



Chemical Materials Department

Molecular Modeling
Part 1. Quantum Chemistry Calculations

Lecture 1

Basis sets for nonempirical (*ab initio*) calculations

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Molecular Modeling

1. “Molecular Dynamic”

Lecturer prof. O. Kalugin

2. “Quantum Chemistry Calculations of molecules”

Lecturer prof. V. Ivanov

The theoretical background of the Quantum Chemistry part of course is knowledge about

- **Schrödinger equation;**
- **Atomic orbitals;**
- **Molecular Orbitals.**



The General Classification of Quantum Chemistry approaches

Semi-empirical methods **currently can be applied to system with large number of atoms (1000-10000).**

In semi-empirical methods for a set of training systems theoretical parameters are adjusted to experimental data.

$$\text{Molecular properties} = F(P_1, P_2, P_3, \dots)$$

P_i – molecular Parameters; Properties: **Heat of formation, Energies of spectral transitions, Dipole moments *etc.***

Nonempirical (*ab initio*) methods **(around 100-500 atoms)**

Program packages: Gaussian, GAMESS, DALTON, COLUMBUS, SAPT, ORCA

We will use GAMESS package

GAMESS

General Atomic and Molecular Electronic Structure System

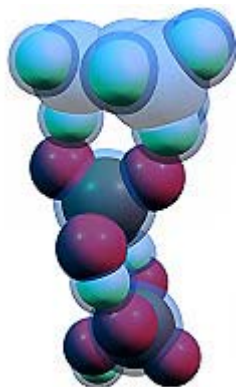
<https://www.msg.chem.iastate.edu/gamess/>

Molecular Graphics



Avogadro

<https://avogadro.cc/>



ChemCraft

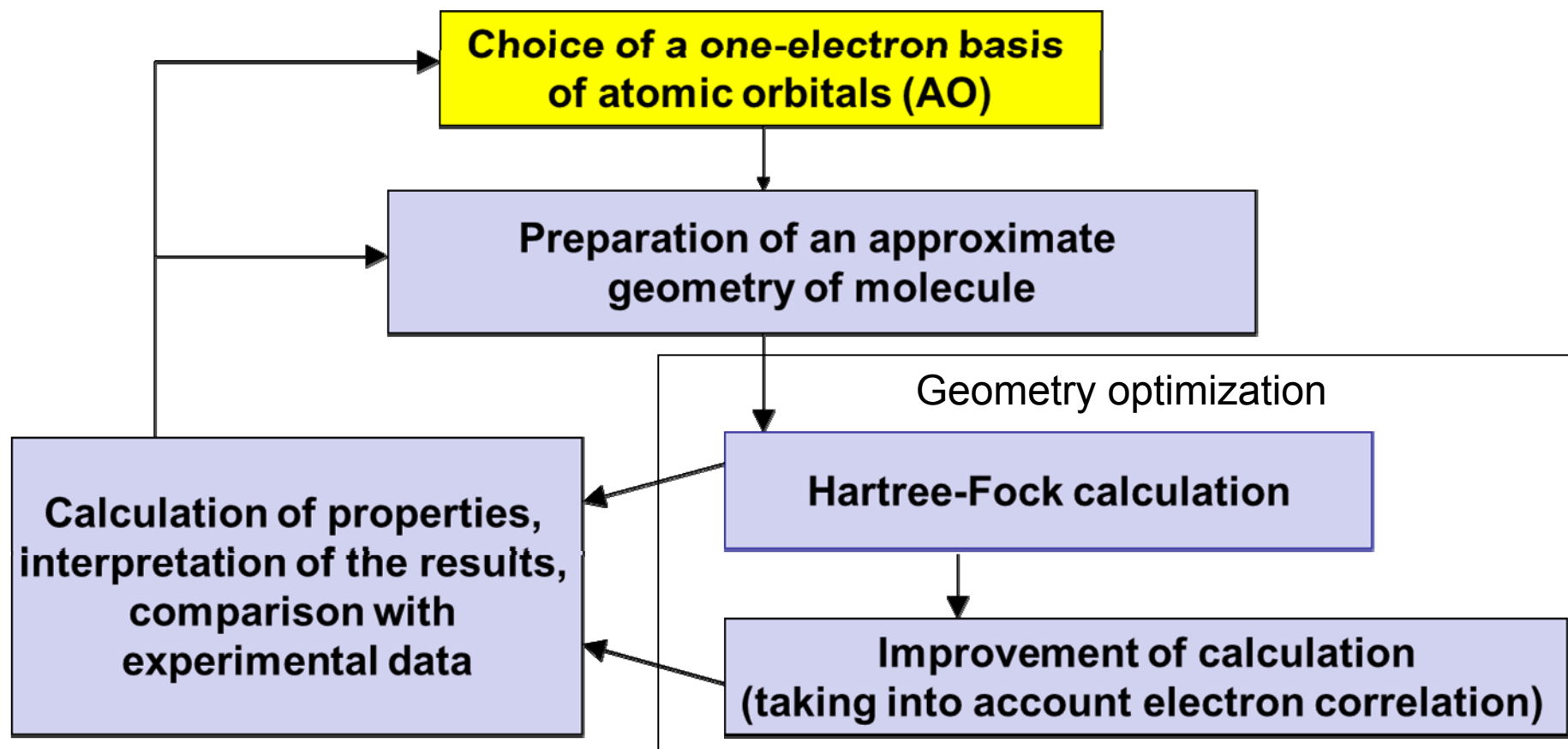
<https://www.chemcraftprog.com/>

What can we get from quantum-chemistry calculations ?

- 1) Optimized geometry of molecules;
- 2) The energies of molecules and complexes, the energies of intermolecular interactions;
- 3) Electronic properties of molecules: charge distributions, dipole moments, *etc.*
- 4) Potential energy surfaces, energies and geometry of reaction transition states, thermodynamics of chemical transformations;
- 5) Vibrational spectra and interpretation of vibrational modes;
- 6) Electronic absorption spectra and fluorescence (ultraviolet and visible region);
- 7) Electrical and magnetic properties of molecules and complexes.

and much more !

