

New tools for chemical bonding analysis

Eduard Matito

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Contents

1	Theoretical Background	4
1.1	The Electron Density	5
1.2	The Pair Density	7
1.3	Electron Correlation	10
2	The Atom in the Molecule	12
2.1	The definition of an atom in a molecule	13
2.2	Hilbert space partition	13
2.3	Real space partition	14
2.3.1	The quantum theory of atoms in molecules (QTAIM)	15
2.3.2	Other real-space partitions	22
2.3.3	References	24
2.4	Population analysis	24
2.4.1	Mulliken population analysis	24
2.4.2	Population from real space partitions	25
2.4.3	The electron-sharing indices (bond orders)	25
2.4.4	Multicenter Indices	27
3	Aromaticity	34
3.1	Geometrical indices	36
3.2	Magnetic indices	36
3.3	Electronic indices	37
3.3.1	The Aromatic Fluctuation Index: FLU	38
3.3.2	A Multicenter based index: I_{ring}	38
3.3.3	The Multicenter Index: MCI	39
3.3.4	The para-Delocalization Index: PDI	39
3.3.5	EXERCISE 8 (Aromaticity)	40
4	Oxidation state	44
4.1	Definition	44
4.2	Computational calculation of Oxidation States	45
4.2.1	Bond Valence Sum	45
4.2.2	Atom Population Analysis	46
4.2.3	Spin Densities	46
4.2.4	Orbital-localization Methods: Effective Oxidation State	49
5	The Electron Localization Function (ELF)	52
5.1	The topological analysis of the electron density	53

6	The local Spin	56
7	Appendices	57
7.1	Appendix I: The use of MAKE	57
7.2	Appendix II: Manual of ESI-3D	57
7.2.1	How to cite the program	57
7.2.2	Compulsory keywords	58
7.2.3	Optional keywords	59

Notation

In the following sections we will often deal with coordinates, usually electronic coordinates. The coordinates of an electron are indicated by a three-dimensional vector $\vec{r} \equiv \mathbf{r}$ (indistinctly indicated by an arrow or boldfaced number) and a spin (α or β , generically indicated by the σ). Therefore, many textbooks indicate the coordinates of electron as \vec{x}_1 or \mathbf{x}_1 , where $\vec{x}_1 = (\vec{r}_1, \sigma_1)$. For the sake of simplification in these notes we have used the short-hand notation $\mathbf{1} \equiv (\vec{r}_1, \sigma_1)$ and $d_1 \equiv d\vec{r}_1 d\sigma_1$ for the derivatives.

N denotes the number of electrons in the system. Ψ is the Greek letter used to represent the electron wavefunction, $\Psi(\mathbf{1}, \mathbf{2}, \dots, \mathbf{N})$. $\phi(\mathbf{1})$ will be used to indicate an orbital: an atomic orbital if we use a Greek letter as a subindex, $\phi_\mu(\mathbf{1})$, or a molecular orbital if we use a Latin letter, $\phi_i(\mathbf{1})$.

Vectors are indicated in bold or using a superscripted arrow, *e.g.*, $\mathbf{n} = \vec{n} = (n_x, n_y, n_z)$. Keep in mind that the nabla operator is a vector, $\nabla = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right)$ and it can be also indicated as $\vec{\nabla}$ in some textbooks.

Chapter 1

Theoretical Background

In this section we will briefly review the notions of quantum mechanics that are needed to follow this course. We assume the basic knowledge of quantum mechanics provided in the bachelor of chemistry or physics, including the quantum nature of matter, the structure of the atom, the concept of the wavefunction, the uncertainty principle and the Pauli principle. Besides, is given for granted that the reader is familiar with the classical concepts of chemistry, such as bond (types of bonds), polarity, ionicity, aromaticity, bond order, the Lewis picture or resonant structures.

In the following we assume the quantum mechanics description of a system of N electrons in terms of an electron wavefunction that depends on the four coordinates of each electron ($\mathbf{1} \equiv (\sigma_1, \vec{r}_1)$: the spin, σ_i , and the three-dimensional vector, \vec{r}_1 , that gives the position of the electron in the space) and parametrically on the nuclei coordinates in the framework of Born-Oppenheimer approximation. The simplest wavefunction in terms of molecular orbitals, $\phi_{k_i}(\mathbf{1})$, that respects the antisymmetry nature of electrons is a Slater determinant:

$$\psi_K(\mathbf{1}, \mathbf{2}, \dots, \mathbf{N}) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_{k_1}(\mathbf{1}) & \phi_{k_1}(\mathbf{2}) & \dots & \phi_{k_1}(\mathbf{N}) \\ \phi_{k_2}(\mathbf{1}) & \phi_{k_2}(\mathbf{2}) & \dots & \phi_{k_2}(\mathbf{N}) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_{k_N}(\mathbf{1}) & \phi_{k_N}(\mathbf{2}) & \dots & \phi_{k_N}(\mathbf{N}) \end{vmatrix}$$

A more accurate description of the system can be obtained by using a wavefunction that includes a linear combination of n_C Slater determinants,

$$\Psi(\mathbf{1}, \mathbf{2}, \dots, \mathbf{N}) = \sum_{K=1}^{n_C} c_K \psi_K(\mathbf{1}, \mathbf{2}, \dots, \mathbf{N}) \quad \text{with} \quad \sum_{K=1}^{n_C} |c_K|^2 = 1 \quad (1.1)$$

The Hartree-Fock (HF) wavefunction and the Kohn-Sham density functional theory (KS-DFT) use wavefunctions with only one Slater determinant, *i.e.*, single-determinant wavefunctions (SD or SD-wfn, hereafter). Wavefunctions composed of more than one Slater determinant are obtained in configuration interaction (CI), complete active space self-consistent field (CASSCF), coupled-cluster (CC), and second-order Moller-Plesset (MP2) calculation, among oth-

ers.^a These wavefunction will be referred as correlated wavefunctions or multideterminant wavefunctions. The name *correlated* is given to emphasize that, unlike HF, these wavefunctions include electron correlation.

1.1 The Electron Density

The electron density is the central quantity of density functional theory (DFT) [1] and the quantum theory of atoms in molecules (QTAIM); *vide infra*. Unlike the wavefunction, which depends on $3N$ spatial coordinates, the density is actually a simple quantity to deal with because only depends on three spatial coordinates. In addition, the density is an observable (a quantity we can measure) often used in experimental analysis through the study of X-ray crystallography.

From Born's rule [2] we know that the probability density of finding one electron at d_1 (the infinitesimal volume around the position of electron 1 with spin σ_1) is given by the square of the wavefunction that describes the system,

$$P(\mathbf{1})d_1 = \int d_2 \int d_3 \dots \int d_N |\Psi(\mathbf{1}, \mathbf{2}, \dots, \mathbf{N})|^2 d_1 \quad (1.2)$$

from which we can define the density

$$\rho(\mathbf{1}) = NP(\mathbf{1}) \quad (1.3)$$

where N is the number of electrons in the system and $P(\mathbf{1})$ is the probability of finding one electron at position $\mathbf{1}$ (*i.e.*, at position \vec{r}_1 with spin σ_1), regardless the position of the other ($N-1$) electrons (*i.e.* they can be everywhere in the space, including d_1). Since electrons are indistinguishable, the previous function is actually accounting for the probability of finding *at least* 1 electron by $\mathbf{1}$. Thus Eq. 1.2 is the probability of *finding at least one electron at d_1* .

The electron density integrated over an arbitrary region Ω of the molecular space gives the *average number of electrons* in that region.

$$N_\Omega \equiv \langle N(\Omega) \rangle = \int_\Omega \rho(\mathbf{1})d_1 \quad (1.4)$$

This is the basis of electronic populations that we will see in section 2.4.

In quantum mechanics the calculation of the electron densities presents no difficulties and in the case of SD-wfn's, the density can be easily constructed from the molecular orbitals:

$$\rho(\mathbf{1}) = \sum_i^N \phi_i^*(\mathbf{1})\phi_i(\mathbf{1}) = \sum_i^N |\phi_i(\mathbf{1})|^2 \quad (1.5)$$

where we have assumed that the system consists of N electrons occupying N orbitals. For closed-shell systems with doubly-occupied orbitals, the expression

^aIn practice, only CI and CASSCF admit straightforward expansions of the wavefunction in terms of Slater determinants. However, CC and MP2 cannot be obtained from the use of a single determinant.

reads:

$$\rho(\mathbf{1}) = 2 \sum_i^{N/2} |\phi_i(\mathbf{1})|^2 \quad (1.6)$$

The two previous expressions are valid for Hartree-Fock (HF) wavefunctions or wavefunctions obtained from Kohn-Sham (KS) formulation of DFT –as these wavefunctions are composed of a single Slater determinant.^b For the sake of generality, hereafter we will not assume doubly-occupied orbitals.

In the case of correlated wavefunctions the density cannot be represented by a linear combination of the square of the molecular orbitals (*i.e.* using Eq. 1.5). For correlated wavefunctions the density is written as:

$$\rho(\mathbf{1}) = \sum_{ij}^M {}^1D_j^i \phi_i^*(\mathbf{1}) \phi_j(\mathbf{1}) \quad (1.7)$$

where M is the *total* number of molecular orbitals in our system. ${}^1D_j^i$ will be called 1-density and it is a matrix representing the electron density in terms of molecular orbitals. Such matrix has a diagonal form for SD-wfns and contains zero in the diagonal for elements greater than N ,

$$\begin{aligned} {}^1D_j^i &= \delta_{ij} & \forall i \leq N \wedge \forall j \leq N \\ {}^1D_j^i &= 0 & \forall i > N \wedge \forall j > N \end{aligned}$$

It is easy to prove that Eq. 1.7 reduces to Eq. 1.5 for SD-wfns. For correlated wavefunctions, we can simplify the calculation of the electron density by using a set of orbitals that *diagonalize* the 1-density.^c These orbitals are called natural orbitals, $\eta_i(\mathbf{1})$, and together with their associated occupancies, n_i , define the density

$$\rho(\mathbf{1}) = \sum_i n_i \eta_i^*(\mathbf{1}) \eta_i(\mathbf{1}) \quad (1.11)$$

Unlike molecular orbitals, natural orbitals do not have an associated energy. Instead, there is an orbital occupancy, n_i , associated to it, which can be interpreted as the probability that an electron occupies this particular natural orbital from the orbital set. Notice that Eq. 1.11 is a general expression that can be also used for single-determinant wavefunctions. Indeed, Eq. 1.5 can be retrieved from Eq. 1.11 by setting the first N occupancies to one (occupied orbital) and the rest to zero (unoccupied).

^bLet us recall that within DFT the density is, in principle, the exact one. However, the orbitals (and the SD-wfn constructed from them) are those that correspond to the fictitious *non-interacting* system, whose density corresponds to the exact density.

$${}^1D\mathbf{L} = \mathbf{L}\mathbf{n} \quad \mathbf{n} = \text{Diag}(n_1, \dots, n_M) \quad (1.8)$$

where

$$\eta = \mathbf{L}\phi \quad \eta_i(\mathbf{1}) = \sum_j L_{ij} \phi_j(\mathbf{1}) \quad (1.9)$$

and

$$\phi = (\phi_1(\mathbf{1}), \dots, \phi_M(\mathbf{1}))^T \quad \eta = (\eta_1(\mathbf{1}), \dots, \eta_M(\mathbf{1}))^T \quad (1.10)$$

Finally, let us give the formula for the first-order reduced density matrix (1-RDM) that will be used to define several chemical bonding tools. The 1-RDM expression reads:

$$\rho_1(\mathbf{1}; \mathbf{1}') = N \int d\mathbf{2} d\mathbf{3} \dots \int d\mathbf{N} \Psi^*(\mathbf{1}, \mathbf{2}, \dots, \mathbf{N}) \Psi(\mathbf{1}', \mathbf{2}, \dots, \mathbf{N}) \quad (1.12)$$

where we have used different coordinates for the first electron of the two wavefunctions that are included in the integrand, so that the 1-RDM depends on two sets of coordinates. The density function (or simply the density), Eq. 1.11, is actually the diagonal part of the 1-RDM, *i.e.*, $\rho(\mathbf{1}) = \rho_1(\mathbf{1}; \mathbf{1})$. In terms of natural orbitals and occupancies the 1-RDM can be written as

$$\rho_1(\mathbf{1}; \mathbf{1}') = \sum_i n_i \eta_i^*(\mathbf{1}) \eta_i(\mathbf{1}') \quad (1.13)$$

1.2 The Pair Density

Born's interpretation can be further extended to include the pair density,

$$\rho_2(\mathbf{1}, \mathbf{2}) = N(N-1)P(\mathbf{1}, \mathbf{2}) \quad (1.14)$$

with

$$P(\mathbf{1}, \mathbf{2}) d_1 d_2 = \int d\mathbf{3} \dots \int d\mathbf{N} \Psi^*(\mathbf{1}, \mathbf{2}, \dots, \mathbf{N}) \Psi(\mathbf{1}, \mathbf{2}, \dots, \mathbf{N}) d_1 d_2 \quad (1.15)$$

where $N(N-1)$ is the number of electron pairs^d and $P(\mathbf{1}, \mathbf{2})$ is the probability of finding two electrons, one at $\mathbf{1}$ and the other at $\mathbf{2}$, regardless of the position of the other $N-2$ electrons [4]. Thus, it represents the probability of finding *at least* a pair of electrons: one in d_1 and the other in d_2 . Notice the difference between the 1-RDM, Eq. 1.12, and the pair density, Eq. 1.14. Analogous definitions and interpretations can be done for the n -densities ($n > 2$) and those are left to the reader.

The expected number of electron pairs in Ω can be calculated from the pair density:

$$N_{\Omega\Omega} \equiv \langle N^2(\Omega) \rangle = \int_{\Omega} \int_{\Omega} \rho_2(\mathbf{1}, \mathbf{2}) d_1 d_2 + N_{\Omega} \quad (1.16)$$

where we have included the last term to account for the self-pairing that is not included in the pair density because wavefunctions attain the Pauli's principle. In the case of two regions Ω_1 and Ω_2 , the expected number of electron pairs with one electron at Ω_1 and another at Ω_2 reads:

$$N_{\Omega_1\Omega_2} \equiv \langle N_{\Omega_1} N_{\Omega_2} \rangle = \int_{\Omega_1} \int_{\Omega_2} \rho_2(\mathbf{1}, \mathbf{2}) d_1 d_2 + N_{\Omega_1 \cap \Omega_2} \quad (1.17)$$

i.e. for non-overlapping regions ($\Omega_1 \cap \Omega_2 = \emptyset$) the expected number of electrons pairs is calculated as the expectation value of the pair density integrated over

^dIt is actually the number of unsorted pairs, the so-called McWeeny (or Dirac) normalization [3] of the pair density. Other textbooks take Löwdin's normalization, *i.e.* the number of sorted pairs, $N(N-1)/2$.

Ω_1 and Ω_2 .

The pair density can be written in a molecular orbital basis using a tensor representation that depends on the four indices:

$$\rho(\mathbf{1}, \mathbf{2}) \equiv \rho_2(\mathbf{1}, \mathbf{2}; \mathbf{1}, \mathbf{2}) = \sum_{\substack{ij \\ kl}}^M {}^2D_{kl}^{ij} \phi_i^*(\mathbf{1}) \phi_j^*(\mathbf{2}) \phi_k(\mathbf{1}) \phi_l(\mathbf{2}) \quad (1.18)$$

where ${}^2D_{kl}^{ij}$ will be called 2-density. The pair density is the diagonal part of the second-order reduced density matrix (2-RDM) that can be calculated as

$$\rho_2(\mathbf{1}, \mathbf{2}; \mathbf{1}', \mathbf{2}') = N(N-1) \int d\mathbf{3} \dots \int d\mathbf{N} \Psi^*(\mathbf{1}, \mathbf{2}, \dots, \mathbf{N}) \Psi(\mathbf{1}', \mathbf{2}', \dots, \mathbf{N}) \quad (1.19)$$

For the calculation of the electronic energy of a molecular system there is no need to know the form of the full 2-RDM. The electronic energy of a molecular system is composed of three ingredients: the kinetic energy, the electron-nucleus attraction and the electron-electron repulsion. The kinetic energy is a known functional of the 1-RDM, the electron-nucleus attraction can be calculated only from the electron density, whereas the electron-electron repulsion is a well-known functional of the pair density. Even though the 2-RDM is not needed to calculate the electronic energy, it is used in quantum mechanics. For instance, the calculation of the total angular spin momentum, $\langle S^2 \rangle$, depends explicitly on the 2-RDM [5].

Unlike the density, the pair density contains *explicit* information about the relative motion of a pair of electrons. A concept which is important to explain, among other things, the so-called electron correlation effects. In order to extract these effects it is customary to define other pair functions. A popular function in DFT is the exchange-correlation density (XCD) [6],

$$\rho_{xc}(\mathbf{1}, \mathbf{2}) = \rho(\mathbf{1})\rho(\mathbf{2}) - \rho_2(\mathbf{1}, \mathbf{2}) \quad (1.20)$$

which is the difference between the pair density and a *fictitious* pair density of independent electrons that do not respect the Pauli principle,

$$\rho_2^{\text{IE}}(\mathbf{1}, \mathbf{2}) = \rho(\mathbf{1})\rho(\mathbf{2}) \quad (1.21)$$

which gives the probably of finding at least one electron at $\mathbf{1}$ and, at the same time, at least one electron at $\mathbf{2}$. The latter probably is usually greater than the exact pair probability, although this is not strictly necessary except for monodeterminantal wavefunctions,

$$\rho_{xc}^{\text{SD}}(\mathbf{1}, \mathbf{2}) = \rho(\mathbf{1})\rho(\mathbf{2}) - \rho_2^{\text{SD}}(\mathbf{1}, \mathbf{2}) = \rho_1(\mathbf{1}; \mathbf{2})\rho_1(\mathbf{2}; \mathbf{1}) = |\rho_1(\mathbf{1}; \mathbf{2})|^2 \geq 0 \quad (1.22)$$

because^e

$$\rho_n^{\text{SD}}(\mathbf{1}, \mathbf{2}) = \begin{vmatrix} \rho(\mathbf{1}) & \rho_1(\mathbf{1}; \mathbf{2}) \\ \rho_1(\mathbf{2}; \mathbf{1}) & \rho(\mathbf{2}) \end{vmatrix} \quad (1.24)$$

where the superscript SD is used to identify a SD-wfn. Therefore, using Eqs. 1.22, 1.16 and 1.17, for a SD-wfn we can prove that

$$N_{\Omega_1 \Omega_2} \leq N_{\Omega_1} N_{\Omega_2} + N_{\Omega_1 \cap \Omega_2} \quad (1.25)$$

so that the maximum number of pairs between two regions is obtained by direct multiplication of its electron averages (plus the population of the intersection of the two regions), and such situation is only given when *the electrons are independent*.^f Taking the definition of the variance of the number of electron in Ω

$$\sigma^2 [N_\Omega] = N_{\Omega\Omega} - N_\Omega^2 \quad (1.26)$$

and using Eq. 1.25 expression we can get an additional relation,

$$0 \leq \sigma^2 [N_\Omega] \leq N_\Omega \quad (1.27)$$

that holds for SD-wfn. The latter inequality puts forward an interesting bound to the uncertainty of the number of electrons in a given region. In particular, from the definition of the variance (and the latter inequality) one can deduce that: 1) the uncertainty in the population of a certain region Ω is only reduced to zero when the XCD (twice) integrated in that region is equal to the number of electrons in that region. The most trivial case when this situation occurs is when the number of electrons outside this region is zero. 2) The uncertainty is maximal, when the electron pairs are maximal, *i.e.*, when the electrons are independent.

