Phi_1 + c_2 \Phi_2 = (\Phi_1 \quad \Phi_2) \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

Linear vector space

Base

$$\psi = c_1\Phi_1 + c_2\Phi_2 = \boxed{\begin{pmatrix}\Phi_1 & \Phi_2\end{pmatrix}} \boxed{\begin{pmatrix}c_1 \\ c_2\end{pmatrix}}$$

Vector representation of the orbital

Vector superposition

$$\mathbf{A} = \mathrm{a}_x\mathbf{i} + \mathrm{a}_y\mathbf{j} + \mathrm{a}_z\mathbf{k}$$

$$\mathrm{a}_x = \mathbf{i}.\mathbf{A}$$

$$|\psi\rangle = c_1\,|\varphi_1\rangle + c_2\,|\varphi_2\rangle + c_3\,|\varphi_3\rangle + \cdots$$

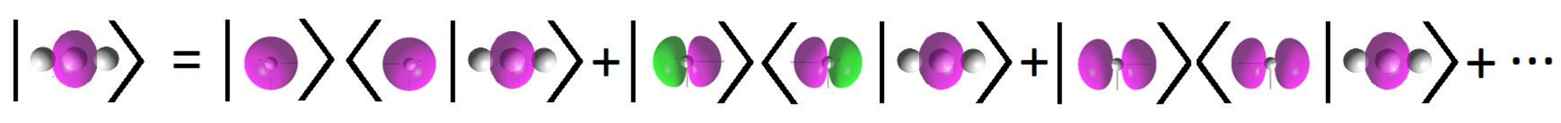
$$\mathrm{c}_1 = \langle\varphi_1\,|\,\psi\rangle$$

The *overlap* between original electronic wave functions and *k*-th resonance configuration

Projection Operator

$$|\psi\rangle = \sum |\varphi_k\rangle c_k = \underbrace{\sum |\varphi_k\rangle\langle\varphi_k|}\psi\rangle$$

$$\mathbf{1} \equiv \sum |\varphi_k\rangle\langle\varphi_k|$$



Change of the base: linear transformation

$$\psi = c_1\Phi_1 + c_2\Phi_2 = (\Phi_1 \quad \Phi_2)\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \mathbf{\Phi c}$$

$$\Phi_1' = T_{11}\Phi_1 + T_{21}\Phi_2$$
$$\Phi_2' = T_{12}\Phi_1 + T_{22}\Phi_2$$

The new base linearly depends to the old one.

$$(\Phi_1' \quad \Phi_2') = (\Phi_1 \quad \Phi_2)\begin{pmatrix} T_{11} & T_{12} \\ T_{21} & T_{22} \end{pmatrix}$$

$$\mathbf{\Phi}' = \mathbf{\Phi T} \quad or \quad \mathbf{\Phi} = \mathbf{\Phi}'\mathbf{T}^{-1}$$

Change of the base: linear transformation

$$\psi = \mathbf{\Phi c} = \mathbf{\Phi' T^{-1} c}$$

On the other hand, $\psi = \mathbf{\Phi' c'}$, therefore:

$$\mathbf{c'} = \mathbf{T^{-1} c}$$

$$\psi = c_1'\Phi_1' + c_2'\Phi_2'$$

Note that the wave function is not changed, it is just rewritten*!*

Why orthonormal base is preferred?

Computational viewpoint:

- Orthogonal bases are mathematically simple to deal with.

Chemical viewpoint:

- Results can be *chemically* interpreted.

Example: two normal vectors

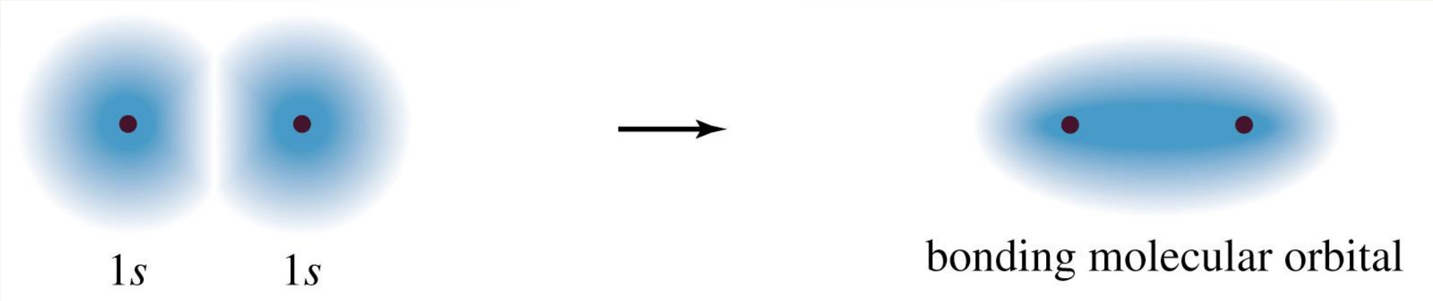
$$\vec{A} = \frac{1}{\sqrt{2}}\vec{i} + \frac{1}{\sqrt{2}}\vec{j} \qquad (\frac{1}{\sqrt{2}})^2 + (\frac{1}{\sqrt{2}})^2 = 1$$

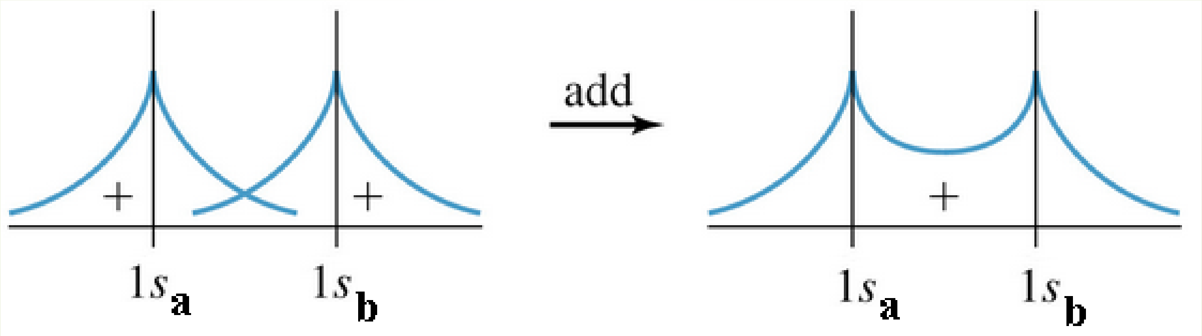
Both i and j unit vectors have equally contributed to the vector, each 1/2.

$$\vec{B} = \frac{1}{\sqrt{3}}\vec{i} + \frac{\sqrt{2}}{\sqrt{3}}\vec{j} \qquad (\frac{1}{\sqrt{3}})^2 + (\frac{\sqrt{2}}{\sqrt{3}})^2 = 1$$

i and j unit vectors have contributed to the vector, 1/3 and 2/3, respectively.