Typical scheme of Quantum Chemistry (*ab initio*) calculation



Slater Type Orbitals, STO

$$\chi_{n,m,l} = N r^{n-1} e^{-\alpha r} Y_{m,l}(\theta, \varphi)$$

l и m – quantum numbers of orbital moment;
 N – normalization constant;
 r – electron-nuclear distance;
 α – orbital exponent.

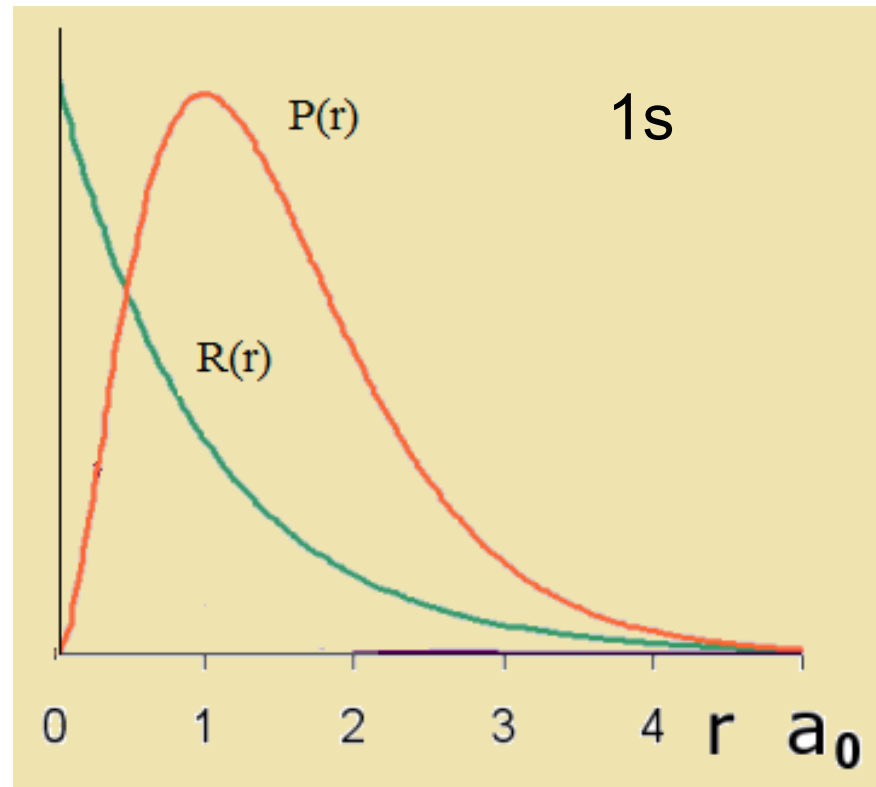
$r^{n-1} e^{-\alpha r}$ - radial part of wave function

$Y_{m,l}(\theta, \varphi)$ - spherical harmonic

The radial part of the wave function describes its dependence on the electron-nuclear distance

