Introduction to Quantum Chemistry

part IV

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Basis functions

INTRODUCTION

Historically:

LCAO MO, i.e. Linear Combination of Atomic Orbitals - Molecular Orbitals.

This means that molecular orbitals are formed as a linear combination of atomic orbitals:

$$\psi_i = \sum_{\mu=1}^{n} c_{\mu i} \phi_\mu \tag{1}$$

where ψ_i is the i-th molecular orbital, $c_{\mu i}$ are the coefficients , ϕ_μ is the μ-th atomic orbital, and n is the number of atomic orbitals.

ATOMIC ORBITALS - AO

STO - Slater Type Orbitals.

$$\phi_\mu = \phi_\mu(\zeta, n, l, m; r, \theta, \phi) = N r^{n-1} exp(-\zeta r) Y_{lm}(\theta, \phi) \tag{2}$$

where ψ_i is the i-th molecular orbital, $c_{\mu i}$ are the coefficients , ϕ_μ is the μ-th atomic orbital, and n is the number of atomic orbitals.

GTO - Gaussian Type Orbitals.

$$g(\alpha, l, m, n; x, y, z) = N exp(-\alpha r^2) x^l y^m z^n \tag{3}$$

where N is the normalisation constant, α is called „exponent", x, y, z are cartesian coordinates. The l, m, n ARE NOT quantum numbers but integral exponents at cartesian coordinates $r^2 = x^2 + y^2 + z^2$.

GTOs vs STOs

Calling gaussians GTOs is probably a misnomer, since they are not really orbitals. They are simpler functions. In recent literature, they are frequently called **gaussian primitives**.
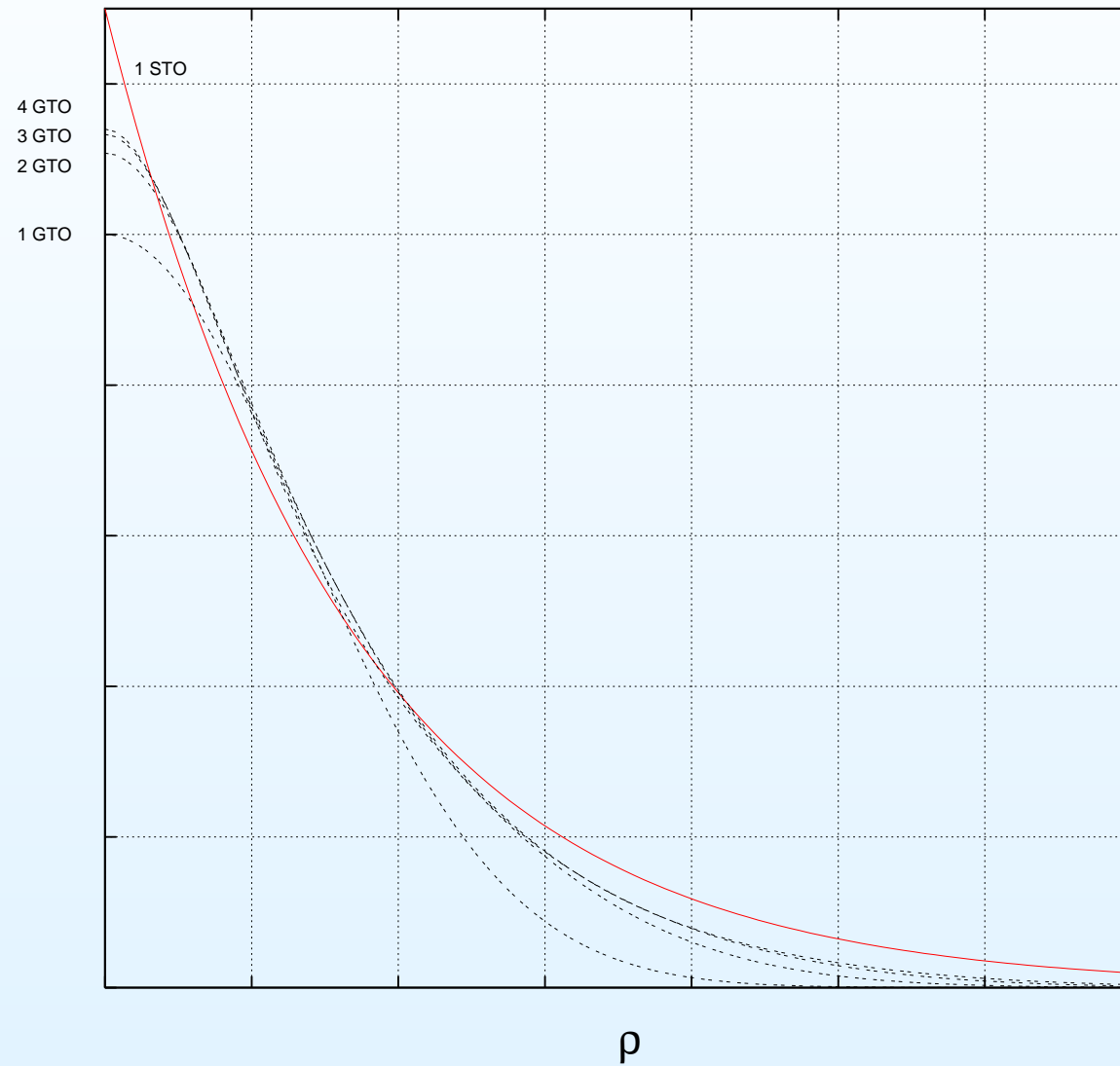
Main differences:

1. in GTOs the r^{n-1} - the preexponential factor - is dropped.
2. the r in the exponential function is squared
3. angular momentum part is a simple function of cartesian coordinates.

The absence of r^{n-1} factor restricts single gaussian primitive to approximating only 1s, 2p, 3d, 4f ... orbitals. It was done for practical reasons, namely, for fast integral calculations.

However, **combinations of gaussians are able to approximate correct nodal properties of atomic orbitals by taking them with different signs**

GTOs vs STOs

Following GTOs are possible

$$1s = Nexp(-\alpha r^2)$$

$$2p_x = Nexp(-\alpha r^2)x$$

$$2p_y = Nexp(-\alpha r^2)y$$

$$2p_z = Nexp(-\alpha r^2)z$$

$$3d_{xx} = Nexp(-\alpha r^2)x^2$$

$$3d_{xy} = Nexp(-\alpha r^2)xy$$

$$3d_{xz} = Nexp(-\alpha r^2)xz$$

$$3d_{yy} = Nexp(-\alpha r^2)y^2$$

$$3d_{yz} = Nexp(-\alpha r^2)yz$$

$$3d_{zz} = Nexp(-\alpha r^2)z^2$$

$$4f_{xxx} = Nexp(-\alpha r^2)x^3$$

$$4f_{xxy} = Nexp(-\alpha r^2)x^2y$$

How are these GAUSSIAN PRIMITIVES derived?

from quantum calculations on atoms (i.e. Hartree-Fock or Hartree-Fock plus some correlated calculations, e.g. CI)

Typically, the exponents are varied until the lowest total energy of the atom is achieved. In some cases, the exponents are optimized independently. In others, the exponents are related to each other by some equation, and parameters in this equation are optimized (e.g. *even-tempered* or *geometrical* and *well-tempered* basis sets).

The primitives so derived describe isolated atoms and cannot accurately describe deformations of atomic orbitals brought by the presence of other atoms in the molecule. Basis sets for molecular calculations are therefore frequently augmented with other functions

Minimum basis set

Only enough functions are employed to contain all the electrons of the neutral atom(s).

Examples:

- for the 0_{th} row in the periodic table (hydrogen and helium): only single s function.
- for the first row: two s functions ($1s$ and $2s$) and one set of p functions ($2p_x$, $2p_y$, $2p_z$). Lithium and berylium formally only require 2 s functions but a set of p functions is also added.
- for the second row elements, three s functions ($1s$, $2s$, $3s$) and two sets of p ($2p$ and $3p$) functions.

Double Zeta (DZ)

Next improvement -> doubling of all basis functions.

Examples:

- for hydrogen and helium: 2 s functions ($1s$ and $1s'$).
- for the first row: 4 s functions and 2 p functions ($1s$, $1s'$, $2s$, $2s'$, $2p$, $2p'$).
- for second row elements: 6 s functions and 4 p functions.

Illustration -> $\mathbf{HCN}$

HCN - Hydrogen cyanide

by the way ...

the prussic acid (brand name Zyklon B) has been selected by Germans as the preferred extermination tool at both the Auschwitz-Birkenau and Majdanek extermination camps during the II World War. The chemical claimed the lives of roughly 1.2 million people at these camps.

Johann Kremer, an SS doctor who oversaw the gassings, testified that: „Shouting and screaming of the victims could be heard through the opening and it was clear that they fought for their lives." When they were removed, if the chamber had been very congested, as they often were, the victims were found half-squatting, their skin colored pink with red and green spots, some foaming at the mouth or bleeding from the ears.

