What Are the Electrons Really Doing in Molecules? A Space-Time Picture

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Abstract

This is a fundamental and pedagogical work in quantum physics/chemistry, where we try to illustrate the Mulliken's question, "*What are the electrons really doing in molecules?*". And we also briefly review the development of the most popular numerical approaches in computational chemistry. We examine in a novel approach, how we can overall describe the electronic interactions in atomic systems with the conceptual help of a space-time picture of quantum mechanics. This is not a research article initially looking for new numerical results, but for the imperative fundamental reinterpretation of the (non-classical and stabilizing) electronic exchange and correlation energies, from the point of view of space-time scattering events between electrons. Consistently, we introduce Feynman type diagrams as pictorial representation of the (abstract) enthalpic integrals, scattering mechanisms, in quantum chemistry. In atomic structures, it is almost impossible to fully understand, covalent bonding, electronic enthalpies, surface science, orbital magnetism, catalysis… without computational chemistry. How well do we know the physical meaning of the quantum mechanisms behind the numerical approaches? We give an educational hit to this question, following the philosophy of R.P. Feynman, "*just recognizing old things from a new point of view*". The possibility of interpreting Coulomb and Fermi holes with space-time diagrams goes deep into the quantum behaviour of electrons, because the Coulomb forces in atomic systems create interreference patterns

and then electrons cannot fill the electrostatic potentials everywhere as in classical mechanics. Quantum mechanics also allows electrons in atoms to collide in scatting events, introducing (dynamic) space-time mechanisms that reduce their repulsion energy; and actual successful computational chemistry methods include an average approximation to these stabilization mechanisms.

Keywords: Path integral formulation, space-time approach to quantum mechanics, computational chemistry, Feynman diagrams.

INTRODUCTION

There are several ways to comprehend quantum mechanics, and then of understanding computational chemistry. One method is to directly formulate an appropriate partial deferential equation, like the Schrödinger equation (Schrödinger, 1926), that describes the state (wave function, amplitude of probability) of the system. This undulatory formulation provides an efficient way to calculate the wave function and how it changes, however, it does not directly say how the electrons behave in the underlying reality behind the amplitude of probability. Another alternative to look at the same physical content is the path integral formulation, developed by P.M.A. Dirac and R.P Feynman (Dirac, 1933),(Feynman, 1948). Both approximations are to some extent completely equivalent; the classical quantum wave mechanics is typically the most useful for doing numerical calculations, but the path integral approach is the best way to gain intuition, physical insight, on what quantum mechanics means.[i] Our propose is to help to develop a novel and more intuitive and realistic picture to the question: *what electrons are doing in atoms*

Lagrangian Approach to Quantum Wave Mechanics

In classical mechanics, particles and forces are exactly defined in space and time. The movement of particles obey Newtonian mechanics, the defined position, $q_0(t)$, of a particle in a scalar field, $U_0(q_0)$, changes because of the action of the force field as

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[i] Reader must have an advanced knowledge of the numerical approaches in computational chemistry to follow the ideas.

$-\nabla U_0(q_0) = F_0(q_0) = m_0 \cdot \frac{\partial^2 q_0(t)}{\partial^2 t}$. The resulting defined path of the particle has minimum action, $S_0 = \int_0^t (\frac{1}{2} \cdot m_0 \cdot \left(\frac{\partial q_0(t)}{\partial t}\right)^2 - U_0(q_0)) \partial t$; any other path $q_i(t)$ has $S_i > S_0$ (Bracken, 2013). In the classical view (Bohr Atomic Model) for a defined energy, the electrons in an atom, with heavy immobile nuclei, under the Coulomb potential $-\frac{Z_A \cdot e^2}{4\pi\epsilon_0 r_{1A}}$ will orbit following exactly the black S_0 lines ($q_0^{e-}(t)$) in Fig. 1 and 2. Any other path, $q_i(t)$, means that electrons do not follow exclusively the expected classical movement according to a defined (in space-time) position, kinetic and potential energy but other orbits with S_i.

P.A.M. Dirac in 1933, introduced the concept that in quantum mechanics every possible path $q_i(t)$ with S_i must be able of contributing to the movement of electrons with a factor $\phi_i = A \cdot e^{\frac{i}{\hbar} S_i[q_i(t)]}$ (Dirac, 1933). In Fig. 2, it means that the electrons, with constant energy, most frequently follow the classical S_0 orbits (black), but any other path (color lines) is also accessible but less probable. The factor $e^{\frac{i}{\hbar} S_i[q_i(t)]}$ indicates that the trajectory of electrons can deviate from the classical path if the difference in the action is roughly within $\hbar$. We can only know the probability of finding the electrons in space-time, because there are no uniquely define paths for the particles in quantum mechanics.

Feynman following the Dirac expression, that every possible path should be able of contributing to go from q to $q + \partial q$, derived the Schrödinger equation (Feynman, 1948). Then a wavefunction, $\Psi_{e-}(q,t)$, solution of the $i\hbar \frac{\partial}{\partial t} \Psi_{e-}(q,t) = \hat{H} \Psi_{e-}(q,t)$ equation actually assign probabilities to different paths for the electrons according to the Dirac exponential factor over the action; and the Hamiltonian of the system consists of defined operators adapted from classical mechanics.