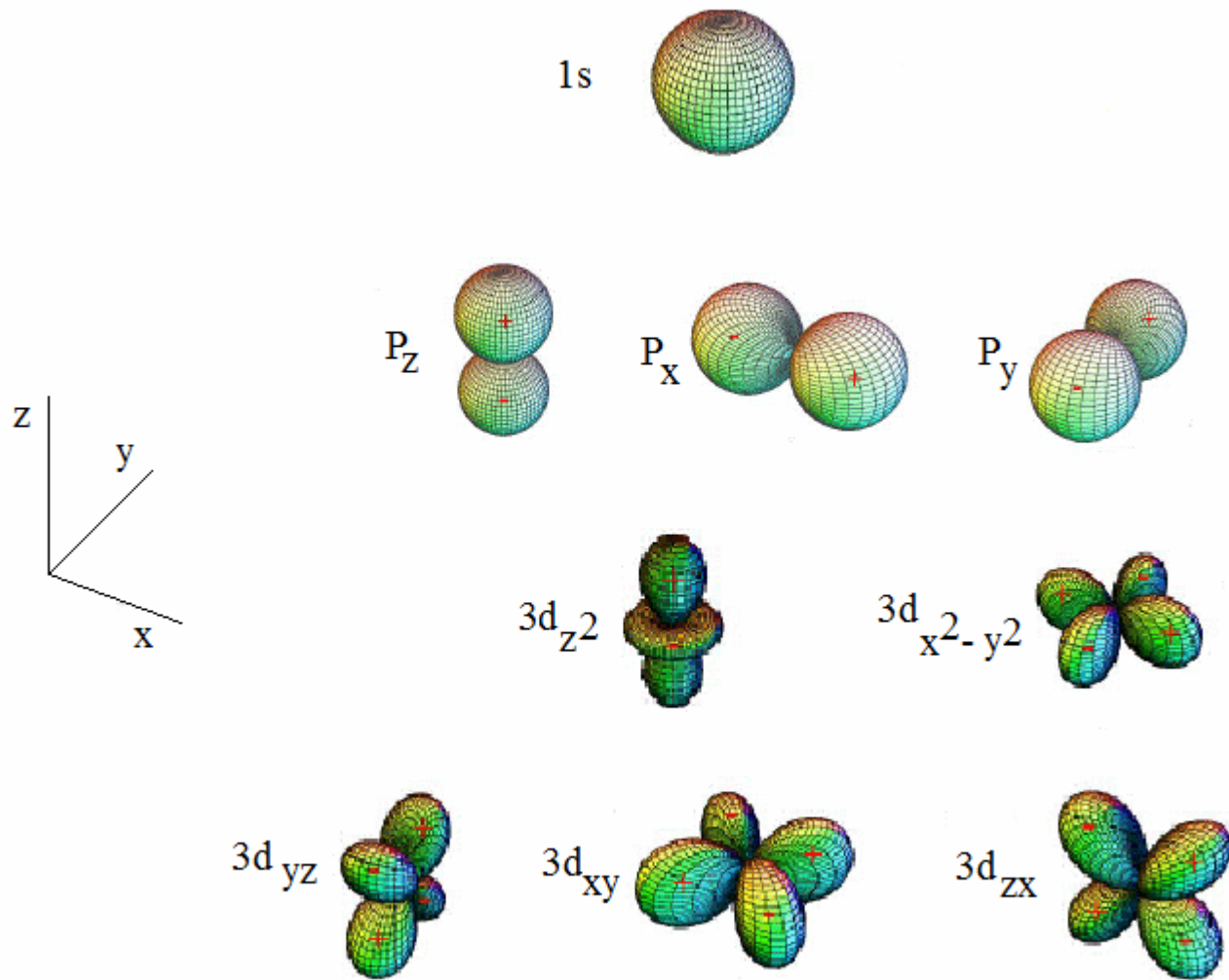
$$R(r) = r^{n-1} e^{-\alpha r}$$

$P(r) = R^2(r)$ the probability of finding an electron at distance r from the nucleus



Spherical Harmonic

$$Y_{m,l}(\theta, \phi)$$



Superposition of functions

$$\text{STO} \quad \chi_{n,m,l} = N r^{n-1} e^{-\alpha r} Y_{m,l}(\theta, \varphi)$$

$$\varphi = \sum_{\mu} C_{\mu} \chi^{(\mu)}$$

C_{μ} α_{μ} **Can be obtained by using variational methods**

$$\min_{C_{\mu}, \alpha_{\mu}} E(C_{\mu}, \alpha_{\mu})$$

Slater Type Orbitals, STO

$$\chi_{n,m,l} = N r^{n-1} e^{-\alpha r} Y_{m,l}(\theta, \phi)$$

Cartesian STO

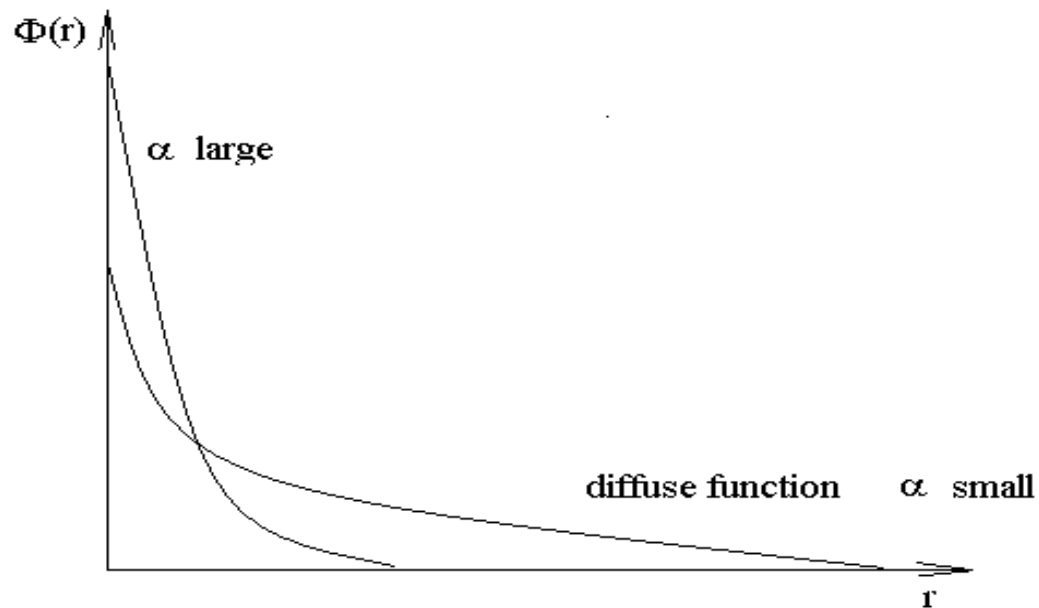
$$\Phi_{n,m,l}^{\text{STO}}(x, y, z) = N x^n y^m z^l e^{-\alpha r}$$

N – normalisation

n, m, l – quantum numbers of angular momentum

$$r^2 = x^2 + y^2 + z^2$$

$$L = n + m + l$$



Main Quantum Chemistry computational problem

Schrödinger equation $H|\psi(123\dots N)\rangle = E|\psi(123\dots N)\rangle$

$$|\psi(123\dots N)\rangle = \dots + \varphi_1(1)\varphi_2(2)\varphi_3(3)\dots\varphi_N(N) + \dots$$

$$H = \sum_{i=1}^N h(i) + \sum_{1 < i < j \leq N} g(ij)$$

$$|\varphi\rangle = \sum_i c_i |\phi_i^{\text{STO}}\rangle$$

Main Quantum Chemistry computational problem

$$H|\psi(123\dots N)\rangle = E|\psi(123\dots N)\rangle$$

$$\langle\psi(123\dots N)|H|\psi(123\dots N)\rangle = E\langle\psi(123\dots N)|\psi(123\dots N)\rangle$$

$$E = \frac{\langle\psi(123\dots N)|H|\psi(123\dots N)\rangle}{\langle\psi(123\dots N)|\psi(123\dots N)\rangle}$$

$$|\varphi\rangle = \sum_i c_i |\phi_i^{\text{STO}}\rangle$$

$$E = \sum \dots [\varphi_r \varphi_s | \varphi_t \varphi_u]$$

**Two electron
integrals**

$$[\varphi_a \varphi_b | \varphi_c \varphi_d] = \int \frac{\varphi_a(1)\varphi_b(1)\varphi_c(2)\varphi_d(2)}{r_{12}} dv_1 dv_2$$

Gauss type AO (GTO)

