# Quantum Chemistry 2023, MOL406, week 3 

November 22, 2023

## Towards Hartree-Fock: diagonalizing $\Lambda$

Unitary operator (here called $\hat{U}$ ):

$$
\hat{U}^{\dagger} \hat{U}=\hat{U} \hat{U}^{\dagger}=\hat{I} \text { i.e. } \hat{U}^{-1}=\hat{U}^{\dagger}
$$

So the adjoint is the inverse.
Remember the definition of the adjoint operator $\hat{U}^{\dagger}$ :

$$
\left\langle\hat{U} \psi_{1}, \psi_{2}\right\rangle=\left\langle\psi_{1}, \hat{U}^{\dagger} \psi_{2}\right\rangle
$$

A unitary matrix (here called $\mathbf{U}$ ):

$$
\mathbf{U}^{\dagger} \mathbf{U}=\mathbf{U U}^{\dagger}=\mathbf{1} \text { i.e. } \mathbf{U}^{-1}=\mathbf{U}^{\dagger}
$$

To get the "Hermitian adjoint" matrix $\mathbf{U}^{\dagger}$ :

$$
U_{i j}^{\dagger}=U_{j i}^{*}
$$

Important properties:

$$
|\operatorname{det}(\mathbf{U})|=1 \text { and } \mathbf{U}=\mathbf{V} \tilde{\mathbf{U}} \mathbf{V}^{\dagger} \text { where } \tilde{\mathbf{U}} \text { is diagonal and } \tilde{\mathbf{V}}^{(\dagger)} \text { and } \tilde{\mathbf{U}} \text { unitary }
$$

## Towards Hartree-Fock: diagonalizing $\Lambda$

Hermitian operator (here called $\hat{H}$ ):

$$
\hat{H}=\hat{H}^{\dagger}
$$

It is self-adjoint.

$$
\left\langle\hat{H} \psi_{1}, \psi_{2}\right\rangle=\left\langle\psi_{1}, \hat{H} \psi_{2}\right\rangle
$$

For an Hermitian matrix $\mathbf{H}$ :

$$
H_{i j}^{\dagger}=H_{j i}^{*}=H_{i j}
$$

It can be diagonalized with a unitary matrix and has real eigenvalues. The determinant (the product of the eigenvalues) is real.

For square matrices:

$$
\operatorname{det}(\mathbf{A B})=\operatorname{det}(\mathbf{A}) \operatorname{det}(\mathbf{B})
$$

## Towards Hartree-Fock: diagonalizing $\wedge$

Let's rotate the orbitals with a unitary matrix $\mathbf{U}$ :

$$
\sum_{\lambda} \chi_{\lambda} C_{\lambda k}^{\prime}=\phi_{k}^{\prime}=\sum_{l} \phi_{l} U_{l k}=\sum_{l} \sum_{\mu} \chi_{\mu} C_{\mu l} U_{l k}=\sum_{\lambda} \chi_{\lambda} \sum_{l} C_{\lambda l} U_{l k}
$$

We did this such that evidently: $\mathbf{C}^{\prime}=\mathbf{C U} \Rightarrow \mathbf{C}=\mathbf{C}^{\prime} \mathbf{U}^{\dagger}$.
We can go back to the spinorbitals $\psi_{i}$ and, in our restricted closed shell HF, get a block diagonal V that transforms the spin orbitals (one block for the $\alpha$, the other for the $\beta$ spin):

$$
\mathbf{V}=\left(\begin{array}{ll}
\mathbf{U} & \mathbf{0} \\
\mathbf{0} & \mathbf{U}
\end{array}\right)
$$

Because the determinant of the product is the product of the determinants

$$
\Phi^{\prime}=\frac{1}{\sqrt{N!}} \operatorname{det}\left|\psi_{1}^{\prime}(1) \psi_{2}^{\prime}(2) \ldots \psi_{N}^{\prime}(N)\right|=\frac{1}{\sqrt{N!}} \operatorname{det}\left|\psi_{1}(1) \psi_{2}(2) \ldots \psi_{N}(N)\right| \operatorname{det}(\mathbf{V})=\Phi \operatorname{det}(\mathbf{V})
$$

So $\Phi^{\prime}= \pm \Phi$, well... $\Phi^{\prime}=\Phi e^{i \tilde{\phi}}$. The fase factors cancel in any expectation value, i.e. chemisty \& physics are unaffected. So also our HF energy is not affected.