Bonding in hydrogen molecule

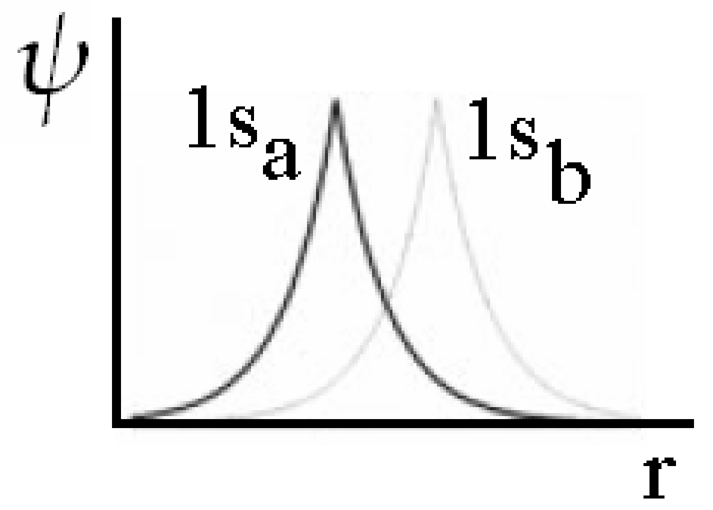




Linear Variation

$$\psi = c_a \psi_{1s_a} + c_a \psi_{1s_a}$$

Orthogonalization of two 1*s* orbitals

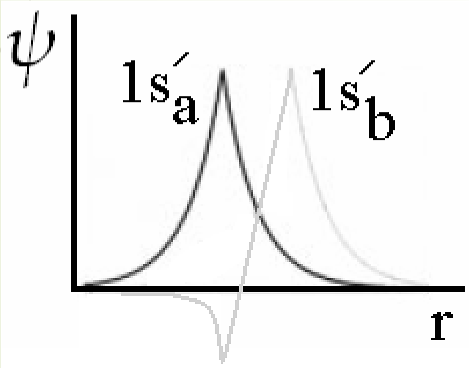


$$\langle \psi_{1s_a} | \psi_{1s_b} \rangle = 0.6781$$

Profile of the two non-orthogonal 1s orbitals

Schmidt vs. symmetric orthogonalization

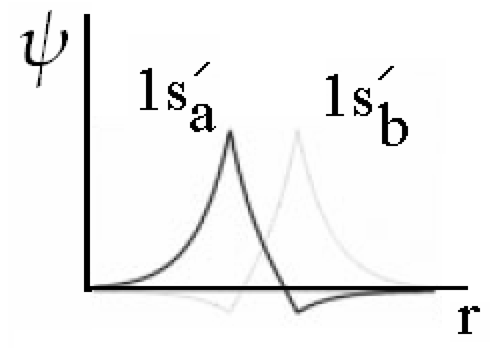
Schmidt



$$\psi'_{1s_a} = \psi_{1s_a}$$

$$\psi'_{1s_b} = c_1\psi_{1s_a} + c_2\psi_{1s_b}$$

Symmetric



$$\psi'_{1s_a} = c_1\psi_{1s_a} + c_2\psi_{1s_b}$$

$$\psi'_{1s_b} = c_2\psi_{1s_a} + c_1\psi_{1s_b}$$

Schmidt vs. symmetric orthogonalization

Schmidt

$$\psi'_{1s_a} = \psi_{1s_a}$$

$$\psi'_{1s_b} = -0.9226\psi_{1s_a} + 1.3606\psi_{1s_b}$$

Symmetric

$$\psi'_{1s_a} = \quad 1.2672\psi_{1s_a} - 0.4953\psi_{1s_b}$$

$$\psi'_{1s_b} = -0.4953\psi_{1s_a} + 1.2672\psi_{1s_b}$$

Symmetric orthogonalization operator

(introduced by Löwdin)

$\mathbf{\Phi} : non-orthogonal\ base$

$\mathbf{\Phi}' : orthogonalized\ base$

$$\mathbf{\Phi}' = \mathbf{\Phi}\mathbf{T}_{sym} \quad where \quad \mathbf{T}_{sym} = \mathbf{S}^{-\frac{1}{2}}$$

$\mathbf{S}^{-\frac{1}{2}}$ is the Taylor expansion of the $f(x) = x^{-\frac{1}{2}}$ function.

It can be shown that $\mathbf{S}^{-\frac{1}{2}} = \mathbf{C}\mathbf{s}^{-\frac{1}{2}}\mathbf{C}^{\dagger}$.

Schmidt vs. symmetric orthogonalization

$$(\psi'_{1s_a} \quad \psi'_{1s_b}) = (\psi_{1s_a} \quad \psi_{1s_b})\begin{pmatrix} 1 & -0.9226 \\ 0 & 1.3606 \end{pmatrix}$$

$\mathbf{T}_{Schmidt}$

$$(\psi'_{1s_a} \quad \psi'_{1s_b}) = (\psi_{1s_a} \quad \psi_{1s_b})\begin{pmatrix} 1.2672 & -0.4953 \\ -0.4953 & 1.2672 \end{pmatrix}$$

$\mathbf{T}_{sym}$

Presence and absence of external electric field

We remember that $\mathbf{c}' = \mathbf{T}^{-1}\mathbf{c}$

	$\mathbf{c}$	$\mathbf{c}'_{Schmidt} = \mathbf{T}^{-1}_{Schmidt}\mathbf{c}$	$\mathbf{c}'_{sym} = \mathbf{T}^{-1}_{sym}\mathbf{c}$
Field free	$\begin{pmatrix} 0.5459 \\ 0.5459 \end{pmatrix}$	$\begin{pmatrix} 0.9160 \\ 0.4012 \end{pmatrix}$	$\begin{pmatrix} 0.7072 \\ 0.7072 \end{pmatrix}$
Electric field	$\begin{pmatrix} 0.4465 \\ 0.6419 \end{pmatrix}$	$\begin{pmatrix} 0.8817 \\ 0.4718 \end{pmatrix}$	$\begin{pmatrix} 0.6496 \\ 0.7604 \end{pmatrix}$

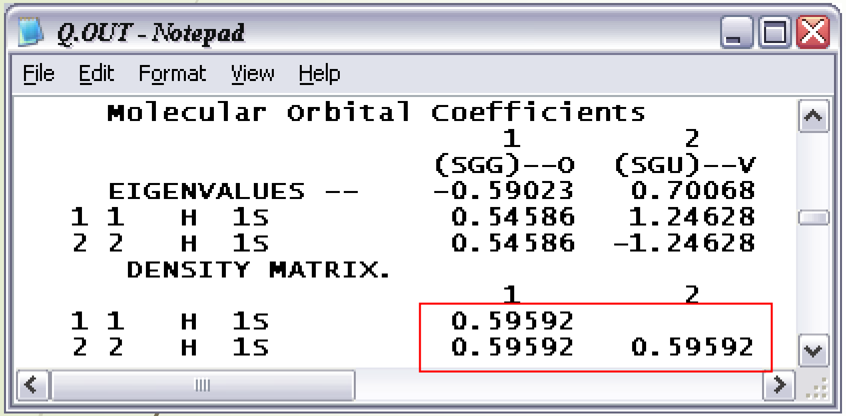
Decomposition into unperturbed states

$$\begin{pmatrix}\psi_{\sigma} & \psi_{\sigma^*}\end{pmatrix} = \begin{pmatrix}\psi_{1s_a} & \psi_{1s_b}\end{pmatrix}\begin{pmatrix}0.5459 & 1.2463\\ 0.5459 & -1.2463\end{pmatrix}$$

$\mathbf{T}_{CMO}$

	$\mathbf{c}$	$\mathbf{c}'_{CMO} = \mathbf{T}_{CMO}^{-1}\mathbf{c}$
Field free	$\begin{pmatrix}0.5459\\ 0.5459\end{pmatrix}$	$\begin{pmatrix}1\\ 0\end{pmatrix}$
Electric field	$\begin{pmatrix}0.4465\\ 0.6419\end{pmatrix}$	$\begin{pmatrix}0.9969\\ -0.0784\end{pmatrix}$

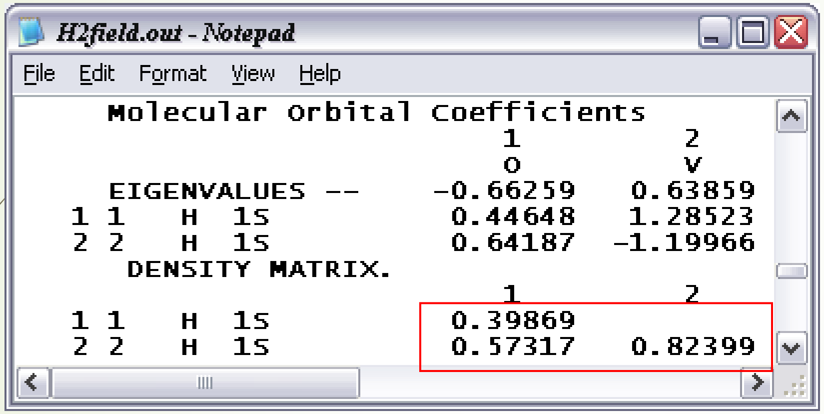
Transformation of density matrix
Example: hydrogen molecule



```
     Molecular Orbital Coefficients
                             1          2
                        (SGG)--O   (SGU)--V
     EIGENVALUES --     -0.59023    0.70068
   1 1    H  1S          0.54586    1.24628
   2 2    H  1S          0.54586   -1.24628
      DENSITY MATRIX.
                             1          2
   1 1    H  1S          0.59592
   2 2    H  1S          0.59592    0.59592
```

$$\mathbf{P} = \begin{pmatrix} 0.59592 & 0.59592 \\ 0.59592 & 0.59592 \end{pmatrix} \xrightarrow{\textit{transformation}} \mathbf{P}' = \begin{pmatrix} 1 & \enclose{circle}{1} \\ \enclose{circle}{1} & 1 \end{pmatrix}$$