HCN - Hydrogen cyanide

$$H-C\equiv N$$

The H-C bond will primarily consist of hydrogen s-orbital and the p_z orbital on C. The π-bond between the C and N will consist of the p_x and p_y orbitals of C and N. The π-bond will have a more electron distribution then the C-H σ-bond.

Thus, optimally, the exponent for the carbon p-orbital should be smaller for x-direction and y-direction then for the z-direction. If **only one set** of p-orbitals is available (minimum basis) it is impossible.

DZ basis, however, has two sets of p orbitals with different exponents. The tighter function (larger exponent) can enter the C-H σ bond with a large coefficient, while the more diffuse function (smaller exponent) can be used primarily for describing the C-N π bond.

Doubling the number of basis functions – different distribution in different directions

VDZ

The chemical bonding occurs between valence orbitals.

A variation of DZ type basis only doubles the number of valence orbitals producing a *split valence basis*. In actual calculations DZ means VDZ, but not always.

the HCN example:
The $1s$ orbitals are independent on the environment of the C atom, being very close to the atomic case. Doubling of carbon $1s$ orbitals does not make sens.

TZ, QZ, 5Z, ...

TZ - Triple Zeta.
Three times as many functions as the minimum basis: (6 s and 3 p functions for the first-row elements, etc.)
Sometimes TZ=VTZ, it means that the term TZ covers these two cases.

QZ - Quadruple Zeta
Four times as many functions as the minimum basis: (8 s and 4 p functions for the first row elements, etc.)

5Z - Quintuple Zeta (5Z not QZ).
Five times as many functions as the minimum basis: (10 s and 5 p functions for the first row elements, etc.)

Polarization functions

One more time **HCN example**:

$$H-C\equiv N$$

The H-C bond is described by s function of H and s and p_z function of C. It is clear, that **the electron distribution along the bond will be different then that perpendicular to the bond**.

A set of s functions on H can not describe this. However, if a set of p orbitals is added to the hydrogen, the p_z component can be used for improving the description of the C-H bond.

similarly
- d orbitals can be used for polarizing p orbitals
- f orbitals can be used for polarizing d orbitals
- etc.

Polarization functions

DZP - Double Zeta plus Polarization = one set of polarizing functions added to the first row of elements, very often neglecting the p polarizing functions on hydrogen and helium.

DZ2P - Double Zeta plus Double Polarization = 2 sets of polarizaing functions with different exponents.

TZ2P - Triple Zeta plus Double Polarization = TZ basis with two sets of polarizing functions.

etc.

For correlated methods the higher angular momentum, polarization functions are especially important.

Problems

1. *overpolarized basis*: too many polarization functions added to a small sp-basis.
   example: **3s2p1d** basis is balanced, while **3s2p2d2f1g** is too heavily polarized.
   A rule of thumb: the number of functions of a given type should at most be one less then the type with one lower angular momentum.

2. *mixed basis sets*: larger basis on the „intersting" atoms and smaller on the „spectators". It CAN lead to artefacts.

Contraction

Why do we contract and split basis sets?

Because many basis functions go into describing the energetically important but chemically unimportant, core electrons.

$$\chi(\text{CGTO}) = \sum_{i}^{k} a_i \chi_i(\text{PGTO}) \tag{4}$$

CGTO = Contracted „Gaussian" Type Orbital

PGTO = Primitive „Gaussian" Type Orbital

a_i = contraction coefficients - we DO NOT optimize them in our calculations; they are frozen and known before.

the DZP, TZ, TZ2P, etc refer to the number of contracted basis functions.

Segmented contraction

$$\chi_1(\text{CGTO}) = \sum_{i=1}^{6} a_i \chi_i(\text{PGTO})$$

$$\chi_2(\text{CGTO}) = \sum_{i=7}^{9} a_i \chi_i(\text{PGTO}) \qquad (5)$$

$$\chi_3(\text{CGTO}) = \chi_{10}(\text{PGTO})$$

Generally: each primitive is only used in one CGTO.

The contraction coefficients a_i are determined by variational procedure (for example atomic HF calculations).