A Novel Alternative View to The Wave-Particle Duality

In a microwave oven, photons carry an individual energy associated with their frequency; while collectively photons create interreference patterns ligated with the resonant cavity, 'Figure 1a: *Standing energy waves determine the overall energy distribution in space-time'*. At the darkest places of a cavity mode, the probability of finding photons is

practically null, no energy; while at the brightest areas a maximum number of photons reinforce the energy density (Yirmiyahu, Niv, Biener, Kleiner & Hasman, 2007). Now, let us imagine that a hydrogen atom is a like a waveguide (microwave cavity); individual virtual photons carry the charge attraction between the proton (p+) and the electron (e-), and collectively these energy carriers create an interference pattern, standing electrostatic energy waves. Then in a hydrogen atom, there will be dark/bright areas in space-time where the probability of finding electrostatic (photons) attractions is null/maximum. Contrary to the classical approximation, the electrostatic potential is not everywhere in an atomic system, see Fig. 1; but the probability of finding the energy associated with the nuclei and electronic interactions (potentials) is determined by amplitudes of probabilities, functions $\Psi_{standing.wave}^{p+e-energy}$.

In the reasonable Born–Oppenheimer (BO) approximation (Born & Oppenheimer, 1927) even for hydrogen atoms, the proton is mainly static while the electron orbits around. According with Fig. 1, electrons do not feel/create the p+-e- attraction at every single point in space; if virtual (electrostatic) energy photons do not accumulate constructively, the electrons (in this picture imagined as classical charged particles) do not feel the Coulomb attraction: *there is no Coulomb attraction at the destructive interreference zones*. Figure 1 represents that the energy density ($\rho_{standing.wave}^{p+e-energy} = \left(\Psi_{standing.wave}^{p+e-energy}\right)^2$) is delocalized and create interreference patterns; but the electrons are localized, can have with specific coordinates [x,y,z,t], and evolve following multiple actual space-time trajectories according to $\rho_{standing.wave}^{p+e-energy}$.
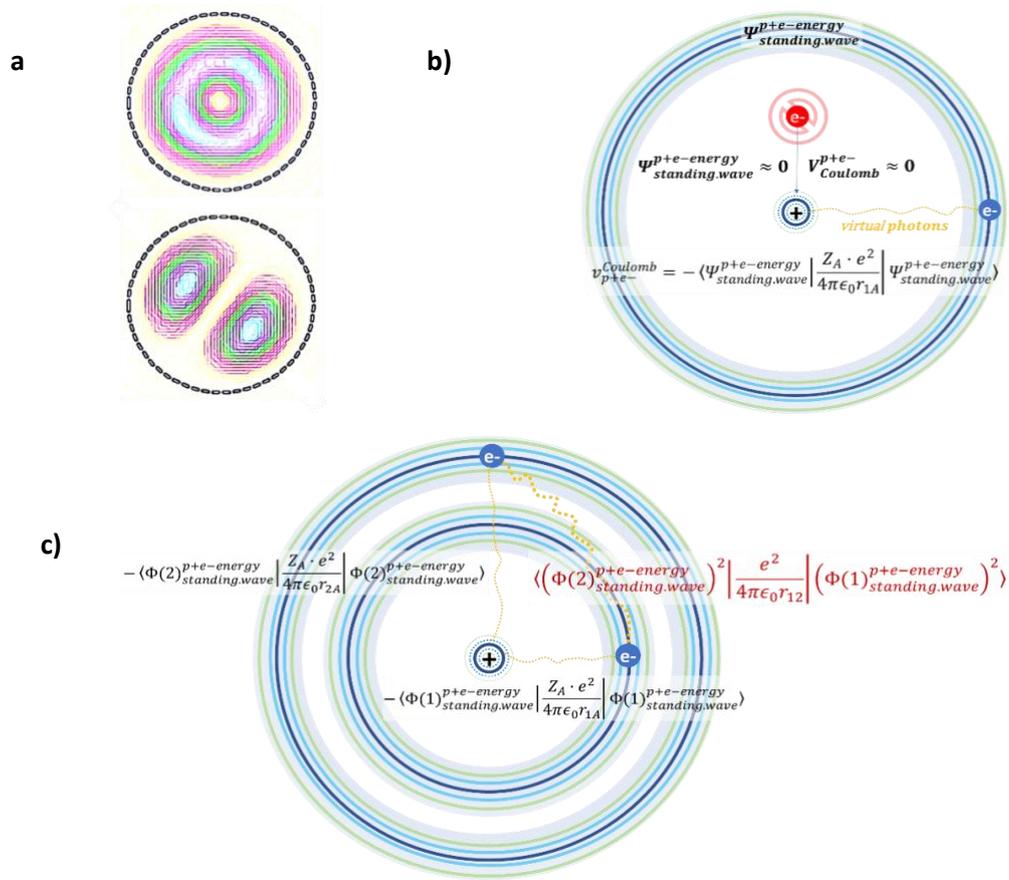
*Figure 1. **a)** Examples of some cylindrical waveguide modes.*(Yirmiyahu, Niv, Biener, Kleiner & Hasman, 2007). ***b)** In a hydrogen atom, we represent with a black line the most probable orbit for an electron (Bohr radius). This actual space-time orbit is not unique, the electrons will occupy all the positions following the amplitude of probability of finding the virtual photons ligated to the quantized Coulomb energy field, $\Psi_{standing.wave}^{p+e-energy}$. Electrons (blue color) expend more time in those positions where they feel more the attraction of the proton; those places with a constructive interference pattern for the virtual photons that carry the energy. Contrary to the classical notion, electrons (with a define position in space-time) will not feel the attraction of the nucleus in the zones with a destructive interference pattern for the Coulomb field (in red in Fig. 1b). Electrons feel a quantized stabilizing Coulomb attraction according to $v_{p+e-}^{Coulomb} = -\langle \Psi_{standing.wave}^{p+e-energy} | \frac{Z_A \cdot e^2}{4\pi\epsilon_0 r_{1A}} | \Psi_{standing.wave}^{p+e-energy} \rangle$. **c)** The same concept of the standing energy wave for the Coulomb attractions applies to the electronic repulsions; electrons in this view are particles, with define position in space-time, that must follow in their trajectories the pattern created by the stable standing energy modes: orbitals.*