## Towards Hartree-Fock: diagonalizing $\Lambda$

Remember:

$$
P_{\mu \lambda}=\sum_{k}^{N / 2} C_{\mu k} C_{\lambda k}^{*}=\sum_{k}^{N / 2} C_{\mu k} C_{k \lambda}^{\dagger} \text { i.e. } \mathbf{P}=\mathbf{C C}^{\dagger}
$$

Transform the density matrix:

$$
\mathbf{P}^{\prime}=\mathbf{C}^{\prime} \mathbf{C}^{\prime \dagger}=\mathbf{C U}(\mathbf{C U})^{\dagger}=\mathbf{C} \mathbf{U U}^{\dagger} \mathbf{C}^{\dagger}=\mathbf{P} \Rightarrow \mathbf{F}^{\prime}=\mathbf{F}
$$

So the Fock matrix is unaffected (as is $\mathbf{S}$ ).

$$
\begin{aligned}
& 2 \mathbf{F C}=\mathbf{S C} \boldsymbol{\Lambda} \\
& 2 \mathbf{F C ^ { \prime }} \mathbf{U}^{\dagger}=\mathbf{S} \mathbf{C}^{\prime} \mathbf{U}^{\dagger} \boldsymbol{\Lambda} \\
& 2 \mathbf{F}^{\prime} \mathbf{C}^{\prime} \mathbf{U}^{\dagger}=\mathbf{S}^{\prime} \mathbf{C}^{\prime} \mathbf{U}^{\dagger} \boldsymbol{\Lambda} \\
& 2 \mathbf{F}^{\prime} \mathbf{C}^{\prime}=\mathbf{S}^{\prime} \mathbf{C}^{\prime} \mathbf{U}^{\dagger} \boldsymbol{\Lambda} \mathbf{U}=\mathbf{S}^{\prime} \mathbf{C}^{\prime} \boldsymbol{\Lambda}^{\prime}
\end{aligned}
$$

We can always choose $\mathbf{U}$ such that it diagonalizes $\boldsymbol{\Lambda}$ (i.e. $\boldsymbol{\Lambda}^{\prime}$ is diagonal) because the latter is hermitian ( $\mathbf{U}$ is unitary, $\boldsymbol{\Lambda}$ is hermitian).

## Towards Hartree-Fock: diagonalizing $\Lambda$

Write (now $\boldsymbol{\Lambda}$ denotes the diagonal matrix):

$$
\boldsymbol{\Lambda} \equiv 2 \boldsymbol{\epsilon}=2\left(\begin{array}{cccc}
\epsilon_{1} & 0 & \ldots & 0 \\
0 & \epsilon_{2} & \ldots & 0 \\
\vdots & \vdots & & \vdots \\
0 & 0 & \ldots & \epsilon_{N / 2}
\end{array}\right)
$$

so that we obtain the Roothaan equations:

$$
\mathrm{FC}=\mathbf{S C} \epsilon \quad, \quad \mathbf{C}=\left(\begin{array}{cccc}
c_{11} & c_{12} & \ldots & c_{1 N / 2} \\
c_{21} & c_{22} & \ldots & c_{2 N / 2} \\
\vdots & \vdots & & \vdots \\
c_{M 1} & c_{M 2} & \ldots & c_{M N / 2}
\end{array}\right)
$$

We can write it for the columns of $\mathbf{C}$ separately:

$$
\mathbf{F c}_{k}=\epsilon_{k} \mathbf{S c}_{k} \text { because } \mathbf{C} \boldsymbol{\epsilon}=\left(\begin{array}{ccccc}
\epsilon_{1} c_{11} & \ldots & \epsilon_{k} c_{1 k} & \ldots & \epsilon_{N / 2} c_{1 N / 2} \\
\vdots & & \vdots & & \vdots \\
\epsilon_{1} c_{M 1} & \ldots & \epsilon_{k} c_{M k} & \ldots & \epsilon_{N / 2} c_{M N / 2}
\end{array}\right)
$$

This is a generalized eigenvalue problem with eigenvalues $\epsilon_{k}$ and eigenvectors $\mathbf{c}_{k}$ and overlap matrix $\mathbf{S}$.