We can also define the covariance of electrons populations

$$\text{cov}(N_{\Omega_1}, N_{\Omega_2}) = N_{\Omega_1 \Omega_2} - N_{\Omega_1} N_{\Omega_2} = N_{\Omega_1 \cap \Omega_2} - \int_{\Omega_1} \int_{\Omega_2} \rho_{xc}(\mathbf{1}, \mathbf{2}) d_1 d_2 \quad (1.28)$$

which gives the measure of how much the number of electrons in Ω_1 and Ω_2 change together. The variance (Eq. ??) is actually a special case of the covariance,

$$\sigma^2 [N_\Omega] = \text{cov}(N_\Omega, N_\Omega) \quad (1.29)$$

and for SD-wfn we can prove the following bound,

$$-\min(N_{\Omega_1 \setminus \Omega_2}, N_{\Omega_2 \setminus \Omega_1}) \leq \text{cov}(N_{\Omega_1}, N_{\Omega_2}) \leq N_{\Omega_1 \cap \Omega_2}. \quad (1.30)$$

^eIn general, a n -RDM can be written in terms of the 1-RDM for a SD-wfn:

$$\rho_2^{\text{SD}}(\mathbf{1}', \mathbf{2}', \dots, \mathbf{N}'; \mathbf{1}, \mathbf{2}, \dots, \mathbf{N}) = \begin{vmatrix} \rho_1(\mathbf{1}'; \mathbf{1}) & \rho_1(\mathbf{1}'; \mathbf{2}) & \cdots & \rho_1(\mathbf{1}'; \mathbf{N}) \\ \rho_1(\mathbf{2}'; \mathbf{1}) & \rho_1(\mathbf{2}'; \mathbf{2}) & \cdots & \rho_1(\mathbf{2}'; \mathbf{N}) \\ \vdots & \vdots & \ddots & \vdots \\ \rho_1(\mathbf{N}'; \mathbf{1}) & \rho_1(\mathbf{N}'; \mathbf{2}) & \cdots & \rho_1(\mathbf{N}'; \mathbf{N}) \end{vmatrix} \quad (1.23)$$

^fNotice that for SD-wfns the electrons are not correlated but their are not independent.

where

$$\Omega_1 \setminus \Omega_2 = \Omega_1 - \Omega_1 \cap \Omega_2$$

In addition, one can use the well-known Cauchy-Schwarz inequality to set new bounds

$$|\text{cov}(N_{\Omega_1}, N_{\Omega_2})| \leq \sqrt{\sigma^2[N_{\Omega_1}] \sigma^2[N_{\Omega_2}]}$$

The XCD is the workhorse for the methods that account for electron localization. Upon integration of the XCD we obtain the density,

$$\int \rho_{xc}(\mathbf{1}, \mathbf{2}) d\mathbf{2} = \rho(\mathbf{1}), \quad (1.31)$$

and, therefore, the XCD fulfills this sum rule:

$$\int \int \rho_{xc}(\mathbf{1}, \mathbf{2}) d\mathbf{1} d\mathbf{2} = N. \quad (1.32)$$

The XCD has been used to define many popular tools in bonding analysis, such as the electron-sharing indices (or bond-orders), [7–10] —as we shall see in section 2.4.3.

1.3 Electron Correlation

The term electron correlation was introduced in quantum chemistry in 1934 by Wigner and Seitz, [11] when they studied the cohesive energy of metals. By 1953, Slater complained about the fuzziness of the concept that received a more solid definition a few years later due to Löwdin [12]

$$E_{\text{CORR}} = E_{\text{FCI}} - E_{\text{HF}} \quad (1.33)$$

where E_{HF} is the Hartree-Fock energy (energy calculated from a SD-wfn) and E_{FCI} is the energy calculated with a full-configuration interaction (FCI) wave-function and, therefore, it is the exact energy of the system. E_{CORR} is called correlated energy.

We will distinguish between *uncorrelated electrons* and *independent electrons*. The electrons are uncorrelated if $E_{\text{CORR}} = 0$, whereas electrons are independent if and only if

$$\rho_2(\mathbf{1}, \mathbf{2}) = \frac{N-1}{N} \rho(\mathbf{1}) \rho(\mathbf{2}) \quad (1.34)$$

where we have taken into account the different normalization factors of the independent-electrons pair density (Eq.1.21) and the actual one (Eq. 1.14). The former is a formal definition that measures the deviation from a SD-wfn and the latter refers to the probabilistic nature of the electrons motion. Independent electrons are uncorrelated but the opposite is usually not true.

It is customary to define a pair function that measures the deviation of the actual pair density and a pair density of uncorrelated electrons,

$$\lambda_2(\mathbf{1}, \mathbf{2}) = \rho_2(\mathbf{1}, \mathbf{2}) - \rho_2^{\text{SD}}(\mathbf{1}, \mathbf{2}) = |\rho_1(\mathbf{1}; \mathbf{2})|^2 - \rho_{xc}(\mathbf{1}, \mathbf{2}) \quad (1.35)$$

and it usually called the cumulant (of the pair density). One can also define the cumulant of the 2-RDM,

$$\begin{aligned}\lambda_2(\mathbf{1}, \mathbf{2}; \mathbf{1}', \mathbf{2}') &= \rho_2(\mathbf{1}, \mathbf{2}; \mathbf{1}', \mathbf{2}') - \rho_2^{\text{SD}}(\mathbf{1}, \mathbf{2}; \mathbf{1}', \mathbf{2}') \\ &= \rho_1(\mathbf{1}; \mathbf{2}')\rho_1(\mathbf{2}; \mathbf{1}') - \rho_{xc}(\mathbf{1}, \mathbf{2}; \mathbf{1}', \mathbf{2}')\end{aligned}\quad (1.36)$$

Several previous bounds can now be set for correlated wavefunctions in terms of the cumulant matrices,

$$\begin{aligned}-\min(N_{\Omega_1 \setminus \Omega_2}, N_{\Omega_2 \setminus \Omega_1}) - \lambda(\Omega_1, \overline{\Omega_2}) &\leq \text{cov}(N_{\Omega_1}, N_{\Omega_2}) \leq N_{\Omega_1 \cap \Omega_2} - \lambda(\Omega_1, \Omega_2) \\ 0 \leq \sigma^2[N_\Omega] &\leq N_\Omega - \lambda(\Omega, \Omega)\end{aligned}\quad (1.37)$$

where

$$\overline{\Omega_2} = \mathbb{R}^3 - \Omega_2 = \mathbb{R}^3 \setminus \Omega_2 \quad (1.38)$$

and

$$\lambda(\Omega_1, \Omega_2) = \int_{\Omega_1} \int_{\Omega_2} \lambda_2(\mathbf{1}, \mathbf{2}) d_1 d_2 \quad (1.39)$$

By measuring the importance of λ_2 we can assess the importance of electron correlation in these quantities. For instance, it is well-known that correlation usually decreases the electron fluctuation between regions [8]. Hence, in atomic regions, the electron correlation usually increase the covariance bound and it tightens the variance bound, thus contributing to a lower uncertainty in the number of electrons [8] (in other words, it contributes to electron localization —as we shall see in section 2.4.3).

Chapter 2

The Atom in the Molecule

The notion of *atom* dates back to the fourth century BC, when Democritus stated that *everything* was composed of atoms. Although his ideas were far from the actual concept of an atom, he was the first to conceive the atoms as the constituents of the nature. Unfortunately, his ideas opposed those of Aristotle and Plato, which were far more known in Athens and, consequently, Democritus' works were mostly ignored on the Ancient Greece.

In 1807 Dalton, the English chemist and physicist, recovered Democritus' ideas and formulated the modern atomic theory. Dalton realized that studying chemistry one should first understand the constituents of matter. Dalton formulated the atoms as indivisible, and his atomic theory provides a formulation of compounds as integer combinations of atoms, introducing the notion of chemical reaction as the process by which atoms are combined to form molecules.

In 1891 Stoney coined the term *electron* to name the unit of charges that should compose the matter according to Faraday's electrolysis experiments. The series of events that led to the discovery of quantum mechanics were partially motivated by the need to suggest a model for the structure of the atom. The experiments of Wilhelm, Goldstein, Crookes and Schuster were culminated by the well-know experiment of J.J. Thompson that proved that atoms are composed of electrons and protons.

In 1913 Bohr's atomic model was formulated, suggesting that electrons in an atom occupy states with quantized energy. In 1916, Lewis suggested that atoms are held together by sharing a pair of electrons between them, giving a first (uncompleted) definition of the chemical bond. The notion of *electron pair* is central in Lewis theory and it remains one of the most important concepts to explain the chemical bonding.

In 1924, Pauli demonstrated that four quantum numbers are necessary to characterize the electrons, thus explaining the shell-like structure of an atom. Actually the contribution of Pauli was the fourth quantum number itself, the *spin*, an intrinsic property of the electron as proved a year later in the experiment of Uhlenbeck and Goudsmit. The spin of the electrons is actually important in order to fully understand the chemical bond; the concept of electron pair would

have not withstood the new discoveries of the atomic structure without the notion of the spin.

2.1 The definition of an atom in a molecule

Since Lewis theory most chemistry have been rationalized using the concept of *an atom in a molecule*. For instance, we know from undergraduate organic courses that carbon binds to itself in many different ways, forming mostly single, double, triple and aromatic bonds. Although the carbon atom is the same building block in all these bonds, the character of each carbon is clearly different. In order to characterize the *electronic structure* of these molecules it is convenient to distinguish and characterize the role of the atoms that form these molecules, *i.e.*, to define *an atom in a molecule* (AIM).

By characterizing atoms inside a molecule we are defining an *atomic partition*. An atomic partition (or partitioning) is a well-defined method to subdivide the atoms in a molecule. An atomic partition provides the means to define atomic properties that can be used to (chemically) rationalize the electronic structure of a given molecule; for instance, they are used to define partial charges, partial multipoles and to perform a bonding analysis.

There is not a unique way to define an atomic partition and, to some extent, all the proposals are, in one way or another, arbitrary. Therefore, it is important to know the limitations and the drawbacks of the partition we employ. There are two ways to define an atomic partition: (i) by partitioning the Hilbert space (the mathematical space where the wavefunction is defined) or (ii) by partitioning the real space that the molecular structure occupies.

2.2 Hilbert space partition

The solution of the Schrödinger equation is often attained by using approximate wavefunctions expanded by a set of basis functions. The basis set functions are usually a set of one-particle functions. In principle one can use any basis sets from the Hilbert space to expand a wavefunction: for instance plane waves (used in solid state) or atomic orbitals constructed from either Slater or Gaussian primitive functions. In gas phase or solution is customary to employ atom-centered functions, making the assignment of the basis set functions to atoms straightforward.

In a Hilbert space partition, the *atom in a molecule* is defined as the set of atomic functions centered over that atom. With such scheme, one only needs to decompose the atomic property into basis functions and then it is easy to calculate the atomic contributions to that property. For instance, if we take the definition of a molecular orbital (MO) in terms of atomic orbitals (AO):

$$\phi_i(\mathbf{1}) \equiv \phi_i^{\text{MO}}(\mathbf{1}) = \sum_{\mu}^m c_{\mu i} \phi_{\mu}^{\text{AO}}(\mathbf{1}) \quad (2.1)$$

we can take the part of the MO that corresponds to atom A as the set of m AO functions centered in A :

$$\phi_i^A(\mathbf{1}) = \sum_{\mu \in A}^m c_{\mu i} \phi_{\mu}(\mathbf{1}) \quad (2.2)$$

It is easy to prove that this assignment provides a partition of the MO:

$$\phi_i^{\text{MO}}(\mathbf{1}) = \sum_A \phi_i^A(\mathbf{1}) = \sum_A \sum_{\mu \in A}^m c_{\mu i} \phi_{\mu}(\mathbf{1}) \quad (2.3)$$

Such atomic decomposition is usually easy to compute and, in particular, the atomic population (see below for a definition) is available in most computational programs under the name of Mulliken population analysis, who first suggested this possibility in 1955 [13].

One of the main advantages of the Hilbert space partition is that for some properties, like the atomic populations, the atomic decomposition can be done analytically, *i.e.*, it bears no significant computational cost and it can be done without committing a numerical error (because the integrals needed can be computed analytically). However, the Hilbert space partition presents two major drawbacks. The first obvious inconvenient is that the method is basis-set dependent, *i.e.*, the result is quite dependent on the quality of the basis set used for the calculation. The second drawback concerns the ambiguity of assigning a basis set function to an atom. Some atomic basis set functions lack a prominent atomic character and, therefore, it is not obvious whether this function can be entirely assigned to one atom. This is the case of diffuse functions, which are assigned to a particular atom but actually are spread over a wider region.

Table 2.1 contains the QTAIM's (see below) and Mulliken atomic charges for methane calculated using three different basis sets (DZ: double zeta, DZP: double zeta with polarization and TZ2P+: triple zeta with double polarization and diffuse functions). QTAIM charges do not depend largely on the basis set used (only DZ basis shows a slightly different result due to the smallness of the basis and, in general, DZ is actually not a good basis set for computational studies), whereas Mulliken's provides quite disparate results, giving an unphysical charge of +0.6 on the carbon atom of methane for the TZ2P+ basis. These results put forward that Mulliken charges should **never be used in the presence of diffuse functions**. Notice that DZP basis is a small but reasonably balanced basis set and provides very similar numbers for both Mulliken and QTAIM charges.

2.3 Real space partition

There are several real-space partition methods. They are based on assigning every three-dimensional point of the real space to a particular atom. In some cases, the partition assigns weight functions to every point in the real space, distributing the importance of the point among the different atoms in the molecule. Among real space analysis we can mention Voronoi cells [14], Hirshfeld partition [15], Becke's partition [16], Bader's atoms [17] and Becke-rho

Atom	Basis set	Mulliken	QTAIM
C	DZ	-0.982	-0.329
	DZP	0.047	0.038
	TZ2P+	0.607	0.047
H	DZ	0.246	0.082
	DZP	-0.012	-0.009
	TZ2P+	-0.152	-0.011

Table 2.1: Bader and Mulliken atomic charges for methane calculated using three different basis sets (DZ: double zeta, DZP: double zeta with polarization and TZ2P+: triple zeta with double polarization and diffuse functions).

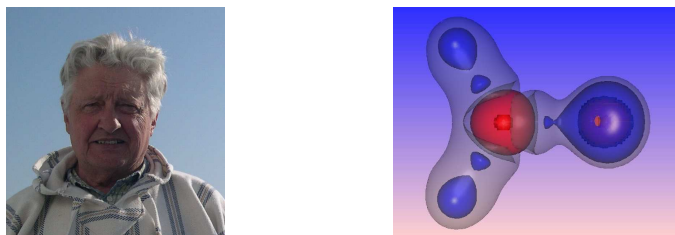


Figure 2.1: **(left)** Richard Bader (1931-2012) from McMaster University is the father of the quantum theory of atoms in molecules (QTAIM). **(right)** A typical molecular plot of QTAIM showing the real-space partition.

methods [8, 18].

2.3.1 The quantum theory of atoms in molecules (QTAIM)

The quantum theory of atoms in molecules (QTAIM) is a very popular theory which, among other things, provides a real-space atomic partition. The theory is due to Richard F.W. Bader and uses as a central concept the electron density. The theory defines the atom through a partitioning of the real space as determined by the *topological* properties of a molecular charge distribution (*i.e.*, the electron density, *c.f.*, Eq. 1.3).

Since the atoms are composed of electrons and most of the chemistry and reactivity can be explained by the behavior and the distribution of the electrons in the molecule, it is natural to take the electron density as the central quantity to define an atomic partition.

In 1972, Bader and Beddall showed that the atom (or a group of atoms) that has the same electron distribution makes the same contribution to the total energy of the system [19]. The *atom in molecule* (AIM) within QTAIM is a quantum subsystem. Quantum subsystems are open systems defined in real space, their boundaries being determined by a particular property of the electronic charge density [17]. In the next section we study the electron density.