The actual standard interpretation of quantum wave mechanics is represented in Fig. 2; the electrons are fully delocalized, with electron density $\rho_{density}^{e-} = \left(\Psi_{probability}^{e-}\right)^2$; while the energy potentials are fully determined having a fix value in space-time according to the classical Coulomb formulas, $-\dfrac{Z_A \cdot e^2}{4\pi\epsilon_0 r_{1A}}$ and $\dfrac{e^2}{4\pi\epsilon_0 \cdot r_{12}}$. The quantum wave–particle duality essentially means that Fig. 1 and 2 are equivalent, the electron amplitude of probability, $\Psi_{probability}^{e-}$, is identical to the energy amplitude of probability $\Psi_{standing.wave}^{energy} \equiv \Psi_{probability}^{e-}$: *evolving electrons in space-time act as mirrors for the energy carriers to create certain standing energy waves*. We can use the mathematical formulation of quantum wave mechanics and use the Feynman Path integrals to reinterpret it according to delocalized energy potentials (standing modes created by the virtual energy carries and not by the electron as a particle) and localized electrons, Figure 1.
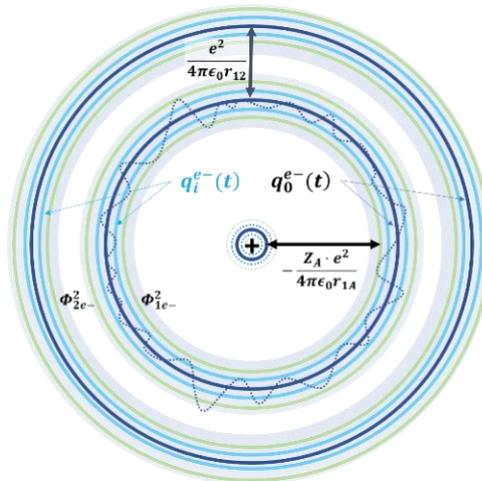

Figure 2. The black lines represent the most probable radius to find the delocalized electrons in the mono-electronic orbitals Φ_{1e-} and Φ_{2e-}, in an atom according to quantum wave mechanics. The electron densities are maximum for those trajectories with minimum action S_0; however, any other alternative path (S_i, color lines) also contributes. In pure wave mechanics, the path integral quantum representation applies to the delocalized electrons; however, the Coulomb potentials (the energy) are always defined in space-time. The interreference patterns are interpreted as created by the electrons.

The idea of introducing alternative ways to understand better the behaviour of electrons in chemical systems, looking for a brief overall pedagogical interpretation of modern Computational Chemistry, will only work if it reduces the complexity of the concepts to follow. We are going adapt the notion behind the Feynman diagrams to represent quantum electronic energy terms (Magnasco, 2009),(Feynman 2011), starting from the Schrödinger equation. This approach offers a space-time view of quantum events, to understand from another approach but necessarily equivalent the quantized electron-electron repulsions. It is important to make evident that the Coulomb field, created by the nuclei and the electrons, creates interference patterns with brighter and darker spots; and the multiple space-time paths of the electrons create and respond to these standing energy wave patterns.

Feynman Diagrams

In computational chemistry, Feynman type diagrams are already a useful tool for algorithmically constructing the k_{th} order term of a perturbation series (Mattuck, 2012). In addition, we are interested in representing any matrix energy term (integral), $\langle \Phi_A | \hat{O} | \Phi_B \rangle$ (scattering matrix), resulting from the introduction of a given electronic wavefunction (any) $\Psi_{e-} = f(\varphi_1, \dots, \varphi_i, \dots)$ as solution to the non-relativistic Schrödinger Hamiltonian $\hat{H}_{e-}^{Schr.} = \hat{T}_{e-}^{kinetic} + \hat{V}_{N+e-}^{Coulomb} + \hat{V}_{e-e-}^{Coulomb}$. The interacting potential $\hat{O}$, evolution operator between the vector states, can be any discrete operator in $\hat{H}_{e-}^{Schr.}$; the kinetic energy of an electron ($\hat{t}_{e-}^{kinetic} = -\frac{\hbar^2}{2\mu}\nabla_1^2$), a nucleus-electron attraction ($\hat{v}_{N+e-}^{Coulomb} = -\frac{Z_A \cdot e^2}{4\pi\epsilon_0 r_{1A}}$), or the electronic repulsion between two electrons ($\hat{v}_{e-e-}^{Coulomb} = \frac{e^2}{4\pi\epsilon_0 \cdot r_{12}}$). Correspondingly, the Φ_A and Φ_B state-vectors include one or two (for $\hat{O} = \hat{v}_{e-e-}^{Coulomb}$) mono-electronic orbitals (φ_i). As in the Heisenberg picture (Weinberg, 1995), Φ_A and Φ_B are time-independent (then defined as real functions) mono- or bi- electronic states, formed by orthonormal φ_i vectors in the same Hilbert space, indicating if the electrons change or remain in the same orbital after the quantum interaction mechanism. The total physical state Ψ_{e-}(wavefunction) is represented in the basis of the mono-electronic vectors; these orbitals, for instance φ_i, individually only represent a partial spacetime history of the electrons.

