• The Koopmans theorem goes at best with chemical harness or aromaticity evaluation by means of LUMO-HOMO gaps when they manifested surprisingly the same for superior orders of IPs-EAs, this way confirming the previous point.

Application on a paradigmatic set of mono and double benzoic rings molecules supported these conclusions, yet leaving enough space for further molecular set extensions and computational various frameworks comparison.

This may lead with the fruitful result according which the Koopmans theorem works better when superior HOMO-LUMO frozen spin-orbitals are considered, probably due to compensating correlating effects such extension implies, see the last section' analytical discussion. In any case, the present molecular illustration of Koopmans' approximations to chemical harness computation clearly shows that, at least for organic aromatic molecules, it works better for superior orders of "freezing" spin-orbitals and is not limitative to the first valence orbitals, as would be the common belief. Moreover, it was also clear the Koopmans theorem finely accords also with more complex ponder of its superior order orbitals in chemical hardness expansions Eq. (4.326), when subtle effects in lone pairing electrons (since remained orbital is frozen upon successive electronic attachment/removals on/from it) or chemical bonding pair of electrons influence the aromatic ring core towards increasing its shielding and the overall molecular reactivity resistance. All these conceptual and computational results should be further extended and tested on increased number of molecules, enlarging their variety too, as well as by considering more refined quantum computational frameworks as the Density Functional Theory and (Hartree-Fock) ab initio schemes are currently compared and discussed for various exchange-correlation and parameterization limits and refutations.

4.6 DENSITY FUNCTIONAL THEORY: OBSERVABLE QUANTUM CHEMISTRY

The main weakness of the Hartree-Fock method, namely the lack in correlation energy, is ingeniously restored by the Density Functional method

through introducing of the so-called effective one-electron exchange-correlation potential, yet with the price of not knowing its analytical form. However, the working equations have the simplicity of the HF ones, while replacing the exchange term in Eq. (4.281) by the exchange-correlation ("XC") contribution; there resulted the (general) unrestricted matrix form of the Kohn-Sham equations (Kohn & Sham, 1965):

$$F_{\mu\nu}^{\uparrow} = H_{\mu\nu}^{\uparrow} + \sum_{\lambda\sigma} P_{\lambda\sigma}^{T} \left(\mu\nu | \lambda\sigma \right) + F_{\mu\nu}^{XC\uparrow} \qquad (4.370)$$

$$F_{\mu\nu}^{\downarrow} = H_{\mu\nu}^{\downarrow} + \sum_{\lambda\sigma} P_{\lambda\sigma}^{T} \left(\mu\nu | \lambda\sigma \right) + F_{\mu\nu}^{XC\downarrow} \qquad (4.371)$$

$$P^{T} \equiv P^{\uparrow+\downarrow} = P^{\uparrow} + P^{\downarrow} \qquad (4.372)$$

in a similar fashion with the Pople-Nesbet equations of Hartree-Fock theory. The restricted (closed-shell) variant is resembled by the density constraint:

$$\rho^{\uparrow} = \rho^{\downarrow} \qquad (4.373)$$

in which case the Roothaan analogous equations (for exchange-correlation potential) are obtained.

Either Eq. (4.370) or (4.371) fulfills the general matrix equation of type (4.279) for the energy solution:

$$E = \sum_{\mu\nu} P_{\mu\nu} H_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma} \left(\mu\nu | \lambda\sigma \right) + E_{XC} \qquad (4.374)$$

that can be actually regarded as the solution of the Kohn-Sham equations themselves. The appeared exchange-correlation energy E_{XC} may be at its turn conveniently expressed through the energy density (per unit volume) by the integral formulation:

$$E_{XC} = E_{XC} \left[\rho^{\uparrow}, \rho^{\downarrow} \right] = \int f \left(\rho^{\uparrow}, \rho^{\downarrow} \right) d\tau \qquad (4.375)$$

once the Fock elements of exchange-correlation are recognized to be of density gradient form (Johnson et al., 1994):

$$F_{\mu\nu}^{XC\uparrow(\downarrow)} = \int \frac{\partial f}{\partial \rho^{\uparrow(\downarrow)}} \phi_\mu \phi_\nu \, d\tau \qquad (4.376)$$

The quest for various approximations for the exchange-correlation energy density $f(\rho)$ had spanned the last decades in quantum chemistry, and will be in the next reviewed (Putz, 2008). Here we will thus present the "red line" of its implementation as will be further used for the current aromaticity applications.

4.6.1 HOHENBERG-KOHN THEOREMS

Unlike the Hartree-Fock method, a completely different approach was invented to overcome from a single shoot both the *exchange and correlation* terms to the total electronic energy. That was possible, however with the price of revisiting the wave function concept, through contracting it into the electronic density:

$$\rho(r) = \sum_i n_i \sum_{\sigma=\alpha,\beta} \left| \chi_i^\sigma (r) \right|^2 \qquad (4.377)$$

written in general terms of the fractional occupancy numbers $n_i \in [0,1]$ so that (Nagy, 1998)

$$N[\rho] = \int \rho(r) dr = \sum_i n_i \qquad (4.378)$$

Worth noting that by introducing of the fractional occupation numbers both the concepts of one-orbitals as well as exact *N*-one-orbitals become generalized to fractionally occupied orbitals and to an arbitrary number of orbitals, hereafter called as *Kohn-Sham orbitals*. This way the distinction respecting the Hartree-Fock approach is made in clear.

The first Hohenberg-Kohn (HK1) theorem gives space to the concept of *electronic density of the system* $\rho(\mathbf{r})$ in terms of the extensive relation

with the N electrons from the system that it characterizes (Bamzai & Deb, 1981):

$$\int \rho(\mathbf{r})d\mathbf{r} = N \qquad (4.379)$$

The relation (4.379) as much simple it could appears stands as the decisive passage from the eigen-wave function level to the level of total electronic density (Parr & Young, 1989; Putz, 2003):

$$\rho(\mathbf{r}) = N\int \Psi^*(\mathbf{r},\mathbf{r}_2,...,\mathbf{r}_N)\Psi(\mathbf{r},\mathbf{r}_2,...,\mathbf{r}_N)d\mathbf{r}_2...d\mathbf{r}_N \qquad (4.380)$$

Firstly, Eq. (4.380) satisfies Eq. (4.379); this can be used also as simple immediate proof of the relation (4.379) itself. Then, the dependency from the $3N$-dimensions of configuration space was reduced at 3 coordinates in the real space, physically measurable.

However, still remains the question: what represents the electronic density of Eq. (4.380)? Definitely, it neither represents the electronic density in the configuration space nor the density of a single electron, since the N-electronic dependency as multiplication factor of the multiple integral in Eq. (4.380). What remains is that $\rho(r)$ *is simple the electronic density (of the whole concerned system) in* "$\mathbf{r}$" space point. Such simplified interpretation, apparently classics, preserves its quantum roots through the averaging (integral) over the many-electronic eigenfunction $\Psi(\mathbf{r}_1,...,\mathbf{r}_N)$ in Eq. (4.380). Alternatively, the explicit non-dependency of density on the wave function is also possible within the quantum statistical approach where the relation with partition function of the system (the global measure of the distribution of energetic states of a system) is mainly considered.

The major consequence of this theorem consists in defining of the total energy of a system as a function of the electronic density function in what is known as the density functional (Parr & Young, 1989; Putz, 2003):

$$E[\rho] = F_{HK}[\rho] + C_A[\rho] \qquad (4.381)$$

from where the name of the theory. The terms of energy decomposition in (4.381) are identified as: the Hohenberg-Kohn density functional (Hohenberg & Kohn, 1964)

$$F_{HK}[\rho] = T[\rho] + V_{ee}[\rho] \tag{4.382}$$

viewed as the summed electronic kinetic $T[\rho]$ and electronic repulsion $V_{ee}[\rho]$, and the so-called *chemical action* term (Putz, 2007a):

$$C_A[\rho] = \int \rho(\mathbf{r})V(\mathbf{r})d\mathbf{r} \tag{4.383}$$

being the only explicit functional of total energy.

Although not entirely known the HK functional has a remarkably property: it is universally, in a sense that both the kinetic and inter-electronic repulsion are independent of the concerned system. The consequence of such universal nature offers the possibility that once it is exactly or approximately knew the HK functional *for a given external potential V(**r**)* remain valuable for any other type of potential *V'(**r**)* applied on the concerned many-electronic system. Let's note the fact that *V(**r**) should be not reduced only to the Coulombic type* of potentials but is carrying the role of the generic potential applied, that could beg of either an electric, magnetic, nuclear, or even electronic nature as far it is external to the system fixed by the N electrons in the investigated system.

Once "in game" the external applied potential provides the second Hohenberg-Kohn (HK2) theorem. In short, HK2 theorem says that "the external applied potential is determined up to an additive constant by the electronic density of the *N*-electronic system ground state". In mathematical terms, the theorem assures the validity of the variational principle applied to the density functional (4.381) relation, i.e., (Ernzerhof, 1994)

$$E[\bar{\rho}] \geq E[\rho] \Leftrightarrow \delta E[\rho] = 0 \tag{4.384}$$

for every electronic test density $\bar{\rho}$ around the real density ρ of the ground state.

