1.1. Theoretical Methods and Computational Chemistry

Theoretical methods and computational techniques are used to model or mimic the behavior of molecules and deliver access to their geometric and electronic structures, allowing the calculation of many properties of chemical systems.

Obviously, atomic entities in molecular systems have to be modeled using a mathematical description within a physical model, coupled to computational tools for solving the subsequent equations. Simplest models describe the atoms as the smallest individual units using classical (*i.e.* Newtonian) mechanics, replacing (and grouping) nuclei and electrons by material points (either charged or not), thereby describing interatomic interaction by parameterized forces (spring-like interactions), constructing a parameterized force field. This method is known as molecular mechanics (MM).

More sharply, a molecular system may be modeled within the physical reality of its constituents, describing explicitly atoms as its constituents, which are electrons moving in the field of positively charged nuclei. Obviously, Newton's laws of physics are no more of help at the atomic scale and these models employ quantum physics.

In this section, elementary quantum mechanics (QM) used in chemistry will be shortly reviewed to lay the foundations for a short theoretical discussion on density functional theory (DFT), later used in this work to assess an interesting regiochemistry question.

The current discussion has been inspired by quantum mechanical and molecular modeling textbooks [1,2,3,4,5,6]. Nevertheless, some landmark papers and important references are explicitly cited in the text.

The present section is obviously not intended for a comprehensive, in depth discussion of quantum physics. Its goal is to expose the fundamental principles needed for the understanding and the practical use of modern quantum chemistry methods.

"Everything we call real is made of things that cannot be regarded as real."

"When it comes to atoms, language can be used only as in poetry. The poet, too, is not nearly so concerned with describing facts as with creating images."

Niels Bohr

1.1.1. Elementary quantum chemistry

In the present section will only be discussed the stationary many-body quantum problem. Evolution of the system with time and solving the time-dependent Schrödinger's equation will not be considered. The time-dependent Schrödinger's wave equation is given for information:

$$\hat{H}\psi_{(r,t)} = \left[-\frac{\hbar^2}{2m}\nabla^2 + V_{(r)}\right]\psi_{(r,t)} = i\hbar\frac{\partial\psi}{\partial t} \quad (1.1)$$

where $\psi_{(r,t)}$ is the wavefunction and ∇^2 is shorthand for $\left(\frac{\partial}{\partial x^2} + \frac{\partial}{\partial y^2} + \frac{\partial}{\partial z^2}\right)$, the Laplacian operator.

1.1.1.1. The time-independent Schrödinger's wave equation

First will be introduced the Born-Oppenheimer approximation which is a central concept in quantum theory and computation. The Born-Oppenheimer approximation has its basis on the fact that the nuclear motion is slower than that of electrons. Within this approximation, the nuclei are considered as fixed for solving the electronic Schrödinger's equation in order to obtain an electronic wavefunction; so that the electrons are moving in a constant external potential due to the nuclei.[1] Therefore, a stationary electronic state is described by an electronic wavefunction $\Psi(\chi_1, \dots, \chi_N)$ satisfying the *N*-electron time-independent Schrödinger equation:

$$\hat{H}_e\,\Psi_{e(\chi_i)} = \left[-\frac{\hbar^2}{2m}\nabla^2 + \hat{V}_{(r)}\right]\Psi_{e(\chi_i)} = E_e\,\Psi_{e(\chi_i)} \quad (1.2)$$

where $\hat{H}_e$ is the electronic Hamiltonian, E_e is the electronic energy, χ_i stands for the three space variables and the spin variable of electron *i*, and $\hat{V}_{(r)}$ is the potential energy operator arising from the external field due to positively charged nuclei. The Hamiltonian operator is a differential operator representing the total energy, which is written in atomic units in a convenient form:

$$\hat{H}_e = \hat{T}_e + \hat{V}_{N,e} + \hat{V}_{e,e} \quad (1.3)$$

$$\hat{H}_e = -\frac{1}{2}\sum_i^N \nabla_i^2 - \sum_A^M\sum_i^N \frac{Z_A}{|R_A - r_i|} - \sum_i^N\sum_{j>i}^N \frac{e^2}{|r_i - r_j|} \quad (1.4)$$

The solution of an electronic Hamiltonian is an electronic wavefunction depending on the electronic spatial and spin coordinates, $\{\vec{r_i}\}$ and $\{s_i\}$, collectively termed $\{\vec{\chi_i}\}$. Atomic units are particularly well adapted