The topological analysis of the electron density

The density is a continuous nonnegative function defined at every point of the real (three-dimensional) space. Therefore, it easily renders to a topological analysis. The calculation of the first derivative (in the present context the gradient because the density depends on three coordinates) of a function provides the set of critical points of the function:

$$\nabla\rho(\mathbf{r}_c) = 0 \quad (2.4)$$

the characterization of these critical points is done through the analysis of the second derivatives of the density at the critical point. All the second derivatives of the density are collected in the so-called Hessian matrix:

$$\mathbf{H}[\rho](\mathbf{r}_c) = \nabla_{\mathbf{r}}^T \nabla_{\mathbf{r}} \rho|_{\mathbf{r}=\mathbf{r}_c} = \begin{pmatrix} \frac{\partial^2 \rho(\mathbf{r})}{\partial x^2} & \frac{\partial^2 \rho(\mathbf{r})}{\partial x \partial y} & \frac{\partial^2 \rho(\mathbf{r})}{\partial x \partial z} \\ \frac{\partial^2 \rho(\mathbf{r})}{\partial y \partial x} & \frac{\partial^2 \rho(\mathbf{r})}{\partial y^2} & \frac{\partial^2 \rho(\mathbf{r})}{\partial y \partial z} \\ \frac{\partial^2 \rho(\mathbf{r})}{\partial z \partial x} & \frac{\partial^2 \rho(\mathbf{r})}{\partial y \partial z} & \frac{\partial^2 \rho(\mathbf{r})}{\partial z^2} \end{pmatrix}_{\mathbf{r}=\mathbf{r}_c} \quad (2.5)$$

that is a real symmetric matrix and thus can be diagonalized through a unitary transformation, \mathbf{L} ,

$$\mathbf{H}[\rho]\mathbf{L} = \mathbf{L}\mathbf{\Lambda} \quad (2.6)$$

i.e., put in a diagonal form,

$$\mathbf{\Lambda} = \begin{pmatrix} \frac{\partial^2 \rho(\mathbf{r})}{\partial x_1^2} & 0 & 0 \\ 0 & \frac{\partial^2 \rho(\mathbf{r})}{\partial y_1^2} & 0 \\ 0 & 0 & \frac{\partial^2 \rho(\mathbf{r})}{\partial z_1^2} \end{pmatrix}_{\mathbf{r}_1=\mathbf{r}_c} = \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{pmatrix} \quad (2.7)$$

where $(\lambda_1 \leq \lambda_2 \leq \lambda_3)$ are the three eigenvalues of the Hessian matrix, *i.e.*, the curvatures. We will label each critical point according its rank and signature as (ω, σ) . Assuming non-zero eigenvalues we can classify the CP by the sign of its curvatures. Each positive curvature contributes +1 to the signature and every negative curvature adds -1, giving four different CPs:

- **(3,-3). Attractor or Nuclear Critical Point (ACP).** All the curvatures are negative in a ACP, and thus this CP is a maximum of the electron density. These regions usually coincide with an atomic position and an atom-in-molecule within QTAIM theory is characterized by one and only one ACP. Although it is not usual one may encounter maxima of the electron density which do not coincide with an atomic position; those are known as non-nuclear maxima (NNA).
- **(3,-1). Bond Critical Point (BCP).** A BCP presents two negative curvatures and a positive one. The BCP is found between two ACP. The positive eigenvalue (λ_3) corresponds to the direction connecting these two ACP and the negative eigenvalues form a plane in the perpendicular direction. The existence of a BCP is often used as an indicator of the presence of a chemical bond between the atoms identified by the two ACPs (see controversy below).

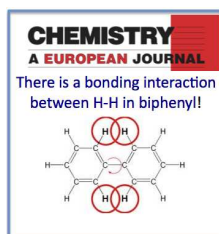


Figure 2.2: The journal *Chemistry a European Journal* published a series of articles discussing the possibility of a bonding interaction between hydrogen atoms in biphenyl molecule. [23–26]

- **(3,+1) Ring Critical Point (RCP)**. A RCP has two positive curvatures and one negative one (λ_1). Its presence indicates a ring structure, which sits in the plane formed by the positive eigenvalues. If the molecule is planar the RCP is located in the minimum of the electron density inside the ring structure.
- **(3,+3) Cage Critical Point (CCP)**. A CCP has three negative eigenvalues and it is thus a minimum of the electron density. Its presence indicates a cage structure and the CCP locates close to its center.

The topology of electron density fulfills the Poincaré-Hopf expression, that gives the relationship that should be fulfilled between the number of critical points:

$$n_{\text{ACP}} - n_{\text{BCP}} + n_{\text{RCP}} - n_{\text{CCP}} = 1 \quad (2.8)$$

If after performing the critical point search the number of points does not fulfill the previous expression we should look carefully at the structure and try to locate the missing critical points.

The critical points are connected between them through gradient lines. For instance, the line that connects two ACPs through a BCP is known as a **bond path** and, according to Bader's theory it *provides a universal indicator of bonding between the atoms so linked* [20]. This statement has not been exempt from controversy. Namely, the bond path found between two hydrogens atoms in biphenyl molecule (see Fig. 2.2 that has been the subject of debate in the literature [21–26]). It is worth mentioning that Bader never claimed that bond paths are indicators of *chemical bond* but indicators of *chemical bonding* or *bonding interaction* [27].

Let us take a look at the two-dimensional representation of the electron density and its critical points. In Fig. 2.3 we can see the density contour plots and the position of ACPs, BCPs and the bond path of NaCl. The gradient lines (perpendicular to the contour lines) are depicted in red and they all end up in the infinity or in the separatrix surface defining the boundaries of the atomic domains. The *atoms in molecules* as defined by QTAIM have its boundaries limited by the *zero-flux* surface in the gradient vector field of the electron density.

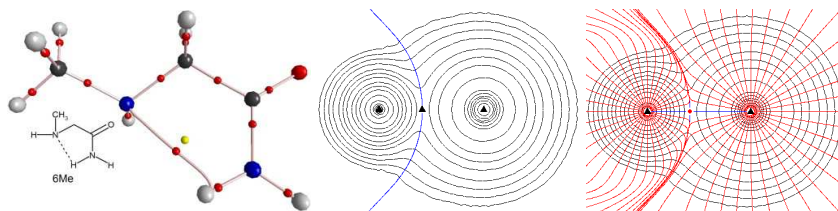


Figure 2.3: **(left)** The molecular representation of a molecule in terms of its CPs. The smallest balls represent the BCP (red) and the RCP (yellow). **(middle)** the contour plot of the electron density for NaCl. The critical points are represented by triangles and the separatrix surface by a blue line. **(right)** the same picture including also the gradient lines (red) and the bond path (light blue). The curvature of the separatrix and the sizes of the atoms are in accord with the electronegativity of the atoms; therefore, it is easy to identify Na in the left and Cl in the right.

This zero-flux surface is given by: [17]

$$\nabla\rho(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = 0 \quad \forall \mathbf{r} \in S(\mathbf{r}) \quad (2.9)$$

where $\mathbf{n}(\mathbf{r})$ is the unit vector perpendicular to the zero-flux surface $S(\mathbf{r})$ or separatrix. These surfaces show the boundaries between AIMs which are, therefore, non-overlapping regions. ^a

To perform a QTAIM analysis of the topology of the electron density we can use many different programs. Here we consider the use of three programs: AIM2000 [28], AIMall [29] and AIMPAC [30]; all of them use a *wavefunction file* (extension wfn) generated by Gaussian [31] (g98 or latter versions) or GAMESS [32]. Exercise 4 is about the use of AIM2000 (even though it can be performed also with the use of AIMall), whereas subsequent exercises can be performed with AIMPAC or AIMall. For molecules containing transition metals (TM) it is customary to use effective core potentials (ECP) or pseudopotentials to account for inner-shell electrons. The wfn-file does not store the ECP information and we need to use a wfx-file (to my knowledge, only produced by Gaussian09c or latter versions) that can only be used by AIMall program or Todd Keith. The wfx-file is obtained by using the keyword *out=wfx* in Gaussian09c.

EXERCISE 4 (AIM2000)

Perform a full topological study of a molecule of your choice. Pick up a molecule with, at least, a ring structure and draw the molecular representation (3D) and the contour plot of the electron density. Include critical points, bond paths, separatrices and gradient lines when possible. Perform integrations over atomic regions to obtain some atomic properties. Follow the following steps:

^aWithin QTAIM, the AIM do not overlap, *i.e.* a given point in the real space belongs to one and only one atom in the molecule. Other atomic partitions, the overlapping ones, assign weights to each point in the real space so that a given point belongs to more than one atom.

- 1.- Run your gaussian calculation (GAMESS also possible) with the keyword **out=wfn** to obtain your wavefunction file (hereafter *wfnline*):

```
#HF/6-31G* out=wfn  
[  
comment  
[  
0 1  
H 0.0 0.0 0.0  
H 0.0 0.0 1.0  
[  
H2.wfn  
[  
_____
```

Figure 2.4: Gaussian input to obtain a wavefunction file for H₂ molecule. Notice the blank lines (marked by blue left bracket, which should not be included in the input) before and after the wavefunction file name.

2.- Open your wfnfile with AIM2000. Calculate first the CPs and bond paths in the molecular representation (they show up in the black window where you can freely rotate the molecule to visualize them).

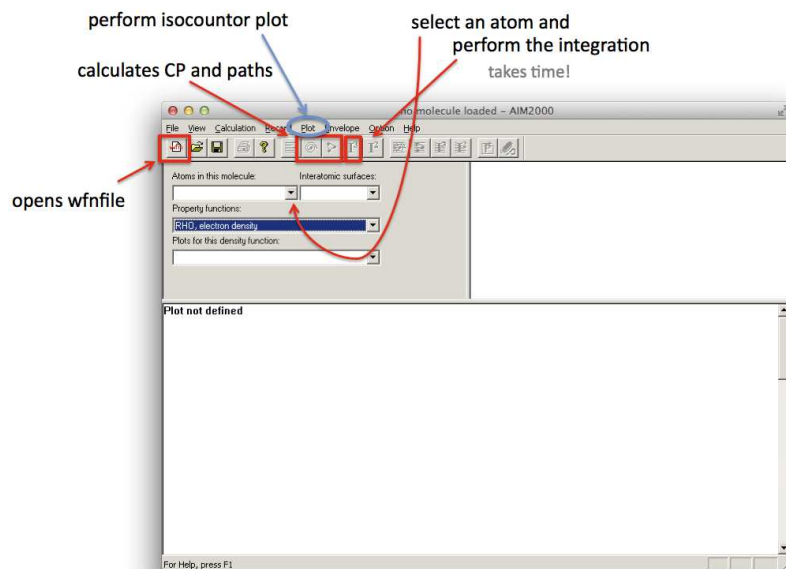


Figure 2.5: Snapshot of AIM2000 program and the most interesting features.

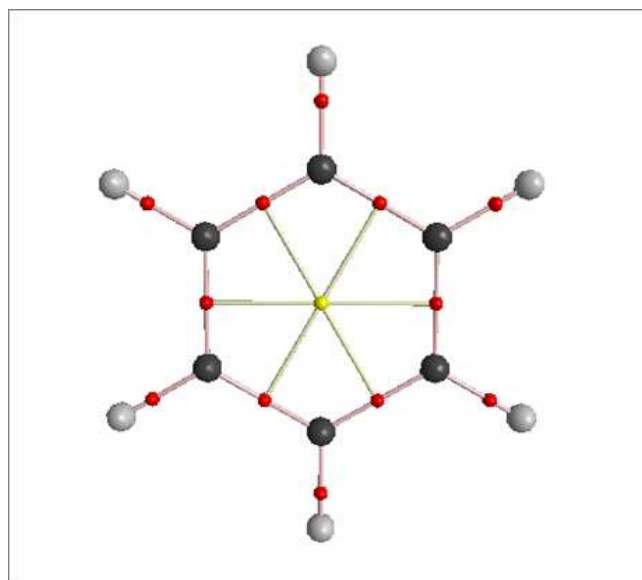


Figure 2.6: Molecular representation of benzene. The atoms (C in black, H in light grey), the BCPs (red), the RCP (yellow) and the paths connecting the CP are presented.

- 3.- In the plot menu select contour plot and construct a two-dimensional plot as this one below:

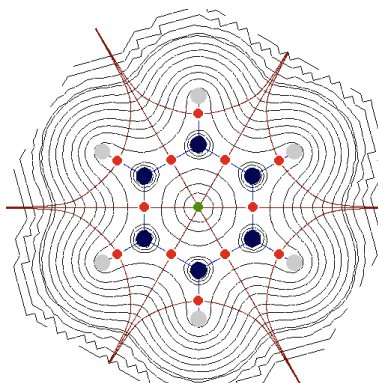


Figure 2.7: The contour plot of the electron density of benzene (contour lines given in black). The molecule is composed of carbon atoms (dark blue) and hydrogens (light grey). The BCPs (red), the RCP (green) and the bond paths (dark blue) connecting C-C and C-H are also given. In brown we can see the separatrix surfaces as they intersect the molecular plane. The spaces left between separatrix surfaces (that extent to infinity in H atoms) define the AIMs.

- 4.- Calculation of properties: Select the atoms you want and perform the integration over them (make sure to integrate in **natural coordinates**).

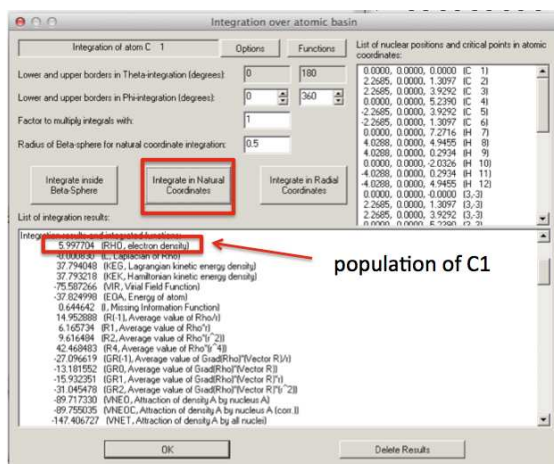


Figure 2.8: Menu on \mathbf{I}^3 (see Fig. 2.5) to perform the integration over C1. Before performing the integration over C1 we should have characterized its topology (ACP, BCP, etc.). NB: the integration takes some computer time. After integration you obtain several atomic properties, here we show the atomic electron population.

The Laplacian of the electron density

Bader's theory goes beyond the concept of an AIM. There are many other aspects that have evolved in useful chemical tools and are widely employed in the literature. The scope of this course is, unfortunately, limited to the aspects of the theory already presented and the discussion of the Laplacian of the electron density.

The second derivative of a function gives the curvature of this function and, therefore, provides information on the concentration or depletion of the quantity represented. Positive second derivatives indicate the presence of a minimum (magnitude depletion) and negative ones show for a maximum of the function (magnitude concentration). Therefore, in the case of the Laplacian of the electron density,

$$\nabla \cdot \nabla \rho(\mathbf{r}) = \nabla^2 \rho(\mathbf{r}) = \frac{\partial^2 \rho(\mathbf{r})}{\partial x^2} + \frac{\partial^2 \rho(\mathbf{r})}{\partial y^2} + \frac{\partial^2 \rho(\mathbf{r})}{\partial z^2} \quad (2.10)$$

we have

- $\nabla^2 \rho(\mathbf{r}) < 0$ electron accumulation \rightarrow localization.
- $\nabla^2 \rho(\mathbf{r}) > 0$ electron depletion \rightarrow delocalization.

Figure 2.9 illustrates the Laplacian of the density for N_2 molecule. In the contour plot we can appreciate large negative values (large localization of electrons) close to the nuclei and in the bonding region above the intermolecular axis. The latter corresponds to the π -electrons of the bond in N_2 . These features are revealed when we choose a medium-range contour value (the largest values correspond to the nuclei) in the three-dimensional plot. Contour pictures can be done with AIM2000. The three-dimensional plot is done with Molekel [33] (using a *cube file* with Laplacian values) but it could be also done with Vmd [34] (*cube file*) or with molden [35] (using a *log file* from Gaussian [31] with the *ginput* keyword).

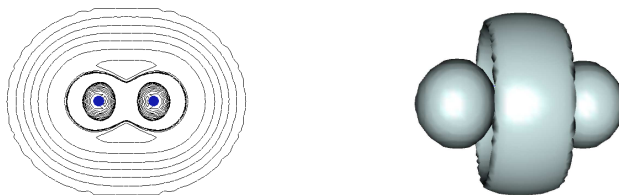


Figure 2.9: The N_2 molecule: (**left**) Contour plot of the negative values (concentration of charge) of the Laplacian of the density. (**right**) three-dimensional representation of the $\nabla^2 \rho(\mathbf{r}) = -0.004$.

2.3.2 Other real-space partitions

There are other important AIMs defined over the real space.

The simplest of the real space methods is perhaps the Voronoi cell. In this scheme the atoms are defined as Voronoi polyhedra that assign the point in the

space to the nearest atom. This method provides a non-overlapping partition of the real space. The partition is thus defined using only the molecular geometry and atom types are not explicitly considered. This partition provides chemically meaningless results in a number of situations.^b

Atoms can be also defined as overlapping regions, *i.e.*, each given point in the real space is assigned to more than one atom. Overlapping atomic partitions define atoms as *fuzzy* entities that interpenetrate each other and extend all over the space. Each atom is assigned a *weight function* (defined between 0 and 1) that gives the contribution of the atom in each point of the molecular space. The simplest of such partitions is Hirshfeld’s which defines the weight functions as follows [15]:

$$w_A(\mathbf{r}) = \frac{\rho_A^0(\mathbf{r})}{\sum_B \rho_B^0(\mathbf{r})} \quad (2.11)$$

where ρ_A^0 is the density of the isolated atom and the sum of atomic densities gives the so-called *promolecular density*.^c The sum of the weights gives the unit:

$$\sum_A w_A(\mathbf{r}) = 1 \quad \forall \mathbf{r} \quad (2.12)$$

The main criticism to this classical Hirshfeld method is that the choice of the electronic state of the isolated atoms can influence the resulting atomic population. This is particularly evident when using ionic atomic densities. This serious drawback has been recently overcome by Bultinck et al. [36] with the *Iterative Hirshfeld approach* or Hirshfeld-I. The essence of the method is that the density of the isolated atoms must integrate to the same population of the atom in the actual molecule. See Refs. [36–38] for further details.

In 1988, Axel Becke defined a multicenter integration technique [16] that assigns weights to atoms in the molecule and it was used by Mayer and Salvador to define the *fuzzy atom* partition [39]. In particular they use the following weight functions:

$$w_A(\mathbf{r}) = \frac{f_A(\mathbf{r})}{\sum_B f_B(\mathbf{r})} \quad (2.13)$$

these functions $f_A(\mathbf{r})$ are obtained from empirical atomic radii. A popular alternative to the *fuzzy atoms* is known as *Becke-rho* partition and uses the BCP (or in the absence of the BCP the point with the lowest density in the straight line connecting two atoms) instead of the atomic radii [8, 18]. *Becke-rho* has the advantage of providing values close to QTAIM ones but using an integration scheme that reduces significantly the computational cost. Recently, Ramos-Córdoba and Salvador have improved the definition of f_A providing a new atomic partition known as *topological fuzzy Voronoi cells* (TFVC) [40]. The use of the latter methodology is recommended over the previous definitions and it is available in program APOST-3D [41].

^bFor instance, Voronoi partition assigns a charge of +0.7 to oxygen in water molecule.

^cThe promolecule is the molecule naively formed by superposing the densities of the isolated atoms (or fragments).