Example of contraction

Four s-type gaussians were used to represent $1s$ orbital of hydrogen as:

$$\psi_{1s} = \begin{aligned} & 0.50907 N_1 e^{-0.123317r^2} + 0.47449 N_2 e^{-0.453757r^2} + \\ & 0.13424 N_3 e^{-2.01330r^2} + 0.01906 N_4 e^{-13.3615r^2} \end{aligned} \qquad (6)$$

N_i is a normalization constant for a given primitive. In the case of gaussians of type s it is equal to $(2\alpha/\pi)^{3/4}$

Now let's make a contraction of these 4 primitives to only two functions:

$$\phi_1 = 0.50907 N_1 e^{-0.123317r^2}$$

$$\phi_2 = N[0.47449 N_2 e^{-0.453757r^2} + 0.13424 N_3 e^{-2.01330r^2} + 0.01906 N_4 e^{-13.3615r^2}] \qquad (7)$$

4 primitives were contracted to 2 basis functions: $(4s) \rightarrow [2s]$ or $(4s)/[2s]$

General contraction

All primitives on a given atom and of a given angular momentum enter all the contracted functions (having the same angular momentum) but with different contraction coefficient.

$$\chi_1(\text{CGTO}) = \sum_{i=1}^{10} a_i \chi_i(\text{PGTO})$$

$$\chi_2(\text{CGTO}) = \sum_{i=1}^{10} b_i \chi_i(\text{PGTO}) \tag{8}$$

$$\chi_3(\text{CGTO}) = \sum_{i=1}^{10} c_i \chi_i(\text{PGTO})$$
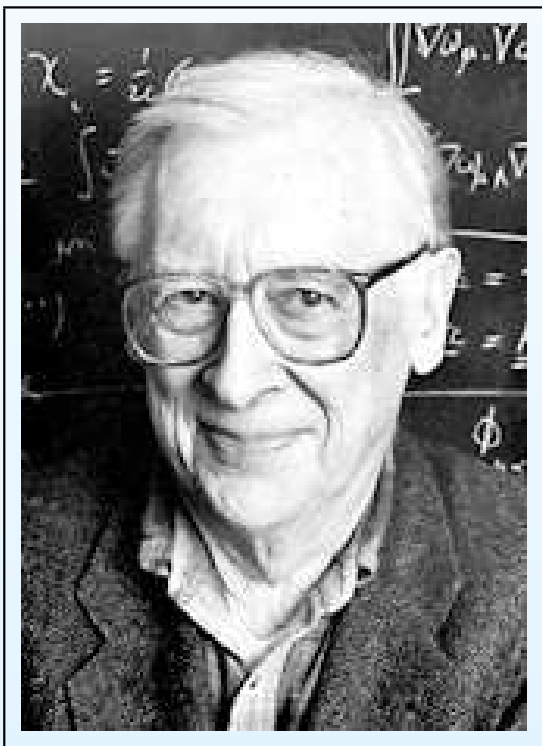
The contraction coefficients a_i, b_i, c_i are determined populary from Atomic Natural Orbitals (ANOs).
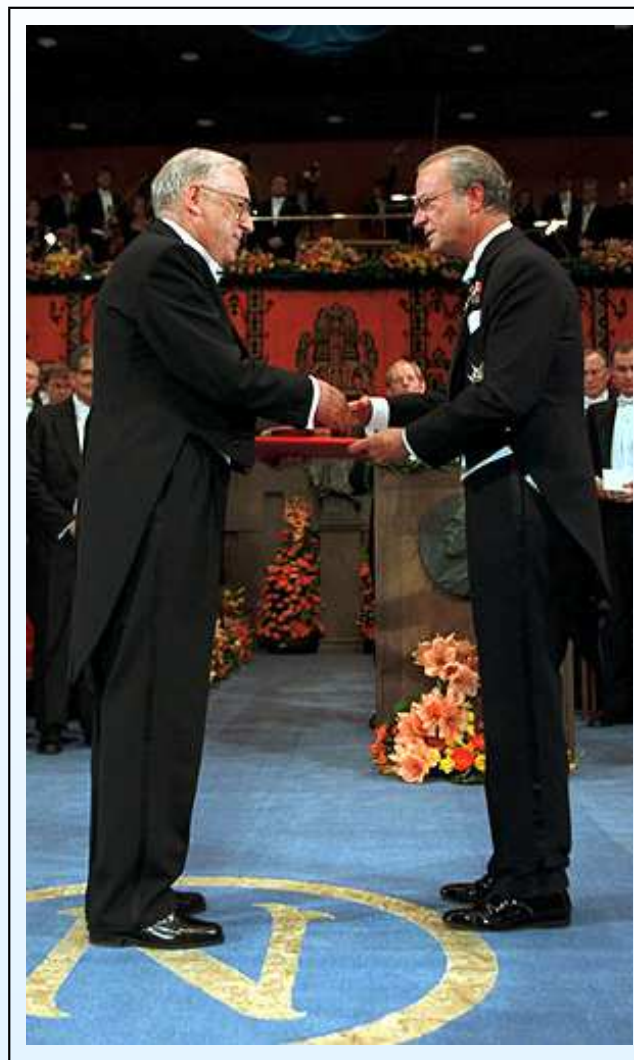
General and segmented contraction