Imagine that the electrons move in defined multiple space-time trajectories, and because of the action of the quantized energy field all the possible paths contribute according to $A \cdot e^{\frac{i}{\hbar}S_i(t)}$. For every matrix element in quantum wave mechanics, integrals in computational chemistry, we can draw an equivalent picture representing the space-time interaction/scattering events for moving electrons: Feynman diagrams serve to represent the possible scattering events, matter---virtual-photon---matter interactions (Ruggenthaler, Tancogne-Dejean, Flick, Appel & Rubio, 2018).

In our interest of understanding better quantum chemistry; this analysis associates the abstract energy integrals with actual space-time propagation/scattering events between electrons in orbitals. Any possible interaction-event between the electrons in the quantized energy field, that will reduce the Coulomb repulsions (the total energy) will occur with a certain probability. The results of the quantum collision mechanisms are different than the expected classical action between delocalized electronic clouds: *quantum electronic correlation energy-mechanisms*.
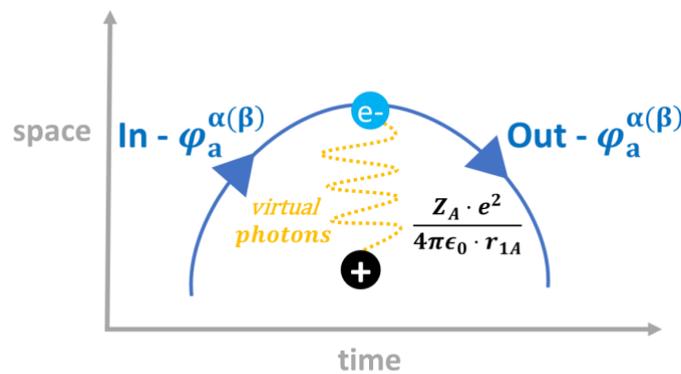
The Non-Relativistic Hydrogen Atom

Figure 3. *Feynman diagram that represent the propagation of an electron in the orbital $\varphi_a^{\alpha(\beta)}$, the line is curved because of the influence of the attractive quantized Coulomb potentials formed with the nuclei:* $t_{e-a}^{kinetic} + v_{N+e-a}^{Coulomb} = \left\langle \Psi_0 \left| -\frac{\hbar^2}{2\mu}\nabla_1^2 \right| \cdot \Psi_0 \right\rangle + \sum_A^M \left\langle \Psi_0 \left| -\frac{Z_A \cdot e^2}{4\pi\epsilon_0 r_{1A}} \right| \cdot \Psi_0 \right\rangle.$

The time-independent Schrödinger equation for an electron in a hydrogen atom, according to the Born-Oppenheimer approximation (Born & Oppenheimer, 1927) is $\widehat{H}_{e-}^{Schr.}(H\,\cdot)\cdot\Psi_n(x_1) = E_n\cdot\Psi_n(x_1)$, with $\widehat{H}_{e-}^{Schr.}(H\,\cdot) = -\frac{\hbar^2}{2\mu}\nabla_1^2 - \frac{Z_A\cdot e^2}{4\pi\epsilon_0 r_{1A}}$ (Schrödinger, 1926). Now, we take the analytical wavefunction for the ground state $\Psi_0(H\,\cdot)$, and in our approximation, the "exact" contribution to the energy due to the proton-electron Coulomb attraction is $\langle\Psi_0(H\,\cdot)|-\frac{Z_A\cdot e^2}{4\pi\epsilon_0 r_{1A}}|\Psi_0(H\,\cdot)\rangle$.

Figure 3 is a Feynman-type space-time diagram to represent a non-relativistic electron in the hydrogen atom. The proton is practically immobile, and the electron propagates in the quantized electrostatic field created together with the nucleus. We represent the evolution of the electron (in the orbitals φ_i) as curved lines, with an arrow indicating the direction; the time axis is in X, flowing from left to right, and the space in Y, bottom to top. Fig. 3 serves to represent any mono-electronic atomic system.