Example: Density matrix of hydrogen molecule in the external field



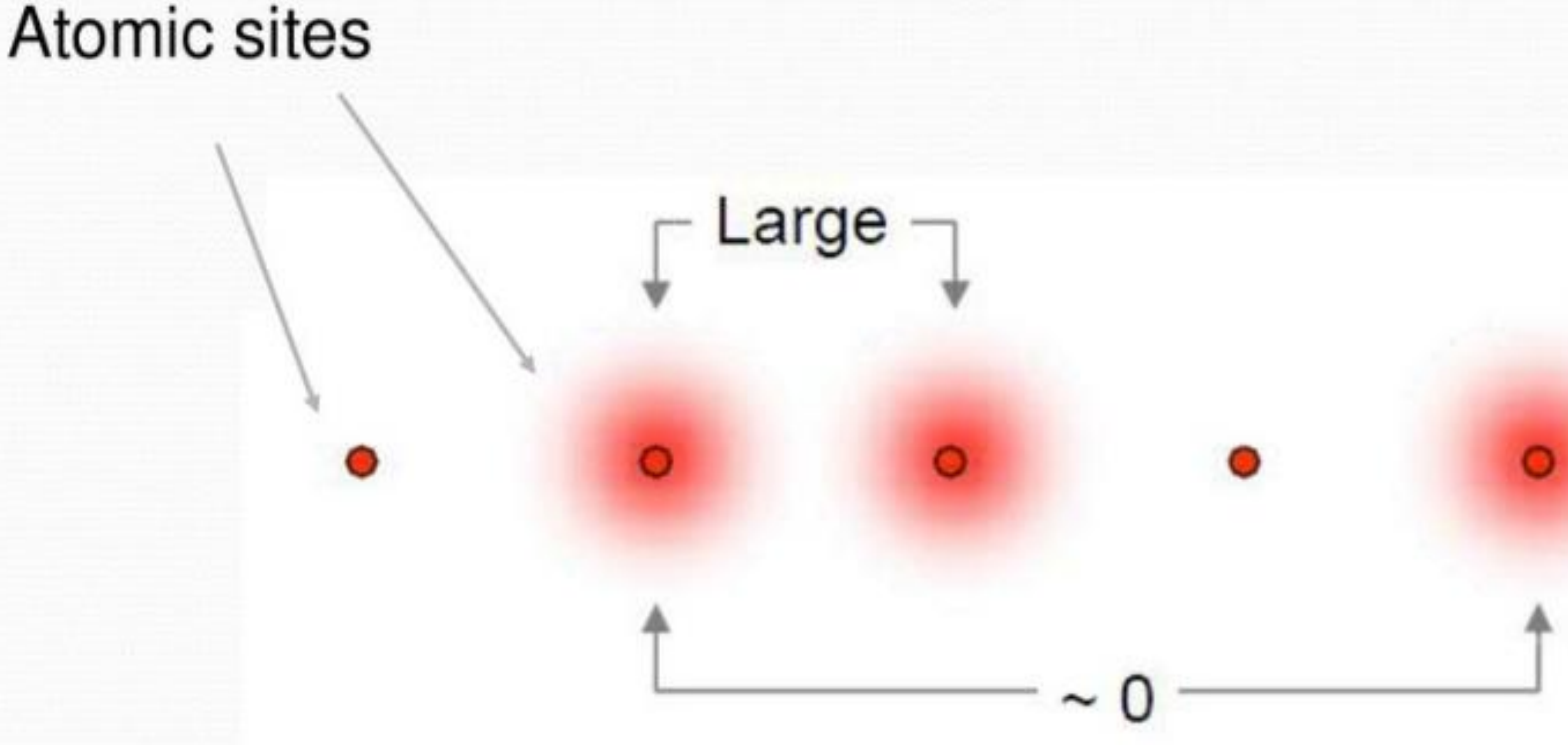
```
     Molecular Orbital Coefficients
                              1          2
                              O          V
     EIGENVALUES --     -0.66259    0.63859
   1 1    H  1S          0.44648    1.28523
   2 2    H  1S          0.64187   -1.19966
      DENSITY MATRIX.
                              1          2
   1 1    H  1S          0.39869
   2 2    H  1S          0.57317    0.82399
```

transformation

$$\mathbf{P}' = \begin{pmatrix} 0.8437 & 0.9877 \\ 0.9877 & 1.1563 \end{pmatrix}$$

Tight-Binding approximation

The interaction between nearest neighbors is large and decrease quickly with the distance



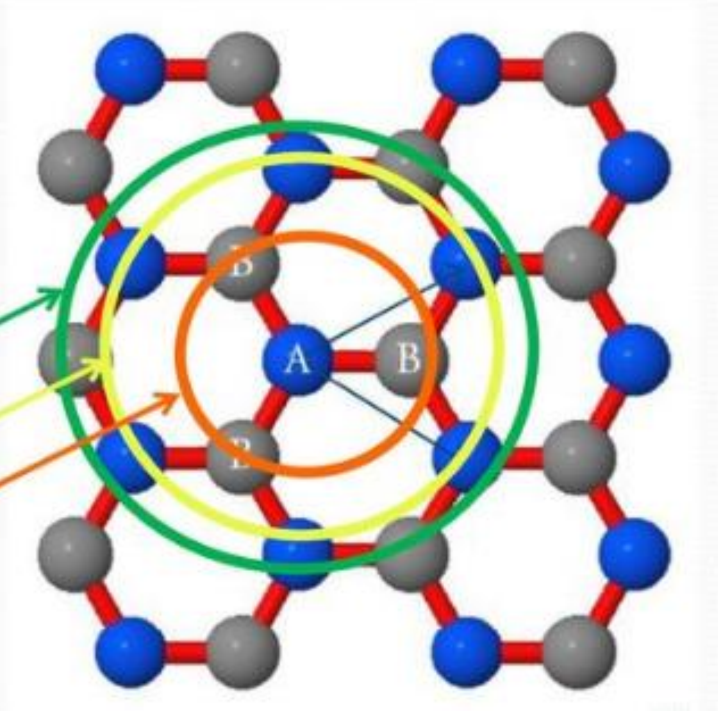
Nearest-Neighbors (N-N)

- One has to choose the extension of the interactions between neighbors

- In general

  first nearest-neighbors (1N-N)

  or third nearest-neighbors (3N-N)