## Towards Hartree-Fock: the Hartree-Fock equation

Help slide:
A standard eigenvalue problem ( $\mathbf{A}$ is a matrix, $\mathbf{v}$ is a vector):

$$
\mathbf{A} \mathbf{v}=\lambda \mathbf{v}
$$

To find the possible eigenvalues $\lambda$ :

$$
\operatorname{det}(\mathbf{A}-\lambda \mathbf{I})=0
$$

A generalized eigenvalue problem ( $\mathbf{A}$ and $\mathbf{B}$ are matrices, $\mathbf{v}$ is a vector):

$$
\mathbf{A} \mathbf{v}=\lambda \mathbf{B} \mathbf{v}
$$

To find the possible eigenvalues $\lambda$ :

$$
\operatorname{det}(\mathbf{A}-\lambda \mathbf{B})=0
$$

## Towards Hartree-Fock: the Hartree-Fock equation

Let's remember how the Fock matrix was defined

$$
\begin{gathered}
F_{\rho \nu}=h_{\rho \nu}+\sum_{\mu \tau} P_{\tau \mu}\langle\rho \mu|\left(2-\hat{P}_{12}\right) \hat{g}|\nu \tau\rangle \text { where } \\
P_{\mu \lambda}=\sum_{k}^{N / 2} C_{\mu k} C_{\lambda k}^{*} \text { and } \phi_{k}=\sum_{\lambda}^{M} \chi_{\lambda} C_{\lambda k}
\end{gathered}
$$

Relabel and expand density matrix and obtain MOs:

$$
\begin{gathered}
F_{\lambda \mu}=h_{\lambda \mu}+\sum_{\nu \tau} P_{\tau \nu}\langle\lambda \nu|\left(2-\hat{P}_{12}\right) \hat{g}|\mu \tau\rangle \text { where } \\
P_{\tau \nu}=\sum_{k}^{N / 2} C_{\tau k} C_{\nu k}^{*} \text { and } \phi_{k}^{*}=\sum_{\nu}^{M} \chi_{\nu}^{*} C_{\nu k}^{*} \text { and } \phi_{k}=\sum_{\tau}^{M} \chi_{\tau} C_{\tau k} \\
\left\langle\chi_{\lambda}\right| \hat{f}\left|\chi_{\mu}\right\rangle \equiv F_{\lambda \mu}=h_{\lambda \mu}+\sum_{\nu \tau} \sum_{k}^{N / 2} C_{\tau k} C_{\nu k}^{*}\langle\lambda \nu|\left(2-\hat{P}_{12}\right) \hat{g}|\mu \tau\rangle \\
=h_{\lambda \mu}+\sum_{k}^{N / 2}\left\langle\chi_{\lambda} \phi_{k}\right|\left(2-\hat{P}_{12}\right) \hat{g}\left|\chi_{\mu} \phi_{k}\right\rangle
\end{gathered}
$$

## Towards Hartree-Fock: the Hartree-Fock equation

$$
\begin{gathered}
\left\langle\chi_{\lambda}(1)\right| \hat{f}(1)\left|\chi_{\mu}(1)\right\rangle=\left\langle\chi_{\lambda}(1)\right| \hat{h}(1)\left|\chi_{\mu}(1)\right\rangle \\
+2 \sum_{k}^{N / 2}\left\langle\chi_{\lambda}(1) \phi_{k}(2)\right| \hat{g}(1,2)\left|\chi_{\mu}(1) \phi_{k}(2)\right\rangle-\sum_{k}^{N / 2}\left\langle\chi_{\lambda}(1) \phi_{k}(2)\right| \hat{P}_{12} \hat{g}(1,2)\left|\chi_{\mu}(1) \phi_{k}(2)\right\rangle
\end{gathered}
$$

We carry out the integration over the second space coordinate and lump it together with the colored parts. We see $\hat{f}$ is a one-electron operator. It is the same operator for all electrons (because we have cancelling self-exchange and self-Coulomb terms). All electrons feel the mean field of all the electrons. There is no electron correlation.

$$
\begin{gathered}
\hat{f}(1)=\hat{h}(1)+\sum_{k=1}^{N / 2}\left(2 \hat{J}_{k}(1)-\hat{K}_{k}(1)\right) \\
\hat{J}_{k}(1) \equiv \int d \mathbf{r}_{2} \frac{\phi_{k}^{*}(2) \phi_{k}(2)}{\left|\mathbf{r}_{1}-\mathbf{r}_{2}\right|}, \quad \hat{K}_{k}(1) \equiv \int d \mathbf{r}_{2} \frac{\phi_{k}^{*}(2) \hat{P}_{12} \phi_{k}(2)}{\left|\mathbf{r}_{1}-\mathbf{r}_{2}\right|}
\end{gathered}
$$