Coulomb Electronic Repulsions

Starting from the Schrödinger Hamiltonian, $\widehat{H}_{e-}^{Schr.} = \widehat{T}_{e-} + \widehat{V}_{N+e-}^{Coulomb} + \widehat{V}_{e-e-}^{Coulomb}$, for a multi-electronic system, the historical improvement in the theoretical descriptions evolved from the introduction of successive better wave-functions:

1) $\widehat{H}_{e-}^{Schr.}\Psi_{e-}^{Hartree} = E_{e-}^{Hartree}\cdot\Psi_{e-}^{Hartree}$, $\quad\Psi_{e-}^{Hartree} = \prod_{i=1}^{n}\varphi_i^{e-}$ (Hartree product) (Hartree, 1928);

2) $\widehat{H}_{e-}^{Schr.}\Psi_{e-}^{Slater} = E_{e-}^{Slater}\cdot\Psi_{e-}^{Slater}$, $\quad\Psi_{e-}^{Slater} = |\varphi_1^{e-},\dots,\varphi_n^{e-}\rangle$ (Slater determinant) (Heisenberg, 1926), (Dirac, 1926).

The difference $E_{e-}^{Slater} - E_{e-}^{Hartree} = QSEI < 0$, always stabilizing, defines exactly the Quantum Spin Exchange Interactions (QSEI) in the Hartree–Fock (HF) approximation (Schrödinger, 1926): *a collision mechanism between electrons with the same spin that allows*

to reduce the Coulomb repulsion energy. QSEI are the most relevant of the correlation effects in atomic systems.

3) $\widehat{H}_{e-}^{Schr.} \cdot \Psi_{e-}^{multi.conf.} = E_{e-}^{multi.conf.} \cdot \Psi_{e-}^{multi.conf.};$ $\Psi_{e-}^{multi.conf.} = \sum_{i=0}^{\infty} C_i |\Psi_i^{Slater}\rangle$
(Schrödinger, 1926).

A multi-determinant expansion of the wavefunction again reduces the energy, $E_{e-}^{multi.conf.} - E_{e-}^{Slater} = E_{e-e-}^{\text{correlation}} < 0$, generally defined as the stabilizing correlation energy.

Electrons in atomic systems are indistinguishable fermions (with the Z-component of the angular momentum $S_Z = \pm \hbar/2$), and the traditional way to introduce such information in the Schrödinger equation is to force an anti-symmetric electronic wavefunction ($\Psi_{e-}^{anti-sym.}$) as solution to $\widehat{H}_{e-}^{Schr.}$ (Slater, 1929). A Slater determinant, as the simplest antisymmetric wave function, appeared independently in 1926 in papers by Heisenberg (Heisenberg, 1926) and Dirac (Dirac, 1926). But the operators in $\widehat{H}_{e-}^{Schr.} = \widehat{T}_{e-} + \widehat{V}_{N+e-}^{Coulomb} + \widehat{V}_{e-e-}^{Coulomb}$ all have a classical origin and are spin independent, the imposed $\Psi_{e-}^{anti-sym.} = f\left(\varphi_1^{\alpha(\beta)}, \dots, \varphi_n^{\alpha(\beta)}\right)$ amplitude of probability generates the (unexpected) non-classical QSEI in multi-electronic systems.

The Hartree $\Psi_{e-}^{Hartree} = \prod_{i=1}^{n} \varphi_i^{e-}$, but it is not antisymmetric, already introduces that for two electrons in the mono-electronic eigen-vectors $\varphi_a^{\alpha(\beta)}$ and $\varphi_b^{\alpha(\beta)}$ independently of the spin, their Coulomb repulsion contribute to the energy with the integral term: $v_{ab}^{Coulomb} = \left\langle \left(\varphi_a^{\alpha(\beta)}\right)^2 \left| \frac{e^2}{4\pi\epsilon_0 \cdot r_{12}} \right| \left(\varphi_b^{\alpha(\beta)}\right)^2 \right\rangle > 0$. Since $\varphi_{a(b)}^{\alpha(\beta)} \cdot \varphi_{a(b)}^{\alpha(\beta)}$ is the real probability of finding the electrons in space according to the stationary $\varphi_{a(b)}^{\alpha(\beta)}$ amplitude, we identify $v_{ab}^{Coulomb}$ as the classical Coulomb repulsions; every electron propagates continuously in its own orbital, see Fig. 4.

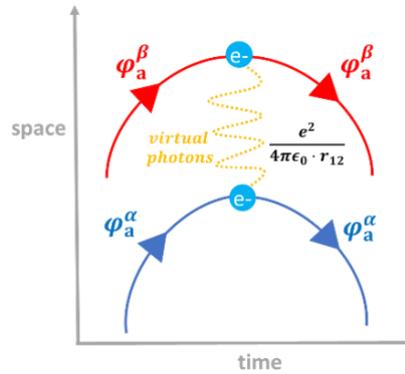**Feynman Diagram for The Classical Coulomb Repulsion**

Figure 4. Feynman diagram that represents the classical Coulomb repulsion between two electrons in the orbital φ_a^α.

