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Are Atoms the Bricks of Molecules?

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ABSTRACT

The celebrations of the International Year of the Periodic Table (IYPT2019) brought to public attention that the 118 atoms, included and systematized in the periodic table, are the building blocks of everything that exists in the universe. We can even go further in that line of thought, by including time, saying that everything that existed in the past, present or the future in the universe is made of atoms: The periodic table is a **Window to Eternity**. Quantum Mechanics changed the paradigm of looking at atomic and molecular structures by creating the concept of probabilistic charge distributions commonly known as the electronic cloud. But this electronic cloud cannot be reproduced from the superposition of atomic charge distributions except at nuclei and core electron levels. The valence electrons have their distributions strongly affected by constructive and destructive interference to a point where there will be no resemblance to their atomic counterparts. Can we recover the concept of atom from that distorted mess? How do we split the charge density of a bond between the two intervening atoms? What are lone pairs? Do they belong to an atom? What's a ring (like in benzene)? We will try to bridge the gap between the quantum formulation and the traditional chemical view.

INTRODUCTION

Chemists are the Architects of the electronic cloud. Solving a problem, in Chemistry is to determine the role of electrons in that problem. Using Quantum Chemistry as a tool, chemists aim at finding a solution for the Schrödinger equation (1), of their particular system

$$(1) \quad H\psi(x,y,z,t) = E\,\psi(x,y,z,t)$$

where $\psi(x,y,z,t)$ is the electron probability distribution function, H is the Hamiltonian of the system (2), having as observable the total energy E (3)

$$(2) \quad H = -\frac{1}{2}\nabla^2 + V$$

$$(3) \quad E = \int_V \psi^* H\psi dV$$

Equations (1), (2) and (3) are a good illustrative example on how space-time coordinates, wavefunctions, operators and observables are related, figure 1.

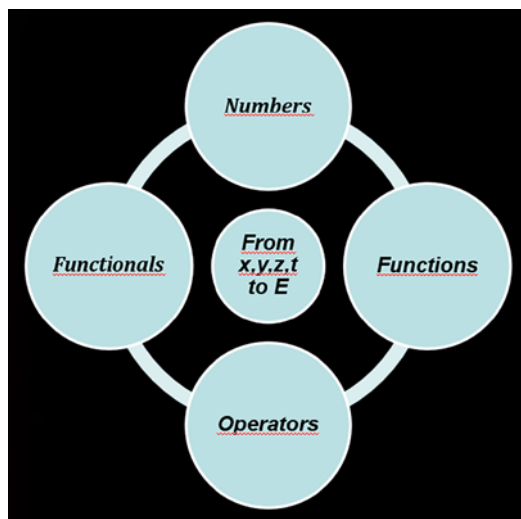[1] Centro de Química Estrutural, Instituto Superior Técnico (IST), Universidade de Lisboa, Lisboa, Portugal

Figure 1.
From space-time coordinates to the observable energy.

Numbers quantify, *functions* transform a set of numbers in another set of numbers, *operators* transform functions in other functions and finally, *functionals* transform functions in numbers. Applying to space time-coordinates (numbers), wavefunctions give the corresponding electron density (functions) which the Hamiltonian (operator) transforms in a density of energy. The last step is to predict the value of the observable energy (again a number) through a functional (3). In this particular case we are obtaining the energy from the corresponding wave-function (orbital in chemical jargon) so equations (1) to (3) are a OFT (Orbital Functional Theory). Of course, distribution functions cannot be measured experimentally but the square of the distribution function has the meaning of an electronic probability and that can be observed by x-ray or electron diffraction techniques. Due to that practicality a new functional theory was developed to compute the energy directly from the charge distribution, $E[\rho]$, so called DFT (Density Functional Theory).

MOLECULES ARE "MANY-BODY" SYSTEMS

Molecules are "Many-Body" systems of N nuclei and n electrons which translates in Schrödinger equations to complex to be solved analytically. The approximations involved and their consequences are well described in any elementary quantum chemistry book such as that of J.P Lowe [1]. The first, and most important, is the Born-Oppenheimer approximation which freezes the nuclei in their equilibrium position. Under this approximation nuclei are mere artifacts to provide the external potential that holds and shapes the electronic cloud. They play a similar function as rebar in concrete, the cement being the electrons.

A more drastic approximation has to be made in relation to the many electrons of a molecule which must be considered independent, each one of them moving in the mean field created by the $n-1$ other electrons. This approximation ignores the dynamic correlation between electrons but can be incorporated in more modern theories such as Coupled Cluster [2] and DFT [3]. Under

this approximation the molecular wave-function is the anti-symmetric product of one-electron solutions (4).

(4) $\psi = A\ (\Pi_i \chi_i)$

Where A is an anti-symmetrizer operator.

If we want to reproduce the molecular wavefunction the χ functions cannot be atomic orbitals or even Linear Combinations of Atomic Orbitals, see figure 2: spherical orbitals are not adequate to model aspherical charge distributions.

