

Since based on fitting with spectroscopic transitions the ZINDO methods are recommended in conjunction with single point calculation and not with geometry optimization, this should be consider by other off-set algorithms.

Beyond either NDO or NDDO methods, the self-consistent computation of molecular orbitals can be made by the so-called ab initio approach, directly relying on the HF equation or on its density functional extension, as will be in next unfolded.

4.5.4 AB INITIO METHODS: THE HARTREE-FOCK APPROACH

The alternative to semi-empirical methods is the full self-consistent calculation or the so-called ab initio approach; it is based on computing of all integrals appearing on Eq. (4.281), yet with the atomic Slater type orbitals (STO), $\exp(-ar)$, being replaced by the Gaussian type orbitals (GTO) (Boys, 1950):

$$\phi_A^{GTO} = x_A^l y_A^m z_A^n \exp(-\alpha r_A^2) \quad (4.312)$$

in molecular orbitals expansion – a procedure allowing for much simplification in multi-center integrals computation. Nevertheless, at their turn, each GTO may be generalized to a contracted expression constructed upon the primitive expressions of Eq. (4.312):

$$\phi_\mu^{CGTO}(r_A) = \sum_p d_{p\mu} \phi_p^{GTO}(\alpha_p, r_A) \quad (4.313)$$

where $d_{p\mu}$ and α_A are called the exponents and the contraction coefficients of the primitives, respectively. Note that the primitive Gaussians involved may be chosen as approximate Slater functions (Szabo & Ostlund, 1996), Hartree-Fock atomic orbitals (Clementi & Roetti, 1974), or any other set of functions desired so that the computations become faster. In these conditions, a minimal basis set may be constructed with one function for H and He, five functions for Li to Ne, nine functions for Na to Ar, 13 functions for K and Ca, 18 functions for Sc to Kr, ..., etc., to describe the core

and valence occupancies of atoms (Hehre et al., 1969; Collins et al., 1976; Stewart, 1970). Although such basis does not generally provide accurate results (because of its small cardinal), it contains the essential information regarding the chemical bond and may be useful for qualitative studies, as is the present case for aromaticity scales where the comparative trend is studied.

Actually, when simple ab initio method is referred it means that the Hartree-Fock equation (4.278) with full Fock matrix elements (Hartree, 1928a-b, 1957; Fock, 1930) of Eqs. (4.280) and (4.281) is solved for a Gaussian contracted basis (4.313). Actually, the method evaluates iteratively the kinetic energy and nuclear-electron attraction energy integrals – for the effective Hamiltonian, along the overlap and electron-electron repulsion energy integrals (for both the Coulomb and exchange terms), respectively written as:

$$T_{\mu\nu} = \langle \mu | \left(-\frac{1}{2} \nabla^2 \right) | \nu \rangle \quad (4.314)$$

$$V_{\mu\nu} = \langle \mu | \frac{Z_A}{r_A} | \nu \rangle \quad (4.315)$$

$$S_{\mu\nu} = \langle \mu | \nu \rangle \quad (4.316)$$

$$(\mu\nu | \lambda\sigma) = (\mu\nu | \frac{1}{r_{12}} | \lambda\sigma) \quad (4.317)$$

until the consistency in electronic population of Eq. (4.280) between two consecutive steps is achieved.

Note that such calculation assumes the total wave function as a single Slater determinant, while the resultant molecular orbital is described as a linear combination of the atomic orbital basis functions (MO-LCAO). Multiple Slater determinants in MO description projects the configurationally and post-HF methods, and will not be discussed here.

4.5.4.1 Hartree-Fock Orbital Energy

Skipping the reference to the electronic (e) subscripts throughout Eqs. (4.250)–(4.262), the Hartree-Fock trial functional can firstly be arranged as by the optimization procedure (Putz & Chiriac, 2008)

$$E_0 \leq E_{trial}^{HF}[\Psi^{HF}] = \langle \Psi^{HF} | \hat{H} | \Psi^{HF} \rangle = \langle \Psi^{HF} | \hat{H}^I | \Psi^{HF} \rangle + \langle \Psi^{HF} | \hat{H}^{II} | \Psi^{HF} \rangle \quad (4.318)$$