2.3.3 References

Recommended bibliography: Bader’s book [17], Bader’s reviews [42,43] and the notes of Ángel Martín-Pendás in Ref. [44]. We will use AIM2000 program [28]. For the historical part we can use Atkins’ [45] or simply browse the relevant concepts in Wikipedia.

2.4 Population analysis

The population analysis is a technique in computational chemistry that assigns a number of electrons, *the atomic population*, to each atom in a molecule. Therefore, it is a way to distribute the N electrons in a molecule among their constituent parts. It is customary to give also the *atomic charge*, which is calculated as the atomic population minus the atomic number (Z_A), *i.e.*,

$$Q_A = Z_A - N_A \quad (2.14)$$

The population analysis are calculated by using the definition of a certain AIM. Therefore, there are as many population schemes as atomic partitions.

2.4.1 Mulliken population analysis

The most popular population analysis is that performed using the Hilbert space partition (see above). It is straightforward to be calculated and thus it is available in any computational chemistry code. Its definition uses the expression of the electron density in terms of the set of atomic orbitals (basis set) used in the calculation. Namely, assuming m number of basis functions (AO) a MO can be expanded in terms of them:

$$\phi_i^{\text{MO}}(\mathbf{1}) = \sum_{\mu}^m c_{\mu i} \phi_{\mu}^{\text{AO}}(\mathbf{1}) \quad (2.15)$$

its squared value reads

$$|\phi_i(\mathbf{1})|^2 = \sum_{\mu\nu}^m c_{\mu i} c_{\nu i} \phi_{\mu}^*(\mathbf{1}) \phi_{\nu}(\mathbf{1}) \quad (2.16)$$

and by using the definition of the electron density, Eq. 1.11, we get:

$$\begin{aligned} N &= \int \rho(\mathbf{1}) d\mathbf{1} = \sum_i^N n_i \int |\phi_i(\mathbf{1})|^2 d\mathbf{1} = \sum_i^N \sum_{\mu\nu}^m c_{\mu i} c_{\nu i} n_i \int \phi_{\mu}^*(\mathbf{1}) \phi_{\nu}(\mathbf{1}) d\mathbf{1} \\ &= \sum_{\mu\nu}^m \left(\sum_i^N c_{\mu i} c_{\nu i} n_i \right) \int \phi_{\mu}^*(\mathbf{1}) \phi_{\nu}(\mathbf{1}) d\mathbf{1} = \sum_{\mu\nu}^m P_{\mu\nu} S_{\mu\nu} = \text{Tr}(\mathbf{P} \cdot \mathbf{S}) \end{aligned} \quad (2.17)$$

where \mathbf{P} and \mathbf{S} are the density matrix (in AO) and the overlap matrix, respectively. The Mulliken population of atom A is defined as

$$N_A = \sum_{\mu \in A} \sum_{\nu}^m P_{\mu\nu} S_{\mu\nu} \quad (2.18)$$

The values of Mulliken populations and charges can be found in the output of Gaussian if we use the keyword **pop=full**. The results of Mulliken population analysis have no numerical error associated because they come from an integral ($S_{\mu\nu}$) that in the case of gaussian functions can be performed analytically. Most computational chemistry codes (Gaussian, GAMESS, NWCHEM, QCHEM, etc.) use gaussian functions as basis sets.

2.4.2 Population from real space partitions

The calculation of populations from a real space partition is a bit more complicated than in the Hilbert space case. In the real space we need to perform a **numerical integration** over the atomic domain of A :

$$N_A = \int_A \rho(\mathbf{1}) d\mathbf{1} = \sum_i n_i \int_A |\phi_i(\mathbf{1})|^2 d\mathbf{1} = \sum_i n_i S_{ii}(A) \quad (2.19)$$

where we need the diagonal part of the **atomic overlap matrix** (AOM):

$$S_{ij}(A) = \int_A \phi_i^*(\mathbf{1}) \phi_j(\mathbf{1}) d\mathbf{1}$$

Since the shape of the AIMs is usually not regular, the calculation of the AOMs is necessarily numerical. The computational cost and the numerical error associated to a population analysis comes from the calculation of the corresponding AOMs. Therefore, it is highly recommended to check the accuracy of the integration after such analysis. The QTAIM population analysis can be obtained from AIMall [29], AIM2000 (see Figure 2.8), using APOST-3D [41] or ESI-3D [46] (by providing the pertinent AOMs).

2.4.3 The electron-sharing indices (bond orders)

The concept of *bond order* is crucial to understand the bonding in molecules and it measures the number of chemical bonds between a pair of atoms. In his seminal work Coulson [47] put forward a measure of the order of a bond, which he applied within Hückel molecular orbital (HMO) theory to explain the electronic structure of some polyenes and aromatic molecules. This measure of the *order of a bond*, more commonly known as Coulson bond order (CBO), has been connected with HMO calculations done so far.

Nowadays very few calculations are performed within the HMO method, as more sophisticated (and now computational affordable) methods are easily available. As a consequence, the CBO has been replaced by what we could call electron sharing indices (ESI), which measure at which extent two atoms are sharing the electrons lying between them.

In this course we will study the ESI that are calculated from the so-called the XCD (Eq. 1.20; see section 1.2). The XCD compares a *fictitious* pair density of independent electron pairs $[\rho(\mathbf{1})\rho(\mathbf{2})]$ with the real pair density, $\rho_2(\mathbf{1}, \mathbf{2})$ [see Eq. 1.14]. The smaller the difference, the more independent the electrons in these positions are. The larger the difference, the more dependent, *i.e.*, the more *coupled* they are. Therefore, for pairs of electrons shared between points

belonging to two different atoms we expect a large XCD value.

The XCD gives rise to the electron sharing indices (ESI). Namely, the delocalization index (DI):

$$\delta(A, B) = 2 \int_A \int_B d\mathbf{1}d\mathbf{2}\rho_{xc}(\mathbf{1}, \mathbf{2}) = 2cov(N_A, N_B) \quad (2.20)$$

and the localization index (LI)

$$\lambda(A) = \int_A \int_A d\mathbf{1}d\mathbf{2}\rho_{xc}(\mathbf{1}, \mathbf{2}) \quad (2.21)$$

The ESI is actually related to the covariance between the population of atoms A and B and it is thus a measure of the number of electrons simultaneously fluctuating between these atoms. It is customary to take this value as the number of electron pairs shared between atoms A and B , a quantity commonly known as the *order of the bond* or simply *bond order* [47].

Since the XCD integrates to the number of electrons, we can classify the electrons as localized and delocalized and assign them to atoms (localized) and pairs of atoms (delocalized). Therefore, the following sum rule is fulfilled:

$$N = \sum_A N_A = \sum_{B, A < B} \delta(A, B) + \sum_A \lambda(A) \quad (2.22)$$

An electron totally localized within an atom contributes 1 to the localization index. A localized pair of electrons contributes 2 to the localization index and an electron shared between two atoms contributes 1/2 the localization index and 1/2 to the delocalization index. [7]

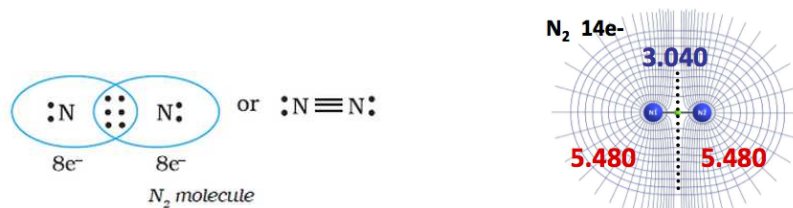


Figure 2.10: The N₂ molecule: **(left)** The Lewis structure. **(right)** Distribution of electrons as localized and delocalized.

Let us take a look at N₂. N has a configuration like this: $1s^2 2s^2 2p^3$ and N₂ shows a triple bond ($2 \times 2p^3$), and each nitrogen has a lone pair ($2s^2$) and two core electrons ($1s^2$). There is a total of 14 electrons that can be thus distributed as 3 delocalized (each of the 3 electrons shared by each nitrogen contribute 1/2, *i.e.*, $2 \times 3 \times 1/2$) and 5.5 localized (2 come from the lone pair, 2 from the core pair and $3 \times 1/2$ from each electron shared). The numbers in Fig. 2.10 match this counting. Single-, double- and triple-, bonds usually exhibit DI values close to 1, 2 and 3; whereas aromatic bonds show DI values around 1.5. The less Lewis-like structure the molecule is, the less predictable the localization and

delocalization indices are.

Finally it is worth defining the total delocalization in a given atom,

$$\delta(A) = \sum_{B \neq A} \delta(A, B) = \frac{1}{2} \sum_{B, A < B} \delta(A, B) \quad (2.23)$$

that some authors [48] relate to the valence of an atom, and provide a natural division of the number of electrons in an atom as the delocalized and the localized ones.

$$N_A = \frac{1}{2} \delta(A) + \lambda(A) = \frac{1}{2} \sum_{B \neq A} \delta(A, B) + \lambda(A) \quad (2.24)$$

By using the bounds established in Section 1.2 for the variance and the covariance we can find some useful bounds for the ESIs,

$$0 \leq \delta(A, B) \leq 2N_A \quad (2.25)$$

$$0 \leq \lambda(A) \leq N_A \quad (2.26)$$

In the case of correlation wavefunctions (see section 1.3), the bounds become more convoluted,

$$\delta^c(A, B) \leq \delta(A, B) \leq 2N_A - \delta^c(A, \overline{B}) \quad (2.27)$$

$$\lambda^c(A) \leq \lambda(A) \leq N_A \quad (2.28)$$

where $\lambda^c(A)$ and $\delta^c(A, B)$ are the correlated parts of the ESI, calculated by replacing ρ_{xc} by λ_2 (Eq. 1.35) in Eqs. 2.20 and 2.21. \overline{B} stays for the region of the molecular space that is complementary to B , *i.e.*, $\overline{B} = \mathbb{R}^3 - B$.

2.4.4 Multicenter Indices

Lewis theory [49] has been one of a few *survivors* to the advent of quantum chemistry. The idea of electron pairs behind Lewis theory has been used to rationalize much of the chemistry known nowadays. In the previous section we have studied a modern tool to characterize the bonding between two atoms, the so-called delocalization index [7], *i.e.*, the generalization of the concept of *bond order*, which gives the electron sharing number between two atoms A and B . Remarkably, a number of molecular species do not fit within the model suggested by Lewis. Most of them involve more than two atoms in the chemical bond. For instance, diborane contains a B_2H_2 ring that is held by four electrons forming two 3-center 2-electrons bonds. Therefore, expressions that account for multicenter bonding are particularly important in order to fully characterize the electronic structure of molecules. There have been a few attempts in the past to characterize multicenter bonds but most of them rely on the molecular orbital picture [50] or 2c-ESIs [51]. To the best of our knowledge the first attempt to use a multicenter expression for the calculation of multicenter bonding is due to Giambiagi [52]. Giambiagi and coworkers developed a formula,

$$I(A_1, A_2, \dots, A_n) = \int_{A_1} d_1 \int_{A_2} d_2 \cdots \int_{A_n} d_N \rho_1(\mathbf{1}; \mathbf{2}) \rho_1(\mathbf{2}; \mathbf{3}) \dots \rho_1(\mathbf{N}; \mathbf{1}) \quad (2.29)$$

that depends on the 1-RDM, $\rho_1(\mathbf{1}; \mathbf{2})$, defined in Eqs. 1.12 and 1.13. Notice that this index depends on the particular order of the atoms in the string for $n > 3$. Following the work of Giambiagi, some authors [53–55] used similar expressions and discovered that the sign of three-center indices was an indicator of the number of electrons involved: three-center two-electron (3c-2e) bonds yield positive I and three-center four-electron (3c-4e) yield negative I ^d [55].

In 1994 Giambiagi [57] reformulated his definition of the multicenter index in terms of the n -order reduced density matrices (n -RDM), which we shall call the n -center ESI (nc -ESI) [58]

$$\delta(A_1, \dots, A_n) = \frac{(-2)^{n-1}}{(n-1)!} \left\langle \prod_{i=1}^n (\hat{N}_{A_i} - \bar{N}_{A_i}) \right\rangle \quad (2.30)$$

Unlike Eq. 2.29 this definition is invariant with respect to the order of the atoms in the ring and is proportional to the n -central moment of the n -variate probability distribution. Eq. 2.30 measures the probability of having simultaneously one electron at A_1 , another at A_2 , etc. regardless of how the remaining $N - n$ electrons of the system distribute in the space. Therefore, $\delta(A_1, \dots, A_n)$ gives a measure of how the electron distribution is skewed from its mean, which may be related to simultaneous electron fluctuation between the atomic population of the basins (A_1, \dots, A_n). Usually the regions A_i are atoms in the molecule, but one could use also molecular fragments or other relevant regions of the space. It was also Giambiagi who pointed out that multicenter indices could be used to account for the aromaticity of molecular species [59] and postulated Eq. 2.29, which he called I_{ring} , as a measure of aromaticity [60]. Afterwards, Bultinck suggested a new aromaticity index, MCI, which is based on the summation of all possible I_{ring} values in a given ring (c.f. Eq. 3.7) [61]. Lately, in our group we suggested a normalization for both Eqs. 2.29 and 2.30 which avoids ring-size dependency [62]. These expressions for multicenter bonding have been used in a number of situations such as the analysis of conjugation and hyperconjugation effects [63], to distinguish agostic bonds [64], to understand aromaticity in organic [65] and all-metal compounds [66–69], and they have also been used to account for electron distributions in molecules [70].

In the next section we will study once again the multicenter indices and we shall see how the same formulae apply to study aromaticity. Of course, the study of aromaticity from multicenter indices will be limited to the electron delocalization aspect of aromaticity.

EXERCISES 5 & 6 (Population analysis, ESIs and multicenters)

Perform a population analysis on both Hilbert space and real space (in the latter case use TFVC and QTAIM). Pick up a molecule of your choice. Follow the following steps:

- 1.- Run you Gaussian09 calculation (GAMESS also possible) with the keyword **out=wfn** (to obtain your wavefunction file; see exercise 4), **fchk=all**

^dOnly for 3c-ESI calculated from single-determinant wavefunctions. [56]

(to obtain the formatted checkpoint file), **iop(6/7=3)** and **ginput** (to give explicit orbital information in the output that can be used to plot the density and the Laplacian with molden), **iop(3/33=4)** (to include the overlap and density matrix that enter Eq. 2.18 and will be used by ESI-3D to perform a Hilbert space calculation), and **pop=full** to obtain a full population analysis in the Hilbert space. If you want to obtain the Mayer bond-orders (which are the definition of DI [Eq. 2.20] for a Hilbert space partition) use **iop(6/80=1)**. You do not need to specify the name of the fchkfile, by default it will be **Test.FChk**. Make sure your script includes a line to move this generic file name to [yourfile.fchk](#). In the following we will use this file name.

- 2.- From the output of gaussian you can already take the Mulliken population analysis data. Look at this extract from gaussian for N₂ molecule:

```

Gross orbital populations:
                                1
  1  1   N   1S                   1.99714
  2                   2S                   0.78709
  3                   2PX                   0.72794
  4                   2PY                   0.72794
  5                   2PZ                   1.10875
  ...
 16  2   N   1S                   1.99714
 17                   2S                   0.78709
 18                   2PX                   0.72794
 19                   2PY                   0.72794
 20                   2PZ                   1.10875

```

It indicates the number of electrons assigned to each function (μ) that is centered in atom A , *i.e.*,

$$N_A^\mu = \sum_\nu^m P_{\mu\nu} S_{\mu\nu} \quad \forall \mu \in A \quad (2.31)$$

Afterwards we see the condensed version, which shows in a matrix form

```

Condensed to atoms (all electrons):
                                1           2
  1  N   6.273954   0.726046
  2  N   0.726046   6.273954

```

and by summing up the condensed fraction we get the Mulliken population on atom A , N_A . In this case $N_N = 6.273954 + 0.726046 = 7$ for both N atoms, which are equivalent by symmetry. Gross orbital populations may give unphysical numbers that violate the Pauli principle, namely, populations below zero or above two. The output also contains the summary of the Mulliken charges, Q_A (see Eq. 2.14) and the summation of them which should coincide with the charge of the molecule.

```

Mulliken charges:
      1
  1  N    0.000000
  2  N    0.000000
Sum of Mulliken charges =  0.000000

```

Finally, Gaussian also prints the DI (Eq. 2.20) in the Hilbert space (commonly known as Mayer Bond Orders [48]):

```

Atomic Valencies and Mayer Atomic Bond Orders:
      1      2
  1  N    2.760249  2.760249
  2  N    2.760249  2.760249

```

$\delta(N, N') = 2.76$, very close to the ideal value of 3 that we can predict from the Lewis theory.

- 3.-** After running gaussian with the option in point 1, the program generates two files: [yourfile.wfn](#) and `Test.FChk` (that you change to [yourfile](#)).fchk. The first will be used with AIMPAC/AIMall to produce the QTAIM results and the second will be used with APOST-3D to generate the TFVC (or Fuzzy or Becke-rho) analysis.

[**3a.-**]AIMall only uses as an input file the [yourfile.wfn](#) or [yourfile.wfx](#) and generates [yourfile.sum](#) file containing the information about QTAIM populations, $N(A)$ [Eq. 2.19], localization indices, $LI(A)$ [Eq. 2.21] and the total delocalization of atom A , $DI(A, A')$ [Eq. 2.23]

```

-----
Atom A          N(A)          LI(A)          DI(A,A')/2    ...
-----
N1             7.0000000752E+00  5.4813310823E+00  1.5186689929E+00...
N2             7.0000000752E+00  5.4813310823E+00  1.5186689929E+00...
-----
Total          1.4000000150E+01  1.0962662165E+01  3.0373379857E+00...

```

as well as delocalization indices, $DI(A, B)$ [Eq. 2.20].

```

-----
Atom A   Atom B       2*D2(A,B)       DI(A,B)       ...
-----
N1       N2          4.7481331985E+01  3.0373381361E+00 ...

```

These results match those already commented in Fig. 2.10. The [yourfile.sum](#) contains additional information about the topology of the electron density and AIM properties that are beyond the contents of this course.