The correct modelling of an actual charge distribution requires extra orbitals to account for polarization or even geminals for pair correlation. As a consequence, we can ask: *If a molecule is not a superposition of atoms, what is an atom in a molecule?*
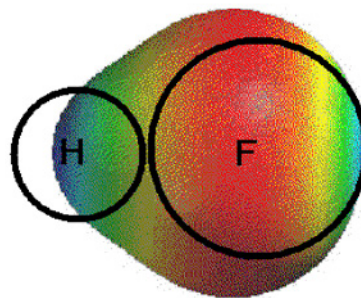

Figure 2.
From space-time coordinates to the observable energy.

THE EXPERIENCE FROM CRYSTALLOGRAPHY.

Let us consider as an example the structure of benzamide determined by neutron diffraction [4]. Neutron diffraction detects nuclei without interfering with the electronic cloud and is depicted in figure 3 at 123 K.
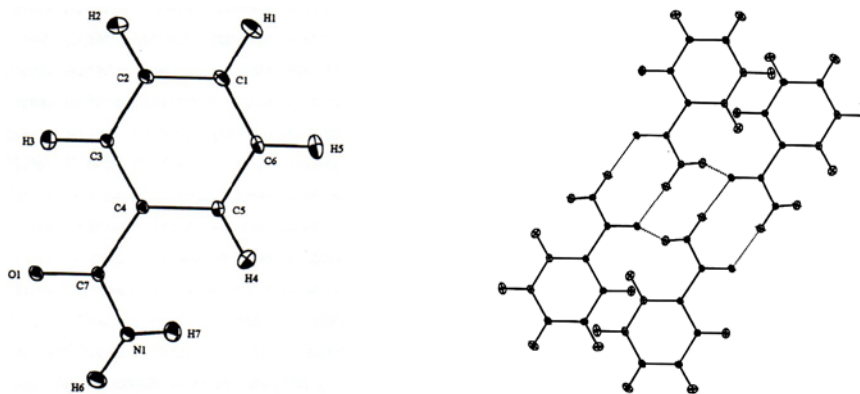

Figure 3.
Neutron diffraction structure of benzamide at 123 K (left) and packing scheme (right).

Neutron scattering provides us with a traditional picture of molecules created by the superposition of atomic cores but, what if we superimpose in this structure the results of x-ray scattering which interfere with the electronic cloud?

Figure 4, shows the difference between the experimental x-ray diffraction and the result of superposition of periodic table atoms [5]. In those maps either within the molecule (right) or the inter--molecular region of hydrogen bonds (left) we can see huge amounts of unexplained density. Within bonds the non-explained density accumulates (right), while in the hydrogen bond system we can detect

non-explained density in the places where the non-bonding pairs of oxygen should be (left). To accurately model the observed x-ray charge density we have to use a multipole expansion centered in each atom that goes beyond the actual *s*, *p*, *d* atomic orbitals, figure 5.
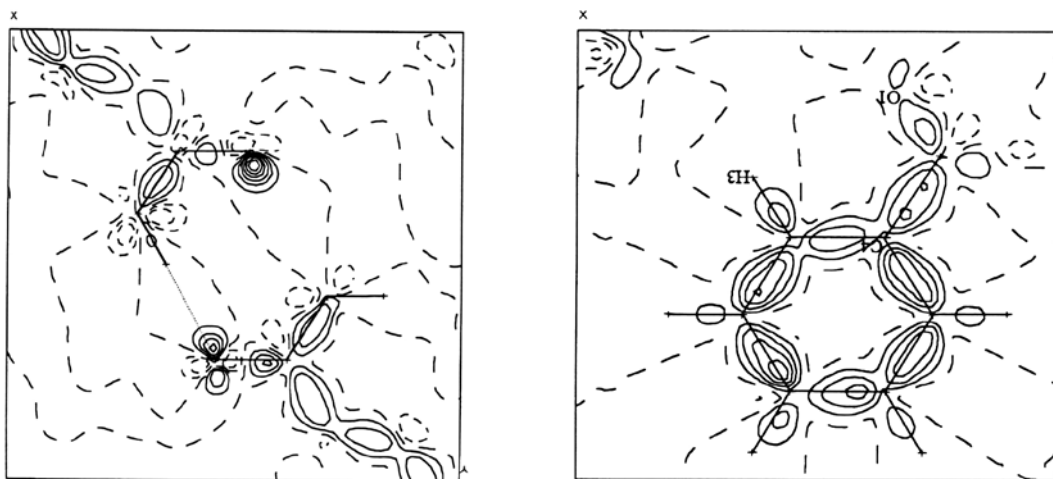
Figure 4.
Difference maps between x-ray diffraction and periodic table atoms. Intramolecular (right), hydrogen bond system (left).
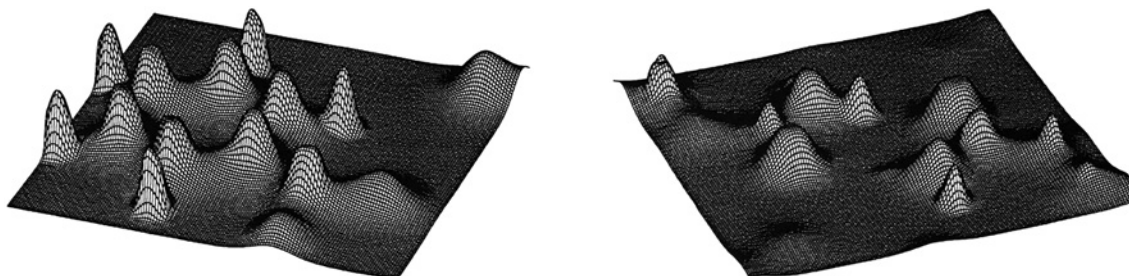
Figure 5.
Multipole modeling of the experimental x-ray diffraction.