The classical electron-electron Coulomb repulsions are represented by a double vertex factor, Fig. 4; the electrons do not change their orbitals. Fig. 5 represents the energy terms that describe the HF ground state for the hydrogen molecule, H_2, for $\Psi_{e-}^{Slater} = |\varphi_a^\alpha \varphi_a^\beta\rangle$.
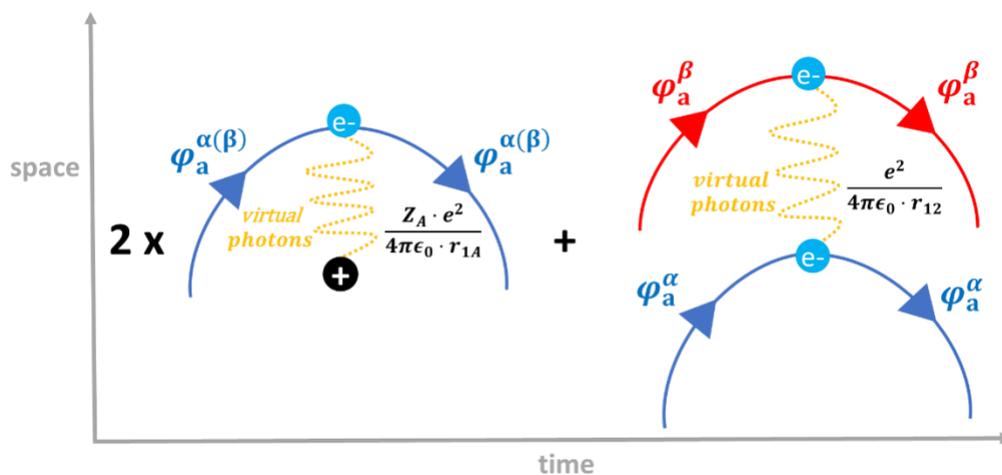

Figure 5. Feynman diagrams that represents the Hartree-Fock energy terms in the H_2 molecule, $\hat{H}_{e-}^{Schr.}\Psi_{e-}^{Slater} = E_{e-}^{Slater} \cdot \Psi_{e-}^{Slater}$.

Quantum Spin Exchange Interactions

What is the physical meaning and origin of the QSEI? If we look to the stabilization energy due to the QSEI, as described in the Hartree-Fock method (Szabo & Ostlund, 2018);

once a Slater determinant is introduced as solution to the $\hat{H}_{e-}^{Schr.}$, if two electrons have the same spin then there is an additional scattering matrix, $QSEI_{ab}^{\alpha\alpha(\beta\beta)} = -\left\langle \varphi_a^{\alpha(\beta)} \varphi_b^{\alpha(\beta)} \middle| \frac{e^2}{4\pi\epsilon_0 \cdot r_{12}} \middle| \varphi_a^{\alpha(\beta)} \varphi_b^{\alpha(\beta)} \right\rangle < 0$ (Szabo & Ostlund, 2018), because of the imposed anti-symmetric solution $\Psi_{e-}^{anti-sym.} = \Psi_{e-}^{Slater}$. Contrary to the Coulomb repulsions, this exchange energy ($QSEI_{ab}^{\alpha\alpha(\beta\beta)}$) is a stabilizing spin-dependent term. From the formulation of the exchange integrals, we can say that the quantum reality introduces the prospect that two electrons with the same spin (indistinguishable) can interchange their orbitals, position and momentum. In every side of the $QSEI_{ab}^{\alpha\alpha(\beta\beta)}$ integrals, the electrons occupy two orbitals, $\varphi_a^{\alpha(\beta)}$ and $\varphi_b^{\alpha(\beta)}$, and this correlation mechanism reduces the Coulomb repulsions. This not intuitive spin phenomenon does not have an apparent classical interpretation; but a space-time approach allows to understand better QSEI: how is possible for the electrons with the same spin to interchange orbitals to reduce their Coulomb repulsions?
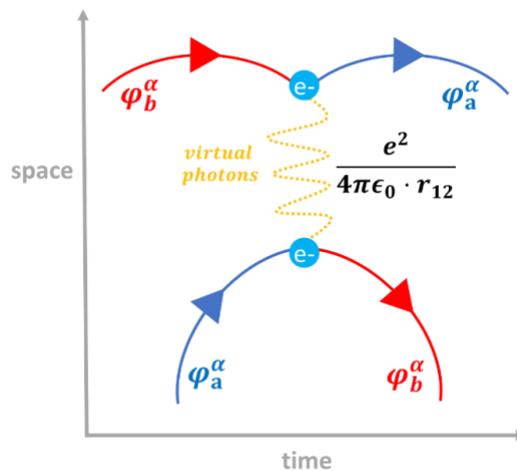
Feynman Diagrams for the QSEI

Figure 6. Feynman diagram that represents the quantum spin exchange interaction between two electrons with the same spin in the orbitals φ_a^α and φ_b^α.

Figure 6 represents that the constructive accumulation of the repulsive energy in the quantified field is released by the interchange of the energy momentum between electrons

with the same spin, mechanism that they use to avoid coming closer (spin correlated movement). At the instant of the space-time scattering event the total energy of the system remains the same, it is an exchange.

With Fig. 3 to 6 just counting electrons and spins, and by adding the Pauli Exclusion principle, we can get all the energy integrals derived in the Hartree-Fock approximation. By adding Feynman type diagrams, just paying attention to the (most likely) scattering events between electrons, we will obtain the energy terms without knowing (imposing) the wavefunction a priory. As we will see, probably the most popular computational chemistry methods are not based, do not have, an associated analytical wavefunction.