STO: $\chi_{n,m,l} = N r^{n-1} e^{-\alpha r} Y_{m,l}(\theta, \phi)$

GTO: $\chi_{n,m,l} = N r^{n-1} e^{-\zeta r^2} Y_{m,l}(\theta, \phi)$

Cartesian GTO

$$\Phi_{n,m,l}^{\text{GTO}}(x, y, z) = N x^n y^m z^l e^{-\zeta r^2}$$

N – normalisation

$$L = n + m + l$$

L = 0 (s-orbitals)

$$e^{-\zeta r^2}$$

L = 1 (p-orbitals)

$$n = 1, m = 0, l = 0 \quad x e^{-\zeta r^2}$$

$$n = 1, m = 0, l = 0 \quad y e^{-\zeta r^2}$$

$$n = 0, m = 0, l = 1 \quad z e^{-\zeta r^2}$$

L = 2 (d-orbitals)

$$x^2 e^{-\zeta r^2} \quad y^2 e^{-\zeta r^2} \quad x y e^{-\zeta r^2}$$

$$x z e^{-\alpha r^2} \quad z^2 e^{-\zeta r^2} \quad y z e^{-\zeta r^2}$$

Main Theorem of GTO

A C B



$$e^{-\zeta_A r_A^2} e^{-\zeta_B r_B^2} = P e^{-\zeta_C r_C^2}$$

$$P = e^{\frac{-\zeta_A \zeta_B}{\zeta_A + \zeta_B} R_{AB}^2} \quad \zeta_C = \zeta_A + \zeta_B \quad z_C = \frac{\zeta_A z_A + \zeta_B z_B}{\zeta_A + \zeta_B}$$

R_{AB} - Internuclear Distance between A and B atoms

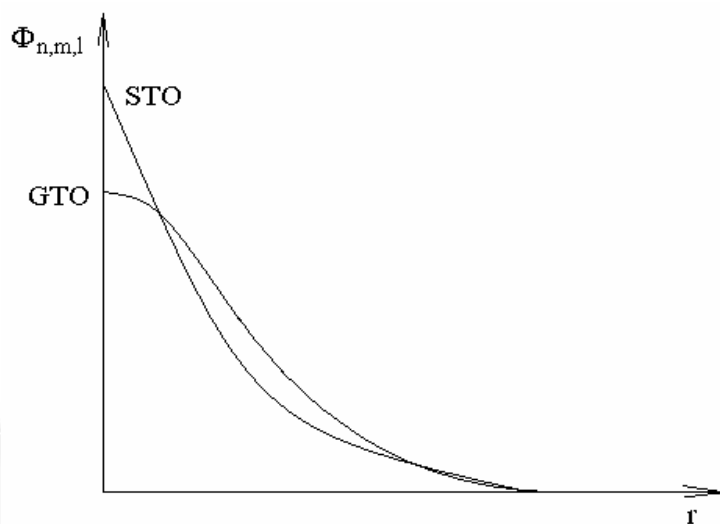
Coordinates of C:

$$x_C = \frac{\zeta_A x_A + \zeta_B x_B}{\zeta_A + \zeta_B} \quad y_C = \frac{\zeta_A y_A + \zeta_B y_B}{\zeta_A + \zeta_B}$$

Main drawback of GTO

$e^{-\zeta r^2}$ **Bad asymptotic** $r \rightarrow \infty$ $r \rightarrow 0$

cusplike condition



$$\text{STO} \approx \sum_{i=1}^N C_i e^{-\zeta_i r^2}$$

$e^{-\zeta_i r^2}$ primitive function
 superposition a set of grouped
 orbitals (compressed or
 contracted).
 C_i – contraction
 coefficients

GTO and STO functions vs electron-nuclear distance

How to calculate compressed (grouped) functions ?

1) Least Squares method:

$$J(C_i, \zeta_i) = \int_0^{\infty} \left(STO - \sum_i C_i e^{-\zeta_i r^2} \right)^2 dr$$

2) Variational principle for electronic shells of atoms $\min E(C_i, \zeta_i)$

Basis set designation

$$(1\ 1s\ 4p\ 2d\ 1f) \rightarrow [4s\ 3p\ 1d\ 1f]$$

John A. Pople Basis sets

John A. Pople Nobel Prize Laureate 1998



(31/10/1925-15/03/2004)

Minimal Basis set, **STO-6G**

Example LiH

Hydrogen – 1s

Lithium – 1s, 2s, 2P_x, 2P_y, 2P_z

$$\varphi_{\text{LiH}} = c_1 \cdot 1s_{(\text{Li})} + c_2 \cdot 2s_{(\text{Li})} + c_3 \cdot 2p_{x(\text{Li})} + c_4 \cdot 2p_{y(\text{Li})} + c_5 \cdot 2p_{z(\text{Li})} + c_6 \cdot 1s_{(\text{H})}$$