---

[1] *The nuclear wavefunction is calculated by solving the nuclear Schrödinger's equation in which the electronic energy E_e of (1.2) appears in the potential term. The BO approximation allows the wavefunction and the total energy of a molecule to be broken into its electronic and nuclear components: $\psi_{total} = \Psi_{electrons}\,\Psi_{nuclei}$ and $E_{total} = E_{electrons} + E_{nuclei}$*

for working with atoms and molecules. In this system, the mass of the electron (m_e), its charge modulus ($|e|$), the permittivity of vacuum ($4\pi\varepsilon_0$), and the reduced Planck's constant ($\hbar = \frac{h}{2\pi}$) are all set to unity.

From now we will only consider the electronic problem, so the subscripts referring to the electronic Schrödinger's equation will be dropped.

Table 1. Atomic units.

Quantity	Atomic unit	Value in SI units	Symbol
Mass	Rest mass of the electron	9.1094 10^{-31} kg	m_e
Charge	Elementary charge	1.6022 10^{-19} C	e
Action	Reduced Planck's constant	1.0546 10^{-34} J s	$\hbar$
Length	$4\pi\varepsilon_0\hbar / m_e e^2$	5.2918 10^{-11} m	a_0
Energy	$\hbar / m_e a_0^2$	4.3597 10^{-18} J	E_h

The wavefunction is not an observable, it is a probability amplitude. Its only physical interpretation is associated with its square modulus:

$$|\Psi(\chi_i)|^2 d\chi = P(\chi_i)d\chi \quad (1.5)$$

The wavefunction is obviously normalized as the probability to find the particle all over the space should be equal to one. So, integration of the probability amplitude over space is necessary equal to unity:

$$\int |\Psi(\chi_i)|^2 d\chi = 1 \quad (1.6)$$

A wavefunction satisfying equation (1.6) is said to be normalized. From now, we will only deal with normalized wavefunctions.

1.1.1.2. The variational principle

The ultimate goal of most quantum mechanical methods is to find a solution to the time-independent Schrödinger's equation. Unfortunately, no analytic solution can be found for systems consisting in more than two particles. Hence, the problem to be solved is the so-called "many-body problem" and an approximate solution of the Schrödinger's equation has to be found. A systematic tool for approaching the exact ground-state wavefunction Ψ_0 lays in the variational principle, a central method in quantum physics.

In quantum mechanics, the expectation value of the observable associated with the operator $\hat{O}$ is given by the following equation:

$$\langle \hat{O} \rangle = \frac{\int \Psi^* \hat{O}\, \Psi d\chi}{\int \Psi^* \Psi d\chi} = \frac{\langle \Psi | \hat{O} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad (1.7)^2$$

Using the Hamiltonian operator in equation (1-7) will return the energy as the expectation value. Then, the variational principle states that, from any guessed Ψ, the related energy eigenvalue will be an upper bound to the exact ground-state energy (unless the trial function is the exact one):

$$\langle \hat{H} \rangle = \frac{\langle \Psi_{trial} | \hat{H} | \Psi_{trial} \rangle}{\langle \Psi_{trial} | \Psi_{trial} \rangle} = E_{trial} \geq \frac{\langle \Psi_0 | \hat{H} | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle} = E_0 \quad (1.8)$$

$$E_{trial} = E_0 \overset{iff}{\leftrightarrow} \Psi_{trial} = \Psi_0 \quad (1.9)$$

Therefore, the strategy for finding the ground-state energy and wavefunction will consist in minimizing the functional $E[\Psi]$ for searching the best wavefunction among acceptable *N*-electron functions.

1.1.1.3. *Spin-orbitals*

For one electron systems (*i.e.* a two particles problem), the Schrödinger's equation can be solved exactly (analytically) and its wavefunctions are called orbitals. However, it is no longer the case when more than two interacting particles are considered and the many-body problem of many-electron atoms needs the use of the orbital approximation. Within this formalism, the many-electron wavefunction is replaced by mono-electronic entities, each electron being treated separately. The total electronic wavefunction is then expressed as a product of mono-electronic functions:

$$\Psi(\chi_i) = \Psi(\chi_1)\Psi(\chi_2) \dots \Psi(\chi_N) \quad (1.10)$$

Let's take a two-electron example for this fundamental approximation used to describe atoms by means of orbital configurations:

$$\Psi(\chi_1, \chi_2) = \Psi(\chi_1)\Psi(\chi_2) \; and \; P(\chi_1, \chi_2) = P_1(\chi_1)P_2(\chi_2) \quad (1.11)$$