## Towards Hartree-Fock: the Hartree-Fock equation

The eigenvalue problem can be written as the HF equation:

$$
\hat{f}(1) \phi_{k}(1)=\epsilon_{k} \phi_{k}(1)
$$

In a basis this boils down to the Roothaan equations, just expand:

$$
\hat{f}(1) \sum_{\lambda} \chi_{\lambda} C_{\lambda k}=\sum_{\lambda} \chi_{\lambda} C_{\lambda k} \epsilon_{k}
$$

Take the inner product with $\left|\chi_{\mu}\right\rangle$ from the left:

$$
\begin{gathered}
\sum_{\lambda} F_{\mu \lambda} C_{\lambda k}=\sum_{\lambda}\left\langle\chi_{\mu}\right| \hat{f}(1)\left|\chi_{\lambda}\right\rangle C_{\lambda k}=\sum_{\lambda}\left\langle\chi_{\mu} \mid \chi_{\lambda}\right\rangle C_{\lambda k} \epsilon_{k}=\sum_{\lambda} S_{\mu \lambda} C_{\lambda k} \epsilon_{k} \\
\text { i.e. } \mathbf{F c}_{k}=\epsilon_{k} \mathbf{S} \mathbf{c}_{k}
\end{gathered}
$$

With the diagonal matrix of Lagrange multipliers $\boldsymbol{\epsilon}=\boldsymbol{\Lambda} / 2$, this can be written:

$$
\begin{aligned}
& \sum_{\lambda} F_{\mu \lambda} C_{\lambda k}= \sum_{\lambda}\left\langle\chi_{\mu} \mid \chi_{\lambda}\right\rangle C_{\lambda k} \epsilon_{k}=\sum_{\lambda} \sum_{\tilde{k}} S_{\mu \lambda} C_{\lambda \grave{k}} \Lambda_{\tilde{k} k} / 2, \\
& \text { i.e. } \mathbf{F C}=\mathbf{S C} \epsilon \quad(\text { Roothaan })
\end{aligned}
$$

## Towards Hartree-Fock: Solving

The Roothaan equations can be solved on a computer. It is a generalized eigenvalue problem, i.e. linear algebra. It can be solved with a LAPACK call. Input: the Fock and overlap matrices. Output: the eigenvector matrix $\mathbf{C}$ and the eigenvalues $\epsilon_{k}$.

Remember: The Fock matrix has greek indices only $\left(F_{\rho \mu}\right)$. Its size, $M \times M$, is defined by the basis (there are $M$ basis functions). The same holds for the overlap matrix $\mathbf{S}$. Matrix $\mathbf{C}$ has dimensions $M \times N / 2 \ldots$ but the computer will give $M$ eigenvectors with their eigenvectors, i.e. return an $M \times M$ matrix for C. The lowest $N / 2$ eigenvalues are with the occupied states (our matrix $\mathbf{C}$ in the HF derivation). So $M$ should be at least $N / 2$. In practise $M>N / 2$ and we also get empty, virtual states (LUMO and higher).

The story isn't complete ... The Fock matrix depends on the density matrix, i.e. on the eigenvector matrix $\mathbf{C}$.

## Towards Hartree-Fock: Solving

The story isn't complete ... The Fock matrix depends on the density matrix, i.e. on the eigenvector matrix $\mathbf{C}$.

So the Roothaan equations are only solved if the output of the diagonalisation yields the same eigenvectors (within a unitary transformation) as were used to build the Fock matrix ... the solution needs to be self-consistent.

To attain self-consistency, in principle, one runs trough a repeated cycle:

$$
\text { guess } \mathbf{C} \rightarrow \text { build } \mathbf{F} \rightarrow \text { solve for } \mathbf{C} \text { and } \epsilon_{k} \rightarrow \text { build } \mathbf{F} \rightarrow \text { etc. }
$$

This is a feedback system: care is needed mixing input \& output (density) matrices to yield stable and "rapid" convergence (instead of divergence). In solids this can be more tricky than in molecules.