The proof of variational principle in Eq. (4.384), or, in other words, the one-to-one correspondence between the applied potential and the ground state electronic density, employs the *reduction ad absurdum* procedure.

That is to assume that the ground state electronic density $\rho(\mathbf{r})$ corresponds to two external potentials (V_1, V_2) fixing two associate Hamiltonians (H_1, H_2) to which two eigen-total energy (E_1, E_2) and two eigen-wave functions (Ψ_1, Ψ_2) are allowed. Now, if eigen-function Ψ_1 is considered as the true one for the ground state the variational principle (4.384) will cast as the inequality:

$$E_1[\rho] = \int \Psi_1^* \hat{H}_1 \Psi_1 d\tau < \int \Psi_2^* \hat{H}_1 \Psi_2 d\tau = \int \Psi_2^* \left[\hat{H}_2 + \left(\hat{H}_1 - \hat{H}_2 \right) \right] \Psi_2 d\tau$$

(4.385)

which is further reduced, on universality reasons of the HK functional in (4.381), to the form:

$$E_1[\rho] < E_2[\rho] + \int \rho(\mathbf{r}) \left[V_1(\mathbf{r}) - V_2(\mathbf{r}) \right] d\mathbf{r}$$

(4.386)

On another way, if the eigen-function Ψ_2 is assumed as being the one true ground state wave-function, the analogue inequality springs out as:

$$E_2[\rho] < E_1[\rho] + \int \rho(\mathbf{r}) \left[V_2(\mathbf{r}) - V_1(\mathbf{r}) \right] d\mathbf{r}$$

(4.387)

Taken together relations (4.386) and (4.387) generate, by direct summation, the evidence of the contradiction:

$$E_1[\rho] + E_2[\rho] < E_1[\rho] + E_2[\rho]$$

(4.388)

The removal of such contradiction could be done in a single way, namely, by abolishing, in a reverse phenomenologically order, the fact that two eigen-functions, two Hamiltonians and respectively, two external potential exist for characterizing the same ground state of a given electronic system. With this statement the HK2 theorem is formally proofed.

Yet, there appears the so-called *V-representability* problem signaling the impossibility of an *a priori* selection of the external potentials types that are in bi-univocal relation with ground state of an electronic system (Chen & Stott, 1991a,b; Kryachko & Ludena, 1991a,b). The problem was revealed as very difficult at mathematical level due to the equivocal

potential intrinsic behavior that is neither of universal nor of referential independent value. Fortunately, such principal limitation does not affect the general validity of the variational principle (4.384) regarding the selection of the energy of ground state level from a collection of states with different associated external potentials.

That because, the problem of *V*-representability can be circumvented by the so-called *N-contingency features of ground state electronic density* assuring that, aside of the $N - integrability\ condition$ (4.379), the candidate ground state densities should fulfill the *positivity condition* (an electronic density could not be negative) (Kryachko & Ludena, 1991a,b):

$$\rho(\mathbf{r}) \geq 0 \ , \ \forall |\mathbf{r}| \in \Re \qquad (4.389)$$

as well as the *non-divergent integrability condition* on the real domain (in relation with the fact that the kinetic energy of an electronic system could not be infinite – since the light velocity restriction):

$$\int_{\Re} \left| \nabla \rho(\mathbf{r})^{1/2} \right|^2 d\mathbf{r} < \infty \qquad (4.390)$$

Both Eqs. (4.389) and (4.390) conditions are easy accomplished by every reasonable density, allowing the employment of the variational principle (4.384) in two steps, according to the so-called *Levy-Lieb double minimization algorithm* (Levy & Perdew, 1985): one regarding the intrinsic minimization procedure of the energetic terms respecting all possible eigen-functions folding a trial electronic density followed by the external minimization over all possible trial electronic densities yielding the correct ground state (GS) energy density functional

$$
\begin{aligned}
E_{GS} &= \min_{\rho} \left[\min_{\Psi \to \rho} \left(\int \Psi^*(T + V_{ee} + V)\Psi d\tau \right) \right] \\
&= \min_{\rho} \left[\min_{\Psi \to \rho} \left(\int \Psi^*(T + V_{ee})\Psi d\tau \right) + \int \rho(\mathbf{r})V(\mathbf{r})d\mathbf{r} \right] \\
&= \min_{\rho} \left(F_{HK}[\rho] + C_A[\rho] \right) = \min_{\rho} \left(E[\rho] \right) \qquad (4.391)
\end{aligned}
$$

One of the most important consequences of the HK2 conveys the rewriting of the variational principle (4.384) in the light of above N-contingency conditions of the trial densities as the working Euler type equation:

$$\delta\{E[\rho] - \mu N[\rho]\} = 0 \qquad (4.392)$$

from where, there follows the Lagrange multiplication factor with the functional definition:

$$\mu = \left(\frac{\delta E[\rho]}{\delta \rho}\right)_{\rho = \rho(V)} \qquad (4.393)$$

this way introducing the *chemical potential* as the fundamental quantity of the theory. At this point, the whole chemistry can spring out since identifying the electronic systems electronegativity with the negative of the density functional chemical potential (Parr & Young, 1989):

$$\chi = -\mu \qquad (4.394)$$

making thus the DFT approach compatible with Hartree-Fock-Koopmans previous formulation of electronagivity for frontier orbital energies, see Eq. (4.352).

However, the Hohenberg-Kohn theorems give new conceptual quantum tools for physico-chemical characterization of an electronic sample by means of electronic density and its functionals, the total energy and chemical potential (electronegativity). Such density functional premises are in next analyzed towards elucidating of the quantum nature of the chemical bond as driven by chemical reactivity (Putz, 2007b).

4.6.2 OPTIMIZED ENERGY-ELECTRONEGATIVITY CONNECTION

Back from Paris, in the winter of 1964, Kohn met at the San Diego University of California his new post-doc Lu J. Sham with who propose to extract from HK1 & 2 theorems the equation of total energy of the ground

state. In fact, they propose themselves to find the correspondent of the stationary eigen-equation of Schrödinger type, employing the relationship between the electronic density and the wave function.

Their basic idea consists in assuming a so-called orbital basic set for the *N*-electronic system by replacing the integration in the relation (4.380) with summation over the virtual uni-electronic orbitals φ_i, $i = \overline{1, N}$, in accordance with Pauli principle, assuring therefore the HK1 frame with maximal spin/orbital occupancy (Janak, 1978):

$$\rho(\mathbf{r}) = \sum_i^N n_i |\varphi_i(\mathbf{r})|^2 \quad , 0 \le n_i \le 1 \ , \ \sum_i n_i = N \qquad (4.395)$$

Then, the *trial* total eigen-energy may be rewritten as density functional of Eq. (4.381) nature expanded in the original form (Moscardo & San-Fabian, 1991; Neal, 1998):

$$
\begin{aligned}
E[\rho] &= F_{HK}[\rho] + C_A[\rho] \\
&= T[\rho] + V_{ee}[\rho] + C_A[\rho] \\
&= T_s[\rho] + J[\rho] + \left\{ (T[\rho] - T_s[\rho]) + (V_{ee}[\rho] - J[\rho]) \right\} + C_A[\rho] \\
&= \sum_i^N \int n_i \varphi_i^*(\mathbf{r}) \left[-\frac{1}{2} \nabla^2 \right] \varphi_i(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 + E_{xc}[\rho] \\
&\quad + \int V(\mathbf{r})\rho(\mathbf{r}) d\mathbf{r}
\end{aligned}
$$

$$(4.396)$$

where, the contribution of the referential uniform kinetic energy contribution

$$T_s[\rho] = \sum_i^N \int n_i \varphi_i^*(\mathbf{r}) \left[-\frac{1}{2} \nabla^2 \right] \varphi_i(\mathbf{r}) d\mathbf{r} \qquad (4.397)$$

with the inferior index "s" referring to the "spherical" or homogeneous attribute together with the classical energy of Coulombic inter-electronic repulsion

$$J[\rho] = \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 \qquad (4.398)$$

were used as the analytical vehicles to elegantly produce the exchange-correlation energy E_{xc} containing exchange ($V_{ee}[\rho] - J[\rho]$) and correlation ($T[\rho] - T_s[\rho]$) heuristically introduced terms as the quantum effects of spin anti-symmetry over the classical interelectronic potential and of corrected homogeneous electronic movement, respectively.

Next, the trial density functional energy (4.396) will be optimized in the light of variational principle (4.392) as prescribed by the HK2 theorem. The combined result of the HK theorems will eventually furnish the new quantum energy expression of multi-electronic systems beyond the exponential wall of the wave function.

An instructive method for deriving such equation assume the same types of orbitals for the density expansion (4.395),

$$\rho(\mathbf{r}) = N\varphi^*(\mathbf{r})\varphi(\mathbf{r}) \tag{4.399}$$

that, without diminishing the general validity of the results, since preserving the N-electronic character of the system, highly simplifies the analytical discourse.