The one-electron (core) energetic component of Eq. (4.318) may be successively unfolded as:

$$\begin{aligned} & \langle \Psi^{HF} | \hat{H}^I | \Psi^{HF} \rangle \\ &= N! \langle \Psi^H | \hat{\phi} \hat{H}^I \hat{\phi} | \Psi^H \rangle \\ &= N! \langle \Psi^H | \hat{H}^I \hat{\phi}^2 | \Psi^H \rangle \\ &= N! \langle \Psi^H | \hat{H}^I \hat{\phi} | \Psi^H \rangle \\ &= \sum_{i=1}^N \sum_P (-1)^P \langle \Psi^H | \left[-\frac{1}{2} \nabla_i^2 - \sum_A \frac{Z_A}{r_{iA}} \right] \hat{\phi} | \Psi^H \rangle \\ &\equiv \sum_{i=1}^N \sum_P (-1)^P \langle \Psi^H | \hat{h}_i(1) \hat{\phi} | \Psi^H \rangle \\ &= \sum_{i=1}^N \langle \Psi^H | \hat{h}_i(1) | \Psi^H \rangle \\ &= \sum_{i=1}^N \langle \chi_i^\sigma(1) | \hat{h}_i(1) | \chi_i^\sigma(1) \rangle \\ &= \sum_{i=1}^N \int \chi_i^{\sigma*}(1) \hat{h}_i(1) \chi_i^\sigma(1) d\tau_1 \\ &\equiv \sum_{i=1}^N h_{ii} \\ &\equiv H_{ii} \end{aligned} \quad (4.319)$$

where it was considered that the introduced one-electron effective operator $\hat{h}_i(\mathbf{1})$ selects from the Hartree wave function (4.259) the associate spin-orbital, for each electron, accordingly.

Similarly, the two-electron energetic component of Eq. (4.318) may be successively transformed as:

$$\begin{aligned}
 & \langle \Psi^{HF} | \hat{H}^{II} | \Psi^{HF} \rangle \\
 &= N! \langle \Psi^H | \hat{\phi} \hat{H}^{II} \hat{\phi} | \Psi^H \rangle \\
 &= N! \langle \Psi^H | \hat{H}^{II} \hat{\phi}^2 | \Psi^H \rangle \\
 &= N! \langle \Psi^H | \hat{H}^{II} \hat{\phi} | \Psi^H \rangle \\
 &= \sum_{\substack{i,j=1 \\ i < j}}^N \sum_P (-1)^P \langle \Psi^H | \frac{1}{r_{ij}} \hat{\phi} | \Psi^H \rangle \\
 &= \sum_{\substack{i,j=1 \\ i < j}}^N \langle \Psi^H | \frac{1}{r_{ij}} (1 - P_{ij}) | \Psi^H \rangle \\
 &= \sum_{\substack{i,j=1 \\ i < j}}^N \langle \Psi^H | \frac{1}{r_{ij}} | \Psi^H \rangle - \sum_{\substack{i,j=1 \\ i < j}}^N \langle \Psi^H | \frac{1}{r_{ij}} P_{ij} | \Psi^H \rangle \\
 &= \sum_{\substack{i,j=1 \\ i < j}}^N \langle \chi_i^\sigma(1) \chi_j^\sigma(2) | \frac{1}{r_{12}} | \chi_i^\sigma(1) \chi_j^\sigma(2) \rangle \\
 &\quad - \sum_{\substack{i,j=1 \\ i < j}}^N \langle \chi_i^\sigma(1) \chi_j^\sigma(2) | \frac{1}{r_{12}} | \chi_j^\sigma(1) \chi_i^\sigma(2) \rangle \\
 &\equiv \sum_{\substack{i,j=1 \\ i < j}}^N \langle \chi_i^\sigma(1) | \hat{J}_j(1) | \chi_i^\sigma(1) \rangle - \sum_{\substack{i,j=1 \\ i < j}}^N \langle \chi_i^\sigma(1) | \hat{K}_j(1) | \chi_i^\sigma(1) \rangle \\
 &= \sum_{\substack{i,j=1 \\ i < j}}^N \iint \chi_i^{\sigma*}(1) \chi_j^{\sigma*}(2) \frac{1}{r_{ij}} \chi_i^\sigma(1) \chi_j^\sigma(2) d\tau_1 d\tau_2 \\
 &\quad - \sum_{\substack{i,j=1 \\ i < j}}^N \iint \chi_i^{\sigma*}(1) \chi_j^{\sigma*}(2) \frac{1}{r_{ij}} \chi_j^\sigma(1) \chi_i^\sigma(2) d\tau_1 d\tau_2
 \end{aligned}$$

$$\begin{aligned}
&\equiv \sum_{\substack{i,j=1 \\ i < j}}^N J_{ij} - \sum_{\substack{i,j=1 \\ i < j}}^N K_{ij} \\
&= \frac{1}{2} \sum_{i,j=1}^N [J_{ij} - K_{ij}] \\
&\equiv U_{ee}
\end{aligned} \tag{4.320}$$

resulting in the effective electron-electron repulsion energy once the quantum exchange terms K_{ij} are subtracted from the classical Coulombic ones J_{ij} . Here we recognize the combined classical (Coulombic) – quantum (exchange) effects that appear in the inter-electronic repulsion Hamiltonian term (4.255).