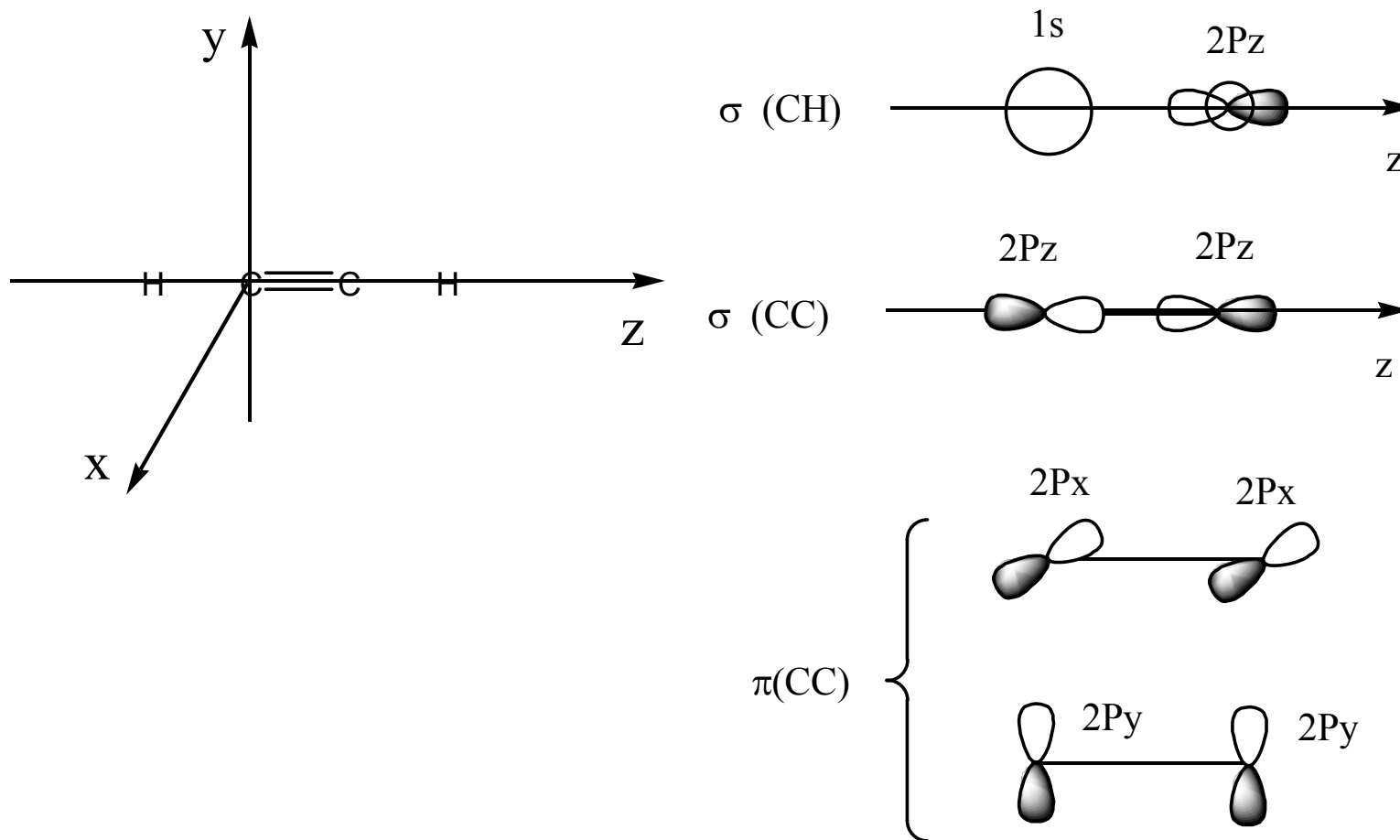
Necessity of valence-split basis sets

In the minimal basis, there is no possibility of changing the size of the orbitals depending on the structure of the molecule. For instance: H_2O and ion H_3O^+ :

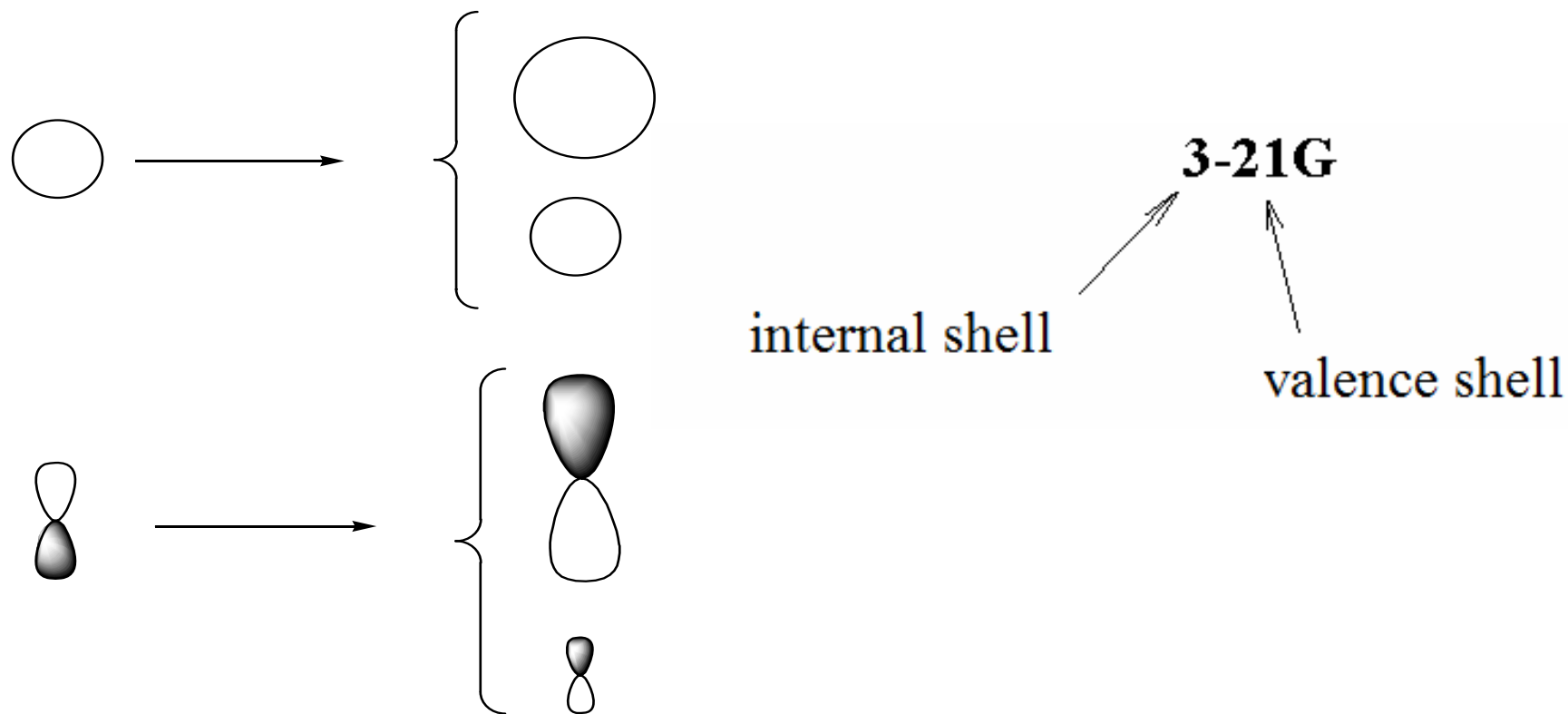


The sizes of P-orbitals are the same, but in H_3O^+ P-orbital must be "pressed" to oxygen !