[**3b.-**]APOST-3D uses the [yourfile.fchk](#) file and an input file named [yourfile.inp](#) with the following contents:

```

# METODEDE #####
TFVC
DOINT
#####

```

The DOINT keyword is used to produce a set of int-files (int extension) that contain the AOMs (Eq. 2.20) that will be used by ESI-3D (see next point). Replace TFVC by BECKE-RHO to produce Becke-Rho results (see above). If no partition keyword is specific the program produces fuzzy-atom partition analysis. The output also contains a Mulliken analysis regardless the partition employed. The output of APOST-3D is self-explanatory and contains populations, charges and the delocalization indices in a BOND ORDER MATRIX form. The program does not provide localization indices, but they can be retrieved from atomic population and total atomic delocalization (Eq. 2.23), which in the output of fuzzy appears as "VALENCES USED IN BONDS" and correspond to $\delta(A)/2$.

- 4.- If you are only interested in populations, delocalization or localization indices you do not need to run any other program. However, if you want to perform multicenter analysis, fragment analysis, aromaticity analysis or decompose into atomic orbitals you need to run ESI-3D program (see Appendix II for a manual with the full list of options). ESI-3D needs the AOMs generated by AIMall/AIMPAC or APOST-3D. APOST-3D and AIMPAC produce the files into the same directory where you run your calculation (`yourfilefuz-*.int` and `yourfile-*.int`, respectively), while AIMall creates a separate folder `yourfile_atomicfiles` with your int-files inside (`*.int`). ESI-3D uses an input file that can have any name but I recommend using `yourfile.bad` for AIMall/AIMPAC inputs and `yourfile.fuz` for APOST-3D. They are executed as follows:

```
[4a.-]ESI yourfile.bad >yourfile_bad.esi
[4b.-]ESI yourfile.fuz >yourfile_fuz.esi
```

A generic input for B₂H₆ looks like this:

```
$TYPE
hf
$BASIS
8
$ATOMS
8
b1.int
b2.int
h3.int
h4.int
h5.int
h6.int
h7.int
h8.int
$MULTICENTER
2
3 5 1 8
3 5 2 8
```

where \$TYPE always precedes *hf* to specify single-determinant wavefunction (replace by *uhf* for open-shell calculations), \$BASIS is used to

introduce the number of occupied orbitals (here 16 electrons occupying 8 orbitals) and \$ATOMS is followed by the number of atoms and the files containing the pertinent AOMs. These three keywords are obligatory. \$MULTICENTER is used to calculate multicenter indices (Eq. 2.29 and Eq. 2.30). See Appendix II for the use of \$MULTICENTER and other options that can be included in the input files for ESI-3D.

- 5.- We have performed a numerical integration over atomic domains so we should first check that the integration is correct (search for WARNING messages, check the magnitude of the error of the integration and the different summation in the outputs of ESI).

The structure of the output of ESI-3D is the same regardless the partition used. Let us analyze here the output for P_4^{2-} :

Integration errors: Error(S), Lapl. (only if QTAIM integration) and the total quantities (*i.e.*, 61.9963 instead of 62)

```

-----
Error(S)=Sum(|I-Sum(S(A))|)=  0.0025945
-----
.....
-----
| Atom  N (Sij)  N (int)  Lapl.   loc.   deloc.   N1     N2
-----
| P   1  15.4991  15.4991  0.0006  13.8377  3.3227  11.9993  3.4998
| P   2  15.4991  15.4991  0.0006  13.8377  3.3227  11.9993  3.4998
| P   3  15.4991  15.4991  0.0006  13.8377  3.3227  11.9993  3.4998
| P   4  15.4991  15.4991  0.0006  13.8377  3.3227  11.9993  3.4998
-----
| -    0  61.9963  61.9963  0.0025  55.3509  13.2910  47.9972  13.9992
-----

```

The first column of the last table gives the population calculated from the AOMs, the second column gives the same quantity as taken from the integration files (they should coincide if the integration is good), the Laplacian of density (for QTAIM we say an integration is acceptable if the quantity is smaller than 0.001), the localization index (Eq. 2.21), the delocalization index (Eq. 2.23), and the populations can be decomposed into two orbital group contributions, N1 (σ orbitals) and N2 (π orbitals). This molecule has D_{4h} and its molecular orbitals can be classified into σ and π orbitals because the symmetry group C_s (with irreducible representations A' [σ] and A'' [π]) is a subgroup of D_{4h} and, therefore, each irreducible representation of this group can be mapped into either A' or A'' . To obtain an orbital decomposition with ESI-3D we should use the keyword \$GROUPS to distribute the orbitals into 2 groups (see Appendix II). The orbital symmetry information can be found in the Gaussian log-file.

Pair	DI	DI1	DI2
P 1-P 1	13.8377	10.8808	2.9569
P 1-P 2	0.4200	0.1620	0.2580
P 1-P 3	1.4504	1.0368	0.4136
P 1-P 4	1.4504	1.0368	0.4136
P 2-P 2	13.8377	10.8808	2.9569

The second table gives the DI and LI values, *i.e.*, Eqs. 2.20 and 2.21. If the pair involves the same atom the value given is the LI, otherwise the corresponding DI. Notice that the last two columns once again represent the A' and A'' contributions.

Finally, we request a multicenter analysis by including the following lines in the input file (either `yourfile.fuz` and `yourfile.bad`):

```
$MULTICENTER
2
4 1 2 3 4
3 1 2 3
```

Please notice that the atoms should be given in the order they are connected in the ring. In this previous lines we request a calculation of two multicenter indices (P-P-P-P and P-P-P):

```
-----
| Multicenter:
| Atom-Group          Iring-like  MCI-like
| P 1-P 2-P 3-P 4 = 0.030794 0.042156
| P 1-P 2-P 3 = 0.019248 0.019248
```

which gives the I_{ring} value, Eq. 2.29, and MCI, Eq. 3.7.

Chapter 3

Aromaticity

Chemistry is essentially an experimental science that evolved through experimentation and it has been built upon a series of empirically proved laws and models. On the other side, quantum mechanics relies on postulates from which a solid theory has been constructed. Both focus on the study of matter, however, quantum mechanics can anticipate the electronic structure of matter and it could, in principle, replace the laws and models of chemistry by physically sound theories. Notwithstanding, after many years of the advent of quantum mechanics, several chemical concepts with high predictable power still prevail. Most of these concepts have not found (and most likely cannot find) a solid root in the quantum theory because there is no observable behind them. One finds many such concepts in the literature (*e.g.*, chemical bonding, bond order, ionicity, electron population, agostic bond, etc.) that are still widely used to predict or explain the electronic structure of molecules or reaction mechanisms [71]. One of the most employed terms in literature —and one of the most controversial [72] ones— is *aromaticity* [73–77]. Aromaticity is associated with cyclic electron delocalization in closed circuits that gives rise to energy stabilization, bond length equalization, large magnetic anisotropies and abnormal chemical shifts, among other effects. Various of these aromaticity manifestations can be measured by appropriate quantities, the aromaticity indices, that allow for aromaticity scales. As a result, nowadays there is a number of indices available in the literature, often offering disparate results about the aromaticity of certain chemical species [78]. The discovery of new aromatic species [79–81] that extend well beyond the realm of organic chemistry has challenged our understanding of aromaticity and it has put forward the limitations of the existing aromaticity indices to deal with these new chemical creatures [69].

Indeed, aromaticity is an *ill-defined* concept. It does not correspond to a physical observable like many other properties that populate the world of tools used in the routine analysis of chemical reactions. Bond orders, reaction concertedness or oxidation states are properties that cannot be measured directly and, therefore, unambiguously assigned. However, aromaticity is still more controverted than other similar quantities like *bond ionicity* or *bond order* because it refers to not one, but several properties that are not necessarily mutually related. Despite its fuzziness, chemists still use this concept to elucidate phenomena such as chemical stability/reactivity, bond length equalization/alternation,

among others. Therefore, aromaticity is a concept used by chemists world wide and it cannot be so easily ignored or put aside.

Aromaticity is a multifold property [78,82–85] because of its different manifestations which range from purely energetical to structural ones. Indeed, the use of different aromaticity measures (even if they are based on the same manifestation) is highly recommended because, as it has been recently proved [67,86], no aromaticity index is infallible. On the other hand, saying that aromaticity is a multidimensional phenomena (an accepted fact), sometimes hinders the drawbacks of certain aromaticity indices, which fail to fulfil this or that feature of aromaticity that any chemist would agree with [86]. These drawbacks should be identified and the limits and features of aromaticity indices established to avoid a wrong use of these quantities. In some cases, we should ask ourselves which manifestation of aromaticity we are looking for. Aromaticity criteria based on electron delocalization are good to identify conjugated-electron circuits, which might play important roles in the electronic distribution of the electrons in a ring, the mobility of the electron cloud or the assignment of electronic spectrum transitions. On the other hand, energetic criteria are important to identify molecules that benefit from extra energy stabilization. In some molecules, conjugated-electron circuits along a ring structure cause bond-length and bond-order equalization as well as an important energy stabilization in the molecule (many organic molecules show this behavior). However, the transition state of the Diels-Alder reaction is the most aromatic point along the intrinsic reaction coordinate (IRC) but there is no bond-length or bond-order equalization and this point is the most energetic point along the IRC.^a

Despite the approximations inherent in the Hückel Molecular Orbital (HMO) approach, organic aromatic molecules are specially well described within the HMO method. It is thus usual to learn the HMO at the same time than $4n + 2$ Hückel's rule and other aromaticity measures given by the HMO method, such as the resonance energy (RE), the RE per electron (REPE) or even the topological REPE (TREPE) [89]. Since the studies of Hückel on organic molecules, the concept of aromaticity has extended importantly including all sort of new aromatic molecules such as metalloaromatic molecules, fullerenes [90], nanotubes, porphyrins [91,92], molecules with a Möbius-like structure [93–95] and all-metal clusters [69], among others.

In the literature there are many indices of aromaticity and they can be classified as either energetic [96], magnetic [75] geometric [76] and electronic indices [77], corresponding to the different manifestations of aromaticity, *i.e.*, energetic stabilization, exalted magnetic susceptibilities, particular geometrical features (such as bond length equalization or planarity) or electron delocalization along the aromatic ring, respectively. There are various energetic criteria to assess aromaticity but perhaps the most popular one is the use of homodesmotic or isodesmotic reactions from which one can calculate the aromatic stabilization energy (ASE) [96]. Among the structural-based (or geometric) indices it is worth to highlight the HOMA index. The most popular index of aromaticity

^aOne could argue that the energy stabilization should be compared with the transition state of similar reactions. Yet, pseudopericyclic reactions are essentially barrierless and produce similar products through a non-aromatic transition state [87,88].

is perhaps the NICS index [97], which belongs to the set of magnetic indices. Finally, among the electronic indices we find the multicenter indices (I_{ring} and MCI), which perform the best among the different aromaticity indices existing in the literature [67, 86].

In this course we will mostly focus on the study of a geometric index of aromaticity (HOMA) [98], a magnetic one (NICS) [97] and several electronic indices of aromaticity, which include FLU [99], I_{ring} [60], MCI [61] and PDI [100].

3.1 Geometrical indices

In this subsection we will analyze the so-called harmonic oscillator model of aromaticity (HOMA) as defined by Kruszewski and Krygowski. [98] The HOMA only relies on geometrical data and it can be computed using this expression:^b

$$\text{HOMA} = 1 - 257.7 \frac{1}{n} \sum_i^n (R_{\text{opt}} - R_i)^2 \quad (3.1)$$

$$= 1 - 257.7 \frac{1}{n} \left((R_{\text{opt}} - \bar{R})^2 + \sum_i^n (R_i - \bar{R})^2 \right) \quad (3.2)$$

$$= 1 - (\text{EN} + \text{GEO}) \quad (3.3)$$

The closer to one the index, the more aromatic. The formula depends on some reference bond distances and, unfortunately, there is a limited number of bonds for which these references have been tabulated (C-C, C-N, C-O, C-P, C-S, N-N and N-O). This set suffices to calculate most organic molecules but imposes a serious drawback to extend the use of HOMA to new aromatic molecules.

3.2 Magnetic indices

If an aromatic molecule is exposed to an external magnetic field, this field induces a π -electron ring current that can be measured and used to characterize aromaticity. The magnetic susceptibility exaltation or the anisotropy of the magnetic susceptibility are measures of aromaticity based on this property of aromatic systems. However, the most important (and by far the most popular) magnetic index of aromaticity is NICS. The nucleus independent chemical shift (NICS) is the negative value of the absolute shielding computed at the center of the ring (or other relevant point of the system, see below). It was defined by Paul Schleyer and coworkers [97] and assesses that the most aromatic molecules will be those with the most negative values. On the contrary, the more positive the NICS values, the more antiaromatic the rings are.

There is many variants of NICS indices, which can be calculated at the ring

^bPlease notice that the step from Eq. 3.1 to Eq. 3.2 assumes that all bonds are of the same type. The expression for rings with different bonding patterns can also be decomposed into EN and GEO terms but its derivation is less straightforward [101].

center [NICS(0)], at one Ångstrom above or below the ring plane [NICS(1)]^c or taking only its out-of-plane tensor component [NICS(0)_{zz} and NICS(1)_{zz}]. Finally, it is worth saying that some authors recommend to compute the NICS not at the geometric center but at the point of the lowest density in the ring plane, *i.e.*, at the RCP [102]. This recommendation proves particularly wise in the case of heterocyclic or metalloaromatic compounds, where the RCP is usually displaced from the geometric ring center.

3.3 Electronic indices

Despite aromaticity does not accept a unique definition, there has been many attempts to define it. Perhaps the most remarkable ones are due to Sondheimer (1963) and Paul Schleyer (1996) in two articles from the official journal of the International Union of Pure and Applied Chemistry (IUPAC) [73,103]:

A compound is considered to be aromatic if there is a measurable degree of delocalization of a π -electron system in the ground state of the molecule.

F. Sondheimer (1963)

Aromaticity is now associated with cyclic arrays of mobile electrons with favorable symmetries. In contrast, the unfavorable symmetry properties of antiaromatic systems lead to localized, rather than to delocalized electronic structures. The "mobile electron" arrays are not restricted to π , but may be σ or mixed in character.

P. Schleyer and H. Jiao (1996)

In this sense, Sondheimer considers aromatic molecules as those that have a *measurable degree of cyclic delocalization of a π -electron system*. Similarly, Schleyer and Jiao think of aromaticity as *associated with cyclic arrays of mobile electrons with favorable symmetries while the unfavorable symmetry properties of antiaromatic systems leads to localized rather than to delocalized electronic structures*. This cyclic mobility of electrons is translated into characteristic aromatic manifestations such as bond-length equalization, abnormal chemical shifts, magnetic anisotropies, and energetic stabilization.

It thus, seems only natural to try to define aromaticity from its origin, the particular electronic distribution, rather than from its consequences. Lately aromaticity indicators based on the electronic structure of molecules are becoming popular, and several research groups have contributed to the issue by providing new aromaticity indices [77]. Among others we can mention the I_{ring} [60] of Giambiagi et al., the MCI [61] of Bultinck and coworkers or the θ index [104] of Matta. More recently, Szczepanik and coworkers have contributed with a index capable of accounting for multicenter bonding [105,106]. Our group has

^cThe NICS(1) should in principle capture the presence of π -electron delocalization because the maximum of the electron of p orbitals is larger at ca. 1Å. NICS(1) is thus more suitable for organic molecules, which exhibit classical π aromaticity.

been also extensively working in this issue [74, 77], and the latest efforts have provided the PDI [100] and FLU [99] aromaticity measures as well as the normalized versions of I_{ring} and MCI [62] and AV1245, which is an index for large porphyrinic rings [107].

Some of the aromaticity indices have been proposed without an exhaustive justification further from the fact that these indices correlate well with previously reported aromaticity indices. It is thus recommended to know the limitations of the existing aromaticity indices. Let us examine several indices. We are concerned with the calculation of the local aromaticity of a given molecule which possesses at least one ring structure. Let us suppose such ring structure consists of n atoms, represented by the following string $\mathcal{A}=\{A_1, A_2, \dots, A_n\}$, whose elements are ordered according to the connectivity of the atoms in the ring. For such system we can calculate the following electronic aromaticity indices.

3.3.1 The Aromatic Fluctuation Index: FLU

Based on the comparison with cyclic electron delocalization of typical aromatic molecules, FLU index is defined as follows [99, 108]:

$$FLU(\mathcal{A}) = \frac{1}{n} \sum_{i=1}^n \left[\left(\frac{\delta(A_i)}{\delta(A_{i-1})} \right)^\alpha \left(\frac{\delta(A_i, A_{i-1}) - \delta_{ref}(A_i, A_{i-1})}{\delta_{ref}(A_i, A_{i-1})} \right) \right]^2 \quad (3.4)$$

where $A_0 \equiv A_n$ and $\delta(A)$ is the atomic valence that for a closed-shell system, Eq. 2.23, and α is a simple function to ensure the first term in Eq. (3.4) is always greater or equal to 1,

$$\alpha = \begin{cases} 1 & \delta(A_{i-1}) \leq \delta(A_i) \\ -1 & \delta(A_i) < \delta(A_{i-1}) \end{cases} \quad (3.5)$$

$\delta(A, B)$, $\delta_{ref}(A, B)$ are quantities that account for the electron sharing of A and B ; the latter is taken from an aromatic molecule which has the pattern of bonding $A - B$. In hydrocarbons, where only C-C bonds will be taken into account, the molecule chosen as an aromatic reference is benzene. FLU is close to zero in aromatic species, and greater than zero for non-aromatic or antiaromatic species.

The aromaticity indices based on references do not actually measure aromaticity but they measure the similarity with respect to some aromatic molecule. In this sense, these indices (HOMA and FLU) are not adequate to describe reactivity. For instance, in the case of the Diels-Alder reaction they cannot recognize the transition state (TS) as the most aromatic point along the reaction path because the product, cyclohexene, is more similar to benzene (the reference molecule for C-C bonds) than the TS, which shows large C-C distance in the bonds that will be formed. [109]

3.3.2 A Multicenter based index: I_{ring}

Based on the multicenter index (which account for the simultaneous electron sharing of various centers) Giambiagi and coworkers, proposed this quantity,

I_{ring} , as a measure of aromaticity. The formula reads as follows [60]:

$$I_{\text{ring}}(\mathcal{A}) = \sum_{i_1, i_2, \dots, i_n}^{\text{occ}} S_{i_1 i_2}(A_1) S_{i_2 i_3}(A_2) \dots S_{i_n i_1}(A_n) \quad (3.6)$$

where $S_{ij}(A)$ is the overlap of molecular orbitals i and j in the atom A . I_{ring} will provide large values (larger simultaneous electron sharing of atoms in the ring) for aromatic molecules. Eq. 3.6 is the single-determinant version of Eq. 2.29.