Correlation Energy

A convenient way for us to introduce $E_{e-}^{\text{correlation}}$ is from perturbation theory. Starting from the single-orbital Hartree-Fock Hamiltonian, $\hat{H}^{HF} = \sum_i (\hat{h}_i + \hat{v}_i^{HF})$, we are interested in the obtaining a perturbation expansion for $E_{e-}^{\text{correlation}}$; which development associates with Rayleigh and Schrödinger (Schrödinger, 1926), (Szabo & Ostlund, 2018), (Mattuck, 2012). The actual effective Hamiltonian change to $\hat{H}^{HF} + \hat{V}^{Correlation}$, the wave function $\Psi_0^{kth} = \Psi_0^{Slater} + \Psi_0^1 + \Psi_0^2 + \cdots$ and the energies $E_0^{kth} = \epsilon_0^{HF} + \epsilon_0^1 + \epsilon_0^2 + \cdots$ improves in an infinite convergent expansion, $E_{e-}^{\text{correlation}} = \epsilon_0^1 + \epsilon_0^2 + \cdots$. In this formulation $\epsilon_0^1 = 0$, and the first meaningful correction is $\epsilon_0^2 =$

$$\frac{1}{2}\sum_{a,b}\sum_{r,s}\frac{\left\langle \varphi_a\,\varphi_b \left|\frac{e^2}{4\pi\epsilon_0 \cdot r_{12}}\right| \varphi_r\,\varphi_s \right\rangle \cdot \left\langle \varphi_r\,\varphi_s \left|\frac{e^2}{4\pi\epsilon_0 \cdot r_{12}}\right| \varphi_a\,\varphi_b \right\rangle}{\varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b}$$; where φ_a and φ_b are occupied orbitals and φ_r and φ_s are unoccupied orbitals in the HF approximation. For higher order corrections we refer to literature, since ϵ_0^2 already indicates the concept that $E_{e-}^{\text{correlation}}$ relates with excitations with respect to the Ψ_0^{Slater} configuration, that reduce the energy.

If we want to understand better the meaning of $E_{e-}^{\text{correlation}}$ using a space-time approach, we need the associated Feynman diagrams. Mono-electronic systems like the hydrogen atom are soluble analytically, a single orbital serves as perfect solution. There is no correlation energy since there is no need to include excites states to improve the wavefunction. In the hydrogen H_2 molecule two electrons are spin-paired so there is no QSEI, however now the

$E_{e-}^{\text{correlation}}$ already appears. Then, the correlation energy is another reduction of the electronic Coulomb repulsions but independent of the spin of the electron.

Feynman Diagrams for the Correlation Energy

If we have chosen to start from previous perturbational convention is because Kelly in 1963 already introduced Feynman type diagrammatic techniques to represent the perturbation energies in atoms (Kelly, 1963), (Paldus & Čížek, 1975), (Ramirez, 1991), (Goldstone, 1957), (Møller & Plesset, 1934). Fig. 7 is an adaptation in our style of the second order energy correction.
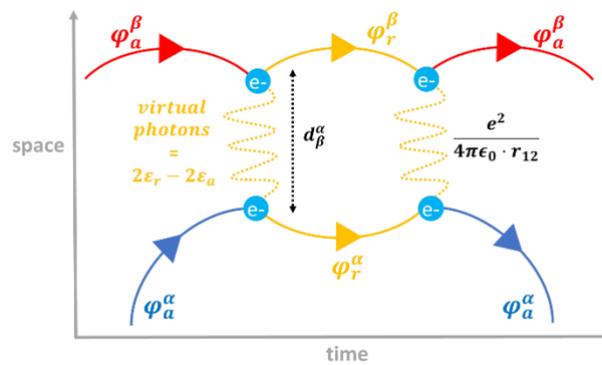

Figure 7. *Feynman type diagram that represents the ϵ_0^2 correlation energy between two paired electrons in the same orbital, φ_a^α and φ_a^β. As the two electrons come closer the quantized Coulomb field constructively accumulate repulsive energy between the electrons; if the Coulomb repulsions reduce in the empty state φ_r , the electrons adsorb energy from the field to propagate in φ_r . Once electrons are further apart their repulsion reduces and the exited configuration is not stable, the interreference energy pattern in the quantum field reorganizes and the electrons come back to their initial more compact orbitals.*

Figure 7 indicates that the electrons in the (occupied) orbital φ_a when they are coming closer, the quantized energy field at some point (in space-time) prefer to change so the Coulomb repulsions can locally reduce by promoting the electrons temporarily in empty orbitals φ_r . In other words, if the two electrons have opposite spins as their charge repulsion increase, QSEI is not possible, the accumulation of repulsive energy at some point changes

the quantized energy field to place electrons in larger empty orbitals where the Coulomb repulsion is less, $\varphi_a \ \varphi_b \ \rightarrow \varphi_r \ \varphi_s$, and the total energy decreases. Once the electrons move away in space-time and the Coulomb repulsions reduce, that exited configuration is not stable, $\varphi_r \ \varphi_s \ \rightarrow \varphi_a \ \varphi_b$. There is some provisional energy penalty due to the increase in the kinetic energy and due to the reduction in the attractive Coulomb nuclei attractions in these temporary-scatter excited states, represented by the energy factor $(\varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b)$ in the denominator.