Actually, with the trial density (4.399) replaced throughout the energy expression in Eq. (4.396) has to undergo the minimization procedure (4.392) with the practical equivalent integral variant:

$$\int \frac{\delta\left(E[\rho] - \mu N[\rho]\right)}{\delta\varphi^*} \delta\varphi^* d\mathbf{r} = 0 \tag{4.400}$$

Note that, in fact, we chose the variation in the conjugated uni-orbital $\varphi^*(\mathbf{r})$ in (4.400) providing from (4.399) the useful differential link:

$$\delta\rho(\mathbf{r}) = N\varphi(\mathbf{r})\delta\varphi^*(\mathbf{r}) \Rightarrow \delta\varphi^*(\mathbf{r}) = N\varphi(\mathbf{r})\frac{1}{\delta\rho(\mathbf{r})} \tag{4.401}$$

Now, unfolding the Eq. (4.400) with the help of relations (4.396) and (4.399), together with fundamental density functional prescription (4.379), one firstly gets (Putz & Chiriac, 2008):

$$\frac{\delta}{\delta\phi^*(\mathbf{r})} \left\{ \begin{array}{l} -\dfrac{N}{2}\int \varphi^*(\mathbf{r})\nabla^2\varphi(\mathbf{r})d\mathbf{r} + J[\rho] + E_{xc}[\rho] \\ +N\int V(\mathbf{r})\varphi^*(\mathbf{r})\varphi(\mathbf{r})d\mathbf{r} - \mu N\int \varphi^*(\mathbf{r})\varphi(\mathbf{r})d\mathbf{r} \end{array} \right\} = 0 \tag{4.402}$$

By performing the required partial functional derivations respecting the uni-orbital $\varphi^*(\mathbf{r})$ and by taking account of the equivalence (4.401) in derivatives relating $J[\rho]$ and $E_{xc}[\rho]$ terms, Eq. (4.402) takes the further form:

$$-\frac{N}{2}\nabla^2\varphi(\mathbf{r}) + N\varphi(\mathbf{r})\frac{\delta J[\rho]}{\delta\rho} + N\varphi(\mathbf{r})\frac{\delta E_{xc}}{\delta\rho} + NV(\mathbf{r})\varphi(\mathbf{r}) - \mu N\varphi(\mathbf{r}) = 0$$

$$(4.403)$$

After immediate suppressing of the N factor in all the terms and by considering the exchange-correlation potential with the formal definition:

$$V_{xc}(\mathbf{r}) = \left(\frac{\delta E_{xc}[\rho]}{\delta\rho(r)}\right)_{V(\mathbf{r})}$$

$$(4.404)$$

Equation (4.403) simplifies as (Flores & Keller, 1992; Keller, 1986):

$$\left[-\frac{1}{2}\nabla^2 + \left(V(\mathbf{r}) + \int\frac{\rho(\mathbf{r}_2)}{|\mathbf{r}-\mathbf{r}_2|}d\mathbf{r}_2 + V_{xc}(\mathbf{r})\right)\right]\varphi(\mathbf{r}) = \mu\varphi(\mathbf{r})$$

$$(4.405)$$

Moreover, once introducing the so-called *effective potential*:

$$V_{eff}(\mathbf{r}) = V(\mathbf{r}) + \int\frac{\rho(\mathbf{r}_2)}{|\mathbf{r}-\mathbf{r}_2|}d\mathbf{r}_2 + V_{xc}(\mathbf{r})$$

$$(4.406)$$

the resulted equation recovers the traditional Schrödinger shape:

$$\left[-\frac{1}{2}\nabla^2 + V_{eff}\right]\varphi(\mathbf{r}) = \mu\varphi(\mathbf{r})$$

$$(4.407)$$

The result (4.407) is fundamental and equally subtle. Firstly, it was proved that the joined Hohenberg-Kohn theorems are compatible with consecrated quantum mechanical postulates, however, still offering a generalized view of the quantum nature of electronic structures, albeit the electronic density was assumed as the foreground reality. In these conditions, the meaning of functions $\varphi(\mathbf{r})$ is now unambiguously producing the analytical passage from configuration (3N-D) to real (3D) space for the whole system under consideration. Nevertheless, the debate may still remain because once equation (4.407) is solved the basic functions $\varphi(\mathbf{r})$ generating the

electronic density (4.399) and not necessarily the eigen-functions of the original system due to the practical approximations of the exchange and correlation terms appearing in the effective potential (4.406). This is why the functions $\varphi(\mathbf{r})$ are used to be called as *Kohn-Sham (KS) orbitals*; they provide the orbital set solutions of the associate KS equations (Kohn & Sham, 1965):

$$\left[-\frac{1}{2}\nabla^2 + V_{eff}\right]\varphi_i(\mathbf{r}) = \mu_i\varphi_i(\mathbf{r}) , \quad i = \overline{1,N} \tag{4.408}$$

once one reconsiders electronic density (4.399) back with general case (4.395). Yet, Eq. (4.408), apart of delivering the KS wave-functions $\varphi_i(\mathbf{r})$, associate with another famous physico-chemical figure, the orbital chemical potential μ_i, which in any moment can be seen as the negative of the orbital electronegativities on the base of the relation (4.394). Going now to a summative characterization of the above optimization procedure worth observing that the *N*-electronic in an arbitrary external *V*-potential problem is conceptual-computationally solved by means of the following self-consistent algorithm:

1. It starts with a trial electronic density (4.395) satisfying the *N*-contingency conditions (4.389) and (4.390);
2. With trial density the effective potential (4.406) containing exchange and correlation is calculated;
3. With computed V_{eff} the Eq. (4.408) are solved for $\varphi_i(\mathbf{r})$, $i = \overline{1,N}$;
4. With the set of functions $\{\varphi_i(\mathbf{r})\}_{i=\overline{1,N}}$ the new density (4.395) is recalculated;
5. The procedure is repeated until the difference between two consecutive densities approaches zero;
6. Once the last condition is achieved one retains the last set $\{\varphi_i(\mathbf{r}), \mu_i = -\chi_i\}_{i=\overline{1,N}}$;
7. The electronegativity orbital observed contributions are summed up from Eq. (4.408) with the expression:

$$-\sum_i^N \langle\chi_i\rangle = \sum_i^N \int n_i \varphi_i^*(\mathbf{r})\left[-\frac{1}{2}\nabla^2 + V_{eff}(\mathbf{r})\right]\varphi_i(\mathbf{r})d\mathbf{r} = T_s[\rho] + \int V_{eff}\rho(\mathbf{r})d\mathbf{r}$$

$$(4.409)$$

8. Replacing in Eq. (4.409) the uniform kinetic energy, $T_s[\rho]$ from the general relation (4.396) the density functional of the total energy for the N-electronic system will take the final figure (Putz, 2008):

$$E[\rho] = -\sum_i^N \langle \chi_i \rangle - \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_{12}|} d\mathbf{r}_1 d\mathbf{r}_2 + \left\{ E_{xc}[\rho] - \int V_{xc}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} \right\}$$

(4.410)

showing that the optimized many-electronic ground state energy is directly related with global or summed over observed or averaged or expected orbital electronegativities. One can observe from Eq. (4.410) that even in the most optimistic case when the last two terms are hopefully canceling each other there still remains a (classical) correction to be added on global electronegativity in total energy. Or, in other terms, electronegativity alone is not enough to better describe the total energy of a many-electronic system, while its correction can be modeled in a global (almost classical) way. Such considerations stressed upon the accepted semiclassical behavior of the chemical systems, at the edge between the full quantum and classical treatments.

However, analytical expressing the total energy requires the use of suitable approximations, whereas for chemical interpretation of bonding the electronic localization information extracted from energy is compulsory. This subject is in next focused followed by a review of the popular energetic density functionals and approximations.

4.6.3   POPULAR ENERGETIC DENSITY FUNCTIONALS

Since the terms of total energy are involved in bonding and reactivity states of many-electronic systems, i.e., the kinetic energetic terms in ELF topological analysis or the exchange and correlation density functionals in chemical reactivity in relation with either localization and chemical potential or electronegativity, worth presenting various schemes of quantification and approximation of these functionals for better understanding their role in chemical structure and dynamics.

4.6.3.1 Density Functionals of Kinetic Energy

When the electronic density is seen as the diagonal element $\rho(\mathbf{r}_1) = \rho(\mathbf{r}_1, \mathbf{r}_1)$ the kinetic energy may be generally expressed from the Hartree-Fock model, through employing the single determinant $\rho(\mathbf{r}_1, \mathbf{r}'_1)$, as the quantity (Lee & Parr, 1987):

$$T[\rho] = -\frac{1}{2} \int \left[\nabla^2_{\mathbf{r}'_1} \rho(\mathbf{r}_1, \mathbf{r}'_1) \right]_{\mathbf{r}_1 = \mathbf{r}'_1} d\mathbf{r}_1 \qquad (4.411)$$

it may eventually be further written by means of the thermodynamical (or statistical) density functional:

$$T_\beta = \frac{3}{2} \int \rho(\mathbf{r}) k_B T(\mathbf{r}) d\mathbf{r} = \frac{3}{2} \int \rho(\mathbf{r}) \frac{1}{\beta(\mathbf{r})} d\mathbf{r} \qquad (4.412)$$

that supports various specializations depending on the statistical factor particularization β.