3.3.3 The Multicenter Index: MCI

With the aim to improve the I_{ring} , Bultinck and coworkers [61] proposed to sum not only the contribution from the Kekulé structures (as I_{ring} does), but also the contribution from all possible structures generated by permuting the position of all the atoms in the ring. Such possibility was already discussed by Ponec and coworkers [55, 110] among others [111]. Thus, the formula reads:

$$MCI(\mathcal{A}) = \sum_{\mathcal{P}(\mathcal{A})} I_{\text{ring}}(\mathcal{A}) = \quad (3.7)$$

$$= \sum_{\mathcal{P}(\mathcal{A})} \sum_{i_1, i_2, \dots, i_n}^{\text{occ}} S_{i_1 i_2}(A_1) S_{i_2 i_3}(A_2) \dots S_{i_n i_1}(A_n) \quad (3.8)$$

where $\mathcal{P}(\mathcal{A})$ stands for $n!$ permutations of elements in the string \mathcal{A} . Although the original proposal of MCI differs from this one in a numerical factor, we will skip it for the reasons already commented in ref. [62]. As I_{ring} , MCI produces large numbers for aromatic species, and the authors claim negative numbers are produced by antiaromatic species [112]. This fact has only been proven for three member rings [55] and heuristically for six-member rings [?].

3.3.4 The para-Delocalization Index: PDI

Based on the finding of Fulton [113] and Bader [114], which showed that benzene has larger para-related atoms electron sharing than meta-related one, the index uses the para-related atoms electron sharing as a measure of aromaticity for six-membered rings:

$$PDI(\mathcal{A}) = \frac{\delta(A_1, A_4) + \delta(A_2, A_5) + \delta(A_3, A_6)}{3} \quad (3.9)$$

thus, the larger the index the greater the aromaticity. Obviously, the index cannot be applied to rings with more or less than six members. The PDI is less reliable for heterocycles and rings made of highly polarizable atoms.

3.3.5 EXERCISE 8 (Aromaticity)

In this exercise we will perform an aromaticity calculation to use all the aforementioned indices. We will take two molecules benzene and cyclohexane.

Electronic aromaticity indices. To obtain the electronic aromaticity indices we just need to perform the same steps that we did to calculate the electronic sharing indices (see exercises 5 and 6) and the output of ESI-3D will include all the electronic aromaticity indices for the rings specified by the keyword \$RING (see Appendix II).

Keep in mind that FLU uses reference values and it only has values for the bonds C-C, C-N, B-N and N-N, any other bond patterns in the rings cannot be calculated with FLU and should be disregarded. On the other hand, PDI can only be calculated in six-member rings. MCI and I_{ring} do not have any limitation and can be calculated in any molecular ring; the only exception being large porphyrinc rings [107].

See below an extract from ESI program:

```
-----  
| Aromaticity indices - FLU [JCP 122, 014109 (2005)]  
|           HOMA [Tetrahedron 52, 10255 (1996)]  
|           PDI [CEJ 9, 400 (2003)]  
|           Iring [PCCP 2, 3381 (2000)]  
|           MCI [JPOC 18, 706 (2005)]  
|           I_NB, I_NG [JPCA 111, 6521 (2007)]  
| For a recent review see: [CSR 44, 6434 (2015)]  
-----  
| FLU      1 = 0.000082  
| TREPE    1 = 0.045432  
-----  
| PDI      1 = 0.103425 ( 0.103427 0.103429 0.103419 )  
| Iring    1 = 0.048553  
| I_NG     1 = 0.041397  
| MCI      1 = 0.072991  
| I_NB     1 = 0.041177  
-----
```

In this case FLU is zero (*i.e.* maximum aromaticity) because the reference molecule is benzene. PDI is 0.1, which is quite large value for a para-DI, thus indicating that benzene is aromatic. The multicenter indices, I_{ring} and MCI, show large numbers, 0.049 and 0.073, respectively. LNG (normalized version of I_{ring} , see Ref. [62]) and LNB (normalized version of MCI, see also Ref. [62]) show also large numbers typical of aromatic molecules. For comparison we add below the extract of cyclohexane:

```
-----  
| FLU      1 = 0.095695  
| TREPE    1 = 0.045432  
-----
```

Ring	EN	GEO	HOMA
1	5.656675	0.000006	-4.656682

PDI	1	=	0.008517	(0.008523	0.008546	0.008482)
Iring	1	=	0.000286					
I_NG	1	=	0.017594					
MCI	1	=	0.000315					
I_NB	1	=	0.016610					

Notice that TREPE produces the same value than benzene because this index only takes into account the connectivity of the atoms and, therefore, should only be used in annulene-like structures.

Geometric indices of aromaticity. The calculation of HOMA can be done using the formulae given in the literature or using the ESI-3D program with the keyword **\$GEOMETRY** (see Appendix II).

benzene:

Ring	EN	GEO	HOMA
1	0.034349	0.000000	0.965651

cyclohexane:

Ring	EN	GEO	HOMA
1	5.656675	0.000006	-4.656682

The total HOMA value for benzene is 0.97, close to the maximum value (one), in accord with the value one would expect for this molecule, which is the reference to set the C-C optimal distance in HOMA (the discrepancy comes from basis set and method effects which are usually small). On the other hand, cyclohexane value is much smaller than zero, indicating that this molecule is not aromatic at all. The geometrical criteria, GEO, (which measures the deviation from the average bond distance in the ring) is zero for both molecules, indicating that all the bonds have the same length and, therefore, as far as the symmetry is concerned, the molecules should be very aromatic. On the other hand, EN is also close to zero because all the C-C are, obviously, very close to the optimal C-C distance, whereas cyclohexane gives a very large EN value, in accord to the C-C distances which are larger than in a typical aromatic molecule.

Magnetic indices of aromaticity. The calculation of NICS has to be done with gaussian by requesting an NMR calculation (keyword to add in the input file: **NMR**) and including a list of the relevant points that we want to specify as **Bq**. See this example for benzene:

```
#HF/6-31G* NMR
```

NICS automatic generation

```
O 1
C   0.00000000   1.38617405   0.00000000
C   1.20046194   0.69308703   0.00000000
C   1.20046194  -0.69308703   0.00000000
C   0.00000000  -1.38617405   0.00000000
C  -1.20046194  -0.69308703   0.00000000
C  -1.20046194   0.69308703   0.00000000
H   0.00000000  -2.46178023   0.00000000
H   2.13196422  -1.23089011   0.00000000
H   2.13196422   1.23089011   0.00000000
H   0.00000000   2.46178023   0.00000000
H  -2.13196422   1.23089011   0.00000000
H  -2.13196422  -1.23089011   0.00000000
Bq   0.00000000   0.00000000   0.00000000
Bq   0.00000000   0.00000000   1.00000000
Bq   0.00000000   0.00000000  -1.00000000
```

In this case, benzene is placed in the XY plane and the NICS(0) point is located at (0,0,0), and NICS(1) can be calculated by placing Bq(s) at (0,0,-1) and (0,0,1). In case your molecule is not symmetric, you need to use a script, NICS.x, that creates an input file for gaussian including a list of Bqs. The script uses the RCP, adjusts the best fitting plane with the atoms in the ring and calculates the points laying 1Å above and below the plane. NICS script needs a [yourfile](#).ring file that assumes the units are Å, unless you specify *au* as a second argument:

```
NICS yourfile au
```

In the case you [yourfile](#).ring is in Å run NICS like this:

```
NICS yourfile
```

The list of Bqs included in the input of gaussian ([yourfile](#)_NICS.com) generated by NICS.x contain in this order: the geometrical center, the position 1Å above the best-fitting ring plane and 1Å below the plane, and the set of RCP contained in [yourfile](#).ring. An example of the contents of [yourfile](#).ring:

```
1 rings found
6 members of 1th ring
2 1 3 7 10 6
12 atoms
C   0.000000   0.000000   1.399576
C   0.000000   1.212026   0.699769
C   0.000000  -1.212026   0.699769
H   0.000000   2.156871   1.245296
H   0.000000  -2.156871   1.245296
C   0.000000   1.212026  -0.699769
C   0.000000  -1.212026  -0.699769
H   0.000000   2.156871  -1.245296
```

```

H      0.000000   -2.156871   -1.245296
C      0.000000    0.000000   -1.399576
H      0.000000    0.000000   -2.490595
H      0.000000    0.000000    2.490595
X      0.000000    0.000000    0.000000

```

The output of gaussian which corresponds to the previous input looks like this:

```

    13 Bq  Isotropic =    11.4581  Anisotropy =    8.5608
XX=    8.6045  YX=    0.0000  ZX=    0.0000
XY=    0.0000  YY=    8.6045  ZY=    0.0000
XZ=    0.0000  YZ=    0.0000  ZZ=   17.1653
Eigenvalues:    8.6045    8.6045   17.1653
    14 Bq  Isotropic =    12.8592  Anisotropy =   29.4313
XX=    3.0487  YX=    0.0000  ZX=    0.0000
XY=    0.0000  YY=    3.0487  ZY=    0.0000
XZ=    0.0000  YZ=    0.0000  ZZ=   32.4800
Eigenvalues:    3.0487    3.0487   32.4800
    15 Bq  Isotropic =    12.8592  Anisotropy =   29.4313
XX=    3.0487  YX=    0.0000  ZX=    0.0000
XY=    0.0000  YY=    3.0487  ZY=    0.0000
XZ=    0.0000  YZ=    0.0000  ZZ=   32.4800

```

We must take the negative value of the Isotropic contribution. Therefore, in this case $\text{NICS}(0)=-11.5$, $\text{NICS}(0)_{zz}=-17.2$, $\text{NICS}(1)=-12.9$ and $\text{NICS}(1)_{zz}=-32.5$. All the values indicate that benzene is an aromatic molecule, the important total and zz-component $\text{NICS}(1)$ values indicate that its aromaticity is due to the π -electron delocalization along the ring.

Chapter 4

Oxidation state

4.1 Definition

Historically, the oxidation state (OS) was defined as the stepwise increase in the amount of oxygen bound by atoms that form more than one oxide. Nowadays, the concept of OS is mostly used for transition metal (TM) complexes and, therefore, the interest on calculating OS is focused on TM atoms. Figure 4.1 summarizes the OS of the first three rows of TM elements.

The OS is a property of an atom within a molecule. As such, its definition is not completely unambiguous and there is a number of cases where the oxidation state cannot be clearly assigned [115]. There are complicated bonding situations involving noninnocent ligands or in intermediates or transition states of reactions, where the formal OS assignment might be rather ambiguous. Therefore, it is important to have reliable methods to assign oxidation states in troublesome cases.

The IUPAC defined the OS as the charge of the central atom (often a TM) after removing its neighbors (the ligands) along with the shared electron pairs. There are a number of papers published by the IUPAC about the OS, but let us stay here with the extensive report of Pavel Karen published in 2014 [115]. For a short account of the OS and its state-of-the-art calculation see the essay

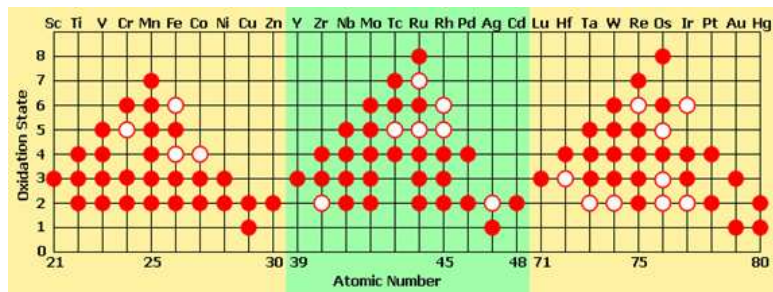


Figure 4.1: The common oxidation states of the first three rows of TM atoms in the periodic table.

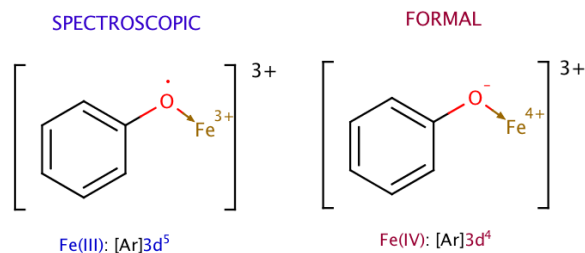


Figure 4.2: The interaction of Fe^{4+} with PhO^- can give rise to two oxidation states. If we consider the *formal* oxidation state, the OS of Fe is IV, whereas the spectroscopic measurements indicate that Fe only populates *d* orbitals with 4 electrons, *i.e.*, the OS of Fe is III.

by the same author, Ref. [116].

There have been attempts to define the OS in a less ambiguous way. For instance, the **physical** or **spectroscopic** OS is the charge of the TM that comes from d^n and can be measured spectroscopically (e.g. Mössbauer).^a Figure 4.2 illustrates one of the few examples where the formal definition of OS states differs from the spectroscopic one.

4.2 Computational calculation of Oxidation States

There are many methods to calculate the OS, for a historical account see Ref. [115] and for a short list see Ref. [116] (see also Refs. [117, 118]). Here we will consider only a few approaches: the empirical approach based on metal-to-ligand distance, the bond valence sum, and three different computational approaches: the population analysis, the spin density and orbital-localization methods.

In order to perform a comparison between the different methods to calculate oxidation states we have chosen a set of TM complexes, taken from Ref. [117]; these TM complexes and the oxidation state of its central atom are collected in Table 4.1.

4.2.1 Bond Valence Sum

The Bond Valence Sum (BVS) method is an empirical technique based on the metal-to-ligand distances (R_i) and some reference values (R_0 , $b=0.37\text{\AA}$).^b The

^aJørgensen, In *Oxidation Numbers and Oxidation States*; Springer; Heildeberg, 1969.

Useful references:

<http://www.edu.upmc.fr/chimie/mc741/PDFs/bond.pdf>

<http://www.chem.umn.edu/groups/harned/classes/8322/lectures/5ElectronCounting.pdf>

^bhttp://www.ccp14.ac.uk/solution/bond_valence/index.html

V ^{II}	[VCl ₆] ⁴⁻	[V(H ₂ O) ₆] ²⁺	[V(CN) ₆] ⁴⁻	[V(CO) ₆] ²⁺
Mn ^{II}	[MnCl ₆] ⁴⁻	[Mn(H ₂ O) ₆] ²⁺	[Mn(CN) ₆] ⁴⁻	[Mn(CO) ₆] ²⁺
Mn ^{III}	[MnCl ₆] ³⁻	[Mn(H ₂ O) ₆] ³⁺	[Mn(CN) ₆] ³⁻	[Mn(CO) ₆] ³⁺
Fe ^{II}	[FeCl ₆] ⁴⁻	[Fe(H ₂ O) ₆] ²⁺	[Fe(CN) ₆] ⁴⁻	[Fe(CO) ₆] ²⁺
Fe ^{III}	[FeCl ₆] ³⁻	[Fe(H ₂ O) ₆] ³⁺	[Fe(CN) ₆] ³⁻	[Fe(CO) ₆] ³⁺
Ni ^{II}	[NiCl ₆] ⁴⁻	[Ni(H ₂ O) ₆] ²⁺	[Ni(CN) ₆] ⁴⁻	[Ni(CO) ₆] ²⁺
Zn ^{II}	[ZnCl ₆] ⁴⁻	[Zn(H ₂ O) ₆] ²⁺	[Zn(CN) ₆] ⁴⁻	[Zn(CO) ₆] ²⁺

Table 4.1: The set of TM complexes from Ref. [117].

BVS expression reads:

$$V = \sum_i \left(\frac{R_i - R_0}{b} \right)$$

This method only needs the computational optimization of the TM complex geometry.

4.2.2 Atom Population Analysis

In section 2.4, we studied different methods to calculate atomic populations. In order to state the OS from atomic populations, we simply need to take the closest integer number to the atomic charge, Eq. 2.14. Although it is a common practice in the literature to estimate the OS from atomic populations, the method is perhaps the least reliable one. The atomic populations have a strong dependency on the method used to perform the atomic partition [119]. Besides, some atomic partitions, such as Mulliken’s (see section 2.4.1) show a strong basis set dependency. In Table 4.2 we collect the OS of the set of TM complexes calculated with Mulliken and TFVC partitions. Mulliken population fails in all cases but TFVC fails more than 50% of the cases [120].

	Cl ⁻	H ₂ O ^{HS}	H ₂ O ^{LS}	CN ⁻	CO	Cl ⁻	H ₂ O ^{HS}	H ₂ O ^{LS}	CN ⁻	CO
V ^{II}	0.98	1.12		0.05	0.64	1.60	1.76	-	1.60	1.64
Mn ^{II}	1.10	1.24	1.18	0.10	0.64	1.36	1.64	1.70	1.53	1.53
Mn ^{III}	0.93	1.58	1.52	0.35	0.80	1.46	2.05	2.09	1.58	1.67
Fe ^{II}	0.86	1.22	1.15	0.01	0.51	1.27	1.63	1.77	1.46	1.44
Fe ^{III}	0.99	1.64	1.48	0.24	0.66	1.44	2.06	1.98	1.49	1.58
Ni ^{II}	0.99		1.08	-0.19	0.31	1.27	-	1.59	1.24	1.30
Zn ^{II}	1.02		1.06	-0.03	0.52	1.25	-	1.45	1.15	1.19

Table 4.2: The OS for set of TM complexes from Ref. [117]. The values on the l.h.s. correspond to Mulliken charges and the ones in the r.h.s. to TFVC, from Ref. [120]. The values marked in green are correctly predicted.

4.2.3 Spin Densities

Crystal Field Theory (CFT) is a model that describes the breaking of degeneracies of electron orbital states, usually *d* or *f* orbitals, due to a static electric field produced by a surrounding charge distribution (anion neighbors). The CFT can

be used in conjunction with the field strength of the complex ligands to predict the occupation of the d orbitals in the TM. From this occupation one can infer the number of unpaired electrons in the TM for each possible oxidation state. From an *unrestricted* computational calculation one can calculate the spin atomic population, *i.e.* the number of unpaired electrons in a given atom. In Fig. 4.3 we find the CFT for the formation of O_h complexes. The l.h.s. depicts the five d orbitals of the isolated metal cation. These orbitals destabilize upon the presence of the negative charges uniformly distributed around the metal due to electron-electron repulsion (these negative charges are a rough representation of the ligands). Upon octahedral organization around the metal, the d -orbitals change their relative energy stabilization. The d_{xy}, d_{xz} and d_{yz} (known as t_{2g}) are stabilized due to the fact the lobes of these orbitals do not face the axial and equatorial positions, where the ligands are placed. Conversely, the d_{z^2} and $d_{x^2-y^2}$ (known as e_g) orbitals have important interactions with the four equatorial ligands, whereas the d_{z^2} orbital also shows important overlap with the ligands in the axial positions. Upon consideration of the favorable electrostatic interactions (the attraction between the TM protons and the ligands' electrons) the five d orbitals stabilize, so that the formation of the TM complex is energetically favorable (see r.h.s. of Fig. 4.3).