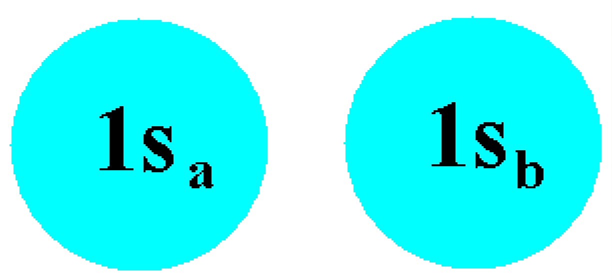
3rd neighbors

2nd neighbors

1st neighbors

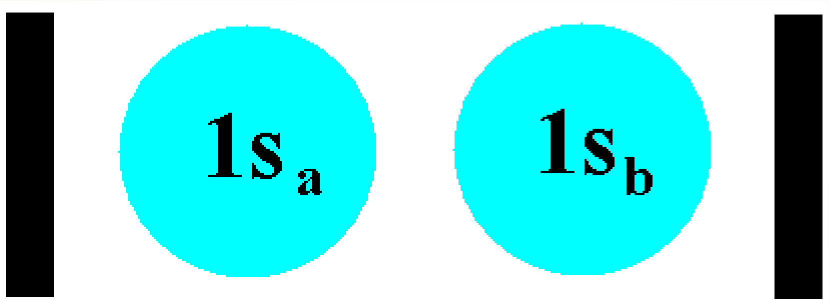
First-Order Reduced Density

$$\rho(1) = n \int_{totalspace} \Psi\Psi^{*} d\tau_2 d\tau_3 \cdots d\tau_n$$



$$\rho_{total} = \rho_{1sa} + \rho_{1sb}$$

$$\Psi = N$$



$$\rho_{total} = N^{2}(\rho_{1sa} + \rho_{1sb} - 2\psi_{1sa}\psi_{1sb})$$

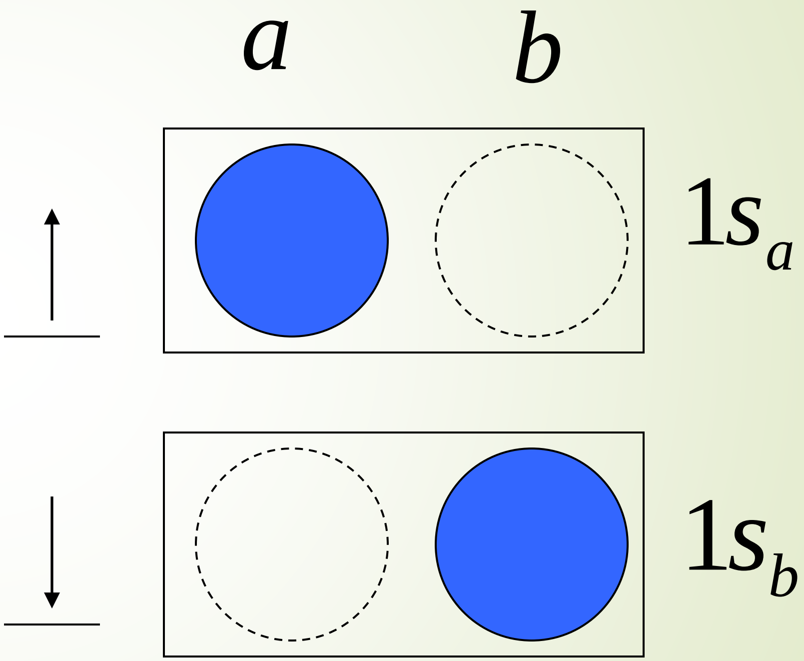
Non-interacting H atoms

(Chemical description)

$1s_a$

$1s_b$

$\psi = |1s_a \quad \overline{1s_b}|$

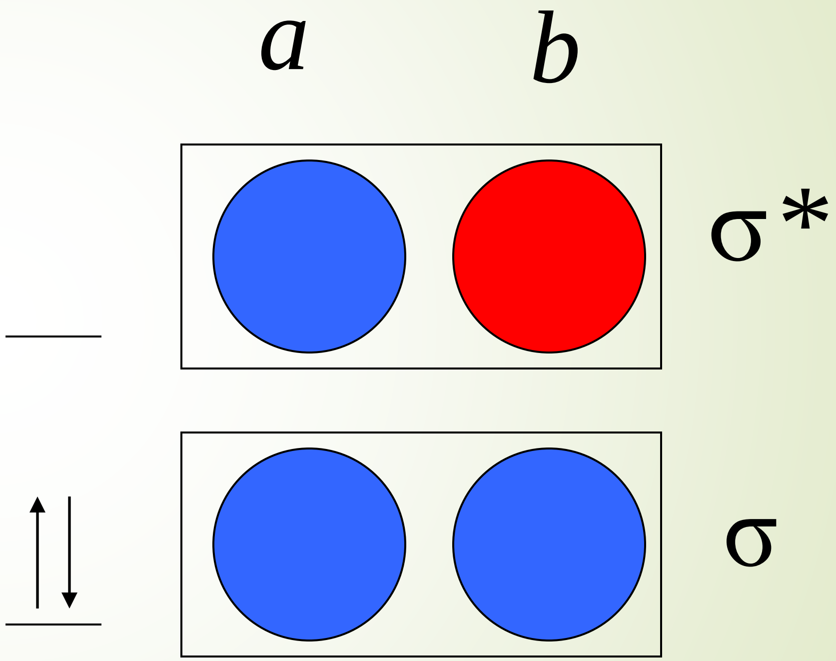


H-H molecule

(MO and chemical description)

$$\sigma^* = 1s_a - 1s_b$$

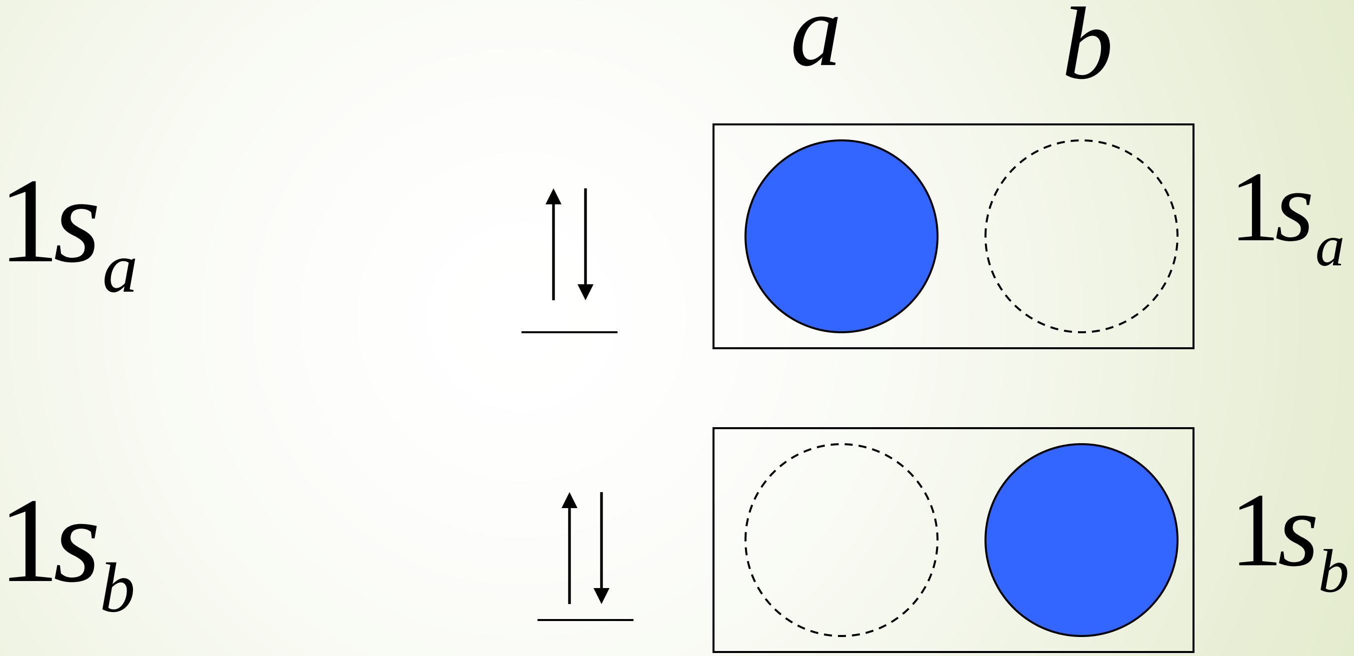
$$\sigma = 1s_a + 1s_b$$



$$\psi = |\sigma \quad \bar{\sigma}|$$

Non-interacting He atoms

(Chemical description)



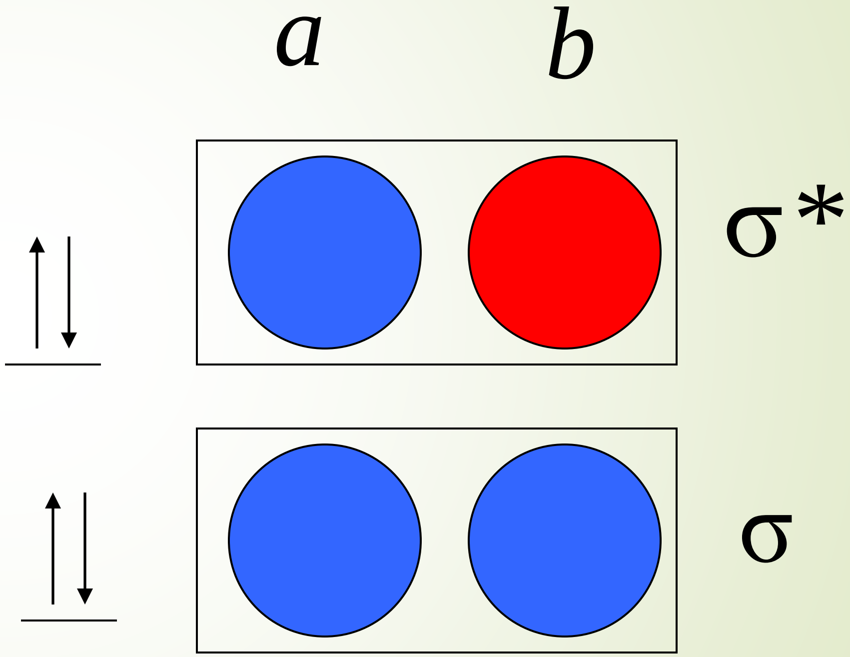
$$\psi = |1s_a \quad \overline{1s_a} \quad 1s_b \quad \overline{1s_b}|$$