We hope that the physical meaning of the perturbation diagrams in literature associated with $E_{e-}^{\text{correlation}}$ is now clearer; and that it is also apparent, there are multiple of this dynamic mechanisms leading to the infinite $E_{e-}^{\text{correlation}} = \epsilon_0^1 + \epsilon_0^2 + \cdots$ expansion, in relation to multiple complex accessible excitations once the electronic repulsions create local interreferences too bright.

But differences in the expansion of the wavefunction and formulation of the $E_{e-}^{\text{correlation}}$, we could also have started from considering the superposition of electronic excitations, interferences, in multi-determinant (anti-symmetric) wavefunctions, eq. 3. Since $\hat{H}_{e-}^{Schr.}$ does not change to be closer to reality: *multi-configurational wavefunctions include a better interpretation of the actual space-time interaction of the electrons in a quantized electromagnetic field*. Conceptually, we can follow the same philosophy, and we can build (sum-over) the most relevant (multiple) Feynman energy terms associated with multi-configurational approaches.

Density Functional Theory

We have seen that the pure $\hat{H}_{e-}^{Schr.}$ necessarily relates with precise wave functions; but we can also try to represent multi-electronic systems by enlarging $\hat{H}_{e-}^{Schr.}$, and then simplifying the wave functions. Why not to try to approximate QSEI and $E_{e-e-}^{\text{correlation}}$ by effective finite one-body operators, maintaining a single Ψ_{e-}^{Slater}. We could try to assign to the Exchange and Correlation interactions an effective space factor, as in Fig. 8, because they introduce a correction that reduces the expected Coulomb repulsions because of the operative larger distance between electrons. This concept is equivalent to the Exchange-

Correlation hole in Density Functional Theory (DFT). DFT actually shows much more, in principle an exact solution to molecular systems based on occupied mono-electronic orbitals is possible, without the need of including excitations (or knowing the exact wavefunction) (Kohn & Sham, 1965), (Pan & Sahni, 2012).
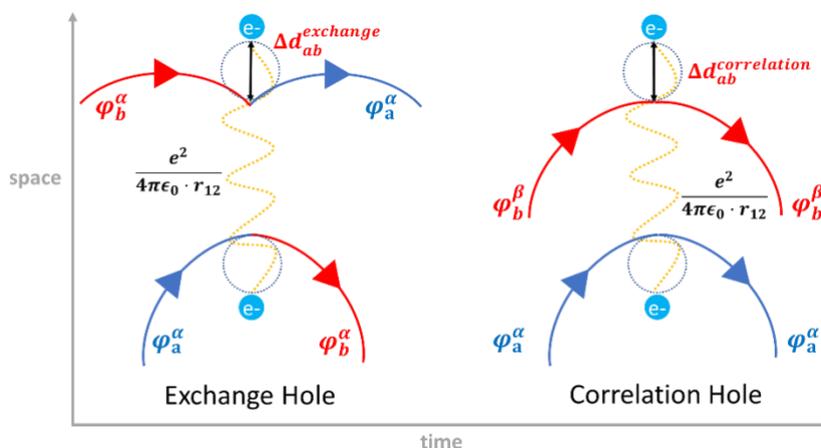

Figure 8. Feynman type diagram of the Correlation and Exchange holes, that in DFT effectively simulate the reduction in the Coulomb repulsions due to electronic correlation.

In DFT, we are used to hear about the exchange-correlation hole (Přecechtělová, Bahmann, Kaupp & Ernzerhof, 2014). The definition inside DFT is more or less close to the quantum reality, electrons in orbitals have dynamical mechanisms to be further apart and avoid partially strong Coulomb repulsions. Each electron effectively creates a depletion, or hole, of electron density around itself as a direct consequence of exchange-correlation effects, Figure 8. We admire that the success of DFT (in its multiple approaches) is also compatible with a quantum space-time interpretation of collision mechanisms between electrons in orbitals. Related with the size-shape of the exchange and correlations holes, every system is going to be different; the DFT exchange-correlation holes must be defined iteratively and approximatively from the solutions.

CONCLUSIONS

R.P. Feynman in 1948 derived the differential Schrödinger equation (Feynman, 1948) recognizing contributions from all possible particle classical paths. His path integral formulation of quantum mechanics offers a point of view that allows to interpret the interactions between electrons from space-time paths.

The electromagnetic fields/interactions between nuclei and electrons are quantized and create interference energy patterns; electrons evolve in space-time following the standing energy-modes that they generate and then suffer scattering events. Feynman diagrams serve to give a visualization of computational chemistry in terms of particle interactions, correlated collision mechanisms in space-time; and that is the second main objective of this illustrative work.

Coming back to the Mulliken's question, *what are the electrons really doing in molecules?* Part of the wave–particle duality picture is that electrons are moving in defined paths in space-time in a quantized energy field, with brighter and darker spots created by the interference patterns of the energy carriers (virtual photons). As they move, electrons can encounter each other and the interference patterns in the quantum field evolve with them. At some point in space-time, if the electrons are too close the quantum field prefers to exchange/give energy: electrons scatter and relax the energy changing their orbitals. An electron as a particle feels and contributes to create a dynamic quantized field; and that is what creates the total vector state of electrons, made from orbitals, where all the possible paths contribute to the electron density as Dirac proposed. It is the awareness that the electrons move in multiple actual space-time paths acting as mirrors for the energy carriers, creating standing energy waves that they must follow when they move, what reconciles the wave-particle duality.

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