The group symmetry of the TM complex determines the particular d -orbital splitting (Δ_o) and, therefore, governs the occupation of d orbitals. The other important factor, is the nature of the ligands that bind to the TM. The ligands can be strong-field (large gap) or weak-field (small gap) ligands and determine the actual energy gap between d orbitals. If a TM is surrounded by weak-field ligands, the electron-electron repulsion among electrons in the same orbitals is stronger than the energy between d -orbitals and, therefore, the TM complex acquires the highest spin state. Conversely, strong-field ligands, generate an important energy gap between d orbitals that is larger than the repulsion energy between electrons in the same orbital and thus the TM complex adopts the lowest spin state possible. *Strong field* is used as synonym of *low spin* and *weak field* is equivalent to *high spin*.

The procedure to determine the OS from spin population is: (i) first determine the d -orbital splitting from the TM complex symmetry using CFT; (ii) determine the nature of the ligands so that we know which d -orbitals are occupied first; (iii) calculate the number of unpaired electrons in the TM for different electron numbers (S_{TM}); (iv) compute the TM spin population from an unrestricted calculation and round to the closest integer number (S_{TM}^{comp}). Match the S_{TM} to the configurations calculated in (iii); once we have the configuration we will assign the OS that results from subtracting the atomic number of the TM from the numbers of electrons in the configuration. Let us consider an example, where the TM is Fe and the ligands are Cl^- (weak-field ligands) organized in a O_h conformation. Fe^0 has an electronic configuration of $[\text{Ar}]3d^64s^2$, *i.e.*, $\text{Fe}^{2+}:[\text{Ar}]3d^6$, which gives a spin population of $S_{TM}^{2+} = 4$; by analogous reasons we find that $S_{TM}^{3+} = 5$ ($3^+:[\text{Ar}]3d^5$). Our unrestricted calculation has produced a $S_{TM}^{\text{comp}} = 4.53 \approx 5$, and therefore the OS of our TM complex is +3.

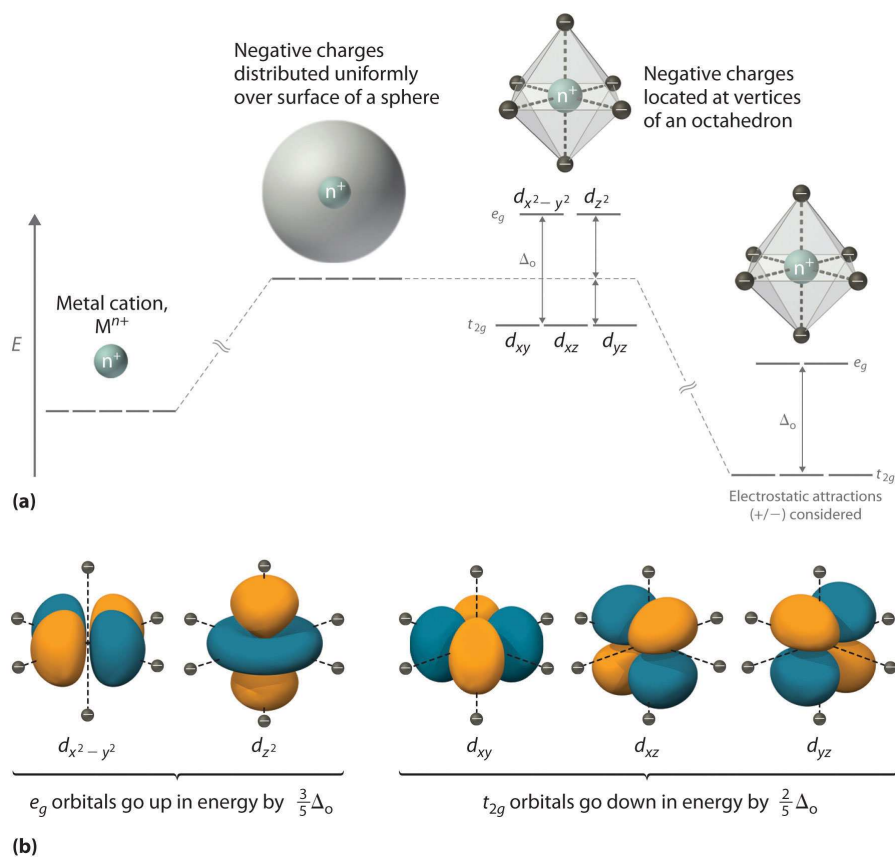


Figure 4.3: O_h complexes d-orbital splitting according to CFT. This figure has been taken from ChemWiki.
http://chemwiki.ucdavis.edu/Core/Inorganic_Chemistry/Crystal_Field_Theory/Crystal_Field_Theory

Unlike total populations, which strongly depend on the atomic partition, spin population are quite more reliable. In Table 4.3 we find the OS of several complexes using Mulliken and TFVC spin atomic populations.

	Cl ⁻	H ₂ O ^{HS}	H ₂ O ^{LS}	CN ⁻	CO	Cl ⁻	H ₂ O ^{HS}	H ₂ O ^{LS}	CN ⁻	CO
V ^{II}	3.06	2.99		2.84	2.79	2.90	2.71	-	2.52	2.44
Mn ^{II}	4.96	4.88	1.01	1.09	1.06	4.86	4.66	0.95	1.01	0.98
Mn ^{III}	4.25	3.85	1.97	2.11	2.16	4.07	3.65	1.84	1.96	2.00
Fe ^{II}	3.86	3.86	0.00	0.00	0.00	3.72	3.71	0.00	0.00	0.00
Fe ^{III}	4.27	4.43	0.89	1.08	1.11	4.17	4.28	0.86	1.01	1.03
Ni ^{II}	1.87		1.84	1.69	1.66	1.84	-	1.77	1.66	1.63
Zn ^{II}	0.00		0.00	0.00	0.00	0.00	-	0.00	0.00	0.00

Table 4.3: The OS for the set of TM complexes from Ref. [117]. The values on the l.h.s. correspond to the OS estimated by Mulliken spin populations and the ones in the r.h.s. to TFVC spin populations, from Ref. [120]. The values marked in green with the number of unpaired electrons of the metal (and, therefore, provide the correct OS).

4.2.4 Orbital-localization Methods: Effective Oxidation State

We are concerned here with the effective oxidation state (EOS) method of Ramos-Cordoba, Postils and Salvador [118] but there are other methods to calculate effective oxidation states, such as the Localized Orbital Bonding Analysis (LOBA) method of Head-Gordon’s group (see Ref. [117]).

Let us consider a spin-unrestricted single-determinant wavefunction built from singly-occupied MOs ($\phi_i^{\text{MO}}(\mathbf{1})$). For each atom in the molecule, A , one can define the intra-atomic part of every MO as

$$\phi_i^A(\mathbf{1}) = w_A(\mathbf{1})\phi_i^{\text{MO}}(\mathbf{1})$$

where w_A is the atomic weight (see section 2.3.2). For each atom we can construct a intra-atomic overlap matrix as

$$Q_{ij}^A = \int \phi_i^A(\mathbf{1})\phi_j^A(\mathbf{1})d\mathbf{1}$$

This matrix is Hermitian and its trace corresponds to the atomic population of atom A (atomic population according to the atomic partition used, which is determined by the weight function, w_A),

$$\text{Tr}\mathbf{Q}^A = N_A$$

The intra-atomic overlap matrix is Hermitian and, therefore, it can diagonalized through a unitary transformation, \mathbf{L}^A ,

$$\mathbf{Q}^A\mathbf{L}^A = \mathbf{L}^A\mathbf{\Lambda}^A$$

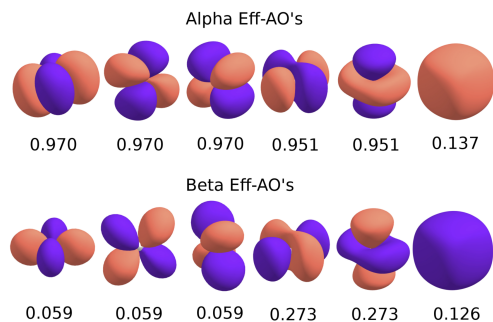


Figure 4.4: A set of eff-AO and their occupation numbers.

producing a set of eigenvalues, $\lambda_i^A \equiv (\mathbf{\Lambda}^A)_{ii}$, and eigenvectors, \mathbf{L}^A . These eigenvectors can be used to produce normalized spin-resolved effective atomic orbitals (eff-AO),

$$\chi_i^A(\mathbf{1}) = \frac{1}{\lambda_i^A} \sum_{\mu}^M U_{\mu i}^A \phi_{\mu}^A(\mathbf{1})$$

whose occupation numbers are λ_i^A . For real-space partitions the occupation numbers are restricted to $0 \leq \lambda_i^A < 1$. These occupation numbers will be used to assign electrons to atoms until a final oxidation state is assigned to each atom. The procedure distributes the electrons among the atoms by comparing the occupations of the eff-AOs on different atoms, rather than independently rounding them [118]. The strategy follows three steps: (i) to collect the alpha eff-AOs that are significantly populated for all centers, (ii) to sort them according to decreasing occupation number, and (iii) to assign integer alpha electrons (I_A^{α}) to the eff-AOs of the centers with higher occupation number, until the total number of alpha electrons is reached. The procedure is repeated for the beta electrons. By this procedure, an effective atomic population $I_A = I_A^{\alpha} + I_A^{\beta}$ is obtained for each atom. From this population the effective oxidation state (EOS) can be readily obtained:

$$\text{EOS}_A = I_A - Z_A$$

The EOS technique of Ramos-Cordoba and coworkers reproduces the correct OS for all the complexes in the test set of Table 4.1 [118]. The EOS can be computed with APOST-3D program. We need to perform a TFVC population analysis (see Exercise 5) but the input file should contain additional information:

```
# METODEDE #####
TFVC
EOS
DOFRAGS
#####
## FRAGMENTS ####
2
1
1
```

12

2 3 4 5 6 7 8 9 10 11 12 13

The EOS is more effective if we define an appropriate set of fragments. We recommend to define a fragment for each ligand (or even a big fragment with all ligands included). The keyword **DOFRAGS** is used to this aim, together with the additional label **## FRAGMENTS ####**, which is followed by the numbers that define our fragments (the way to include this information is the same used for \$FRAGMENTS or \$RINGS keywords in the ESI-3D program). The best working DFT functionals for the calculation of EOS are UB3LYP and UM062X, even though the EOS can be calculated with any method. The output of APOST-3D for an EOS calculation looks like this (both the input above and the output below correspond to a UB3LYP calculation of Cr(CO)₆ taking two fragments: one for Cr and the other for (CO)₆):

```
-----
      DOING EFFAO-3D GENERAL FORMULATION
-----
...
EOS ANALYSIS  FOR ALPHA ELECTRONS
  Fragm  Elect  Last occ.  First unocc
-----
    1    7.00      0.516      0.207
    2   42.00      0.715      0.412
-----
      RELIABILITY INDEX R(%) =  60.418
...
FRAGMENT  OXIDATION STATES

  Frag  Oxidation State
-----
    1      0.00
    2      0.00
-----
Sum    0.0

      OVERALL RELIABILITY INDEX R(%) =  60.418
```

The oxidation states of Cr within Cr(CO)₆ are correctly predicted to be 0. From the occupation numbers of the frontier eff-AOs (the orbital around the last orbital assigned to a given atom), a simple global reliability index is constructed. The index quantifies how reliable the formal oxidation states assignment is. For each spin case, one can compute the following quantity

$$R_{\alpha}(\%) = 100 \min(1, \max(0, \lambda_{\alpha}^{LO} - \lambda_{\alpha}^{FU} + 1/2))$$

where λ_{α}^{LO} is the last-occupied eff-AO and λ_{α}^{FU} is the first-unoccupied eff-AO. The last-occupied and the first-unoccupied orbitals are determined by the occupation numbers of *all* the atomic simultaneously. The reliability index is the lowest such number of both spin cases: $R = \min(R_{\alpha}, R_{\beta})$.

Chapter 5

The Electron Localization Function (ELF)

The first to recognize the importance of the electron pair in chemical bonding was Lewis 100 years ago [49]. His model of chemical bonds formed by (shared) electron pairs is one of the most successful in modern chemistry. The electron pair is a powerful concept to rationalize and understand the molecular structure, *e.g.*, through the valence shell electron pair repulsion (VSEPR) theory [121]. The electron pair concept is found in quantum mechanics through the pair density or some of its variants. Perhaps a most useful quantity related to the pair density is the conditional pair density [122,123]. The definition of the conditional probability (CP), *i.e.*, the probability density of finding electron 2 nearby, $\mathbf{2}$, when electron 1 is at $\mathbf{1}$, reads

$$P(\mathbf{1}, \mathbf{2}) = \frac{\rho_2(\mathbf{1}, \mathbf{2})}{\rho(\mathbf{1})} \quad (5.1)$$

Both the pair density and the CP contain all the necessary information about the relative motion of pairs of electrons. However, the advantage of the CP function is that it is actually measuring the probability with respect to the position of a reference electron and, therefore, is a it is not including the information concerning the position of the reference electron, which is superfluous.

The CP was used by Becke and Edgecombe to define the electron localization function (ELF) [124]. Namely, they used the spherical average of the CP expanded by Taylor series around the position of the reference electron

$$\begin{aligned} \langle e^{s \cdot \nabla} P^{\sigma\sigma}(\mathbf{1}, \mathbf{1} + \mathbf{s}) \rangle &= \frac{1}{4\pi} \left(\int_{-1}^1 \int_0^{2\pi} e^{s \nabla \theta} d\theta d\phi \right) P^{\sigma\sigma}(\mathbf{1}, \mathbf{1} + \mathbf{s})|_{\mathbf{s}=\mathbf{0}} \\ &= \frac{\sin(s \nabla)}{s \nabla} P^{\sigma\sigma}(\mathbf{1}, \mathbf{1} + \mathbf{s})|_{\mathbf{s}=\mathbf{0}} \end{aligned} \quad (5.2)$$

which after applying the Taylor expansion of sinh around the reference electro

(*i.e.*, $\mathbf{s} = \mathbf{0}$) gives:

$$\langle e^{\mathbf{s} \cdot \nabla} P^{\sigma\sigma}(\mathbf{1}, \mathbf{1} + \mathbf{s}) \rangle = \left(1 + \frac{1}{6} s^2 \nabla^2 + \dots \right) P^{\sigma\sigma}(\mathbf{1}, \mathbf{1} + \mathbf{s})|_{\mathbf{s}=\mathbf{0}} \quad (5.3)$$

$$\approx \frac{1}{6} \nabla_s^2 P^{\sigma\sigma}(\mathbf{1}, \mathbf{1} + \mathbf{s})|_{\mathbf{s}=\mathbf{0}} \quad (5.4)$$

Notice that the first term of expansion are zero because of the Pauli principle ($\rho_2(\mathbf{1}, \mathbf{1}) = 0$) and thus the leading term of the expansion depends on the Laplacian of the CP (or, equivalently, the Laplacian of the pair density). Becke and Edgecombe used this term as the principal ingredient to construct the ELF; namely, they did the ratio between this quantity (D_σ) and the same value calculated for the homogenous electron gas (HEG), D_σ^0 ,

$$D(\mathbf{1}) = \frac{D_\sigma(\mathbf{1})}{D_\sigma^0(\mathbf{1})} = \frac{\langle e^{\mathbf{s} \cdot \nabla} P^{\sigma\sigma}(\mathbf{1}, \mathbf{1} + \mathbf{s}) \rangle / ((s^2/3)|_{\mathbf{s}=\mathbf{0}})}{3/5(6\pi^2)^{2/3} \rho_\sigma^{5/6}} = \frac{\nabla_s^2 \rho_2(\mathbf{1}, \mathbf{1} + \mathbf{s})|_{\mathbf{s}=\mathbf{0}}}{c_F 2 \rho_\sigma^{8/3}} \quad (5.5)$$

where $c_F = (3/10)(3\pi^2)^{3/2}$ is the Fermi constant. The conditional probability of finding an electron with spin σ when there is already another electron with the same spin nearby is lower when the former is localized. Therefore, the ratio in Eq. 5.5 accounts for electron localization, *i.e.*, the higher it is, the lower the localization. Becke and Edgecombe decided to apply a Lorentz transformation to the previous formulation so that the ELF would be defined in the interval $[0, 1]$.

$$\text{ELF}(\mathbf{1}) = \frac{1}{1 + D(\mathbf{1})^2} \quad (5.6)$$

thus ELF=1 corresponds to a completely localized situation whereas ELF=0 is a fully delocalized system and ELF=0.5 is the value that matches the result for the HEG. Becke and Edgecombe did their derivation for single-determinant wavefunctions and using the HEG as a reference, however, several authors have given a most general (and equivalent!) derivation valid of the ELF for correlated wavefunctions [125–127] that does not need to use the HEG as a reference [125, 126]. The ELF becomes computationally expensive for correlated wavefunctions (wavefunction beyond the single-determinant approximation) because one should compute the pair density. Opportuntely, there exist some approximations to the pair density that can be used to simplify the calculation of the ELF for correlation wavefunction [128].