He-He molecule

(MO description)

$$\sigma^* = 1s_a - 1s_b$$

$$\sigma = 1s_a + 1s_b$$



$$\psi = |\sigma \quad \bar{\sigma} \quad \sigma^* \quad \bar{\sigma}^*|$$

Equivalent MO and VB-type

He-He system

$$\psi = |\sigma \quad \bar{\sigma} \quad \sigma^* \quad \bar{\sigma}^*|$$

$$\psi = |1s_a \quad \overline{1s_a} \quad 1s_b \quad \overline{1s_b}|$$

Linear transformation

$$\begin{pmatrix} 1s_a & 1s_b \end{pmatrix} = \begin{pmatrix} \sigma & \sigma^* \end{pmatrix} \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{pmatrix}$$

Unitary matrix

$$\mathbf{U}^{\dagger} = \mathbf{U}^{-1}$$

Unitary transformation

$$\begin{pmatrix} 1s_a & 1s_b \end{pmatrix} = \begin{pmatrix} \sigma & \sigma^* \end{pmatrix} \mathbf{U}$$

Any U is acceptable! The ONLY requirement is that it must be unitary.

How to define U ?

1- Chemical interpretation

2- Physical imposition

3- Mathematical restriction

Chemical interpretation

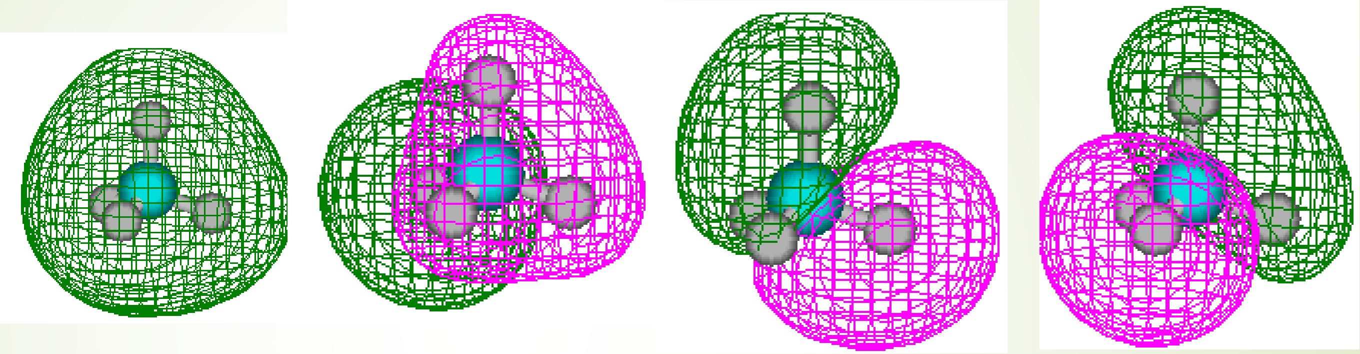
(example: localization)

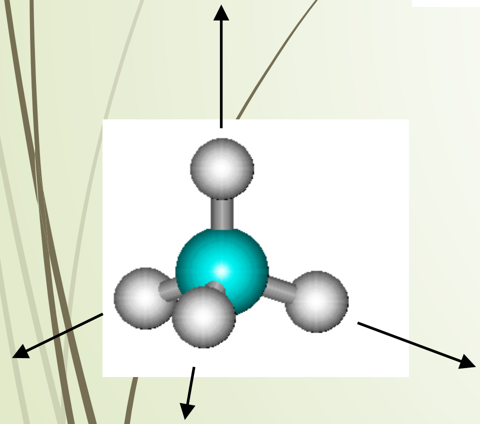
1- Chemical interpretation ⟶ Localization

2- Physical imposition ⟶ ???

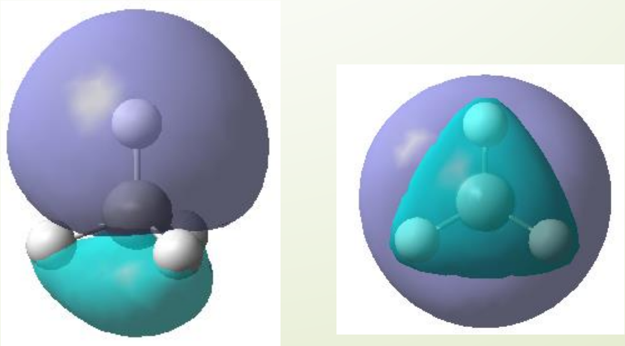
3- Mathematical restriction ⟶ $\mathbf{U}^{\dagger} = \mathbf{U}^{-1}$

Find U so that the resultant orbitals provide eigenfunctions of certain symmetry operator.





Equivalent orbitals



Electron density

$$\rho = \int \Psi^* \Psi d\mathbf{r}_2 \ldots d\mathbf{r}_N$$

For closed-shell single determinantal wave function:

$$\rho = \sum_{k=1}^{occ} 2\chi_k \chi_k^* = \sum_{k=1}^{occ} 2 |\chi_k|^2$$

Where the summation is over CMOs.

Electron density

For many determinantal wave function, it can be shown that:

$$\rho = \sum_{k=1}^{basis} n_k \theta_k \theta_k^* = \sum_{k=1}^{basis} n_k \,|\, \theta_k \,|^2$$

θ_k is called Natural Orbital.

n_k is called Occupancy.

Matrix representation of density

$$\chi_k = \sum_{j=1}^{n} c_{jk} \Phi_j$$

$$\chi_k = \begin{pmatrix} \Phi_1 & \cdots & \Phi_n \end{pmatrix} \begin{pmatrix} c_{1k} \\ \vdots \\ c_{nk} \end{pmatrix} = \mathbf{\Phi} \mathbf{c}_k$$

$$\mathbf{\Phi} = \begin{pmatrix} \Phi_1 & \cdots & \Phi_n \end{pmatrix}$$

Matrix representation of density

$$\rho = \sum_{ij}^{n} P_{ij} \Phi_i \Phi_j^*$$

$$\rho = \mathbf{\Phi P \Phi}^\dagger$$

$$\rho = \begin{pmatrix} \Phi_1 & \cdots & \Phi_n \end{pmatrix} \begin{pmatrix} P_{11} & \cdots & P_{1n} \\ \vdots & \ddots & \vdots \\ P_{n1} & \cdots & P_{nn} \end{pmatrix} \begin{pmatrix} \Phi_1^* \\ \vdots \\ \Phi_n^* \end{pmatrix}$$

Comparison of electron density of interacting and non-interacting systems

$$\rho_0 = |\psi_{1s_a}|^2 + |\psi_{1s_b}|^2$$ non-interacting

$$\psi_\sigma = N(\psi_{1s_a} + \psi_{1s_b})$$ interacting

$$\rho_\sigma = |\psi_\sigma|^2 = 2N^2(\psi_{1s_a}^2 + \psi_{1s_b}^2 \boxed{+\psi_{1s_a}\psi_{1s_b}})$$

Responsible for the interaction *!!*

Density matrix representation

$$\mathbf{P} = \begin{array}{cc|c} \Phi_1 & \Phi_2 & \\ \hline P_{11} & P_{12} & \Phi_1 \\ P_{21} & P_{22} & \Phi_2 \end{array}$$

$$\rho = P_{11}\Phi_1^*\Phi_1 + P_{12}\Phi_1^*\Phi_2 + P_{21}\Phi_2^*\Phi_1 + P_{22}\Phi_2^*\Phi_2$$

Comparison of density matrices of interacting and non-interacting systems

$$\mathbf{P}_0 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

non-interacting

$$\mathbf{P}_\sigma = \begin{pmatrix} 2N^2 & \boxed{2N^2} \\ \boxed{2N^2} & 2N^2 \end{pmatrix}$$

interacting

In matrix representation, the off-diagonal elements are responsible for the interaction.

