

Electron as a Wave: An Activating Messenger. Beyond their Bouncing Electronic Objects Representation, Could it be that Reactive Molecules Behave as Wave-Interconnected Objects?

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Abstract

In this paper, a new mechanism explaining chemical reactions is proposed. The statistical process of “bouncing” molecules is completed by a matching procedure between wave-compatible molecules. This mechanism is elaborated in the light of the wave-particle duality of quantum physics, a property not as much used in chemistry as it has been in other domains, despite the advances permitted by Schrödinger’s equation. Numerical values for the hydrogen atom illustrate the mechanism which is then applied to offer a new representation of reactions between molecules. This representation converges with the HOMO LUMO approaches of reactivity. The concept could help in narrowing the gap between chemistry and biology.

Keywords: Electron as a wave; Connected molecules; New representation of reactions; HOMO and LUMO; Molecular communication

In 1990, when the article “One electron more, one electron less. What does it change? The electron as an activating messenger” was published [1], the perception of the electron among most chemists was mainly that of a particle. In operational terms, De Broglie’s proposition “to any particle a wave is associated” was somewhat “forgotten” [2,3]. The only part in chemistry teaching material taking seriously into account De Broglie’s proposition was the one devoted to “Theoretical Chemistry”. In theoretical chemistry teaching, a mandatory step was the demonstration showing that Schrödinger’s equation, when solved for the hydrogen atom, provides an elegant and spectacular rationalization of its experimental spectroscopic properties [4]. It was not often stressed, however, that Schrödinger, when proposing his equation, had thought the electron as an essentially wave like object, rather than as a particle. The charged particle aspect was, however, taken into account in the Hamiltonian part of the equation, as it includes a kinetic term and the electrostatic interaction between the electron and the proton [5].

The Heisenberg, Born, Jordan approach of quantum chemistry which led, under the hands of Pauli, Eckart and Dirac, to an equally good rationalization of the hydrogen atom spectroscopic properties, did not need to introduce the wave particle duality for the electron [6]. Therefore the proposition developed in this report is mainly heuristic: “reactive molecules as bouncing-ball quantum objects or reactive molecules as bats-like quantum objects?”

Twenty six years after the 1990 Tetrahedron Report, let us return to some aspects of chemical reactivity which hint that the present representations of molecules have underestimated the wave character of these objects. Within this representation, the electron’s messenger function sounds more natural.

In radio technology, a radio emitting center sends waves in all directions. Receiver radio sets, all over a more or less extended area, receive and decode these waves provided that they are tuned at the right frequency. The receiving radio set receives a given program depending upon the frequency at which it has been tuned. Changing the frequency selected might give access to a different message.

Could it be that a molecule in a given environment might behave simultaneously as an emitting and a receiving center, possibly via its outer electrons or outer empty energy levels?

In the Schrödinger’s representation of the hydrogen atom, the stress was laid on the wave nature of the electron. Light waves are viewed as traveling through space along a linear path. Schrödinger’s equation somewhat views the hydrogen electron as a wave traveling along a circular path around the proton due to the electron proton attraction. Let’s imagine an electron as a particle moving on its circular orbit. If a wave accompanies it, something like a standing wave settles. The stability condition of such a standing wave is that there be a whole number of wavelengths in the complete circle, so that the wave can interfere constructively with itself. This wave displays varying wavelengths depending upon the fact that the hydrogen atom is in its fundamental or in an excited state [5].

According to the quantum theory, the circular orbit of the electron is only statistical. Therefore the outer electron of a molecule may sometimes escape this theoretical circular orbit, leaving the “ring” motion for a “chain” motion. A statistical ring-chain equilibrium exists. This would mean that the wave associated with this electron may reversibly transform its circular path into a linear one. Therefore the molecule emits from time to time a wave which explores the space immediately surrounding it. During this exploration this wave may meet a molecule offering no possibility of resonance with itself. In such a case it will return to its circular path and emitting center state. If, however, it meets a molecule which welcomes a wave having precisely its characteristics, it may abandon the emitting center state and migrate to this welcoming center.

De Broglie’s equation allows the calculation of wavelength λ associated to a given electron of mass m . It provides a guess of which type of electrons could leave a molecule to generate exploring waves

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of wavelength λ comprised between 3 and 10 angströms (in MKSA units 3E-10 meters and 10E-10 meters). The wavelength of an electron moving at speed v is equal to

$$\lambda = h/mv$$

where h is the Plank constant 6.625 E-34 Joule.sec, $m=9.11E-31$ kg.

then $v=h/\lambda m$ where v is given in m/s.