For instance, in LDA approximation, the temperature at a point is assumed as a function of the density in that point, $\beta(\mathbf{r}) = \beta(\rho(\mathbf{r}))$; this may be easily reached out by employing the scaling transformation to be (Ou-Yang & Levy, 1990)

$$\rho_\lambda(\mathbf{r}) = \lambda^3 \rho(\lambda \mathbf{r}) \Rightarrow T[\rho_\lambda] = \lambda^2 T[\rho], \; \lambda = ct \qquad (4.413)$$

providing that

$$\beta(\mathbf{r}) = \frac{3}{2} C \rho^{-2/3}(\mathbf{r}) \qquad (4.414)$$

a result that helps in recovering the traditional (Thomas-Fermi) energetic kinetic density functional form

$$T[\rho] = C \int \rho^{5/3}(\mathbf{r}) d\mathbf{r} \qquad (4.415)$$

while the indeterminacy remained is smeared out in different approximation frames in which also the exchange energy is evaluated. Note that the kinetic energy is generally foreseen as having an intimate relation with

the exchange energy since both are expressed in Hartree-Fock model as determinantal values of $\rho(\mathbf{r}_1, \mathbf{r'}_1)$, see below.

Actually, the different LDA particular cases are derived by equating the total number of particle N with various realization of the integral

$$N = \frac{1}{2} \iint |\rho(\mathbf{r}_1, \mathbf{r'}_1)|^2 \, d\mathbf{r}_1 d\mathbf{r}_1' \qquad (4.416)$$

by rewriting it within the inter-particle coordinates frame:

$$\mathbf{r} = 0.5(\mathbf{r}_1 + \mathbf{r}_1'), s = \mathbf{r}_1 - \mathbf{r}_1' \qquad (4.417)$$

as:

$$N = \frac{1}{2} \iint |\rho(\mathbf{r} + s/2, \mathbf{r} - s/2)|^2 \, d\mathbf{r} ds \qquad (4.418)$$

followed by spherical averaged expression:

$$N = 2\pi \iint \rho^2(\mathbf{r}) \Gamma(\mathbf{r}, s) d\mathbf{r} s^2 ds \qquad (4.419)$$

with

$$\Gamma(\mathbf{r}, s) = 1 - \frac{s}{\beta(\mathbf{r})} + \dots \qquad (4.420)$$

The option in choosing the $\Gamma(\mathbf{r}, s)$ series (4.420) so that to converge in the sense of charge particle integral (4.419) fixes the possible cases to be considered (Lee & Parr, 1987):

1. the Gaussian resummation uses:

$$\Gamma(\mathbf{r}, s) \cong \Gamma_G(\mathbf{r}, s) = \exp\left(-\frac{s^2}{\beta(\mathbf{r})}\right) \qquad (4.421)$$

2. the trigonometric (uniform gas) approximation looks like:

$$\Gamma(\mathbf{r}, s) \cong \Gamma_T(\mathbf{r}, s) = 9 \frac{(\sin t - t \cos t)^2}{t^6}, t = s\sqrt{\frac{5}{\beta(\mathbf{r})}} \qquad (4.422)$$

In each of (4.421) and (4.422) cases the LDA-β function (4.414) is firstly replaced; then, the particle integral (4.419) is solved to give the constant C and then the respective kinetic energy density functional of Eq. (4.415) type is delivered; the results are (Lee & Parr, 1987):

1. in Gaussian resummation:

$$T_G^{LDA} = \frac{3\pi}{2^{5/3}} \int \rho^{5/3}(\mathbf{r}) d\mathbf{r} \tag{4.423}$$

2. whereas in trigonometric approximation

$$T_{TF}^{LDA} = \frac{3}{10} \left(3\pi^2\right)^{2/3} \int \rho^{5/3}(\mathbf{r}) d\mathbf{r} \tag{4.424}$$

one arrives to the Thomas-Fermi original density functional formulation.

Next on, one will consider the non-local functionals; this can be achieved through the gradient expansion in the case of slowly varying densities – that is assuming the expansion (Murphy, 1981):

$$
\begin{aligned}
T &= \int d\mathbf{r} \left[\tau(\rho_\uparrow) + \tau(\rho_\downarrow) \right] \\
&= \int d\mathbf{r} \sum_{m=0}^{\infty} \left[\tau_{2m}(\rho_\uparrow) + \tau_{2m}(\rho_\downarrow) \right] \\
&= \int d\mathbf{r} \sum_{m=0}^{\infty} \tau_{2m}(\rho) \\
&= \int d\mathbf{r} \tau(\rho)
\end{aligned}
\tag{4.425}
$$

The first two terms of the series respectively covers: the Thomas Fermi typical functional for the homogeneous gas

$$\tau_0(\rho) = \frac{3}{10} \left(6\pi^2\right)^{2/3} \rho^{5/3} \tag{4.426}$$

and the Weizsäcker related first gradient correction:

$$\tau_2(\rho) = \frac{1}{9} \tau_W(\rho) = \frac{1}{72} \frac{|\nabla\rho|^2}{\rho} \tag{4.427}$$

They both correctly behave in asymptotic limits:

$$\tau(\rho) = \begin{cases} \tau_0(\rho) = \tau_2(\rho) & \dots \ \nabla\rho << \ (far \ from \ nucleus) \\ 9\tau_2(\rho) = \tau_W(\rho) = \dfrac{1}{8}\dfrac{|\nabla\rho|^2}{\rho} & \dots \ \nabla\rho >> \ (close \ to \ nucleus) \end{cases}$$

$$(4.428)$$

However, an interesting resummation of the kinetic density functional gradient expansion series (4.425) may be formulated in terms of the Padé-approximant model (DePristo & Kress, 1987):

$$\tau(\rho) = \tau_0(\rho)P_{4,3}(x) \tag{4.429}$$

with

$$P_{4,3}(x) = \frac{1 + 0.95x + a_2x^2 + a_3x^3 + 9b_3x^4}{1 - 0.05x + b_2x^2 + b_3x^3} \tag{4.430}$$

and where the *x*-variable is given by

$$x = \frac{\tau_2(\rho)}{\tau_0(\rho)} = \frac{5}{108}\frac{1}{\left(6\pi^2\right)^{2/3}}\frac{|\nabla\rho|^2}{\rho^{8/3}} \tag{4.431}$$

while the parameters a_2, a_3, b_2, and b_3 are determined by fitting them to reproduce Hartree-Fock kinetic energies of He, Ne, Ar, and Kr atoms, respectively (Liberman et al., 1994). Note that Padé function (4.430) may be regarded as a sort of generalized electronic localization function (ELF) susceptible to be further used in bonding characterizations.

4.6.3.2　Density Functionals of Exchange Energy

Starting from the Hartree-Fock framework of exchange energy definition in terms of density matrix (Levy et al., 1996),

$$K[\rho] = -\frac{1}{4}\iint \frac{|\rho(\mathbf{r}_1,\mathbf{r'}_1)|^2}{|\mathbf{r}_1-\mathbf{r'}_1|}d\mathbf{r}_1 d\mathbf{r}_1' \qquad (4.432)$$

within the same consideration as before, we get that the spherical averaged exchange density functional

$$K = \pi \iint \rho^2(\mathbf{r})\Gamma(\mathbf{r},s)d\mathbf{r}sds \qquad (4.433)$$

takes the particular forms (Lee & Parr, 1987):

1. in Gaussian resummation:

$$K_G^{LDA} = -\frac{1}{2^{1/3}}\int \rho^{4/3}(\mathbf{r})d\mathbf{r} \qquad (4.434)$$

2. and in trigonometric approximation (recovering the Dirac formula):

$$K_D^{LDA} = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\int \rho^{4/3}(\mathbf{r})d\mathbf{r} \qquad (4.435)$$

Alternatively, by paralleling the kinetic density functional previous developments the gradient expansion for the exchange energy may be regarded as the density dependent series (Cedillo et al., 1988):

$$\begin{aligned} K &= \sum_{n=0}^{\infty} K_{2n}(\rho) \\ &= \int d\mathbf{r}\sum_{n=0}^{\infty} k_{2n}(\rho) \\ &= \int d\mathbf{r}k(\rho) \end{aligned} \qquad (4.436)$$

while the first term reproduces the Dirac LDA term (Perdew & Yue, 1986; Manoli & Whitehead, 1988):

$$k_0(\rho) = -\frac{3}{2}\left(\frac{3}{4\pi}\right)^{1/3}\rho^{4/3} \qquad (4.437)$$

and the second term contains the density gradient correction, with the Becke proposed approximation (Becke, 1986):

$$k_2(\rho) = -b \frac{\dfrac{|\nabla\rho|^2}{\rho^{4/3}}}{\left(1 + d\dfrac{|\nabla\rho|^2}{\rho^{8/3}}\right)^a}$$

(4.438)

where the parameters b and d are determined by fitting the $k_0 + k_2$ exchange energy to reproduce Hartree-Fock counterpart energy of He, Ne, Ar, and Kr atoms, and where for the a exponent either 1.0 or 4/5 value furnishes excellent results. However, worth noting that when analyzing the asymptotic exchange energy behavior, we get in small gradient limit (Becke, 1986):

$$k(\rho) \xrightarrow{\nabla\rho \ll} k_0(\rho) - \frac{7}{432\pi\left(6\pi^2\right)^{1/3}} \frac{|\nabla\rho|^2}{\rho^{4/3}}$$

(4.439)

whereas the adequate large-gradient limit is obtained by considering an arbitrary damping function as multiplying the short-range behavior of the exchange-hole density, with the result:

$$k(\rho) \xrightarrow{\nabla\rho \gg} c\rho^{4/5}|\nabla\rho|^{2/5}$$

(4.440)

where the constant c depends of the damping function choice.