LONDON					Price
Sydney	OG4G	Thu Oct 10	Mon Oct 21 or 28	11 or 18 days	**999GBP**
		Thu Oct 17	Mon Oct 21 or 28	4 or 11 days	**999GBP**
	OG7A	Sun Oct 13	Mon Oct 21 or 28	8 or 15 days	**999GBP**
		Sun Oct 20	Mon Oct 28	8 days	**999GBP**

Pople-style basis functions

John Pople

31.10.1925 - 15.03.2004

1998 Nobel Laureate in Chemistry for his development of computational methods in quantum chemistry. Prize Co-recipient: Walter Kohn

STO-nG

A minimum type basis.

The exponents of the PGTO are determined by fitting them to the STO rather then optimizing them by a variational procedure.

Most popular is the **STO-3G**.

(6s3p/3s) $\rightarrow$ [2s1p/1s]

Derived for many elements of the periodic table.

k-nlmG

k PGTOs represent core electrons.

nlm after the dash indicates both
- how many functions the valence orbitals are split into
- and how many PGTOs are used for their representation

Two values, i.e. **nl** indicate split valence.

Three values, i.e. **nlm** indicate a triple split valence.

Values before the **G** indicate s and p functions

Values after the **G** indicate polarization functions.

Here, the same exponent is used both in s and in p the valence functions.

The most popular basis sets.

3-21G

Split valence basis set

The core orbitals are a contraction of three PGTOs.

The inner part of the valence orbitals is a contraction of two PGTOs.

The outer part of the valence is represented by one PGTO.

(6s3p/3s) → [3s2p/2s]

Note. The 3-21G basis contains the same number of PGTOs as the STO-3G, but there are twice as many valence functions which can combine more flexibly to make MOs. (STO-3G: [2s1p/1s], 3-21G: [3s2p/2s]).

6-31G

Split valence basis set

The core orbitals are a contraction of 6 PGTOs.

The inner part of the valence orbitals is a contraction of 3 PGTOs

The outer part of the valence orbitals is represented by one PGTO.

(10s4p/4s) → [3s2p/2s]

Note. In terms of contracted basis functions it contains the same number of functions as 3-21G but the representation of each CGTO is better since more PGTOs are used.

6-311G

Triple split valence basis set

The inner part of the valence orbitals is represented by 3 PGTO.

The middle part of the valence orbitals is represented by one PGTO.

The outer part of the valence orbitals is represented by one PGTO.

$(11s,5p/5s) \rightarrow [4s,3p/3s]$

Polarization and diffusion functions

Diffuse functions are normally s and p functions and consequently go before the **G**. They are denoted by **+**.

One **+** indicates one set of diffuse functions on atoms heavier then hydrogen and helium.

Two **+**, i.e. **++** indicates additionaly the s functions on hydrogens and heliums.

Polarization functions are indicated after the G, with a separate designation for heavy atoms and hydrogens.

Examples:
6-31G(2df) is a 6-31G basis with additional 2 d and 1 f function on atoms heavier then hydrogen or helium.

6-311G(2d,2p) is a 6-311G basis with additional 2 d on heavy atoms and 2 p on hydrogens.

Polarization and diffusion functions

Sometimes, instead of (d) we write an asterisk * and instead of (d,p) we write double asterisk, i.e. **.

6-31G(d) = 6-31G*
6-31G(d,p) = 6-31G**

other examples: **6-31G+(d,p), 6-31G++(2df,2p), 4-31+G*.**

66-31G example

Shell	Exponent	s coefficient	p coefficient
1 S	1.61921(+4)	1.94924(-3)	
	2.43609(+3)	1.48559(-2)	
	5.56001(+2)	7.25689(-2)	
	1.56813(+2)	2.45655(-1)	
	5.01692(+1)	4.86060(-1)	
	1.70300(+1)	3.25720(-1)	
2 SP	2.93350(+2)	-2.82991(-3)	4.43334(-3)
	7.01173(+1)	-3.60737(-2)	3.24402(-2)
	2.24301(+1)	-1.16808(-1)	1.33719(-1)
	8.19425	9.35768(-2)	3.26780(-1)
	3.14768	6.01705(-1)	4.51139(-1)
	1.21515	4.22207(-1)	2.64105(-1)
3 SP	1.65370	-2.40600(-1)	-1.51774(-2)
	5.40760(-1)	7.37953(-2)	2.75139(-2)
	2.04406(-1)	1.04094	7.83008(-1)
3 SP	7.23837(-2)	1.00000	1.00000

MINI-i, MIDI-i

MINI-i $(i = 1, 2, 3, 4)$.