All together, with the results of Eqs. (4.319) and (4.320) back in Eq. (4.318), we get for the trial Hartree-Fock functional the expression:

$$E_{trial}^{HF}[\Psi^{HF}] = \sum_{i=1}^N h_{ii} + \frac{1}{2} \sum_{i,j=1}^N [J_{ij} - K_{ij}] \tag{4.321}$$

In next, we are going to apply the variational principle respecting the variations of the spin-orbitals in terms of Lagrange multipliers ε_{ij} that widely demands that:

$$\delta \left\{ E_{trial}^{HF}[\Psi^{HF}] - \sum_{i,j=1}^N \varepsilon_{ij}^{HF} \left(\langle \chi_i^\sigma(1) | \chi_j^\sigma(1) \rangle - 1 \right) \right\} = 0 \tag{4.322a}$$

However, by employing the canonical transformation, i.e., the N^2 parameters may be considered as the elements of a Hermitian matrix which through a unitary transformation become a diagonal matrix, the outset form of the variational principle (4.322) now reads:

$$\delta \left\{ E_{trial}^{HF}[\Psi^{HF}] - \sum_{i=1}^N \varepsilon_i^{HF} \left(\langle \chi_i^\sigma(1) | \chi_i^\sigma(1) \rangle - 1 \right) \right\} = 0 \tag{4.322b}$$

Note that performing a unitary transformation will not affect the average of the electronic Hamiltonian but only the HF wave function by a phase factor of unity modulus. Under these circumstances, the famous Hartree-Fock equation results from the successive equivalent forms:

$$\sum_{i=1}^N \frac{\delta}{\delta \chi_i^{\sigma*}(1)} \left\{ \begin{aligned} & -\frac{1}{2} \int \chi_i^{\sigma*}(1) \nabla_i^2 \chi_i^\sigma(1) d\tau_1 - \sum_A Z_A \int \chi_i^{\sigma*}(1) \frac{1}{r_{iA}} \chi_i^\sigma(1) d\tau_1 \\ & + \frac{1}{2} \sum_{j=1}^N \iint \chi_i^{\sigma*}(1) \chi_j^{\sigma*}(2) \frac{1}{r_{ij}} \chi_i^\sigma(1) \chi_j^\sigma(2) d\tau_1 d\tau_2 \\ & - \frac{1}{2} \sum_{j=1}^N \iint \chi_i^{\sigma*}(1) \chi_j^{\sigma*}(2) \frac{1}{r_{ij}} \chi_j^\sigma(1) \chi_i^\sigma(2) d\tau_1 d\tau_2 \\ & - \varepsilon_i^{HF} \int \chi_i^{\sigma*}(1) \chi_i^\sigma(1) d\tau_1 \end{aligned} \right\} = 0$$

$$\Leftrightarrow \left[-\frac{1}{2} \nabla_i^2 - \sum_A \frac{Z_A}{r_{iA}} \right] \chi_i^\sigma(1) + \left[\sum_{j=1}^N \int \chi_j^{\sigma*}(2) \frac{1}{r_{ij}} \chi_j^\sigma(2) d\tau_2 \right] \chi_i^\sigma(1)$$

$$- \left[\sum_{j=1}^N \int \chi_j^{\sigma*}(2) \frac{1}{r_{ij}} \chi_i^\sigma(2) d\tau_2 \right] \chi_j^\sigma(1) = \varepsilon_i^{HF} \chi_i^\sigma(1) \quad (4.322c)$$

Still, a more compact form of *HF* equation (4.322c) may be achieved since specific potential notations are introduced. For instance, the electrostatic repulsion potential (i.e., the Coulombic interaction) can be shortened as:

$$V_j^{ee}(1) = \int \chi_j^{\sigma*}(2) \frac{1}{r_{ij}} \chi_j^\sigma(2) d\tau_2 \quad (4.323)$$

while for the exchange potential (i.e., non-local interaction) we can define it as satisfying the relation:

$$V_j^{ex}(1) f(1) = \left[\int \chi_j^{\sigma*}(2) \frac{1}{r_{ij}} f(2) d\tau_2 \right] \chi_j^\sigma(1) \quad (4.324)$$