## Towards Hartree-Fock: the eigenvalues

Once we have the converged orbitals, inserting in $h_{k k}$, etc., yields the (ground state) energy of our system:

$$
E=\epsilon=\langle\Psi| \hat{H}|\Psi\rangle=\sum_{k}^{N / 2} 2 h_{k k}+\sum_{k}^{N / 2} \sum_{l}^{N / 2}\left(2 J_{k l}-K_{k l}\right)
$$

We also have the eigenvalues. Per eigenvalue we have an $\alpha$ and a $\beta$ spin. We can add:

$$
\tilde{\epsilon} \equiv \sum_{k}^{N / 2} 2 \epsilon_{k} \neq \epsilon
$$

$$
\begin{aligned}
& \text { To see why, } \\
& \qquad\left\langle\phi_{k}(1) \mid \hat{f}(1) \phi_{k}(1)\right\rangle=\left\langle\phi_{k}(1) \mid\left[\hat{h}(1)+\sum_{l=1}^{N / 2}\left(2 \hat{\jmath}_{l}(1)-\hat{K}_{l}(1)\right)\right] \phi_{k}(1)\right\rangle=\left\langle\phi_{k}(1) \mid \epsilon_{k} \phi_{k}(1)\right\rangle=\epsilon_{k} \Rightarrow
\end{aligned}
$$

$$
\tilde{\epsilon}=2 \sum_{k}^{N / 2}\left\langle\phi_{k}(1)\right| \hat{f}(1)\left|\phi_{k}(1)\right\rangle=2 \sum_{k}^{N / 2}\left\{\left\langle\phi_{k}(1)\right| \hat{h}(1)\left|\phi_{k}(1)\right\rangle+\sum_{l=1}^{N / 2}\left(2\left\langle\phi_{k}(1)\right| \hat{J}_{l}(1)\left|\phi_{k}(1)\right\rangle-\left\langle\phi_{k}(1)\right| \hat{K}_{l}(1)\left|\phi_{k}(1)\right\rangle\right)\right\}
$$

$$
\text { hence: } \epsilon=\tilde{\epsilon}-\sum_{k}^{N / 2} \sum_{l}^{N / 2}\left(2 J_{k l}-K_{k l}\right) \quad \text { Double counting! }
$$

This comes from the minimization where the derivative w.r.t. $C_{\rho m}^{*}$ was taken (week 2). The 2-electron term depends on a product of density matrices, yielding the same contribution twice.

## Towards Hartree-Fock: the eigenvalues

Help slide:

$$
\frac{\partial}{\partial C_{\rho m}^{*}}\left(\sum_{\lambda \mu \nu \tau} P_{\nu \lambda} P_{\tau \mu}\langle\lambda \mu|\left(2-\hat{P}_{12}\right) \hat{g}|\nu \tau\rangle\right)=2 \sum_{\nu} \sum_{\mu \tau} P_{\tau \mu}\langle\rho \mu|\left(2-\hat{P}_{12}\right) \hat{g}|\nu \tau\rangle C_{\nu m}
$$

## Towards Hartree-Fock: the eigenvalues

Remember: if $M>N / 2$ diagonalization of the Roothaan problem will also yield unoccupied orbitals and eigenvalues.

## Koopmans' theorem

We remove an electron $i$ from the system and assume that the orbitals are unaffected. Subtracting the HF energies of both systems, we find an expression (previous slide) exactly equal to the orbital eigenvalue $\epsilon_{i}$. Hence, if $\epsilon_{i}$ is in the HOMO eigenvalue:

$$
\mathrm{IP}=-\epsilon_{i}
$$

I.e., the ionization potential is minus the HOMO eigenvalue. This is Koopman's theorem. One can also add an electron to a virtual orbital $v$. For the LUMO:

$$
\mathrm{EA}=-\epsilon_{v}
$$

EA is the electron affinity. Both IP and EA are positive.
Note: we neglect relaxation of the depleted state... i.e. the calculated IP is too large. However, we also neglect electron correlation, which works the other way, making Koopman's IP often a reasonable number.

The $\epsilon_{v}$ (of neutral molecules) are often positive in HF, yielding unphysical negative EA. The HOMO-LUMO gap in HF is often (much) too large.