Minimum basis sets with 3 PGTOs describing 2s CGTO and varying numbers of PGTOs describing 1s and 2p CGTOs.

1. **MINI-1** . (3s,3s,3p) PGTOs.
2. **MINI-2** . (3s,3s,4p) PGTOs.
3. **MINI-3** . (4s,3s,3p) PGTOs.
4. **MINI-4** . (4s,3s,4p) PGTOs.

MIDI. Identical to MINI-i, except that the outer valence basis is decontracted.

MAXI-i

MAXI-i.

Four PGTOs for the 2s CGTO and 5-7 PGTOs to represent the 1s and 2p CGTOs.

Valence orbitals are split into three or four functions.

1. **MAXI-1** . (9s,5p) $\rightarrow$ [4s,3p], contraction 5,2,1,1 and 3,1,1.
2. **MAXI-3** . (10s,6p) $\rightarrow$ [5s,4p], contraction 6,2,1,1 and 3,1,1.
3. **MAXI-5** . (12s,7p) $\rightarrow$ [5s,4p], contraction 7,2,1,1,1 and 4,1,1,1.

Correlation Consistent basis sets

Basis sets of segmented contraction type. Optimized using so called ANOs from correlated calculations on the free atom, typically at the CISD level.

Addition of polarization functions is done in the order: 1d, 2d1f, 3d2f1g, etc.

basis	primitive functions	contracted functions
cc-pVDZ	9s,4p,1d/4s,1p	3s,2p,1d/4s,1p
cc-pVTZ	10s,5p,2d,1f/5s,2p,1d	4s,3p,2d,1f/3s,2p,1d
cc-pVQZ	12,6p,3d,2f,1g / 6s,3p,2d,1f	5s,4p,3d,2f,1g/4s,3p,2d,1f
cc-pV5Z	14s,9p,4d,3f,2g,1h/8s,4p,3d,2f,1g	6s,5p,4d,3f,2g,1h/5s,4p,3d,2f,1g
cc-p6Z	16s/10p,5d,4f,3g,2h,1i/10s,5p,4d,3f,2g,1h	7s,6p,5d,4f,3g,2h,1i/6s,5p,4d,3f,2g,1h

Effective Core Potentials - ECPs

Core (inner) orbitals are in most cases not affected significantly by changes in chemical bonding. This prompted the development of Effective Core Potential (ECP) or Effective Potentials (EP) approaches

They allow treatment of inner shell electrons as if they were some averaged potential rather than actual particles.

ECP's are not orbitals but modifications to a hamiltonian, and as such are very efficient computationally.

They can incorporate relativistic effects into ECP, while all-electron relativistic computations are very expensive. The relativistic effects are very important in describing heavier atoms, and luckily ECP's simplify calculations and at the same time make them more accurate with popular non-relativistic ab initio packages

ECPs - continuation

$$ECP(r) = \sum_{i=1}^{M} d_i r^{n_i} \exp(-\zeta_i r^2) \qquad (9)$$

To specify ECP for a given atomic center, one need to include typically:

1. the number of core electrons that are substituted by ECP,
2. the largest angular momentum quantum number included in the potential (e.g., 1 for s only, 2 for s and p, 3 for s, p, and d; etc.),
3. and number of terms in the "polynomial gaussian expansion" shown above.

Basis Set Superposition Error (BSSE)

$$\Delta E_{A-B} = E_{A-B} - (E_A + E_B) = [E_{A-B} - (\tilde{E}_A + \tilde{E}_B)] + (\tilde{E}_A - E_A) + (\tilde{E}_B - E_B)$$

$$\delta E_{A-B} = [\tilde{E}_A(\chi_A \cup \chi_B) - \tilde{E}_A(\chi_A)] + [\tilde{E}_B(\chi_A \cup \chi_B) - \tilde{E}_B(\chi_B)]$$