With these the above *HF* equation (4.322c) reduces to its most simple form:

$$\hat{F}(1) \chi_i^\sigma(1) = \varepsilon_i^{HF} \chi_i^\sigma(1) \quad (4.325)$$

where the one-electronic Fock operator

$$\hat{F}(1) = -\frac{1}{2} \nabla_i^2 + V_i^{HF\text{eff}}(1) \quad (4.326)$$

was introduced in terms of the effective-one potential

$$V_i^{HFeff}(\mathbf{1}) = -\sum_A \frac{Z_A}{r_{iA}} + \sum_{j=1}^N V_j^{ee}(\mathbf{1}) - \sum_{j=1}^N V_j^{ex}(\mathbf{1}) \quad (4.327)$$

Now, since the spin-orbitals satisfies the normalization condition

$$\int |\chi_i^\sigma(\mathbf{1})|^2 d\tau_1 = 1 \quad (4.328)$$

the orbital energies look like:

$$\varepsilon_i^{HF} = \int \chi_i^{\sigma*}(\mathbf{1}) \hat{F}(\mathbf{1}) \chi_i^\sigma(\mathbf{1}) d\tau_1 = h_{ii} + \sum_{j=1}^N [J_{ij} - K_{ij}] \quad (4.329)$$

while the total HF energy will take the form:

$$E^{HF}[\Psi^{HF}] = \sum_{i=1}^N \varepsilon_i^{HF} - U_{ee} \quad (4.330)$$

where

$$\sum_{i=1}^N \varepsilon_i^{HF} = \sum_{i=1}^N h_{ii} + \sum_{i,j=1}^N [J_{ij} - K_{ij}] \quad (4.331)$$

Remarkably, one can clearly see that the predicted *HF* energy (4.330) differs from the simple sum over the *HF* orbital energies (4.331) by the effective electron-electron interaction energy U_{ee} . We will return on this matter with more subtle consequences on Section 4.4.4.3.

4.5.4.2 About Correlation Energy

The post self-consistent era was mainly dedicated to the implementation of the so nominated *correlation energy* in the computation (Putz & Chiriac, 2008).

Firstly, it was noticed that a single Slater determinant (on which base the current *HF* analysis was exposed) can never account for a complete description of the many-electronic interaction. That is, the correlation

energy can be introduced as the difference between the exact eigen-value and the Hartree-Fock energy of the same Hamiltonian for the concerning state:

$$E_{corr} = E - E^{HF} \quad (4.332)$$

The next step was sustained by the assumption that the correlation energy can be seen as the perturbation of the self-consistent-field energy, which is associated with a wave function derived for a single electronic configuration. At this point the basic methods of approximation used in quantum chemistry, namely the *perturbation* and *variational*, can be considered.

In the case that perturbation method is employed, assuming the unperturbed wave function and energy as the HF solutions the exact eigen-functions and eigen-values can be written as expanded series

$$\Psi_e = \Psi_e^{HF} + \ell \Psi_e^{(1)} + \ell^2 \Psi_e^{(2)} + \dots \quad (4.333)$$

$$E_e = E^{HF} + \ell E_e^{(1)} + \ell^2 E_e^{(2)} + \dots \quad (4.334)$$

by introducing the ordering parameter ℓ . Through truncating the series in the second, third or fourth order generates the so-called Møller-Plesset MP2, MP3, and MP4 perturbative approximations, respectively.

On the other side, the linear variational method can be practiced within the *configuration interaction (CI)* approach of the many-electronic wave-function:

$$\Psi_e^{CI} = c_0 \Psi_e^{HF} + \sum_s c_a^s \Psi_a^s + c_{ab}^{sd} \Psi_{ab}^{sd} + c_{abc}^{sdt} \Psi_{abc}^{sdt} + \dots \quad (4.335)$$

where the $\Psi_0, \Psi_a^s, \Psi_{ab}^{sd}, \Psi_{abc}^{sdt}$ stands for the ground, single excited, double excited, and triple excited N -electron trial wave functions, respectively, for a given spin state. While the *CI* wave function is the subject of the eigen-problem:

$$\hat{H}_e \Psi_e^{CI} = \tilde{E}_0 \Psi_e^{CI} \quad (4.336)$$

the correlation correction to HF energy can be achieved through subtracting the HF energy from last equation

$$\left(\hat{H}_e - E^{HF} \right) \Psi_e^{CI} = \left(\tilde{E}_0 - E^{HF} \right) \Psi_e^{CI} = E_{corr} \Psi_e^{CI} \quad (4.337)$$

However, although, starting from this point, many sophisticated methods for wave function expansion, for example, the coupled cluster approach, multi-configuration self-consistent-field method or multi-reference CI methods, have been developed, the correlation problem faced many computational limitation, some of them almost insurmountable, due to the immense number of integrals to be evaluated.