5.1 The topological analysis of the electron density

The ELF is a one-coordinate function and likewise the density it admits a topological analysis. The procedure to perform an analysis of the topology of the ELF follows the same procedure already described in section 5.1 of this text. The position of the atomic nuclei also correspond to maxima of this function, which often exhibits maxima in other positions. Typically, the ELF is also maximum in the bonding regions of covalent bonds and in the nonbonded regions where electron accumulate, such as the lone pairs. In this regard, ELF basins

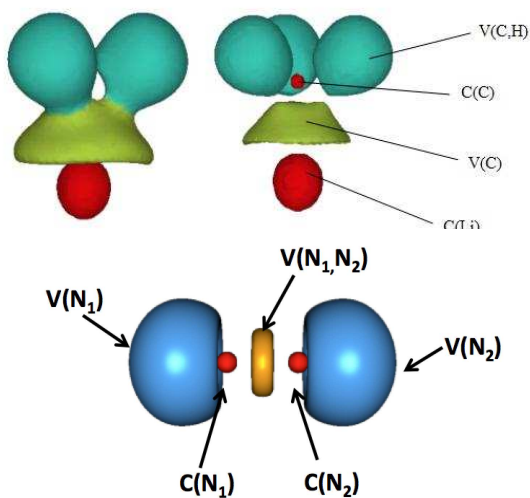


Figure 5.1: **(top)** The $\text{ELF}(\mathbf{1}) = 0.6$ (top-left) and $\text{ELF}(\mathbf{1}) = 0.8$ (top-right) isosurface plots of the CH_3Li molecule using different color for ELF basins. The core basins of Li [C(Li)] and carbon [C(C)], the valence basin of C [V(C)] and the three valence basins of the C-H bonds [V(C,H)] are displayed. Figures taken from Ref. [129]. **(right)** The $\text{ELF}(\mathbf{1}) = 0.8$ isosurface plot of N_2 molecule, where we can see the core basins of N [C(N)], the valence basins of N [V(N)] corresponding to N's lone pairs and the valence bonding basin [V(N₁,N₂)].

can be defined as regions in the molecular space surrounded by zero-flux surfaces of this function. The topological analysis thus provides a decomposition of the molecular space into basins. Typically, there exist two kinds of ELF basins: the core (C) basins, which contain core electrons and are centered in atomic positions and the valence (V) basins, which are all the other basins and are populated with valence electrons. The synapticity characterizes the nature of the ELF basin. Core basins are always monosynaptic, whereas valence basins are said to be monosynaptic if they do not belong to more than one valence shell. Lone-pairs are usually represented by monosynaptic basins, while 2c-2e bonds are characterized by disynaptic basins. Multicenter bonds would present polysynaptic basins. Unlike QTAIM's partition (which is an *atomic* partition of the molecular space), the topological analysis of the ELF reveals several concepts from classical bonding theory such as lone pairs, bonds and core electrons. The density can be integrated into these ELF basins providing core, bonds and lone-pairs population analysis. Since there exist bonding basins that do not belong exclusively to one atom, the ELF partition cannot be used to provide an atomic population analysis. However, the ELF provides a powerful tool to visualize the bonds. These tools can be used together to get a complete electron structure picture of complicated bonding patterns [129]. In atoms, the ELF provides the shell structure of atoms [130, 131].

The ELF have found a plethora of application to analyze chemical bonding

and reactivity, linking some classical concepts of traditional chemistry models such as the Lewis picture or the resonant structures [132]. The ELF has been used to analyze all sort of systems, from solids [133] to organometallic complexes [134] and its application include aromaticity analysis [74, 135, 136], electronic structure studies along the IRC [137, 138] and the mechanism of electrocyclic reactions [87, 88], among many others [74, 134, 139].

The ELF has been implemented in the TopMod package [140] and other codes such as DGRID [141]. Both program use wavefunction files as those provided by Gaussian and Gamess.

Chapter 6

The local Spin

Lately, [5, 142–146] there has been an interest in assigning local spin values by decomposing the expectation value of the total spin angular momentum as

$$\langle \hat{S}^2 \rangle = \sum_A \langle \hat{S}^2 \rangle_A + \sum_{A, B \neq A} \langle \hat{S}^2 \rangle_{AB}$$

where A and B are atoms or molecular fragments and $\langle \hat{S}^2 \rangle_A$ is the local spin of fragment A . There are infinitely many ways [145] to define the terms entering the r.h.s. of the latter expression. In a recent work some of us have suggested a proper general definition of $\langle \hat{S}^2 \rangle$ that avoids the arbitrariness by imposing a number of physical requirements and for pure singlet states yields: [145, 146]

$$\langle \hat{S}^2 \rangle_A = \frac{3}{4}u_A + \Lambda_{AA} + \Lambda'_{AA} \quad (6.1)$$

and

$$\langle \hat{S}^2 \rangle_{AB} = \Lambda_{AB} + \Lambda'_{AB} \quad (6.2)$$

where the following compact forms in terms of the matrix representation (in molecular or natural orbitals) of the 1-RDM (\mathbf{D}), the 2C (Γ) and the fragment overlap matrix (\mathbf{S}^A) are used,

$$u_A = \left(2 \text{Tr}(\mathbf{D}\mathbf{S}^A) - \text{Tr}(\mathbf{D}\mathbf{S}^A\mathbf{D}) \right) \quad (6.3)$$

$$\Lambda_{AA} = \frac{1}{2} \sum_{ijkl} \Gamma_{ij;kl} S_{ki}^A S_{lj}^A \quad \Lambda'_{AA} = -\frac{1}{2} \sum_{ijkl} \Gamma_{ij;kl} S_{li}^A S_{kj}^A \quad (6.4)$$

$$\Lambda_{AB} = \frac{1}{2} \sum_{ijkl} \Gamma_{ij;kl} S_{ki}^A S_{lj}^B \quad \Lambda'_{AB} = -\frac{1}{2} \sum_{ijkl} \Gamma_{ij;kl} S_{li}^A S_{kj}^B \quad (6.5)$$

Chapter 7

Appendices

7.1 Appendix I: The use of MAKE

The MAKE is an script constructed to simplify the process between the obtaining the avefunction and running the ESI-3D program. It handles wfnfiles and checkpoint files. It assumes that all the files have the name `yourfile.extension`, *e.g.* the log file from gaussian should be called `yourfile.log`, the formatted checkpoint file should be name `yourfile.fchk` and the wavefunction file `yourfile.wfn`. MAKE uses options from the following menu:

```
-n name-of-wfn      specify the name of the wfn file (compulsory!)
-u first-beta       the wfn is unrestricted and gives first beta
                    orbital
-s point-group      specify the subgroup of symmetry to perform
                    orbital decomposition
-f                 use fchk and only produce files for ESI-3D
                    (default if wfn not available)
-p                 request promega algorithm in input files
-h                 print this menu
```

7.2 Appendix II: Manual of ESI-3D

ESI-3D program performs the calculation of real-space indices from the AOMs and density matrices (for correlated cases). The AOMs should be collected in separated files and formatted in the AIMPAC way. Currently ESI-3D accepts AOMs from AIMPAC, APOST-3D and AIMall. It can perform population analysis, calculation of the electron sharing indices, multicenter indices and various electronic aromaticity indices (MCI, I_{ring} , FLU, PDI and TREPE). It can decompose these quantities into orbital contributions and permits the construction of fragments (groups of atoms).

7.2.1 How to cite the program

Please if you are publishing the results obtained with ESI-3D remember to cite correctly the program:

Matito, E. ESI-3D: Electron Sharing Indices Program for 3D Molecular Space Partitioning; Institute of Computational chemistry and Catalysis (IQCC), University of Girona, Catalonia, Spain, 2006; <http://iqc.udg.es/eduard/ESI>

and please also cite the papers that deal with the most important features of the program:

Matito E., Duran M., Solà M. The aromatic fluctuation index (FLU): A new aromaticity index based on electron delocalization. *J. Chem. Phys.* 122, 014109 (2005)

Matito E., Solà M., Salvador P., Duran M.; Electron Sharing Indexes at the Correlated Level. Application to Aromaticity Measures. *Faraday Discuss.* 135, 325-345 (2007)

7.2.2 Compulsory keywords

These keywords are only compulsory if **\$READLOG** keyword is not used. If we use **\$READLOG** keyword is because we want to perform a Hilbert space partition analysis and all the information can be extracted from the log file of Gaussian. Therefore, we only need to include the following lines:

```
$READLOG
name_of_logfile
```

\$ATOMS. The number of atoms and the files containing the atomic overlap matrices.

```
$ATOMS
number of atoms (n)
file_1.int
file_2.int
...
file_n.int
```

The user can calculate all the atoms in the molecule are just a small subset of them. In the latter case the accuracy of the integration can only be assessed by the value of the Laplacian in the QTAIM partition. In the former case the integration to the number of electrons, the inspection of the total overlap matrix or the sum rule fulfilled by the delocalization indices can be used as additional criteria to assess the accuracy of the integration, regardless of the atomic partition used.

\$BASIS. The number of occupied molecular orbitals (or spinorbitals if open-shell).

```
$BASIS
number of occupied (spin)orbitals
```

\$TYPE. Type of wave function: restricted (hf) or unrestricted (uhf) single-determinant wave function (HF or Kohn-Sham DFT), or natural orbitals (no) expected. If uhf then the program reads the number of the first beta spinorbital. If *no* the program expects the name of the wavefunction file. If the user has access to DM*n* program he can also use the *dmn*-files as input. The wavefunction type will be specified as *dm1*, *dm2*, *dm3* or *dm4* and the user will provide the name of this and lower densities (e.g. for dm2 one provides the name of dm1-file first and dm2-file second). For higher order the program will only read the highest order density matrix file.

```
$TYPE
hf, uhf, no or dmn
(first beta spinorbital) (wavefunction file) (dm1/dmn file)
(the dm2 file) etc.
```

7.2.3 Optional keywords

\$NOWARN. Prints no warning messages.

\$RING. Needed for the calculation of aromatic properties. Holds the information of the connectivity of the ring(s). Important: the atoms of each ring must be specified according to the connectivity of each ring.

```
$RING
number of rings (nr)
number of members in the first ring (nm1)
1 2 ... nm1 (the atom number according to their connectivity)
...
number of members in the n-th ring (nmn)
1 2 ... nmn
```

\$GROUPS. Needed for the orbital decomposition of the ESI and the aromatic indices. First we must provide the number of groups, and afterwards the number assigned to each orbital according to the group they belong. For $\sigma - \pi$ separation of 5 occupied orbitals it might read:

```
$GROUPS
2
1 1 2 1 2
```

The decomposition applied is only exact in the case where $S_{ij} = 0$ for any i and j belonging to different groups (In the case of sigma-pi orbitals separation the decomposition is only exact for planar molecules). In any other cases the decomposition cannot be attained exactly and the orbital contributions to the ESIs are approximated. We assume the terms $S_{ij}(A)S_{ij}(B)$ can be assigned half to orbital i and half to orbital j . Since ideally the overlap between i and j should be zero, the larger the overlap the more crude the approximation. We can estimate the error committed in the approximation into two ways: *a*) by the absolute sum of the $\frac{1}{2}S_{ij}(A)S_{ij}(B)$ terms, given in the output as *Difference* and *b*) by recalculating the population contribution of different orbitals by summing up the approximated delocalization indices. Since the decomposition

of atomic population into orbitals contributions is exact, by comparison with these populations from approximate delocalization indices we have an estimate of the error committed. This information is given in the output as *Error (from population)*. If we use the keyword **\$DEBUG** the program will also print the approximate atomic populations under the columns tagged n1, n2, etc. Note that the population will be only a good estimate in case we integrate all the atoms in the molecule, otherwise the sum-rule needs not to be fulfilled and thus there is no guarantee we can reproduce the atomic populations from the delocalization indices.

In addition, one can specify a negative number of groups. By doing so, one requests a full decomposition (i.e. orbital by orbital, rather than by group of orbitals) into atomic orbitals. The program will take the negative of this number to estimate the number of basis set to decompose (this integer should be larger than the one specified in **\$BASIS**). The program will produce a file **decompose.out** which contains the 2c-ESI and their orbital contributions up to the specified orbital number. Please notice that the program will fail if it tries to read the INT file beyond the number of orbitals included there. Make sure the integration program (FUZZY/PROAIM/etc.) includes the integration over these many orbitals.

\$FUZZY. If the program finds this keyword it uses the ESI references calculated with Fuzzy-atom partition for the calculation of FLU.

\$MULLIKEN. We should specify this keyword for the program to perform the correct calculation with Mulliken's partition (e.g. Mulliken's atomic overlap matrices are not symmetric).

\$HIRSH. If the program finds this keyword it uses the references of HIRSHFELD-ESI for the calculation of FLU. Nowadays these references are not included the keyword is left for completeness.

\$I-HIRSH. If the program finds this keyword it uses the references of iterative-Hirschfeld-ESI for the calculation of FLU. Nowadays these references are not included the keyword is left for completeness.

\$NELECT. It reads the number of electrons in the molecule. Sometimes (e.g. we do not provide the full list of atoms in the molecule) the program cannot guess correctly this number and we need to provide the correct number.

\$NOMCI. Avoids the MCI calculation.

\$NOHYDROGENS. It does not include hydrogens in the output.

\$OVERLAP. Provides a file with partial and total overlap matrices.

\$DEBUG. Debug-mode on. Provide some extra information to help locating errors.

\$SIC. No idea what it is... check!

\$FMO. Frontier Molecular Orbital analysis. It will print extra information regarding the FMO. It needs at least the overlap elements involving the LUMO orbital (nb! not provided by default in any program). The FMO numbers are tightly related to the concept of softness kernel (see J. Phys. Chem. A, 115, 12459 (2011)).

\$THRESOUT. Provide the threshold of significant values to be printed in the output file.

```
$THRESOUT
(threshold)
```

\$MULTICENTER. *I_{ring}* and MCI values are printed for all the rings list in \$RING. If we want to perform the calculation of these indices for another combination of atoms we shall use this keyword.

```
$MULTICENTER
number of measures
number of atoms in the first measure (nm1)
1 2 ... nm1 (the atom number according to the order requested)
...
number of atoms in the nth-measure (nmn)
1 2 ... nmn
```

\$RENORM. Renormalizes the overlaps so that the trace of the total overlap corresponds to the total number of electrons. This option should only be used when all the atoms in the molecule are integrated.

\$FRAGMENTS. Calculates properties of a user-made fragment. Notice that population are additive properties, but delocalization/localization are not additive (delocalization between elements in the fragment are, obviously, not reflected in the delocalization of the fragment).

```
$FRAGMENTS
number of fragments
number of atoms in the first fragment (nm1)
1 2 ... nm1 (the atom number according to the order requested)
...
number of atoms in the nth-fragment (nmn)
1 2 ... nmn
```

\$MCIALG. Developers option (in progress, unpublished). Use MCIALG and 2 below if run into trouble when calculating MCI.

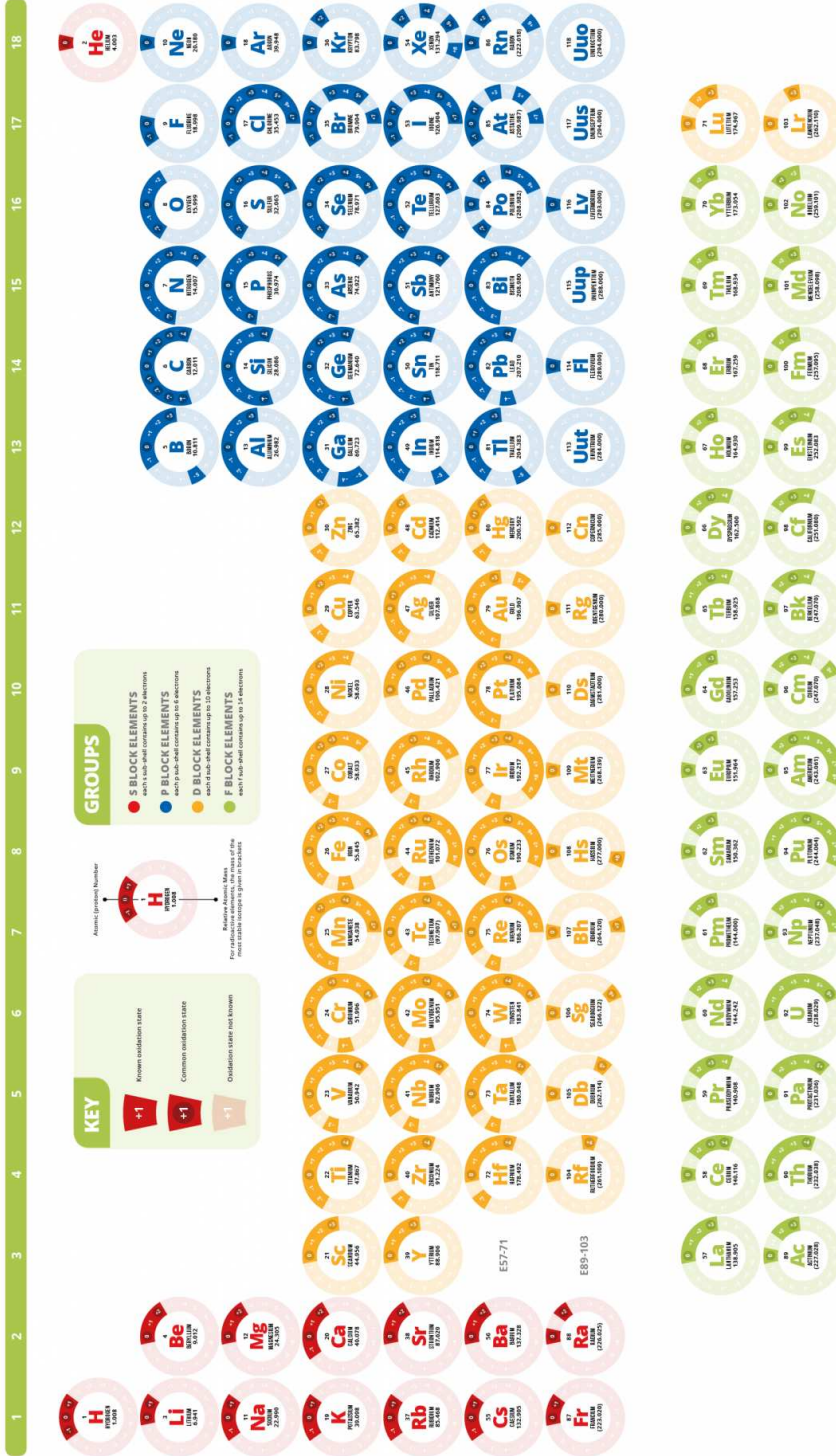
```
$GROUPS
2
1 1 2 1 2
```

\$GEOMETRY. Inputs the geometry of the molecule in free format (atom symbol and three Cartesian coordinates in Å). Together with **\$RING** it produces the HOMA aromaticity index.

\$FULLOUT. It produces a full output for ESI-3D. By default some details (FLU specifications, thresholds, etc.) are omitted.

\$FLUREFS. It gives the two-center electron sharing indices that should be used as a reference. We will enter them as they appear listed in **\$RING** (make sure to include all rings).

THE PERIODIC TABLE OF OXIDATION STATES



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