Necessity of valence-split basis sets



Valence double zeta basis sets



4-21G, 3-21G mean error in geometry - 0.071 Å

6-31G mean error in geometry - 0.035 Å

6-31G basis set for Hydrogen atom

$$\text{STO} \approx \sum_{i=1}^N C_i e^{-\zeta_i r^2} \quad (4s) \rightarrow [2s]$$

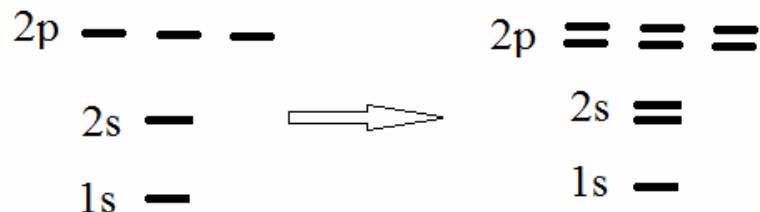
orbital	No	ζ_i	C_i
S	1	18.73113700	0.0334946000
	2	2.825393700	0.2347269500
	3	0.640121700	0.8137573300
S	1	0.161277800	1.0000000000

6-31G basis set for Lithium atom

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$$(10s, 4p) \rightarrow [3s, 2p]$$

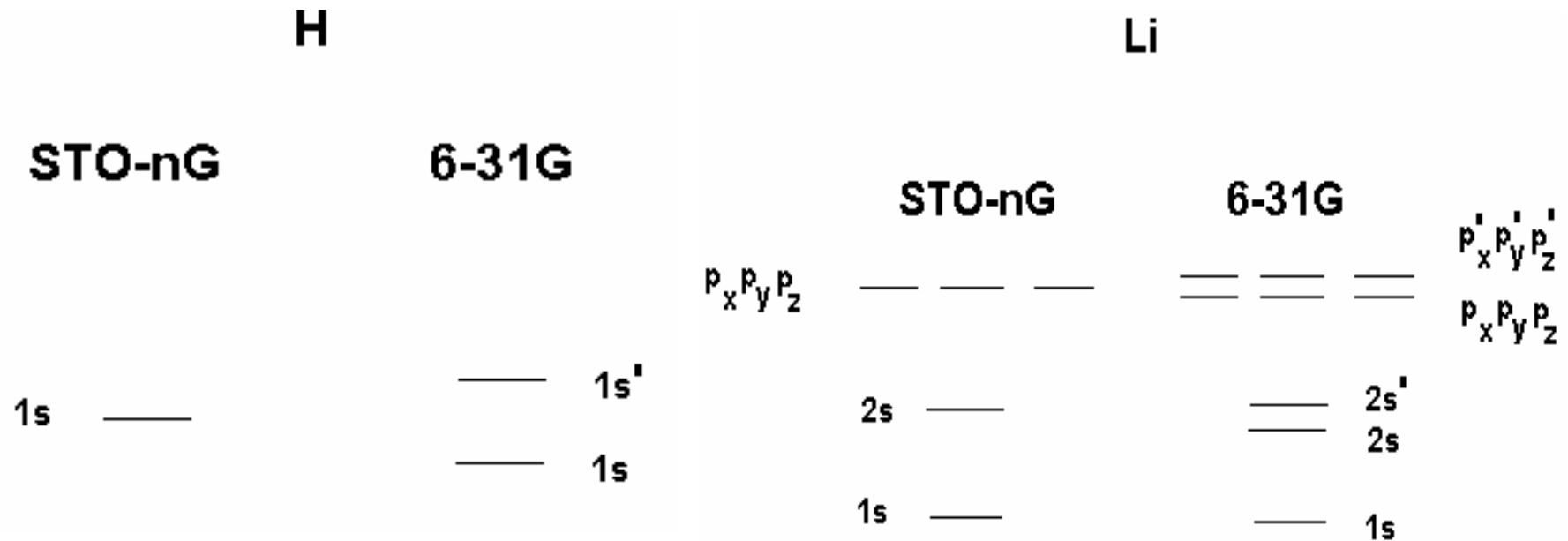
$$\text{STO} \approx \sum_{i=1}^N C_i e^{-\zeta_i r^2}$$



орбіталь	№	ζ_i	C_i
S	1	642.41892	0.0021426
	2	96.798515	0.0162089
	3	22.091121	0.0773156
	4	6.2010703	0.2457860
	5	1.9351177	0.4701890
	6	0.6367358	0.3454708
S, P	1	2.3249184	-0.0350917
	2	0.6324306	-0.1912328
	3	0.0790534	1.0839878
S, P	1	0.0359620	1.0000000