4.5.4.3 Koopman's Orbital Theorem with Hartree-Fock Picture

Now one will make the essential difference between (Putz, 2013):

- the entire orbital spectrum available to a many-body systems, which include *occupied orbitals* + *unoccupied orbitals (up to infinity)*, denoted by $|\psi_i\rangle_{i=1,\dots,N \rightarrow \infty}$ which generates the Hartree-Fock energy
- the occupied orbitals on the many-body system, which will determine the total energy of the system, denoted by $|\psi_a\rangle_{i=1,\dots,N}$

All together, we can deal with the first lowest N spin-orbitals occupied in the overall wave-function $|\Psi_0^{(N)}\rangle = |\psi_1 \dots \psi_a \dots \psi_N\rangle$, while the rest (from N up to infinity) virtual or unoccupied orbitals, formally denoted as ψ_r, ψ_s, \dots (see Figure 4.3)

The conceptual difference consist in the fact that when dealing with infinite number of orbitals one does not avoid the double counting since there will be always available virtual orbitals to be occupied since the infinite cardinal of this set of orbitals; so we have with the actual subtle (mixed) notations:

$$\begin{aligned} \varepsilon_{i=1,\dots,\infty}^{HF} &= \langle \psi_i | \hat{f} | \psi_i \rangle \\ &= \langle \psi_i | \left(\hat{h} + \sum_{b=1}^N \left[\hat{J}_b - \hat{K}_b \right] \right) | \psi_i \rangle \end{aligned}$$

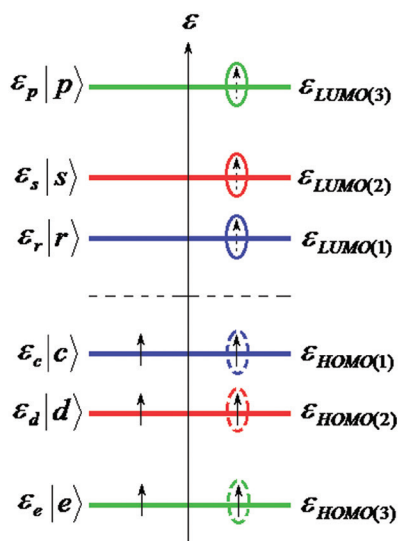


FIGURE 4.3 The paradigmatic *in silico* spectra of the first three highest occupied and lowest unoccupied molecular orbitals HOMOs and LUMOs illustrating the respective, successive, ionization and affinities energies as provided by Koopmans' theorem. Note KT implies ionization and affinity of one electron on successive levels and not of successive electrons on levels- see the marked occupied and virtual spin-orbitals (Putz, 2013).

$$\begin{aligned}
 &= \langle \psi_i | \hat{h} | \psi_i \rangle + \sum_{b=1}^N \left[\langle \psi_i | \hat{J}_b | \psi_i \rangle - \langle \psi_i | \hat{K}_b | \psi_i \rangle \right] \\
 &\equiv \langle i | \hat{h} | i \rangle + \sum_{b=1}^N \left[\langle ii | bb \rangle - \langle ib | bi \rangle \right] \\
 &\equiv \langle i | \hat{h} | i \rangle + \sum_{b=1}^N \langle ib | ib \rangle
 \end{aligned} \tag{4.338}$$

Here one remarks that the Coulombic inter-electronic

$$J_b(1) = \int d^2\psi_b^*(2) r_{12}^{-1} \psi_b(2) \tag{4.339}$$

and exchange terms

$$K_b(1) = \int d^2\psi_b^*(2) r_{12}^{-1} \psi_b(1) = \int d^2\psi_b^*(2) r_{12}^{-1} \phi_{12} \psi_b(2) \tag{4.340}$$

were remained with occupied orbitals' notation since they are readily computed among existing electrons.

Interesting, when the orbital energy (4.338) is summed just over occupied Hartree-Fock orbitals, as done in Eq. (4.331), now we equivalently obtain, yet under new notation revealing the restraint to the occupied orbitals

$$\sum_{a=1}^N \varepsilon_a = \sum_{a=1}^N \langle a | \hat{h} | a \rangle + \sum_{a=1, b=1}^N \langle ab | ab \rangle \quad (4.341)$$