Next, the Padé-resummation model of the exchange energy prescribes the compact form (Cedillo et al., 1988):

$$k(\rho) = \frac{10}{9} \frac{k_0(\rho)}{P_{4,3}(x)}$$

(4.441)

with the same Padé-function (4.430) as previously involved when dealing with the kinetic functional resummation. Note that when $x=0$, one directly obtains the Ghosh-Parr functional (Ghosh & Parr, 1986):

$$k(\rho) = \frac{10}{9} k_0(\rho)$$

(4.442)

Moreover, the asymptotic behavior of Padé exchange functional (4.441) leaves with the convergent limits:

$$
k(\rho) = \begin{cases}
\dfrac{10}{9} \dfrac{\left(k_0 + \dfrac{15}{17} \dfrac{7}{432\pi \left(6\pi^2\right)^{1/3}} \right)}{\dfrac{|\nabla\rho|^2}{\rho^{4/3}}} & ... \; x \to 0 \; (SMALL \;\; GRADIENTS) \\[6ex]
-12\pi \dfrac{\rho^2}{|\nabla\rho|^2} & ... \; x \to \infty \, (LARGE \;\; GRADIENTS)
\end{cases}
$$

$$(4.443)$$

Once again, note that when particularizing small or large gradients and fixing asymptotic long or short range behavior, we are discovering the various cases of bonding modeled by the electronic localization recipe as provided by electronic localization function limits, see Volume II of the present five-volumes set (Putz, 2016b).

   Another interesting approach of exchange energy in the gradient expansion framework was given by Bartolotti through the two-component density functional (Bartolotti, 1982):

$$
K[\rho] = C(N) \int \rho(\mathbf{r})^{4/3} d\mathbf{r} + D(N) \int \mathbf{r}^2 \frac{|\nabla\rho|^2}{\rho^{2/3}} d\mathbf{r} \tag{4.444}
$$

where the N-dependency is assumed to behave like:

$$
C(N) = C_1 + \frac{C_2}{N^{2/3}}, \; D(N) = \frac{D_2}{N^{2/3}} \tag{4.445}
$$

while the introduced parameters C_1, C_2, and D_2 were fond with the exact values (Perdew et al., 1992; Wang et al., 1990; Alonso & Girifalco, 1978):

$$
C_1 = -\frac{3}{4}\pi^{1/3}, \; C_2 = -\frac{3}{4}\pi^{1/3}\left[1 - \left(\frac{3}{\pi^2}\right)^{1/3}\right], \; D_2 = \frac{\pi^{1/3}}{729} \tag{4.446}
$$

Worth observing that the exchange Bartolotti functional (4.444) has some important phenomenological features: it scales like potential energy,

fulfills the non-locality behavior through the powers of the electron and powers of the gradient of the density, while the atomic cusp condition is preserved (Levy & Gorling, 1996).

However, density functional exchange-energy approximation with correct asymptotic (long range) behavior, i.e., satisfying the limits for the density

$$\lim_{r \to \infty} \rho_\sigma = \exp(-a_\sigma r) \tag{4.447}$$

and for the Coulomb potential of the exchange charge, or Fermi hole density at the reference point $\mathbf{r}$

$$\lim_{r \to \infty} U_X^\sigma = -\frac{1}{r}, \sigma = \alpha \,(or \uparrow), \beta \,(or \downarrow)...spin\ states \tag{4.448}$$

in the total exchange energy

$$K[\rho] = \frac{1}{2} \sum_\sigma \int \rho_\sigma U_X^\sigma d\mathbf{r} \tag{4.449}$$

was given by Becke *via* employing the so-called semiempirical (SE) modified gradient-corrected functional (Becke, 1986):

$$K^{SE} = K_0 - \beta \sum_\sigma \int \rho_\sigma^{4/3} \frac{x_\sigma^2(\mathbf{r})}{1 + \gamma x_\sigma^2(\mathbf{r})} d\mathbf{r}, K_0 = \int d\mathbf{r} k_0[\rho(\mathbf{r})], x_\sigma(\mathbf{r}) = \frac{|\nabla \rho_\sigma(\mathbf{r})|}{\rho_\sigma^{4/3}(\mathbf{r})} \tag{4.450}$$

to the working single-parameter dependent one (Becke, 1988):

$$K^{B88} = K_0 - \beta \sum_\sigma \int \rho_\sigma^{4/3}(\mathbf{r}) \frac{x_\sigma^2(\mathbf{r})}{1 + 6\beta x_\sigma(\mathbf{r}) \sinh^{-1} x_\sigma(\mathbf{r})} d\mathbf{r} \tag{4.451}$$

where the value $\beta = 0.0042[a.u.]$ was found as the best fit among the noble gases (He to Rn atoms) exchange energies; the constant a_σ is related to the ionization potential of the system.

Still, having different exchange approximation energetic functionals as possible worth explaining from where such ambiguity eventually comes.

To clarify this, it helps in rewriting the starting exchange energy (4.432) under the formally exact form (Taut, 1996):

$$K[\rho] = \sum_\sigma \int \rho_\sigma(\mathbf{r}) k[\rho_\sigma(\mathbf{r})] g[x_\sigma(\mathbf{r})] d\mathbf{r} \qquad (4.452)$$

where the typical components are identified as:

$$k[\rho] = -A_X \rho^{1/3}, \; A_X = \frac{3}{2}\left(\frac{3}{4\pi}\right)^{1/3} \qquad (4.453)$$

while the gradient containing correction $g(x)$ is to be determined.

Firstly, one can notice that a sufficiency condition for the two exchange integrals (4.449) and (4.452) to be equal is that their integrands, or the exchange potentials, to be equal; this provides the leading gradient correction:

$$g_0(x) = \frac{1}{2}\frac{U_X(\mathbf{r}(x))}{k[\rho(\mathbf{r}(x))]} \qquad (4.454)$$

with $\mathbf{r}(x)$ following from $x(\mathbf{r})$ by (not unique) inversion.

Unfortunately, the above "integrity" condition for exchange integrals to be equal is not also necessary, since any additional gradient correction

$$g(x) = g_0(x) + \Delta g(x) \qquad (4.455)$$

fulfills the same constraint if it is chosen so that

$$\int \rho^{4/3}(\mathbf{r}) \Delta g(x(\mathbf{r})) d\mathbf{r} = 0 \qquad (4.456)$$

or, with the general form:

$$\Delta g(x) = f(x) - \frac{\int \rho^{4/3}(\mathbf{r}) f(x(\mathbf{r})) d\mathbf{r}}{\int \rho^{4/3}(\mathbf{r}) d\mathbf{r}} \qquad (4.457)$$

being $f(x)$ an arbitrary function.

Nonetheless, if, for instance, the function $f(x)$ is specialized so that

$$f(x) = -g_0(x) \tag{4.458}$$

the gradient correcting function (4.455) becomes:

$$g(x) = -\frac{1}{2A_X} \frac{\int \rho(\mathbf{r}) U_X(\mathbf{r}) d\mathbf{r}}{\int \rho^{4/3}(\mathbf{r}) d\mathbf{r}} \equiv \alpha_X \tag{4.459}$$

recovering the Slater's famous X_α method for exchange energy evaluations (Slater, 1951; Slater & Johnson, 1972):

$$K[\rho] = -\alpha_X A_X \int \rho^{4/3}(\mathbf{r}) d\mathbf{r} \tag{4.460}$$

Nevertheless, the different values of the multiplication factor α_X in Eq. (4.460) can explain the various forms of exchange energy coefficients and forms above. Moreover, following this conceptual line the above Becke'88 functional (4.451) can be further rearranged in a so-called Xα-Becke88 form (Lee & Zhou, 1991):

$$K^{XB88} = \alpha_{XB} \sum_\sigma \int \rho_\sigma^{4/3}(\mathbf{r}) \left[2^{1/3} + \frac{x_\sigma^2(\mathbf{r})}{1 + 6\beta_{XB} x_\sigma(\mathbf{r}) \sinh^{-1} x_\sigma(\mathbf{r})} \right] d\mathbf{r} \tag{4.461}$$

where the parameters α_{XB} and β_{XB} are to be determined, as usually, throughout atomic fitting; it may lead with a new workable valuable density functional in exchange family.