The total wavefunction depending on spatial and spin coordinates of both electrons is then expressed as a product of two functions, depending only on the position and spin coordinates of one electron. The probability amplitude of the total wavefunction is therefore approximated to the product of probabilities of finding each electron at given points independently. If this approximation may, at first glance, give the impression that repulsion between electrons is not taken into account, it is evidently not true, since the two orbitals are not solutions of a one-electron Schrödinger's equation. The functions $\Psi(\chi_1)$ and $\Psi(\chi_2)$ of equation (1.11) indeed include electronic repulsion in an averaged manner. However, it lacks of electronic

---

[2] Dirac's bra-ket notation.

correlation as the motion of an electron is not correlated to the motion of the other, but only "feels" this electron as an average field.

Within the orbital approximation, we can write the ground-state electronic configuration of helium as:

$$\text{He: } 1s^2 = 1s_1^\alpha \, 1s_2^\beta = 1s(1) \, 1\bar{s}(2) = \Psi_{\text{He}} \quad (1.12)$$

where α and β superscripts stand for the two spin states whether $1s(1)$ and $1\bar{s}(2)$ are associated with α and β spins of electrons 1 and 2. But one can see that this expression of the helium wavefunction does not fulfill Pauli's antisymmetry principle. Indeed, when interchanging a pair of electrons (and moreover, fermions), the wavefunction must change sign. So an acceptable form for the two-electron wavefunction is:

$$\Psi_{\text{He}} = \frac{1}{\sqrt{2}} \left[1s(1) \, 1\bar{s}(2) - 1s(2) \, 1\bar{s}(1) \right]^3 \quad (1.13)$$

Hopefully we can write this in a convenient form as these products are the expansion of a determinant:

$$\Psi_{\text{He}} = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1) & 1s(2) \\ 1\bar{s}(1) & 1\bar{s}(2) \end{vmatrix} \quad (1.14)$$

We may generalize the expression (1.14) to heavier atoms. We will therefore have to write each permutation of electrons, which leads to $N!$ products whether the normalizing constant becomes $1/\sqrt{N!}$. So more generally, we obtain the Slater determinant, Φ_{SD}:

$$\Psi(\chi_1, \chi_2, \ldots, \chi_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(\chi_1) & \cdots & \varphi_1(\chi_N) \\ \vdots & \ddots & \vdots \\ \varphi_N(\chi_1) & \cdots & \varphi_N(\chi_N) \end{vmatrix} = |\varphi_1 \, \varphi_2 \ldots \varphi_N| = \Phi_{SD} \quad (1.15)$$

Hence, the goal of computational methods is to find the mono-electronic φ_i of any chemical or atomic system. It should be reminded that replacement of the true *N*-electron wavefunction by a single Slater determinant consists in a fairly drastic approximation.

Historically, Douglas Hartree firstly computed numerical functions [7], later fitted to analytical forms by John Slater to obtain the so-called Slater orbitals [8]. These functions depend on the three spatial coordinates (r, θ, ϕ) [4] and one spin coordinate and have the general form of:

$$\varphi_i = (normalization\ constant).(exponential\ function\ of\ r).(spherical\ harmonic)$$

$$\varphi_i = R_n(r)\, Y_m^l(\theta, \phi) = N\, r^{n-1}\, e^{-\zeta r}\, Y_m^l(\theta, \phi) \quad (1.16)\text{ [5]}$$

One would notice that the radial part of these wavefunctions is responsible for the atom-to-atom variations. The spherical harmonic part of these orbitals is identical to the one of hydrogen, for which the exact analytical forms are known. This is made possible by adopting the central field approximation, so that each electron feels a potential that only depends on its radial distance from the nucleus.