Actual system: hydrogen molecule

$$\mathbf{P}_0 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

non-interacting

$$\mathbf{P}_\sigma = \begin{pmatrix} 0.596 & 0.596 \\ 0.596 & 0.596 \end{pmatrix}$$

interacting

Wiberg bond index

Wiberg bond index, simply adds up squares of density matrix off-diagonal elements:

$$W_{AB} = \sum_{i \in A} \sum_{j \in B} | P_{ij} |^2$$

Wiberg (H2): $P_{12}^2 + P_{21}^2 = 0.71$ $\mathbf{P}_\sigma = \begin{pmatrix} 0.596 & 0.596 \\ 0.596 & 0.596 \end{pmatrix}$

Natural Orbitals

It can be shown that **b** is eigenvector of the density matrix, whose eigenvalue is its occupancy.

$$\mathbf{P}\mathbf{b}_k = n_k \mathbf{b}_k$$

Matrix representation of natural orbitals

$$\theta_k = \sum_{j=1}^{n} b_{jk} \Phi_j$$

$$\theta_k = \begin{pmatrix} \Phi_1 & \cdots & \Phi_n \end{pmatrix} \begin{pmatrix} b_{1k} \\ \vdots \\ b_{nk} \end{pmatrix} = \mathbf{\Phi b}_k$$

Natural Orbitals

$$\mathbf{PB} = \mathbf{nB}$$

$$\mathbf{B} = \begin{array}{c} \begin{pmatrix} b_{11} & b_{12} & \vdots & b_{1n} \\ b_{21} & b_{22} & \vdots & b_{2n} \\ \vdots & \vdots & \vdots & \vdots \\ b_{n1} & b_{n2} & \vdots & b_{nn} \end{pmatrix} \\ \begin{array}{cccc} \uparrow & \uparrow & & \uparrow \\ \mathbf{b}_1 & \mathbf{b}_2 & & \mathbf{b}_n \end{array} \end{array}$$

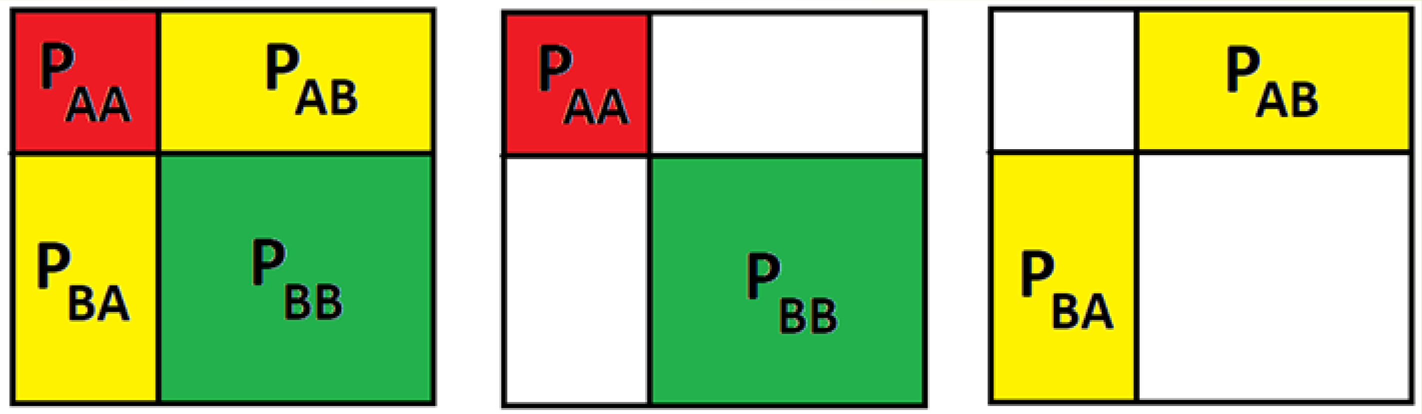
Natural Orbitals with overlap taken into consideration

$$\mathbf{PSB} = \mathbf{Bn}$$

Where S is the overlap matrix.

In practice, to diagonalize a matrix using standard mathematical softwares, P can be diagonalized in some orthonormal basis.

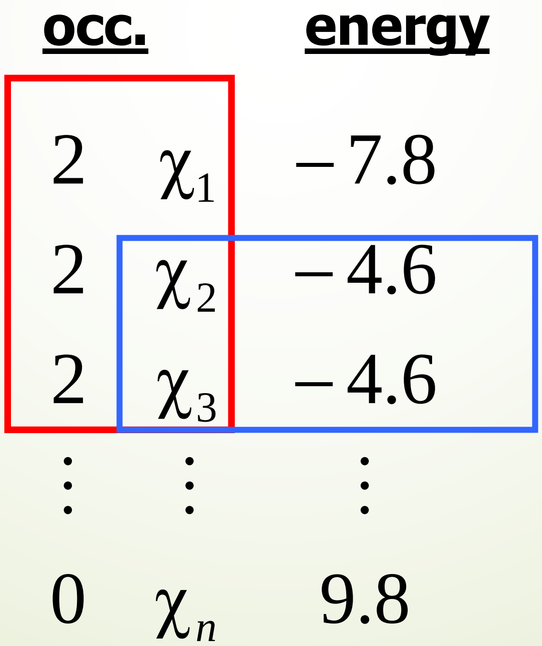
Density Matrix Blocks



F and P

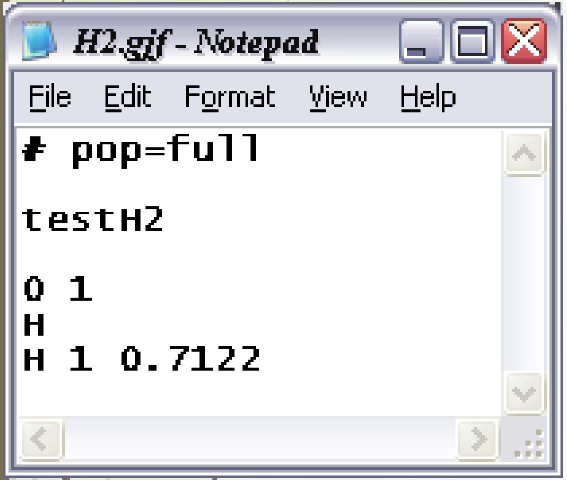
For single determinantal wave functions, F commute with P; which means that they share the same eigenvectors.

BUT, be careful with degenerate ones!

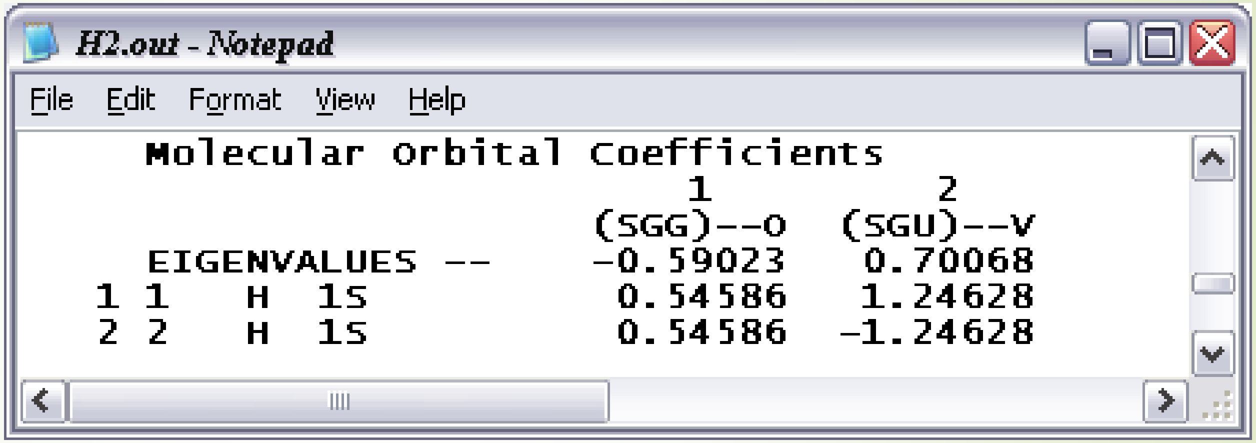


occ.		energy
2	χ_1	-7.8
2	χ_2	-4.6
2	χ_3	-4.6
$\vdots$	$\vdots$	$\vdots$
0	χ_n	9.8