Instead, when searched for total energy of the system one should avoid double counting and deal with occupied only orbitals to successively get within the actual notations

$$\begin{aligned} E_N &= \langle \Psi_0^{(N)} | \hat{H} | \Psi_0^{(N)} \rangle \\ &= \sum_{a=1}^N \langle \psi_a | \left(\hat{h} + \sum_{b=1}^N [\hat{J}_b - \hat{K}_b] \right) | \psi_a \rangle \\ &= \sum_{a=1}^N \langle \psi_a | \hat{h} | \psi_a \rangle + \frac{1}{2} \sum_{a=1, b=1}^N \left[\langle \psi_a | \int d2 \psi_b^*(2) r_{12}^{-1} \psi_b(2) | \psi_a \rangle \right. \\ &\quad \left. - \langle \psi_a | \int d2 \psi_b^*(2) r_{12}^{-1} \rho_{12} \psi_b(2) | \psi_a \rangle \right] \\ &= \sum_{a=1}^N \langle \psi_a | \hat{h} | \psi_a \rangle + \frac{1}{2} \sum_{a=1, b=1}^N \left[\int d1 d2 \psi_a^*(1) \psi_b^*(2) r_{12}^{-1} \psi_b(2) \psi_a(1) \right. \\ &\quad \left. - \int d1 d2 \psi_a^*(1) \psi_b^*(2) r_{12}^{-1} \rho_{12} \psi_b(2) \psi_a(1) \right] \\ &= \sum_{a=1}^N \langle \psi_a | \hat{h} | \psi_a \rangle + \frac{1}{2} \sum_{a=1, b=1}^N \left[\int d1 d2 \psi_a^*(1) \psi_b^*(2) r_{12}^{-1} \psi_b(2) \psi_a(1) \right. \\ &\quad \left. - \int d1 d2 \psi_a^*(1) \psi_b^*(2) r_{12}^{-1} \psi_b(1) \psi_a(2) \right] \\ &= \sum_{a=1}^N \langle \psi_a | \hat{h} | \psi_a \rangle + \frac{1}{2} \sum_{a=1, b=1}^N \left[\int d1 d2 \psi_a^*(1) \psi_a(1) r_{12}^{-1} \psi_b^*(2) \psi_b(2) \right. \\ &\quad \left. - \int d1 d2 \psi_a^*(1) \psi_b(1) r_{12}^{-1} \psi_b^*(2) \psi_a(2) \right] \\ &\equiv \sum_{a=1}^N \langle \psi_a | \hat{h} | \psi_a \rangle + \frac{1}{2} \sum_{a=1, b=1}^N [\langle aa | bb \rangle - \langle ab | ba \rangle] \\ &\equiv \sum_{a=1}^N \langle a | \hat{h} | a \rangle + \frac{1}{2} \sum_{a=1, b=1}^N \langle ab | ab \rangle \end{aligned} \quad (4.342)$$

In obvious difference respecting Eq. (4.341), as already anticipated from the Eqs. (4.330) & (4.331).

Eq. (4.341) does not exactly recovering the above total energy of the N -occupied spin-orbitals Eq. (4.342), when they were considered “free (not depending)” of computation (basis set); however, this may be considered as *in silico* manifestation of quantum “observability” (once a basis set representation applies) which destroys the quantum system in itself’s (or eigen) manifestation. Here the mathematical properties of eigen-function computed upon a given basis on Hilbert-Banach spaces determine the “shift” or the “unrealistic” energies of orbitals since spanning those occupied and unoccupied alike; from the present dichotomy basically follows all critics on the Hartree-Fock formalism and of allied molecular orbital theory, Koopmans’ “theorem” included (see below); instead, there seems that such departure of the computed from the exact energy orbitals is inherent to quantum formalism and not necessary a weakness of the Hartree-formalism itself, since it will appear to any quantum many-particle problem involving eigen-problems.

Now, returning to the above occupied and unoccupied orbital energy, one may assume (*Koopmans’ ansatz*) that, on the frontier levels of a many-electronic system, extracting or adding of an electron (or even few of them, but lesser than the total number of valence electrons) will not affect the remaining (or $N \pm 1, N \pm 1 \pm 1', \dots$ electronic orbitals) states, on successive levels and not successive electrons on levels (see Figure 4.3).

This approach allows simplifying of the common terms and emphasizing only on the involving frontier orbitals participating in chemical reactivity. Accordingly, for the first ionization potential one successively obtains the first highest occupied molecular orbital (HOMO), see Figure 4.3:

$$\begin{aligned} IP_1 &= E_{N-1} - E_N \\ &= \langle \Psi_c^{(N-1)} | \widehat{H} | \Psi_c^{(N-1)} \rangle - \langle \Psi_0^{(N)} | \widehat{H} | \Psi_0^{(N)} \rangle \\ &= \left\{ \sum_{\substack{a=1 \\ a \neq c}}^N \langle a | \widehat{h} | a \rangle + \frac{1}{2} \sum_{\substack{a=1, b=1 \\ a \neq c, b \neq c}}^N \langle ab | ab \rangle \right\} \end{aligned}$$

$$\begin{aligned}
& - \left[\sum_{\substack{a=1 \\ a \neq c}}^N \langle a | \hat{h} | a \rangle + \langle c | \hat{h} | c \rangle \right] + \frac{1}{2} \left[\sum_{\substack{a=1, b=1 \\ a \neq c, b \neq c}}^N \langle ab | ab \rangle + \sum_{\substack{a=1, b=1 \\ a \neq c, b=c}}^N \langle ac | ac \rangle \right. \\
& \left. + \sum_{\substack{a=1, b=1 \\ a=c, b \neq c}}^N \langle cb | cb \rangle \right] \\
& = -\langle c | \hat{h} | c \rangle - \sum_{b=1}^N \langle cb | cb \rangle \\
& = -\mathcal{E}_c \\
& = -\mathcal{E}_{HOMO(1)} \tag{4.343}
\end{aligned}$$