1.1.1.4. Molecular orbitals (MOs)

Once dealing with molecules (rather than atoms), one would expect the molecular wavefunctions Ψ to have the same appearance than the atomic wavefunctions $\varPsi$. So, applying the orbital approximation, we write the total molecular wavefunction as a product of mono-electronic molecular spin-orbitals, $\varPhi_i$:

$$\Psi = \varPhi_1 \varPhi_2 \dots \varPhi_N \quad (1.17)$$

If the ultimate objective of molecular computational methods is to compute the molecular wavefunction Ψ, the problem is usually solved by firstly transferring it one step further, expressing the molecular spin-orbitals as linear combinations of known atomic orbitals φ_j:

$$\varPhi_i = \sum_j c_{ij}\, \varphi_j \quad (1.18)$$

This is the basis of the so-called linear combination of atomic orbitals (LCAO) method. Finding the molecular wavefunction is then reduced to the determination of the c_{ij} coefficients from the expansion of molecular spin-orbitals in terms of atomic orbitals. The j index range depends on how big an expansion is taken, in other words on the size of an atomic orbitals basis set (see 1.5.4).

Applying the variational principle to the LCAO coefficients will therefore produce the lowest energy wavefunction inside the use of a particular basis set. Indeed, increasing the set of atomic orbitals for the calculation of a wavefunction will add more flexibility to it, and the variational procedure will deliver a lower energy function. The more flexible the wavefunction (*i.e.* the larger the basis set expansion), the lower the wavefunction energy. As a result, the computed Slater determinant will be closer to the exact solution.

1.1.2. The Hartree-Fock method and the self-consistent molecular orbitals

The Hartree-Fock (HF) approximation is a corner stone in all computational techniques in quantum chemistry and quantum physics. It has originally been developed in the late 1920s, soon after the publication of the Schrödinger's equation in 1926 [9]. However its usage only spread later with the advent of computer electronics, making the calculation feasible. So, considering molecular calculations, the variational principle

---

[5] *ζ is a constant related to the effective charge of the nucleus. Indeed, the total nuclear charge felt by a particular electron is decreased due to the presence of a shielding electron cloud in poly-electronic atoms.*

has to be applied to the linear coefficients c_{ij} of the molecular spin-orbitals as they represent the only flexible components of the Slater determinant. Within the HF approximation, the energy is computed as the eigenvalue of a particular one-electron operator, the Fock operator:

$$E_{HF} = \min E[\Phi_{SD}] \ \text{ and } \ \hat{F}_i \Phi_i = \varepsilon_i \Phi_i \quad (1.19)$$

$$\hat{F}(i) = \hat{h}(i) + \sum_j^N [\hat{J}_j(i) - \hat{K}_j(i)] = \hat{h}(i) + V_{HF}(i) \quad (1.20)$$

where $\hat{F}_i$ is the Fock operator for the ith electron, ε_i is the energy of the HF spin-orbital i, $\hat{h}(i)$ is the one-electron Hamiltonian, $\hat{J}_j(i)$ is the Coulomb operator representing the repulsive potential between electrons i and j, $\hat{K}_j(i)$ is the exchange operator accounting for the energy associated with the quantum effect produced by exchanging two electrons. The expression of the Coulomb and exchange operators will not be discussed here, but it is important to mention that the HF potential (V_{HF}) depends on the spin-orbitals themselves. Solving the HF equations thus requires an initial guess of the orbitals, allowing the energy to be computed. Consequently, the calculation is carried out through an iterative fashion, using an initial guess which is refined at each iteration and hopefully converges to the HF solution.

Most importantly, the Coulomb operator represents the repulsive potential experienced by electron i, due to the average charge distribution of electron j. Therefore, movements of electrons i and j are not correlated as both experience each other fields in an average manner. This rough approximation constitutes the major limit of the HF method, and is the reason for the implementation of post-HF methods that may partly include electronic correlation.

Numerous post-HF methods exist, such as Möller-Plesset perturbation theory [10], coupled clusters [11] and configuration interaction [12,13]. These correlated approaches will not be discussed here.

1.1.3. Density functional theory

From the early development of quantum physics, the wavefunction evidently retained all attention and has been the source point for computational methods. If the conventional approach to quantum chemistry indeed uses the wavefunction as the fundamental quantity to solve the quantum problem and to access information about any physical system state, one may wonder if another quantity (possibly simpler) may be used to achieve that goal. This assumption is motivated by the need to lower calculation costs of elaborate wavefunction techniques. Indeed, including correlation energy beyond the HF approximation requires the use of computationally complex methods which are responsible for a high increase of computational time. This inevitably restrains the size of molecular systems that can be tackled by such post-HF methods.