Molecular orbitals of LiH molecule

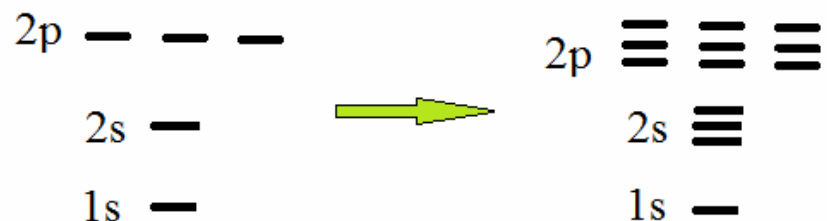
6-31G basis set



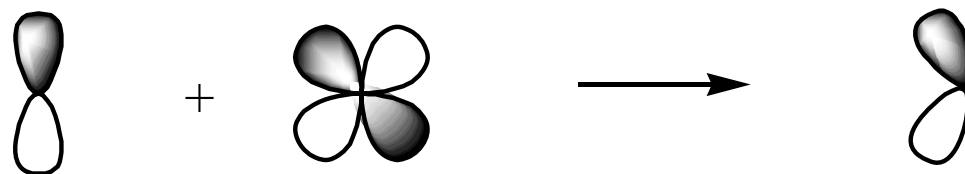
(базис 6-31G) linear combination of 11 basis functions

$$\begin{aligned} \varphi_{\text{LiH}} = & c_1 \cdot 1s_{(\text{Li})} + c_2 \cdot 2s_{(\text{Li})} + c_3 \cdot 2s'_{(\text{Li})} + c_4 \cdot 2p_{x(\text{Li})} + c_5 \cdot 2p_{y(\text{Li})} + c_6 \cdot 2p_{z(\text{Li})} \\ & + c_7 \cdot 2p'_{x(\text{Li})} + c_8 \cdot 2p'_{y(\text{Li})} + c_9 \cdot 2p'_{z(\text{Li})} + c_{10} \cdot 1s_{(\text{H})} + c_{11} \cdot 1s'_{(\text{H})} \end{aligned}$$

Valence triple zeta basis sets (6-311G)



Basis sets with polarization functions



For only heavy atoms (all the atoms except light atoms: hydrogen and helium):

Designations: 6-31G*, 6-311G* or 6-31G(d) i 6-311G(d)

For heavy and light atoms:

Designations: 6-31G**, 6-311G** or 6-31G(d,p) i 6-311G(d,p)

Basis sets with diffuse functions

$$\text{STO} \approx \sum_{i=1}^N C_i e^{-\zeta_i r^2} \quad \zeta_i = 0.1 - 0.01$$

**Valence split basis sets with diffuse functions
(necessary in calculations of anions, electronically excited states,
polarizabilities, intermolecular interactions)**

Examples:

Diffuse functions only for heavy atoms 6-31+G, 6-311+G

Diffuse functions and for heavy and for light atoms 6-31++G, 6-311++G

Huzinaga-Dunning basis sets

double zeta: DZ, triple zeta: TZ.

Valence double zeta: VDZ, Valence triple zeta: VTZ.

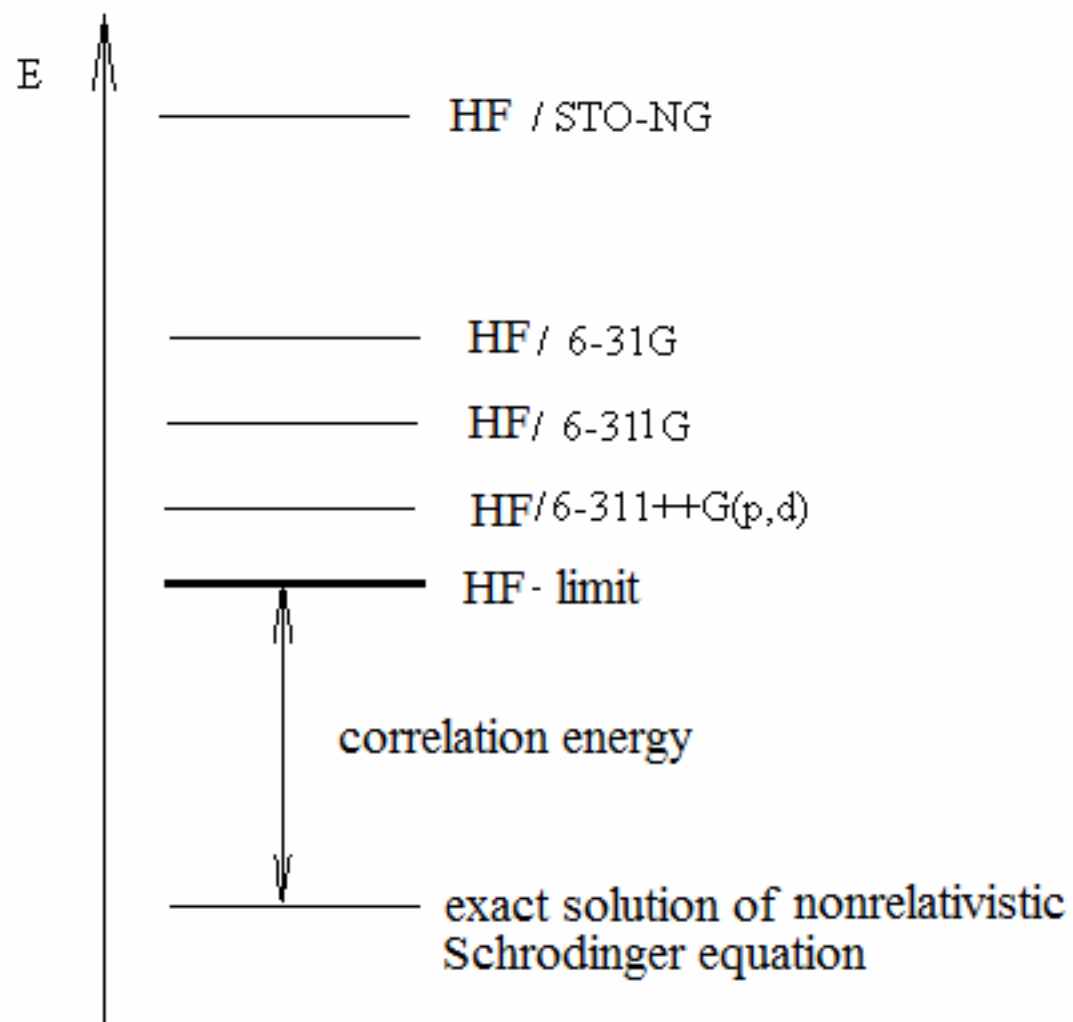
Correlation consists X-zeta basis sets: cc-pVXZ, X=D,T,Q,5,6

aug-cc-pVXZ–augmented basis set

cc-pCVXZ – for best description of core orbitals

Basis	Primitive	Contract	Polariz	aug	cc-pCVXZ
cc-pVDZ	(9s4p)	[3s2p]	[1d]	[1s1p1d]	[1s1p]
cc-pVTZ	(10s5p)	[4s3p]	[2d1f]	[1s1p1d1f]	[2s2p1d]
cc-pVQZ	(12s6p)	[5s4p]	[2d2f1g]	[1s1p1d1f1g]	[3s3p2d1f]