Example: hydrogen molecule



```
# pop=full

testH2

0 1
H
H 1 0.7122
```



```
     Molecular Orbital Coefficients
                                   1          2
                               (SGG)--O   (SGU)--V
     EIGENVALUES --           -0.59023    0.70068
   1 1   H  1S                 0.54586    1.24628
   2 2   H  1S                 0.54586   -1.24628
```

$$\psi_\sigma = 0.54586\ \psi_{1s_a} + 0.54586\ \psi_{1s_b}$$

$$0.54586^2 + 0.54586^2 \neq 1$$

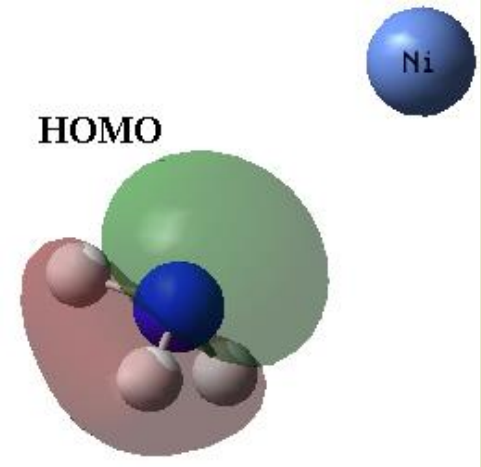
Although the base is not orthogonal, the symmetry implies equal contribution from the two atoms.

Decomposition of CMOs into localized orbitals and vice versa

To study certain cases e.g., chemical reactivity, it would be more helpful to understand how the localized orbitals construct HOMO or LUMO.

On the other hand, one might be interested to know components of some localized orbitals.

Question: Is HOMO the lone pair?



Definition of matrices

Base $\mathbf{\Phi} = \begin{pmatrix} \Phi_1 & \cdots & \Phi_n \end{pmatrix}$

CMO $\boldsymbol{\chi} = \begin{pmatrix} \chi_1 & \cdots & \chi_n \end{pmatrix}$

LMO $\boldsymbol{\theta} = \begin{pmatrix} \theta_1 & \cdots & \theta_n \end{pmatrix}$

$$\mathbf{C} = (\mathbf{c}_1 \quad \cdots \quad \mathbf{c}_n)$$

Transformation matrix

Elements are *functions !*

Elements are *scalars !*

Transformation and back-transformation

$$\begin{tikzcd}
\begin{aligned} \boldsymbol{\chi} &= \boldsymbol{\theta}\mathbf{C}_{LMO}^{-1}\mathbf{C}_{CMO} \\ &= \boldsymbol{\theta}\mathbf{T}_{LMO\to CMO} \end{aligned} & & \\
& \boldsymbol{\chi} = \boldsymbol{\Phi}\mathbf{C}_{CMO} \arrow[ul] \arrow[r] & \boldsymbol{\Phi} = \boldsymbol{\chi}\mathbf{C}_{CMO}^{-1} \\
\boldsymbol{\Phi} = \boldsymbol{\theta}\mathbf{C}_{LMO}^{-1} & \boldsymbol{\theta} = \boldsymbol{\Phi}\mathbf{C}_{LMO} \arrow[l] \arrow[dr] & \\
& & \begin{aligned} \boldsymbol{\theta} &= \boldsymbol{\chi}\mathbf{C}_{CMO}^{-1}\mathbf{C}_{LMO} \\ &= \boldsymbol{\chi}\mathbf{T}_{CMO\to LMO} \end{aligned}
\end{tikzcd}$$

Localized orbitals are not necessarily orthogonal !

$\mathbf{S}_{ij}^{\{\theta\}} = \langle \theta_i | \theta_j \rangle$ and $\boldsymbol{\theta} = \boldsymbol{\Phi}\mathbf{C}_{LMO}$

$$\boldsymbol{\theta}' = \boldsymbol{\theta}\mathbf{S}^{\{\theta\}^{-\frac{1}{2}}} = \boldsymbol{\Phi}\mathbf{C}_{LMO}\mathbf{S}^{\{\theta\}^{-\frac{1}{2}}}$$

$$\boldsymbol{\chi} = \boldsymbol{\theta}\mathbf{C}_{LMO}^{-1}\mathbf{C}_{CMO} = \boldsymbol{\theta}\mathbf{T}_{LMO\to CMO}$$

$$\boldsymbol{\chi} = \boldsymbol{\theta}'(\mathbf{C}_{LMO}\mathbf{S}^{\{\theta\}^{-\frac{1}{2}}})^{-1}\mathbf{C}_{CMO} = \boldsymbol{\theta}'\mathbf{T}'_{LMO\to CMO}$$

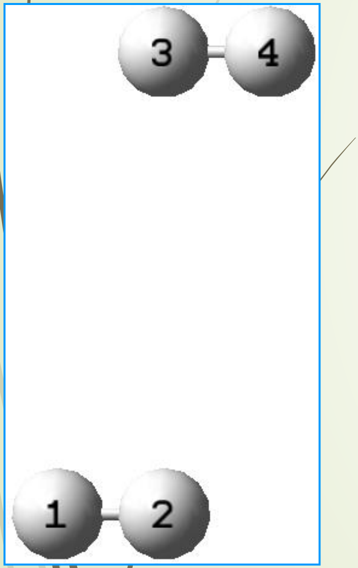
$$\boxed{\mathbf{T}'_{LMO\to CMO} = (\mathbf{C}_{LMO}\mathbf{S}^{\{\theta\}^{-\frac{1}{2}}})^{-1}\mathbf{C}_{CMO}}$$

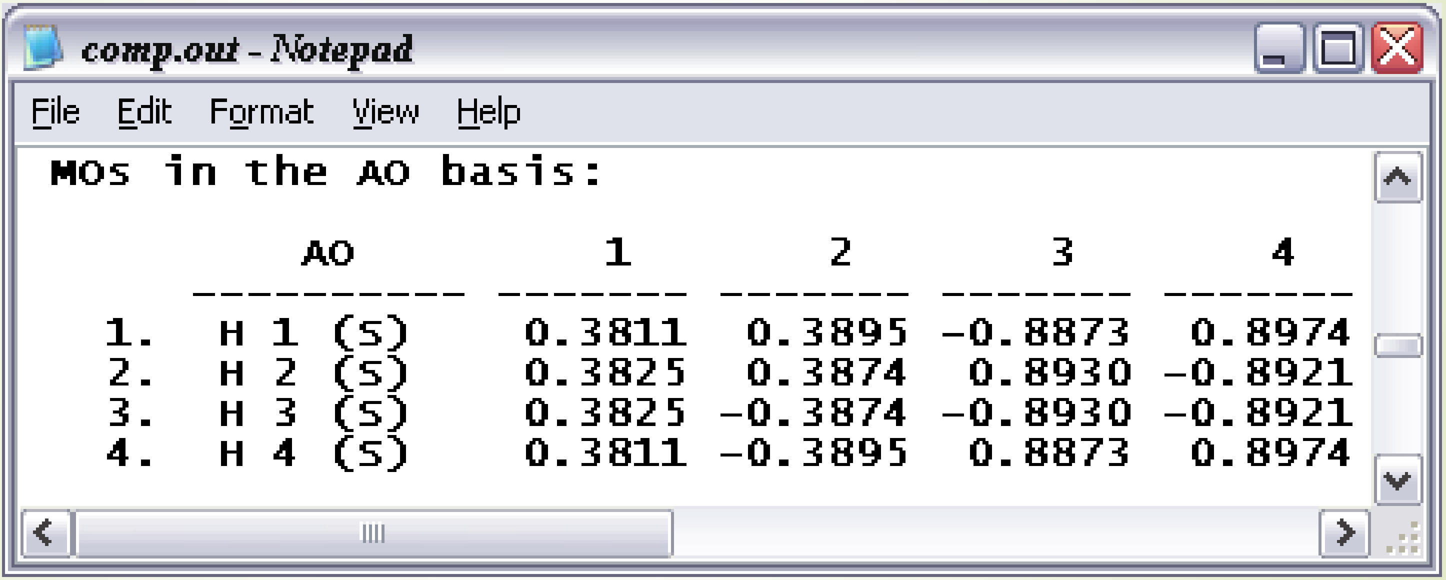
The three transformations

$$\mathbf{S}^{\{\theta\}} = \mathbf{C}^{\dagger}_{LMO}\mathbf{S}\mathbf{C}_{LMO}$$ where $$\mathbf{S}_{ij} = \langle \Phi_i \,|\, \Phi_j \rangle$$