The electronic density will naturally come to minds when addressing this question: can we possibly replace the *N*-electron wavefunction with its dependence on *3N* spatial plus one spin variables (so *4N* variables) by a simpler quantity, the electron density?

Is the electron density able to fully and uniquely describe the ground state of a system? Some clues are given by simple arguments. If the Hamiltonian operator is entirely determined by the positions and atomic numbers of nuclei and the total number of electrons, these three are also unambiguously assigned by the electron density. Actually, the integration of electron density over space gives the number of electrons and local maxima of electron density correspond to the positions of nuclei. Moreover, information about nuclear charges (*i.e.* the atomic number, Z) is also contained in the electron density, as the density at the nuclei positions depends on the atomic number. Yet a rigorous foundation has been set by the two Hohenberg-Kohn's theorems [14], marking the advent of electron density-based computational methods and making DFT possible.

The first theorem is an existence theorem as it demonstrates that the electron density uniquely determines the Hamiltonian operator, and consequently all properties accessible through that operator, including the system energy.

The second theorem proves that the density obeys a variational principle, just as does MO theory. It means that any well-behaved trial density integrating to the proper number of electrons, determines a trial Hamiltonian and wavefunction that will return an energy which is an upper bound to the exact energy, unless it is the exact Hamiltonian and wavefunction (see equation 1.21).

$$\rho_{trial}(r) \rightarrow \hat{H}_{trial}, \Psi_{trial} \ \ and \ \ \langle\Psi_{trial}|\hat{H}|\Psi_{trial}\rangle = E_{trial} \geq E_0 \ \ \ (1.21)$$

So, the starting point of DFT comes from the fact that the specification of the ground state density $\rho(r)$ uniquely determines the external potential $V(r)$ and therefore the Hamiltonian operator. The ground state energy is then a functional of the ground state density:

$$E[\rho(r)] = T[\rho(r)] + V_{Ne}[\rho(r)] + V_{ee}[\rho(r)] \ \ \ (1.22)$$

In this equation, $T[\rho]$ accounts for the kinetic energy, and $V_{Ne}[\rho]$, $V_{ee}[\rho]$ represent the potential energy of the electron-nucleus and electron-electron interactions, respectively. The latter may in turn be subdivided in two contributions arising from the Coulomb interaction plus a second term accounting for exchange and correlation effects, which are of a purely quantum nature:

$$V_{ee}[\rho(r)] = V_{Coulomb}[\rho(r)] + V_{xc}[\rho(r)] \ \ \ (1.23)$$

The above discussion led to the conclusion that the electron density determines the potential which in turns uniquely determines the Hamiltonian and thus the wavefunction. However it does not provide at this stage any simplification over MO theory, as one would have to solve the Schrödinger's equation with the density-derived Hamiltonian. But a major breakthrough appeared with the development of self-consistent equations by Kohn and Sham [15], treating an inhomogeneous system of interacting electrons using the Hohenberg-Kohn formalism. The crucial idea was to take a fictitious system of non-interacting electrons (but

with a density identical to the real system) as a starting point, then separating the energy functional into well-chosen components:

$$E[\rho(r)] = T_{ni}[\rho(r)] + V_{Ne}[\rho(r)] + V'_{ee}[\rho(r)] + \Delta T[\rho(r)] + \Delta V_{ee}[\rho(r)] \quad (1.24)$$

where $T_{ni}[\rho(r)]$ represents the kinetic energy of non-interacting electrons, $V'_{ee}[\rho(r)]$ is the classical electron-electron repulsion, $\Delta T[\rho(r)]$ is the correction to the kinetic energy due to the electronic interaction and $\Delta V_{ee}[\rho(r)]$ regroups all quantum corrections to the electron-electron interaction. So, the first three terms of equation (1.24) are known and one may write an eigenvalue expression of (1.24) using orbitals, more precisely using the Kohn-Sham (KS) orbitals which are density orbitals:

$$\hat{h}_i^{KS}\emptyset_i = \varepsilon_i\emptyset_i \quad (1.25)$$

The one-electron KS operator is defined for an *N*-electron and *M*-nuclei system as:

$$\hat{h}_i^{KS} = -\frac{1}{2}\nabla_i^2 - \sum_A^M \frac{Z_A}{|r_i - r_A|} + \int \frac{\rho_{r'}}{|r_i - r'|} dr' + V_{xc} \quad (1.26)$$

where V_{xc} is responsible for the $\Delta T[\rho(r)]$ and $\Delta V_{ee}[\rho(r)]$ contributions to the energy and typically called the exchange-correlation energy (even if it also consists in the correction to the kinetic energy of non-interacting particles).