From figure 5 we can make a first attempt to produce a definition of atom since near the position of each nuclei the charge density has a cusp and this cusp verifies the boundary condition of (5).

$$(5) \quad \lim_{rA \to 0}[\nabla_r + 2z_A]\rho(\mathrm{r}) = 0$$

From (5) we can define an atom in a molecule by a point in space where the ratio between the gradient and the charge density is two times the symmetric of the nuclear charge.

BADER'S THEORY "ATOMS IN MOLECULES"

Richard Bader [6] in 1990 introduced an interpretative tool to help us in bridging the gap between quantum Chemistry and old classical chemistry concepts such as atom, bond, ring, lone pair, etc, based on the topological analysis of the charge density. The process starts with the mapping of all the critical points in

the charge density map. A critical point is any point in space where the gradient of the charge density is zero. At each one of these points we compute the Hessian (second derivatives matrix) of the charge density and extract the corresponding eigenvalues (λ_1, λ_2 and λ_3) and eigenvectors. The *rank* of the critical point will be defined by the number of non-zero curvatures (eigenvalues). The *signature* will be the sum of the signs of the curvatures. The pair (*rank*, *signature*) will define the chemical interpretation. For instance a (3, -3) critical point is a maximum in all three space directions, figure 6 (left), which defines an atom; a (3, -1) is a minimum in one direction (saddle), figure 6 (right), and topologically defines the existence of a bond.
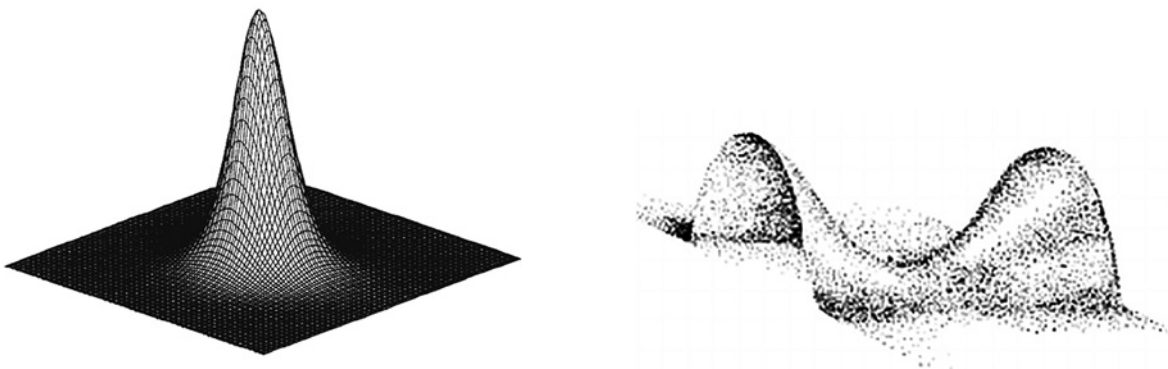

Figure 6.
(3, -3) atom critical point (left); (3,-1) bond critical point (right).

The eigenvectors of the Hessian at the critical points define the directions in which the gradients are higher. If we follow those gradients along the steepest descend line from a pair of atoms to the bond critical point that joins them, we define the bond lines of our traditional molecular drawings. Curiously the bond critical point will be closer to the most electropositive atom. A scale of electronegativities can be defined by the lever rule applied to the bond critical point as the fulcrum of the lever.

At the bond critical points, the gradient lines bend to form a zero flow surface, (6). The volume encompassed by that zero-flow surface is what we call an atom in a molecule.

(6) $\quad \int_s \nabla\rho.ndS = 0$

Finally, the topology of the Laplacian of the charge density controls the reactivity. The Laplacian is negative in points where charge accumulates (prone to electrophilic attack), while is positive in areas of charge depletion (prone to nucleophilic attack).

CONCLUDING REMARKS

Although quantum chemistry had provided us with a powerful tool to study chemical molecular systems it lacks in providing intuitive representations of the traditional chemical features such as atoms, bonds, lone pairs, etc. The topological analysis of the charge density provides that intuitive tool bridging the gap between the bench chemist and the theoretician. With this tool, atoms remain the building blocks of all the mater that exists although reshaped to better fit its molecular function.

ACKNOWLEDGEMENTS

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