The values of v displayed in the following table are in the range of what is admitted for the speed of the electron in hydrogen atoms: $c/137$ (where c is the speed of light), i.e., 2200 km/s. These amazing values hint that, represented as a particle, the electron performs about 8 E15 turns/second around the proton [7]. So even if the ring-chain mechanism postulated in the preceding paragraph is very largely biased towards the ring shape (for example 100000 ring for 1 chain) there still remains a considerable amount of linear waves leaving the atom every second to explore the surroundings.

h (Joule.sec)	λ (m)	m (kg)	$v=h/\lambda m$ (m/s)	v (km/s)
6,63E-34	3,00E-10	9,11E-31	2,42E+06	2,424
6,63E-34	1,00E-09	9,11E-31	7,27E+05	727

The 1990 Tetrahedron Report gathered examples where the addition or removal of a single electron to a given molecule (whatever the molecule's size) could drastically affect its reactivity (measured in terms of kinetic rate constant for a given reaction). Spectacular examples were provided in terms of fantastic enhancement of associative reactivity (tendency to associate with another molecule) or dissociative reactivity (tendency to dissociate into smaller fragments). The term "electron as an activating messenger" was proposed because the selected examples showed that the transfer of an electron from one molecule to another one introduced drastic changes in the reactivity (activation) of the Donor-Acceptor couple [1].

Theoretical processing of the electron transfer kinetics of rate constants (Marcus) is in the line of Eyring's transition state theory [8,9]. Molecules in this representation are essentially viewed as bouncing projectiles hitting each other. A very small percentage of these hits create couples (transition states) whose energy is far higher than that of the average surrounding molecules. Boltzmann's law of energy distribution accounts for the very low values of this percentage. From such a transition state, the couple of reactants may either evolve towards a new products or return to the initial reactants status. Higher is the energy of this transition state, smaller is the constant rate of electron transfer.

Electron transfer reactions described in the preceding paragraph were first studied in redox reactions occurring in an outer sphere electron transfer. Taube classified this large set of reactions involving inorganic substrates into two main groups 1) outer sphere 2) inner sphere electron transfer [10]. This classification was then extended to organic and organometallic substrates [11-13]. Photon induced electron transfer cover a very large class of transformations [14]. If one accepts Pross's concept of "electron shift", it becomes clear that the travel of electrons between reactive partners plays a central role in the occurrence of most chemical transformations [15].

Hoffman and Fukui streamlined an astonishing observation. The reactivity of some couples of molecules could be rationalized considering only their frontier orbital. Everything is going on as if, of the whole set of electrons in the electronic cloud, only the ones occupying either the highest occupied molecular orbital (HOMO) or the lowest unoccupied molecular orbital (LUMO) matter to understand some

reactivity trends [16-18]. This is a very considerable simplification for modeling the reactive behavior in physical systems whose complexity seems beyond the grasp of any "clean" mathematical streamlining (remember that only the hydrogen atom with its unique electron is "cleanly" dealt with through Schrödinger's equation processing).

This astonishing observation may be described as an illustration of the concept of "spatially connected molecules behaving as emitting or receiving centers of information". In the Donor molecule where the HOMO sits, waves of given wavelengths would be emitted by an electron in the outer occupied electronic level. There could be a slight dispersion in the values of the wavelength because the rate of displacement of this electron is not sharply defined: however it stays in a given range of values for a given electronic level. The wave explores the space surrounding the ever moving molecule. If, during this exploration, it meets an Acceptor molecule whose LUMO suits for the emitted wavelength it may abandon the emitting molecule and add to the electronic cloud of the Acceptor molecule.

The slight dispersion in the wavelength values explains the rate constants variation in series of structurally related couples of reactants.

This representation provides molecules displaying more "character" than simple objects bouncing blindly against each other in a given medium. With this possibility of exploring waves carrying information which may or may not be caught by other molecules, a far richer world of communication is opened (exploration of the space via specific infrared vibrations could, along similar lines, help refining the representations of molecular recognition). This perspective could have applications in the field of biochemistry where information transfer events play such an important role to understand the fine-tuned biological machines based on elaborate chemical systems [19,20].

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