## Basis sets

## Basis sets

Our MOs $\left|\phi_{k}\right\rangle$ are linear combinations of atom-centred basis functions $\chi_{\lambda}(\mathbf{r})$ :

$$
\phi_{k}(\mathbf{r})=\sum_{\lambda}^{M} C_{\lambda k} \chi_{\lambda}(\mathbf{r})
$$

The sum is a double sum: it runs over all atoms and over all the orbitals belonging to the atoms. This is common practise in most molecular quantum chemical programs (other choices for $\chi_{\lambda}(\mathbf{r})$ are possible).
Slater type orbitals (STOs):

$$
\chi(\mathbf{r})=r^{n-1} e^{-\zeta r} Y_{l m}(\theta, \phi)
$$

( $n \sim$ principal quantum number)
E.g., the $1 s$ in hydrogen with nucleus sitting at $\mathbf{R}$ :

$$
\phi_{1 s}(\mathbf{r}-\mathbf{R})=\sqrt{\zeta^{3} / \pi} e^{-\zeta|\mathbf{r}-\mathbf{R}|}
$$

Note that $d \phi_{1 s} / d r \neq 0$ at $r=|\mathbf{r}-\mathbf{R}|=0$. Cusp!
Slater type orbitals are very suitable to quantum chemical problems, but computationally awkward. Most chemists use Gaussians. You can use them to approxmate STOs.

## Basis sets

A general Gaussian type orbital (GTO), Cartesian:

$$
\eta\left(\mathbf{r} ; \alpha_{i}\right)=x^{\prime} y^{m} z^{n} e^{-\alpha_{i} r^{2}}
$$

- $I+m+n=0$, i.e. $I=m=n=0$ gives an $s$-orbital
- $I+m+n=1$, i.e. $n=1$ or $m=1$, or $I=1$ gives the $3 p$-orbitals
- $1+m+n=2$, gives $x^{2}, x y, y^{2}, y z, z^{2}$ or $x z$. These are proportional to linear combinations of the 5 (angular) $d$-functions: $d_{x y}, d_{y z}, d_{z x}, d_{x^{2}-y^{2}}$ and $d_{3 z^{2}-r^{2}}$, who, in turn, are a linear mix of the five spherical harmonics $Y_{2 m}$, with $m=-2, \ldots, 2$. There is one additional combination: $x^{2}+y^{2}+z^{2}=r^{2}$ that yields and extra function of $s$ symmetry.


## Basis sets

STO minimal basis sets: the minimum number of STOs needed to accommodate all electrons, e.g. C: $1 s, 2 s$ and $2 p: 1+1+3=5$ STOs.
Optimizing the coefficients (the "zeta"s, i.e. " $\zeta$ "s) in a series of HF calculations on the atom $\rightarrow$ "energy-optimized single-zeta STO basis".

Approximate the STOs as a sum of Gaussians with (optimized) coefficients:

$$
\mathrm{STO}=\sum_{i=1}^{L} d_{i} \eta\left(\mathbf{r} ; \alpha_{i}\right)
$$

Fix the $d_{i}$ (called "contraction") and $\alpha_{i}$ in subsequent molecular calculations. If, e.g., $L=4$, we have a STO-4G basis.

So the STO-4G basis gives a small set of element-specific exponents and contraction coefficients.

## Basis sets

Gaussian basis sets (Pople). Consider, e.g., for C:
SV 4-31G

- "4" the $1 s$ is a contraction of 4 Gaussians (" $G$ "). A single basis function. For a general element: each core state is a contraction of 4 Gs .
- "SV" we have "split valence", i.e. two (radial) basis functions for the valence $2 s$ and $2 p$.
- "31" tells us how the valence is split: One contraction of 3 Gaussians, and one of a single Gaussian. So for $2 s$ we get 2 basis functions, for $2 p$ we get 6 . One calls this "double zeta". One can add, e.g. "SV 6-311" is "triple zeta". More variational freedom!
- Pople cs did not base their basis functions on STOs, but optimized their contraction coefficients and exponents directly on the atom.
- We need many GTOs to approximate the cusp in the $1 s$. An "SV 6-31G" is better in this respect. A contraction of 6 functions mimics the $1 s$.
- SV 4-31G* We can add "polarization functions", i.e. AOs with / quantum number of the first "empty shell", so in this case $d$ functions. To add also on hydrogen: SV 4-31G**
- SV $4-31+$ G has diffusive functions added. With SV 4-31++G also for hydrogen.