Hartree-Fock limit



Atom Unit System (Hartree atomic units)

$$\hbar = 1, m_e = 1, e = 1$$

$$1 \text{ a.u. (energy)} = 1 \text{ hartree} = 2625.5 \text{ kJ/mol} = 627.5 \text{ kcal/mol} \\ = 27.21138 \text{ eV} = 219474.6 \text{ cm}^{-1}.$$

$$1 \text{ a.u. (distance)} = 0.529177 \text{ \AA}$$

(average distance electron-nuclear in hydrogen atoms)

$$\text{HF/6-31G } E(\text{H}_2\text{O}) = -75.985359 \text{ a.u.}$$



online Physical Values Converter:

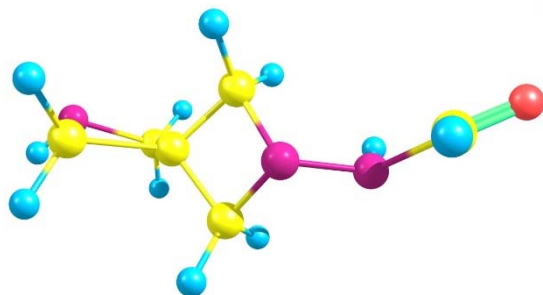
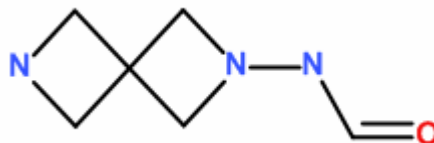
[http://www-](http://www-chemo.univer.kharkov.ua/ivanov/energy_converter.html)

[chemo.univer.kharkov.ua/ivanov/energy_converter.html](http://www-chemo.univer.kharkov.ua/ivanov/energy_converter.html)

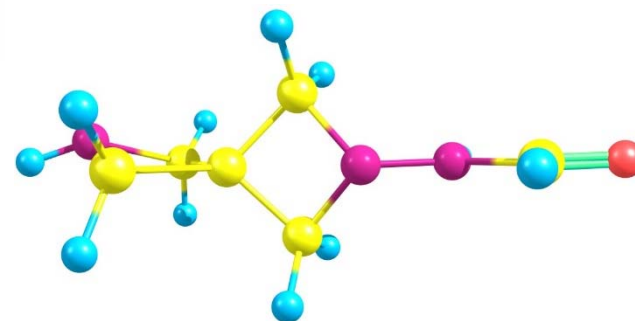
An example – water molecule

Basis	\angle HOH	R_{OH}	μ (D)	E(a.u.)
STO-3G	100.0	0.989	1.709	-74.965901
STO-6G	100.0	0.986	1.754	-75.681200
6-31G	111.5	0.950	2.501	-75.985359
6-31G(d)	105.5	0.947	2.199	-76.010747
6-31G(p,d)	106.0	0.943	2.148	-76.023615
6-31++G(p,d)	107.1	0.943	2.227	-76.031309
6-311G	111.9	0.945	2.488	-76.010955
6-311G(p,d)	105.5	0.941	2.139	-76.047092
6-31G++(p,d)	106.2	0.941	2.196	-76.053446
6-311G++(3p,3d,f)	106.3	0.940	1.968	-76.059488
experimental	104.5	0.957	1.833	HF limit -76.066³⁰

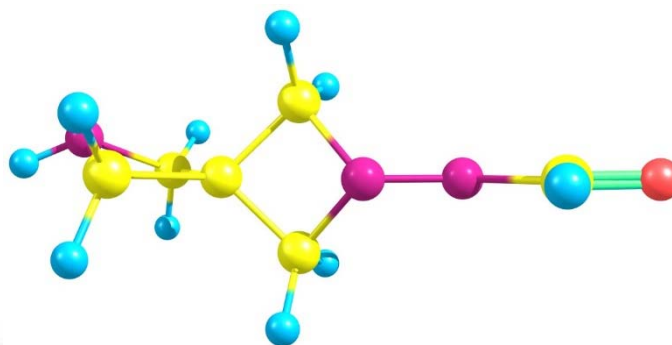
N-(2,6-diazaspiro[3.3]heptan-2-yl)formamide



STO-3G



6-31G



6-31G(d,p)

Dipole moment CO

STO-1G	6-31G	6-311G	6-311G(3d)	6-311+G(3d,1f)	C-O ⁺
+0.730	-0.573	-0.477	-0.080	-0.147	+0.112

Harmonic Freq. (cm⁻¹). Water. (in parenthesis abs. differences relative experiment data)

basis	valence (asym)	valence (sym.)	Deform.
STO-6G	4351.4(596)	4101.5(445)	2161.5(568)
6-31G	4145.4(390)	3988.5(332)	1736.9(143)
6-311G	4172.1(416)	4016.6(360)	1737.0(149)
6-311G**	4225.1(469)	4153.9(497)	1782.4(188)
Exprl.	3755.8	3656.7	1594

Internet resources with information about *ab initio* basis sets

<http://www.re3data.org/repository/r3d100011165>

<https://www.basissetexchange.org/>

<http://www.emsl.pnl.gov/forms/basisform-orig.html>

To be continued

“Geometry Optimization”