4.6.3.3   Density Functionals of Correlation Energy

The first and immediate definition of energy correlation may be given by the difference between the exact and Hartree-Fock (HF) total energy of a poly-electronic system (Senatore & March, 1994):

$$E_c[\rho] = E[\rho] - E_{HF}[\rho] \tag{4.462}$$

Instead, in density functional theory the correlation energy can be seen as the gain of the kinetic and electron repulsion energy between the full

interacting ($\lambda = 1$) and non-interacting ($\lambda = 0$) states of the electronic systems (Liu et al., 1999):

$$E_c^\lambda[\rho] = \left\langle \psi^\lambda \left| \left(\hat{T} + \lambda \hat{V}_{ee} \right) \right| \psi^\lambda \right\rangle - \left\langle \psi^{\lambda=0} \left| \left(\hat{T} + \lambda \hat{V}_{ee} \right) \right| \psi^{\lambda=0} \right\rangle \quad (4.463)$$

In this context, taking the variation of the correlation energy (4.463) respecting the coupling parameter λ (Ou-Yang & Levy, 1991; Nagy et al., 1999),

$$\lambda \frac{\partial E_c^\lambda[\rho]}{\partial \lambda} = E_c^\lambda[\rho] + \int \rho(\mathbf{r})\mathbf{r} \cdot \nabla \frac{\delta E_c^\lambda[\rho]}{\delta \rho(\mathbf{r})} d\mathbf{r} \quad (4.464)$$

by employing it through the functional differentiation with respecting the electronic density,

$$\lambda \frac{\partial V_c^\lambda[\rho]}{\partial \lambda} - V_c^\lambda[\rho] = \mathbf{r} \cdot \nabla V_c^\lambda + \int \rho(\mathbf{r}_1)\mathbf{r}_1 \cdot \nabla_1 \frac{\delta^2 E_c^\lambda[\rho]}{\delta \rho(\mathbf{r})\delta \rho(\mathbf{r}_1)} d\mathbf{r}_1 \quad (4.465)$$

one obtains the equation to be solved for correlation potential $V_c^\lambda = \delta E_c^\lambda[\rho]/\delta\rho$; then the correlation energy is yielded by back integration:

$$E_c^\lambda[\rho] = \int V_c^\lambda(\mathbf{r},[\rho])\rho(\mathbf{r})d\mathbf{r} \quad (4.466)$$

from where the full correlation energy is reached out by finally setting $\lambda = 1$.

When restricting to atomic systems, i.e., assuming spherical symmetry, and neglecting the last term of the correlation potential equation above, believed to be small (Liu et al., 1999), the equation to be solved simply becomes:

$$\lambda \frac{\partial V_c^\lambda[\rho]}{\partial \lambda} - V_c^\lambda[\rho] = r\nabla V_c^\lambda \quad (4.467)$$

that can really be solved out with the solution:

$$V_c^\lambda = A_p \lambda^{p+1} r^p \quad (4.468)$$

with the integration constants A_p and p.

However, since the Eq. (4.467) is a homogeneous differential one, the linear combination of solutions gives a solution as well. This way, the general form of correlation potential looks like:

$$V_c^\lambda = \sum_p A_p \lambda^{p+1} r^p \tag{4.469}$$

This procedure can be then iterated by taking further derivative of Eq. (4.465) with respect to the density, solving the obtained equation until the second order correction over above first order solution (4.469),

$$V_c^\lambda = \sum_{p1} A_{p1} \lambda^{p1+1} r^{p1} + \sum_{p2} A_{p2} \lambda^{2p1+1} r^{p2} \left\langle r^{p2} \rho \right\rangle \tag{4.470}$$

By mathematical induction, when going to higher orders the K-truncated solution is iteratively founded as:

$$V_c^\lambda = \sum_p \sum_{k=1}^K A_{pk} \lambda^{pk+1} r^p \left\langle r^p \rho \right\rangle^{k-1} \tag{4.471}$$

producing the λ-related correlation functional:

$$E_c^\lambda[\rho] = \sum_p \sum_{k=1}^K \frac{1}{k} A_{pk} \lambda^{pk+1} \left\langle r^p \rho \right\rangle^k \tag{4.472}$$

and the associate full correlation energy functional (λ=1) expression:

$$E_c[\rho] = \sum_p \sum_{k=1}^K \frac{1}{k} A_{pk} \left\langle r^p \rho \right\rangle^k \tag{4.473}$$

As an observation, the correlation energy (4.473) supports also the immediate not spherically (molecular) generalization:

$$E_c[\rho] = \sum_{lmn} \sum_{k=1}^K \frac{1}{k} A_{lmnk} \left\langle x^l x^m x^n \rho \right\rangle^k \tag{4.474}$$

Nevertheless, for atomic systems, the simplest specialization of the relation (4.473) involves the simplest density moments $\left\langle \rho \right\rangle = N$ and $\left\langle r\rho \right\rangle$ that gives:

$$E_c[\rho] = A_{c0} N + A_{c1} \left\langle r\rho \right\rangle \tag{4.475}$$

Unfortunately, universal atomic values for the correlation constants A_{c0} and A_{c1} in Eq. (4.475) are not possible; they have to be related with the atomic number Z that on its turn can be seen as functional of density as well. Therefore, with the settings

$$A_{c0} = C_{c0} \ln Z, \; A_{c1} = C_{c1} Z \qquad (4.476)$$

the fitting of Eq. (4.475) with the HF related correlation energy (4.462) reveals the atomic-working correlation energy with the form (Liu et al., 1999):

$$E_c = -0.16569 N \ln Z + 0.000401 Z \langle r\rho \rangle \qquad (4.477)$$

The last formula is circumvented to the high-density total correlation density approaches rooting at their turn on the Thomas-Fermi atomic theory. Very interesting, the relation (4.477) may be seen as an atomic reflection of the (solid state) high-density regime ($r_s < 1$) given by Perdew et al. (Perdew, 1986; Wang & Perdew, 1989; Seidl et al., 1999; Perdew et al., 1996):

$$E_c^{PZ\infty}[\rho] = \int d\mathbf{r}\rho(\mathbf{r})\left(-0.048 - 0.0116 r_s + 0.0311 \ln r_s + 0.0020 r_s \ln r_s\right)$$
$$(4.478)$$

in terms of the dimensionless ratio

$$r_s = \frac{r_0}{a_0} \qquad (4.479)$$

between the Wigner-Seitz radius $r_0 = (3/4\pi\rho)^{1/3}$ and the first Bohr radius $a_0 = \hbar^2/me^2$.

Instead, within the low density regime ($r_s \geq 1$) the first approximation for correlation energy goes back to the Wigner jellium model of electronic fluid in solids thus providing the LDA form (Perdew et al., 1998; Wilson & Levy, 1990):

$$E_c^{W-LDA}[\rho] = \int \varepsilon_c[\rho(\mathbf{r})]\rho(\mathbf{r})d\mathbf{r} \qquad (4.480)$$

where

$$\varepsilon_c[\rho(\mathbf{r})] = -\frac{0.44}{7.8 + r_s} \qquad (4.481)$$

is the correlation energy per particle of the homogeneous electron gas with density ρ (Zhao et al., 1994; Gritsenko et al., 2000; Zhao & Parr, 1992; Lam et al., 1998; Gaspar & Nagy, 1987; Levy, 1991).

However, extended parameterization of the local correlation energy may be unfolded since considering the fit with an LSDA ($\rho_\uparrow$ and $\rho_\downarrow$) analytical expression by *Vosko, Wilk and Nusair* (VWN) (Vosko et al., 1980),

$$E_c^{VWN}[\rho_\uparrow, \rho_\downarrow] = \int \varepsilon_c[\rho_\uparrow(\mathbf{r}), \rho_\downarrow(\mathbf{r})]\rho(\mathbf{r})d\mathbf{r} \qquad (4.482)$$

while further density functional *gradient corrected Perdew* (GCP) expansion will look like:

$$E_c^{GCP}[\rho_\uparrow, \rho_\downarrow] = \int d\mathbf{r}\varepsilon_c[\rho_\uparrow(\mathbf{r}), \rho_\downarrow(\mathbf{r})]\rho(\mathbf{r}) + \int d\mathbf{r}B[\rho_\uparrow(\mathbf{r}), \rho_\downarrow(\mathbf{r})]|\nabla\rho(\mathbf{r})|^2 + ... \qquad (4.483)$$

where the Perdew recommendation for the gradient integrant has the form (Perdew, 1986):

$$B_c^P[\rho_\uparrow(\mathbf{r}), \rho_\downarrow(\mathbf{r})] = B_c[\rho]\frac{\exp\left(-b[\rho]f|\nabla\rho|\rho^{-7/6}\right)}{d(m)} \qquad (4.484)$$

with

$$B_c[\rho] = \rho^{-4/3}C[\rho] \qquad (4.485)$$

being the electron gas expression for the coefficient of the gradient expansion. The normalization in Eq. (4.484) is to the spin degeneracy:

$$d(m) = 2^{1/3}\left[\left(\frac{1+m}{2}\right)^{5/3} + \left(\frac{1-m}{2}\right)^{5/3}\right]^{1/2}$$

$$m = \frac{\rho_\uparrow - \rho_\downarrow}{\rho}, \rho = \rho_\uparrow + \rho_\downarrow \qquad (4.486)$$

while the exponent containing functional

$$b[\rho] = (9\pi)^{1/6} \frac{C[\rho \to \infty]}{C[\rho]} \tag{4.487}$$

is written as the ratio of the asymptotic long-range density behavior to the current one, and is controlled by the cut-off f exponential parameter taking various values depending of the fitting procedures it subscribes (0.17 for closed shells atoms and 0.11 for Ne particular system (Savin et al., 1986, 1987)).