Similarly to MO theory, the KS orbitals may be expressed within a basis set of functions and the individual orbital coefficients are determined variationally such as in the HF procedure. Also, the Kohn-Sham process is carried out using an iterative self-consistent field (SCF) procedure.

It is worth notice that DFT is an exact theory. So far no approximations were done and the minimal energy $E[\rho(r)]$ is associated with the exact density. But DFT equations has to be solved in an approximate manner as the key operator (V_{xc}) is not exactly known. This constitutes the crux of the problem and the main difference with the HF method. HF theory is intrinsically an approximate theory, however it is solved exactly.[6] Hence, if DFT is often capable of producing much better results than the HF procedure with a comparable computational cost, the entire difficulty lays in the determination of the exchange-correlation functionals. The different types of functionals and the way they are build will not be discussed here, as it is a vast question (sometimes named the "functional zoo"…) and once again, it appears to be out of scope. The functional that was used in the present work is the so-called B3LYP (see 3.3).

As a concluding remark, DFT may be regarded as the most cost-effective method to achieve a given level of accuracy, provided that the exchange-correlation functional is well chosen.

1.1.4. Basis sets

As stated in section 1.5.1.4, constructing a molecular wavefunction needs a set of functions describing atomic orbitals to be used in the LCAO expression of MOs. Such a set of mathematical functions is called a basis set. Basis sets' efficiency obviously implies two main considerations: accuracy and computational cost. Evidently, increasing the number of basis functions will increase the physical accuracy of the computed MO, but will negatively impact the computational time.

1.1.4.1. Slater-type orbitals (STOs)

Slater-type orbitals have already been introduced in section 1.5.1.3 when discussing the spin-orbital approximation. If STOs are attracting when considering their resemblance to hydrogenic spherical harmonics, there is no analytical solutions to the integrals generated for calculating the energy (both from HF and DFT equations), and these should therefore be computed numerically, which drastically slows down calculations. This problem was addressed by replacing STOs by Gaussian functions, which mainly differ by

---

[6] *These remarks are physically sound if an infinite basis set is used.*

their radial decay (e^{-r} vs e^{-r^2}) and the presence (or absence) of cusp; this method was first proposed by Boys in 1950 [16].

1.1.4.2.   Gaussian-type orbitals (GTOs)

If Gaussian functions are attractive when looking at their mathematical properties, such as their integration and their product (the product of two Gaussians is another Gaussian), they do not describe AOs as STOs do. Their decay is faster than exponentials and they flatten near zero.
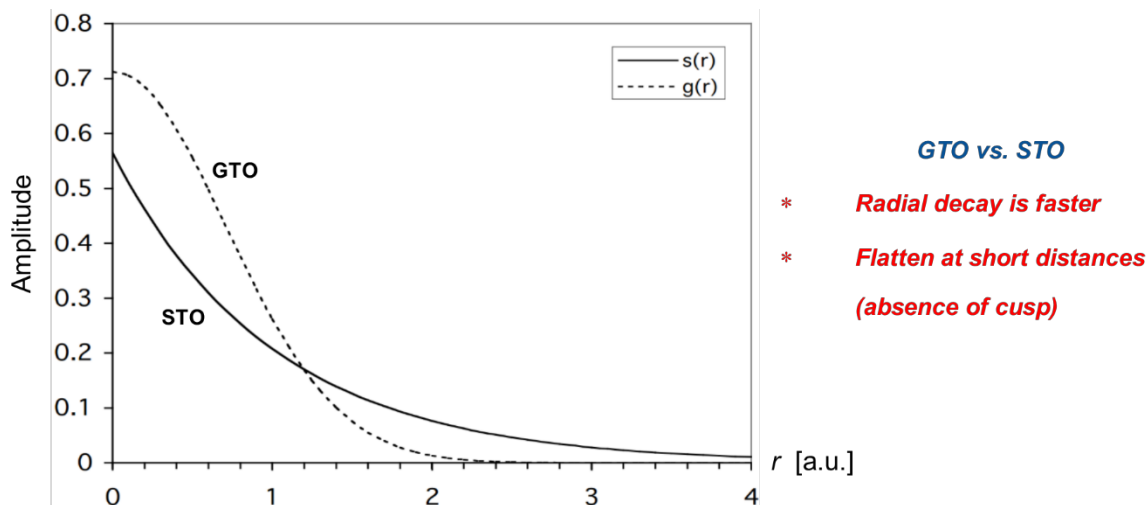

Figure 1. Behavior of a Slater type orbital s(r) and a Gaussian type orbital g(r), showing the stronger r-dependency and the flattening at short distances of the GTO.