Remarkable, in this analytics, one starts with *in se* quantum expression of total energies of the N and $(N-1)$ systems and ends up with a result characteristic to the computational (shifted) realm since recovering the orbital energy of the *in silico* state from which the electron was removed. Yet, one may ask how such *in se-to-in silico* quantum chemical passage is possible; the answer is naturally positive since the above derivation associates with the ionization process which is basically an observer intervention to the genuine quantum system, from where the final result will reflect the energetic deviation from *in se-to-in silico* as an irrefutable quantum manifestation of electronic system.

Similarly, for electronic affinity, one will act on the *in se* quantum system to add an electron at the frontier level and, under the “frozen spin-orbitals” physical-chemical assumption, one gets the energetic turn from the genuine HF expression to the *in silico* orbital energy on which the “action” was undertaken towards the first lowest occupied molecular orbital (LUMO), see Figure 4.3:

$$\begin{aligned}
EA_1 & = E_N - E_{N+1} \\
& = -\langle r | \hat{h} | r \rangle - \sum_{b=1}^N \langle rb | rb \rangle \\
& = -\mathcal{E}_r \\
& = -\mathcal{E}_{LUMO(1)} \tag{4.344}
\end{aligned}$$

These results are usually considered as defining the popular Koopmans theorem, used for estimating the observable quantities as ionization

potential and electronic affinity in terms of “artefactual” computed orbital energies (first approximation) and in the spin-orbitalic frozen framework during the electronic extraction or addition (the second approximation).

However one may ask whether this approximation is valid and in which conditions. This can be achieved by reconsidering the above Koopmans first order IP and EA to the superior differences within Hartree-Fock framework; as such, for the second order of ionization potential one gets the second highest occupied molecular orbital ($HOMO_2$), see Figure 4.3:

$$\begin{aligned}
 IP_2 &= E_{N-2} - E_{N-1} \\
 &= \left\{ \begin{array}{l} \sum_{\substack{a=1 \\ a \neq c \\ a \neq d}}^N \langle a | \hat{h} | a \rangle \\ + \frac{1}{2} \sum_{\substack{a=1, b=1 \\ a \neq c, b \neq c \\ a \neq d, b \neq d}}^N \langle ab | ab \rangle \end{array} \right\} - \left\{ \begin{array}{l} \sum_{\substack{a=1 \\ a \neq c}}^N \langle a | \hat{h} | a \rangle \\ + \frac{1}{2} \sum_{\substack{a=1, b=1 \\ a \neq c, b \neq c}}^N \langle ab | ab \rangle \end{array} \right\} \\
 &= \left\{ \begin{array}{l} \sum_{\substack{a=1 \\ a \neq c \\ a \neq d}}^N \langle a | \hat{h} | a \rangle + \frac{1}{2} \sum_{\substack{a=1, b=1 \\ a \neq c, b \neq c \\ a \neq d, b \neq d}}^N \langle ab | ab \rangle \end{array} \right\} \\
 &\quad - \left\{ \begin{array}{l} \sum_{\substack{a=1 \\ a \neq c \\ a \neq d}}^N \langle a | \hat{h} | a \rangle + \langle d | \hat{h} | d \rangle + \frac{1}{2} \sum_{\substack{a=1, b=1 \\ a \neq c, b \neq c \\ a \neq d, b \neq d}}^N \langle ab | ab \rangle \\ + \frac{1}{2} \sum_{\substack{a=1, b=1 \\ a \neq c, b \neq c \\ a=d, b \neq d}}^N \langle db | db \rangle + \frac{1}{2} \sum_{\substack{a=1, b=1 \\ a \neq c, b \neq c \\ a \neq d, b=d}}^N \langle ad | ad \rangle \end{array} \right\} \\
 &= -\langle d | \hat{h} | d \rangle - \sum_{\substack{a=1, b=1 \\ b \neq d}}^N \langle db | db \rangle \\
 &= -\mathcal{E}_d \\
 &= -\mathcal{E}_{HOMO(2)} \tag{4.345}
 \end{aligned}$$