More specifically, we list bellow some nonlocal correlation density functionals in the low density (gradient corrections over LDA) regime:

- the Rasolt and Geldar paramagnetic case ($\rho_\uparrow = \rho_\downarrow = \rho / 2$) is covered by correlation energy (Rasolt & Geldart, 1986):

$$E_c^{RG}[\rho] = c_1 + \frac{c_2 + c_3 r_s + c_4 r_s^2}{1 + c_5 r_s + c_6 r_s^2 + c_7 r_s^3} \tag{4.488}$$

with c_1=1.667×10^{-3}, c_1=2.568×10^{-3}, c_3=2.3266×10^{-2}, c_4=7.389×10^{-6}, c_5=8.723, c_6=0.472, c_7=7.389×10^{-2} (in atomic units).
- The gradient corrected correlation functional reads as (Savin et al., 1984):

$$E_c^{GC} = \int d\mathbf{r} \varepsilon_c[\rho_\uparrow, \rho_\downarrow] \rho(\mathbf{r}) + \int d\mathbf{r} B_c^P[\rho_\uparrow, \rho_\downarrow] \Big|_{C[\rho] = \sqrt{2}\pi/4\left(6\pi^2\right)^{4/3}, f=0.17} |\nabla \rho(\mathbf{r})|^2$$

$$+ 9 \frac{\pi}{4\left(6\pi^2\right)^{4/3}} (0.17)^2 \int d\mathbf{r} \left(|\nabla \rho_\uparrow|^2 \rho_\uparrow^{-4/3} + |\nabla \rho_\downarrow|^2 \rho_\downarrow^{-4/3} \right) \tag{4.489}$$

- The *Lee, Yang, and Parr* (LYP) functional within Colle-Salvetti approximation unfolds like (Lee et al., 1988):

$$E_c^{LYP} = -a_c b_c \int d\mathbf{r} \gamma(\mathbf{r}) \xi(\mathbf{r}) \left(\begin{array}{c} \sum_\sigma \rho_\sigma(\mathbf{r}) \sum_i |\nabla \varphi_{i\sigma}(\mathbf{r})|^2 - \frac{1}{4} \sum_\sigma \rho_\sigma(\mathbf{r}) \Delta \rho_\sigma(\mathbf{r}) \\ -\frac{1}{4} |\nabla \rho(\mathbf{r})|^2 + \frac{1}{4} \rho(\mathbf{r}) \Delta \rho(\mathbf{r}) \end{array} \right)$$

$$-a_c \int d\mathbf{r} \frac{\gamma(\mathbf{r})}{\eta(\mathbf{r})} \rho(\mathbf{r}) \tag{4.490}$$

where

$$\gamma(\mathbf{r}) = 4\frac{\rho_\uparrow(\mathbf{r})\rho_\downarrow(\mathbf{r})}{\rho(\mathbf{r})^2}, \, \eta(\mathbf{r}) = 1 + d_c \rho(\mathbf{r})^{-1/3}, \, \xi(\mathbf{r}) = \frac{\rho(\mathbf{r})^{-5/3}}{\eta(\mathbf{r})}\exp\left[-c_c\rho(\mathbf{r})^{-1/3}\right]$$

(4.491)

and the constants: a_c=0.04918, b_c=0.132, c_c=0.2533, d_c=0.349.

- The open-shell (OS) case provides the functional (Wilson & Levy, 1990):

$$E_c^{OS} = \int d\mathbf{r} \frac{a_s\rho(\mathbf{r}) + b_s\left|\nabla\rho(\mathbf{r})\right|\rho(\mathbf{r})^{-1/3}}{c_s + d_s\left(\left|\nabla\rho_\uparrow\right|\rho_\uparrow^{-4/3} + \left|\nabla\rho_\downarrow\right|\rho_\downarrow^{-4/3}\right) + r_s}\sqrt{1-\zeta^2}$$

(4.492)

with the spin-dependency regulated by the factor $\zeta = (\rho_\uparrow - \rho_\downarrow)/(\rho_\uparrow + \rho_\downarrow)$, approaching zero for closed-shell case, while the specific coefficients are determined through a scaled-minimization procedure yielding the values: a_s=–0.74860, b_s=–0.06001, c_s=3.60073, d_s=0.900000.

- Finally, Perdew and Zunger (PZ) recommend the working functional (Perdew & Zunger, 1981):

$$E_c^{PZ0}[\rho] = \int d\mathbf{r}\rho(\mathbf{r})\frac{\alpha_p}{1 + \beta_{1p}\sqrt{r_s} + \beta_{2p}r_s}$$

(4.493)

with the numerical values for the fitting parameters founded as: α_p=-0.1423, β_{1p}=1.0529, β_{2p}=0.3334.

4.6.3.4 Density Functionals of Exchange-Correlation Energy

Another approach in questing exchange and correlation density functionals consists in finding them both at once in what was defined as exchange-correlation density functional (4.404). In this regard, following the Lee and Parr approach (Lee & Parr, 1990), the simplest starting point is to rewrite the inter-electronic interaction potential

$$V_{ee} = \iint \frac{\rho_2(\mathbf{r}_1,\mathbf{r}_2)}{r_{12}}d\mathbf{r}_1 d\mathbf{r}_2$$

(4.494)

and the classical (Coulombic) repulsion

$$J = \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 \qquad (4.495)$$

appeared in the formal exchange energy $(V_{ee} - J)$ in Eq. (4.396), by performing the previously introduced coordinate transformation (4.417), followed by integration of the averaged pair and coupled densities (denoted with over-bars) over the angular components of $\mathbf{s}$:

$$V_{ee} = 4\pi \int d\mathbf{r} \int s\,ds\,\overline{\rho}_2(\mathbf{r},s) \qquad (4.496)$$

$$J = 2\pi \int d\mathbf{r} \int s\,ds\,\overline{\rho(\mathbf{r}+\mathbf{s}/2)\rho(\mathbf{r}-\mathbf{s}/2)} \qquad (4.497)$$

Now, the second order density matrix in Eq. (4.496) can be expressed as

$$\overline{\rho}_2(\mathbf{r},s) = \frac{1}{2}\overline{\rho(\mathbf{r}+\mathbf{s}/2)\rho(\mathbf{r}-\mathbf{s}/2)}[1+F_1(\mathbf{r},s)] \qquad (4.498)$$

with the help of the introduced function $F_1(\mathbf{r},s)$ carrying the form

$$F_1(\mathbf{r},s) = -\frac{\exp[-\alpha(\mathbf{r})s]}{1+\alpha(\mathbf{r})}\left\{1+[\alpha(\mathbf{r})s]^2 F_2(\mathbf{r},s)\right\} \qquad (4.499)$$

so that the cusp condition for $\overline{\rho}_2(\mathbf{r},s)$

$$\left.\frac{\partial \ln \overline{\rho}_2(\mathbf{r},s)}{\partial s}\right|_{s=0} = 1 \qquad (4.500)$$

to be satisfied for a well behaved function of a Taylor series expansion type

$$F_2(\mathbf{r},s) = \sum_{k=0}^{\infty} a_k(\mathbf{r})[\alpha(\mathbf{r})s]^k \qquad (4.501)$$

when $\alpha(\mathbf{r})$ stands for a suitable function of $\mathbf{r}$ as well, see bellow.

On the other side, the average $\overline{\rho(\mathbf{r}+\mathbf{s}/2)\rho(\mathbf{r}-\mathbf{s}/2)}$ in (4.497) and (4.498) supports a Taylor expansion (Berkowitz, 1986):

$$\overline{\rho(\mathbf{r}+\mathbf{s}/2)\rho(\mathbf{r}-\mathbf{s}/2)} = \rho^2(\mathbf{r})\left[1 - \frac{2\tau_w(\mathbf{r})}{3\rho(\mathbf{r})}s^2 + ...\right] \qquad (4.502)$$

with

$$\tau_w(\mathbf{r}) = \frac{1}{8}\frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})} - \frac{1}{8}\nabla^2\rho(\mathbf{r}) \qquad (4.503)$$

being the Parr modified kinetic energy of Weizsäcker type (Parr & Young, 1989).