The general form of a normalized, atom-centered GTO in Cartesian coordinates is:

$$g(x, y, z; \alpha, i, j, k) = \left(\frac{2\alpha}{\pi}\right)^{3/4} \left[\frac{(8\alpha)^{i+j+k} i! \, j! \, k!}{(2i)! \, (2j)! \, (2k)!}\right]^{1/2} x^i y^j z^k e^{-\alpha(x^2 + y^2 + z^2)} \quad (1.27)$$

where the exponent α is controlling the width of the Gaussian, i, j and k integers dictate the nature of the orbital (*i.e. s, p, d,* etc…). If these three are equal to zero, we obtain a Gaussian with a spherical symmetry, which is therefore an *s*-type function. If one of them is equal to one we obtain a *p*-type function, and a *d*-type function with a sum equal to two.

To alleviate the shape problems of GTOs, one may use them as building blocks to approximate a STO, combining the computational advantages of GTOs with the physical accuracy of STOs.
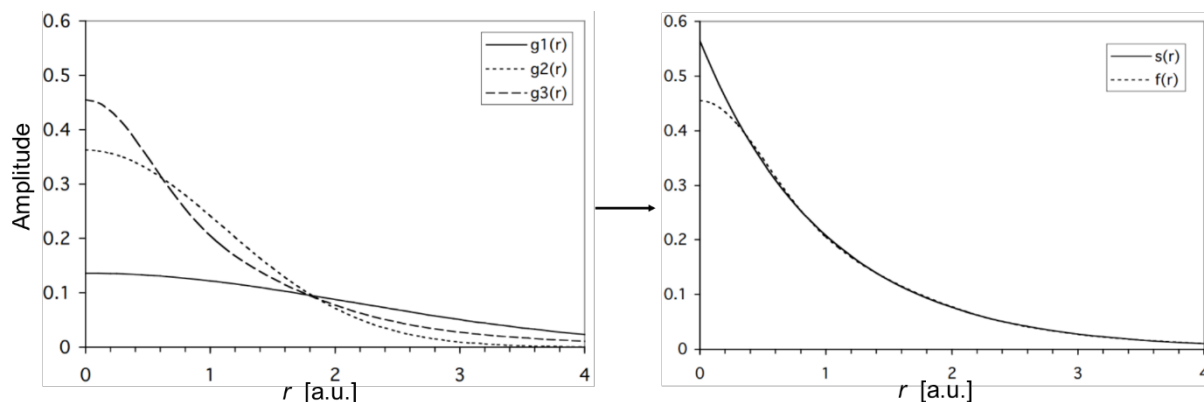
Figure 2. Contraction of three GTOs, namely g1(r), g2(r) and g3(r), to fit a STO (s(r), bold solid line in the right-hand graph). The contracted GTOs form the minimal basis set which is noted STO-3G.

These contracted GTOs may be written as:

$$\varphi(x, y, z; \alpha, i, j, k) = \sum_{a=1}^{u} c_a \, g(r) \quad (1.28)$$

An important feature of equation (1.28) is that it may add the necessary radial nodes by introducing negative c_a coefficients.

Multiple-ζ basis sets. The minimal basis set (STO-3G) consists in only 1 basis function for each type of orbital, from core to valence. This means that taking oxygen as an example, the basis set will consists in one 1s, one 2s, one 2p_x, one 2p_y *and* one 2p_z basis function, each of them constructed from three Gaussians. In order to increase the flexibility of the basis set (which is ultimately intended to be used in a variational calculation), one may decontract it. For instance, a 2s orbital from the STO-3G could be separated as a two Gaussians orbital and a second orbital made of the third primitive Gaussian. This would of course neither increase the size of the basis sets nor its accuracy to fit the exact AO, but it will add an orbital to the HF (or KS) equations for computing the energy (*i.e.* in the secular equations) and the computed energy will be lowered, as more flexibility will be given to the Slater determinant. A basis set including two functions for each AO is called a double-ζ basis set; if there is three functions then it is a triple-ζ basis set; and so on. Such a splitting of the basis set is usually achieved for the valence-shell orbitals.