$$\boxed{\begin{aligned}
\mathbf{T}_{CMO\to LMO} &= \mathbf{C}^{-1}_{CMO}\mathbf{C}_{LMO} \\
\mathbf{T}_{LMO\to CMO} &= \mathbf{C}^{-1}_{LMO}\mathbf{C}_{CMO} \\
\mathbf{T}'_{LMO\to CMO} &= (\mathbf{C}_{LMO}(\mathbf{C}^{\dagger}_{LMO}\mathbf{S}\mathbf{C}_{LMO})^{-\frac{1}{2}})^{-1}\mathbf{C}_{CMO}
\end{aligned}}$$

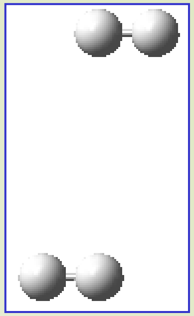
H2-H2 interaction as vdW complex:

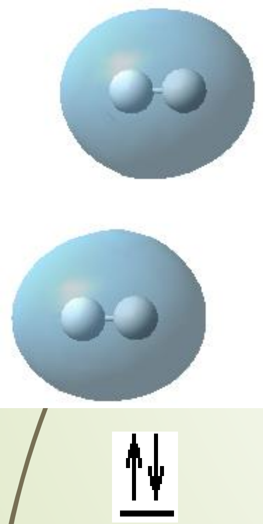




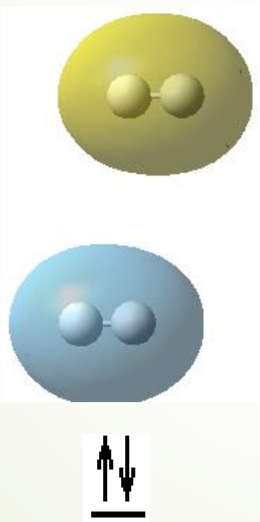
```
 MOs in the AO basis:

                AO            1        2        3        4
           ----------- -------- -------- -------- --------
     1.     H 1 (S)      0.3811   0.3895  -0.8873   0.8974
     2.     H 2 (S)      0.3825   0.3874   0.8930  -0.8921
     3.     H 3 (S)      0.3825  -0.3874  -0.8930  -0.8921
     4.     H 4 (S)      0.3811  -0.3895   0.8873   0.8974
```

Visual decomposition of complex' CMOs into fragments' CMOs

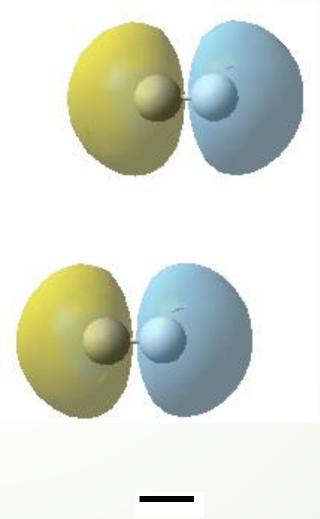




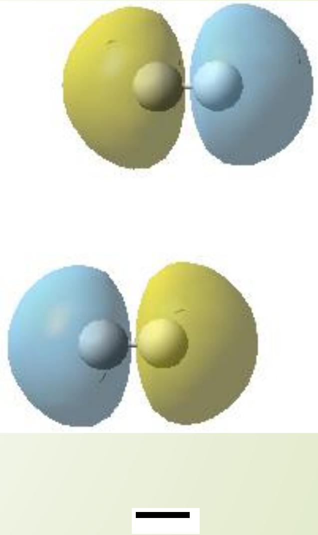
$\sigma_{1,2}+\sigma_{3,4}$



$\sigma_{1,2}-\sigma_{3,4}$



$\sigma^{*}_{1,2}+\sigma^{*}_{3,4}$



$\sigma^{*}_{1,2}-\sigma^{*}_{3,4}$

Decomposition of complex' CMOs into fragments' CMOs

$$\chi_{comp} = \mathbf{\Phi C}_{comp} =$$

$$\begin{pmatrix} 1s_1 & 1s_2 & 1s_3 & 1s_4 \end{pmatrix}\begin{pmatrix} 0.3811 & 0.3895 & -0.8873 & 0.8974 \\ 0.3825 & 0.3874 & 0.8930 & -0.8921 \\ 0.3825 & -0.3874 & -0.8930 & -0.8921 \\ 0.3811 & -0.3895 & 0.8873 & 0.8974 \end{pmatrix}$$

$$\chi_{frag1} = \mathbf{\Phi}_{frag1}\mathbf{C}_{frag1} =$$

$$\begin{pmatrix} 1s_1 & 1s_2 \end{pmatrix}\begin{pmatrix} 0.5459 & 1.2463 \\ 0.5459 & -1.2463 \end{pmatrix}$$

$$\chi_{frag2} = \mathbf{\Phi}_{frag2}\mathbf{C}_{frag2} =$$

$$\begin{pmatrix} 1s_1 & 1s_2 \end{pmatrix}\begin{pmatrix} 0.5459 & 1.2463 \\ 0.5459 & -1.2463 \end{pmatrix}$$

Rewriting of fragments' matrices

$$\chi_{frag1} = \begin{pmatrix} 1s_1 & 1s_2 & 1s_3 & 1s_4 \end{pmatrix} \begin{pmatrix} 0.5459 & 1.2463 \\ 0.5459 & -1.2463 \\ 0 & 0 \\ 0 & 0 \end{pmatrix}$$

$$\chi_{frag2} = \begin{pmatrix} 1s_1 & 1s_2 & 1s_3 & 1s_4 \end{pmatrix} \begin{pmatrix} 0 & 0 \\ 0 & 0 \\ 0.5459 & 1.2463 \\ 0.5459 & -1.2463 \end{pmatrix}$$

Unification of the fragments

$$\chi_{frags} =$$

$$\begin{pmatrix} 1s_1 & 1s_2 & 1s_3 & 1s_4 \end{pmatrix} \begin{pmatrix} 0.5459 & 1.2463 & 0 & 0 \\ 0.5459 & -1.2463 & 0 & 0 \\ 0 & 0 & 0.5459 & 1.2463 \\ 0 & 0 & 0.5459 & -1.2463 \end{pmatrix}$$

$$= \mathbf{\Phi C}_{frags}$$

Transformation into fragments

$$\chi_{comp} = \mathbf{\Phi C}_{comp}$$

$$\chi_{frags} = \mathbf{\Phi C}_{frags}$$

$$\Rightarrow$$

$$\chi_{comp} = \chi_{frags}\mathbf{C}_{frags}^{-1}\mathbf{C}_{comp}$$

$$\mathbf{T}_{frags\rightarrow comp} = \mathbf{C}_{frags}^{-1}\mathbf{C}_{comp}$$

If desired, fragments’ orbitals can be orthogonalized with the same procedure as localized orbitals.

Are off-diagonal elements of density matrix “physical” ?

Matrix representation of first-order density

$$\rho = \int \Psi^* \Psi d\mathbf{r}_2 \ldots d\mathbf{r}_N$$

$$\rho = \begin{pmatrix} \Phi_1 & \cdots & \Phi_n \end{pmatrix} \begin{pmatrix} P_{11} & \cdots & P_{1n} \\ \vdots & \ddots & \vdots \\ P_{n1} & \cdots & P_{nn} \end{pmatrix} \begin{pmatrix} \Phi_1^* \\ \vdots \\ \Phi_n^* \end{pmatrix}$$

Matrix representation of time-independent Schrodinger equation **HC=SCE**


Thank you