Inserting relations (4.496)–(4.503) in $(V_{ee} - J)$ difference it is eventually converted from the "genuine" exchange meaning into practical exchange-correlation energy characterized by the density functional form:

$$\begin{aligned}
E_{xc} &= 2\pi\int d\mathbf{r}\int s\,ds\,\overline{\rho(\mathbf{r}+\mathbf{s}/2)\rho(\mathbf{r}-\mathbf{s}/2)}F_1(\mathbf{r},s) \\
&= -2\pi\int d\mathbf{r}\frac{\rho^2(\mathbf{r})}{1+\alpha(\mathbf{r})}\int ds\,s\exp[-\alpha(\mathbf{r})s]\left\{1 - \frac{2\tau_w(\mathbf{r})}{3\rho(\mathbf{r})}s^2 + ...\right\} \\
&\qquad \left\{1 + [\alpha(\mathbf{r})s]^2\sum_{k=0}^{\infty}a_k(\mathbf{r})[\alpha(\mathbf{r})s]^k\right\}
\end{aligned} \qquad (4.504)$$

Making use of the two possible multiplication of the series in Eq. (4.504), i.e., either by retaining the $\alpha(\mathbf{r})$ containing function only or by including also the density gradient terms in the first curled brackets, thus retaining also the term containing $\tau_w(\mathbf{r})$ function, the so-called *I-xc or II-xc type functionals* are respectively obtained.

Now, laying aside other variants and choosing the simple (however meaningfully) density dependency

$$\alpha(\mathbf{r}) = \kappa\rho^{1/3}(\mathbf{r}), \kappa = \text{constant} \qquad (4.505)$$

the provided exchange-correlation functionals are generally shaped as (Lee & Parr, 1990):

$$E_{xc}^{I} = -\frac{1}{\kappa^2} \int d\mathbf{r} \rho^{4/3}(\mathbf{r}) \frac{A_{xc}(\mathbf{r})}{1+\kappa\rho^{1/3}(\mathbf{r})}$$

$$E_{xc}^{II} = -\frac{1}{\kappa^2} \int d\mathbf{r} \frac{\rho^{4/3}(\mathbf{r})}{1+\kappa\rho^{1/3}(\mathbf{r})} \left[B_{xc}(\mathbf{r}) + \frac{2}{3}\frac{\tau_w(\mathbf{r})}{\rho^{5/3}(\mathbf{r})} C_{xc}(\mathbf{r}) \right] \qquad (4.506)$$

These functionals are formally exact for any κ albeit the resumed functions $A_{xc}(\mathbf{r})$, $B_{xc}(\mathbf{r})$, and $C_{xc}(\mathbf{r})$ are determined for each particular specialization.

Going now to the specific models, let's explore the type I of exchange-correlation functionals (4.506). Firstly, they can further undergo simplification since the reasonable (atomic) assumption according which

$$\kappa\rho^{1/3}(\mathbf{r}) << 1, \forall \mathbf{r} \qquad (4.507)$$

Within this frame the best provided model is of $X\alpha$-Padé approximation type, containing N-dependency (Lee & Parr, 1990):

$$E_{xc}^{I(X\alpha)} = -a_0^{X\alpha} \frac{1+a_1^{X\alpha}/N}{1+a_2^{X\alpha}/N} \int \rho^{4/3}(\mathbf{r}) d\mathbf{r} \qquad (4.508)$$

with $a_0^{X\alpha}$=0.7475, $a_1^{X\alpha}$=17.1903, and $a_2^{X\alpha}$=14.1936 (atomic units).

When the condition (4.507) for κ is abolished the Wigner-like model results, again, having the best approximant exchange-correlation model as the Padé form (Lee & Parr, 1990):

$$E_{xc}^{I(Wig)} = -a_0^{Wig} \frac{1+a_1^{Wig}/N}{1+a_2^{Wig}/N} \int \frac{\rho^{4/3}(\mathbf{r})}{1+\kappa^{I(Wig)}\rho^{1/3}(\mathbf{r})} d\mathbf{r} \qquad (4.509)$$

with a_0^{Wig}=0.76799, a_1^{Wig}=17.5943, a_2^{Wig}=14.8893, and $\kappa^{I(Wig)}$=4.115·10⁻³ (atomic units).

Turning to the II-type of exchange-correlation functionals, the small density condition (4.507) delivers the gradient corrected $X\alpha$ model, taking its best fitting form as the N-dependent Padé approximant (Lee & Parr, 1990):

$$E_{xc}^{II(X\alpha)} = -b_0^{X\alpha} \frac{1 + b_1^{X\alpha}/N}{1 + b_2^{X\alpha}/N} \int \rho^{4/3}(\mathbf{r})d\mathbf{r} - c_0^{X\alpha} \int \rho^{-1/3}(\mathbf{r})\tau_w(\mathbf{r})d\mathbf{r} \quad (4.510)$$

with $b_0^{X\alpha}$=0.7615, $b_1^{X\alpha}$=1.6034, $b_2^{X\alpha}$=2.1437, and $c_2^{X\alpha}$=6.151×10^{-2} (atomic units), while when laying outside the Eq. (4.507) condition the gradient corrected Wigner-like best model is proved to be without involving the N-dependency (Lee & Parr, 1990):

$$E_{xc}^{II(Wig)} = -b_0^{Wig} \int \frac{\rho^{4/3}(\mathbf{r})}{1 + \kappa^{II(Wig)}\rho^{1/3}(\mathbf{r})} d\mathbf{r} - c_0^{Wig} \int \frac{\rho^{-1/3}(\mathbf{r})\tau_w(\mathbf{r})}{1 + \kappa^{II(Wig)}\rho^{1/3}(\mathbf{r})} d\mathbf{r} \quad (4.511)$$

with b_0^{Wig} =0.80569, c_0^{Wig} =3.0124×10^{-3}, and $\kappa^{II(Wig)}$=4.0743×10^{-3} (atomic units).

Still, a Padé approximant for the gradient-corrected Wigner-type exchange-correlation functional exists and it was firstly formulated by (Rasolt & Geldar, 1986) with the working form (Lee & Bartolotti, 1991):

$$E_{xc}^{RG} = E_{xc}^{LDA(or\, X\alpha)} + \int B_{xc}^{RG}[\rho(\mathbf{r})] \frac{|\nabla\rho(\mathbf{r})|^2}{\rho^{1/3}(\mathbf{r})} d\mathbf{r} \quad (4.512)$$

with B_{xc}^{RG} given with the Padé form:

$$B_{xc}^{RG}[\rho(\mathbf{r})] = -1\times10^{-3} c_1^{RG} \frac{1 + c_2^{RG} r_s + c_3^{RG} r_s^2}{1 + c_4^{RG} r_s + c_5^{RG} r_s^2 + c_6^{RG} r_s^3} \quad (4.513)$$

having the fitted coefficients c_1^{RG}=2.568, c_2^{RG}=9.0599, c_3^{RG}=2.877×10^{-3}, c_4^{RG}=8.723, c_5^{RG}=0.472, and c_3^{RG}=7.389×10^{-2} (atomic units). Some studies also consider the nonlocal correction in Eq. (4.512) premultiplied by the 10/7 factor, which was found as appropriate procedure for atomic systems.

Finally, worth noting the Tozer and Handy general form for exchange-correlation functionals viewed as a sum of products of powers of density and gradients (Tozer & Handy, 1998):

$$E_{xc}^{TH} = \int F_{xc}\left(\rho_\uparrow, \rho_\downarrow, \zeta_\uparrow, \zeta_\downarrow, \zeta_{\uparrow\downarrow}\right) d\mathbf{r} \qquad (4.514)$$

with

$$F_{xc} = \sum_{abcd} \omega_{abcd} R^a S^b X^c Y^d = \sum_{abcd} \omega_{abcd} f_{abcd}(\mathbf{r}) \qquad (4.515)$$

Where $R^a = \rho_\uparrow^a + \rho_\downarrow^a$, $S^b = m^{2b}$, see Eq. (4.486) for m definition, along the notations

$$X^c = \frac{\zeta_\uparrow^c + \zeta_\downarrow^c}{2\rho^{c4/3}}, \; Y^d = \left(\frac{\zeta_\uparrow^2 + \zeta_\downarrow^2 - 2\zeta_{\uparrow\downarrow}}{\rho^{8/3}}\right)^d \qquad (4.516)$$

and

$$\zeta_\uparrow = \left|\nabla\rho_\uparrow\right|, \; \zeta_\downarrow = \left|\nabla\rho_\downarrow\right|, \; \zeta_{\uparrow\downarrow} = \nabla\rho_\uparrow \cdot \nabla\rho_\downarrow, \; \rho = \rho_\uparrow + \rho_\downarrow \qquad (4.517)$$

The coefficients ω_{abcd} of Eq. (4.515) are determined through minimization procedure involving the associated exchange-correlation potentials $V_{xc\uparrow(\downarrow)}^{abcd}(\mathbf{r}) = \delta f_{abcd}(\mathbf{r})/\delta\rho_{\uparrow(\downarrow)}(\mathbf{r})$ in Eq. (4.514) functional. The results would depend upon the training set of atoms and molecules but presents the advantage of incorporating the potential information in a non-vanishing asymptotical manner, with a semi-empirical value. Moreover, its exact asymptotic exchange-correlation potential equals chemical hardness (Putz, 2003, 2007a,b) for open-shell being less than that for closed shell systems, thus having the merit of including chemical hardness as an intrinsic aspect of energetic approach, a somewhat absent aspect from conventional functionals so far.

However, since electronegativity and chemical hardness closely relate with chemical bonding, their relation with the total energy and component functionals is in next at both conceptual and applied levels explored.