Diffuse and polarization functions. In order to better describe long-distance interactions and chemical bonding, basis sets may be augmented with diffuse and polarization functions. The former being GTOs with a slower radial decay and the latter are usually GTOs of higher secondary quantum numbers (for example a d-type orbital is added to a p-type orbital). Diffuse functions will help for long distances interactions. Indeed, it will not be possible to describe long range interactions if the basis set tends to zero too rapidly. Polarization functions will add angular flexibility to the calculated MOs, as these may largely differ in their shape when compared to the AOs used to construct them from the LCAO method.

Notation for GTOs. Amongst the most used basis sets are the ones from Pople and co-workers. As an example, the Pople's 6-311++G(2d,2p) basis set was used in Chapter 3:

- 6 Gaussians forms the core orbitals (thus single-ζ orbitals).
- A triple-ζ basis set consisting in 3 orbitals built from 3, one and one primitive Gaussian functions for the valence shell.
- The first + indicates the presence of one set of diffuse *s*-type and *p*-type functions for the heavy atoms, the second + stands for the presence of diffuse *s*-type functions on hydrogens.
- The (2d,2p) bracket enumerates the polarization functions. So two sets of *d*-type functions are added to the heavy atoms and two sets of *p*-type functions are added to hydrogen atoms.

Beside the largely spread Pople's basis sets, Dunning's basis are also under intensive use. These are noted, for example, as: cc-pV*n*Z where *n* indicates the "ζ state". Polarization functions are consistently added with respect to *n* and the "Aug" prefix indicates the addition of diffuse functions.

[1] C.J. Cramer, Essentials of Computational Chemistry, second ed., J. Wiley & Sons, Chichester, 2004.

[2] W. Koch, M.C. Holthausen, A Chemist's Guide to Density Functional Theory, second ed., Wiley-VCH, Weinheim, 2000.

[3] Density functional methods in chemistry and Physics, in: P. Geerlings, F. De Proft, W. Langenaeker (Eds.), Density Functional Theory: A Bridge between Chemistry and Physics, VUB University Press, 1999, Brussels, pp. 15-85.

[4] N.J.B. Green, Quantum Mechanics 1: Foundations, first ed., Oxford University Press, Oxford, 1997.

[5] G.H. Grant, W.G. Richards, Computational Chemistry, first ed., Oxford University Press, Oxford, 1995.

[6] A.R. Leach, Molecular Modelling: Principles and Applications, second ed., Pearson Education, Harlow, 2001.

[7] D.R. Hartree, The calculation of atomic structures, Rep. Prog. Phys. 11 (1946) 113-143.

[8] J.C. Slater, Atomic shielding constants, Phys. Rev. 36 (1930) 57-64.

[9] E. Schrödinger, An ondulatory theory of the mechanics of atoms and molecules, Phys. Rev. 28 (1926) 1049-1070.

[10] C. Møller, M.S. Plesset, Note on an approximation for many-electrons systems, Phys. Rev. 46 (1934) 618-622.

[11] G.D. Purvis, R.J. Bartlett, A full coupled-cluster singles and doubles model: The inclusion of disconnected triples, J. Chem. Phys. 76 (1982) 1910-1918.

[12] J.A. Pople, Electron interaction in unsaturated hydrocarbons, Trans. Faraday Soc. 49 (1953) 1375-1385.

[13] C.D. Sherrill, H.F. Schaefer, The configuration interaction method: advances in highly correlated approaches, in: P.-O. Löwdin, J.R. Sabin, M.C. Zerner and Erkki Brändas (Eds), Advances in Quantum Chemistry, Academic Press, 1999, Volume 34, pp. 143-269.

[14] P. Hohenberg, W. Kohn, Inhomogeneous electron gas, Phys. Rev. 136 (1964) 864-871.

[15] W. Kohn, L.J. Sham, Self-consistent equations including exchange and correlation effects, Phys. Rev. 140 (1965) A1133-A1138.

[16] S.F. Boys, Electronic wave functions. I. A general method of calculation for the stationary states of any molecular system, Proc. R. Soc. London Ser. A. 200 (1950) 542-554.