Note that this derivation eventually employs the equivalency for the Coulombic and exchange terms for orbitals of the same nature (with missing the same number of spin-orbitals, see Figure 4.3). However, in the case

this will be further refined to isolate the first two orders of highest occupied molecular orbitals, the last expression will be corrected with HOMO₁/HOMO₂ (Coulombic and exchange) interaction to successively become

$$\begin{aligned}
 IP_2 &= E_{N-2} - E_{N-1} \\
 &= -\langle d | \hat{h} | d \rangle - \left\{ \begin{aligned} &\frac{1}{2} \sum_{\substack{a=1, b=1 \\ a \neq c, \\ a=d, b \neq d}}^N \langle db | db \rangle + \frac{1}{2} \langle dc | dc \rangle \\ &+ \frac{1}{2} \sum_{\substack{a=1, b=1 \\ b \neq c, \\ a \neq d, b=d}}^N \langle ad | ad \rangle + \frac{1}{2} \langle cd | cd \rangle \end{aligned} \right\} \\
 &= -\langle d | \hat{h} | d \rangle - \sum_{\substack{a=1, b=1 \\ b \neq d}}^N \langle db | db \rangle + \langle cd | cd \rangle \\
 &= -\varepsilon_d + \langle cd | cd \rangle \\
 &= -\varepsilon_{HOMO(2)} + \langle HOMO_1 HOMO_2 | HOMO_1 HOMO_2 \rangle \quad (4.346)
 \end{aligned}$$

However, reloading this procedure for electronic affinity process too, one gets

$$\begin{aligned}
 EA_2 &= E_{N+1} - E_{N+2} \\
 &= -\varepsilon_{LUMO(2)} + \langle LUMO_1 LUMO_2 | LUMO_1 LUMO_2 \rangle \quad (4.347)
 \end{aligned}$$

When combining Eq. (4.347) with its IP counterpart (4.346) there appears that the simple Koopmans' orbitals energy difference is corrected by the HOMO₁/HOMO₂ vs. LUMO₁/LUMO₂

$$\begin{aligned}
 IP_2 - EA_2 &= \varepsilon_{LUMO(2)} - \varepsilon_{HOMO(2)} \\
 &\quad + \left(\langle HOMO_1 HOMO_2 | HOMO_1 HOMO_2 \rangle \right) \\
 &\quad - \left(\langle LUMO_1 LUMO_2 | LUMO_1 LUMO_2 \rangle \right) \quad (4.348)
 \end{aligned}$$

This expression is usually reduced to the superior order LUMO-HOMO difference

$$IP_2 - EA_2 \cong \varepsilon_{LUMO(2)} - \varepsilon_{HOMO(2)} \quad (4.349)$$

due to the energetic spectra symmetry of Figure 4.3 relating on the bonding vs. anti-bonding displacements of orbitals, specific to molecular orbital theory. Therefore, with the premise that molecular orbital theory itself is correct, or at least a reliable quantum undulatory modeling of multi-electronic systems moving in a nuclei potential, the above IP-EA differences in terms of Koopmans' *in silico* LUMO-HOMO energetic gaps holds also for superior orders.

4.5.4.4 Chemical Reactivity Indices in Orbital Energy Representation

Koopmans' theorem entered on the quantum chemistry as a versatile tool for estimating the ionization potentials for closed-shells systems, and it was widely confirmed for organic molecular systems, due to the inner usually separation between sigma (core) and pi (valence) sub-electronic systems, allowing to treat the "frozen spin-orbitals" as orbitals not essentially depending on the number of electrons in the valence shells, when some of them are extracted (via ionization) or added (via negative attachments); this approximation ultimately works for Hartree-Fock systems when electronic correlation may be negligible or cancels with the orbital relaxations during ionization or affinity processes, respectively; naturally, it works less when correlation is explicitly counted, as in Density Functional Theory, where instead the exchange energies are approximated or merely parameterized so that "loosing" somehow on the genuine spin-orbital nature of the mono-determinantal approach of the Hartree-Fock, with a natural energetic hierarchy included.

Beside the many concepts in modeling the chemical reactivity and interaction electronegativity and chemical hardness are by far the most versatile measures, to be detailed in the next volumes of this set, since their direct connection with total, valence or orbital energies of atoms and molecules via the first and the second derivative of such energies with respecting the available or concerned electrons therein. Actually, such derivatives, may use the molecular frontier orbitals when based on differential expansion of the energy around its isolated value to account both for the electrophilic (electrons accepting) and nucleophilic (electrons donating) states.

Starting from the general mathematical framework, given the values of a function $f(n)$ on a set of nodes $\{\dots, n-3, n-2, n-1, n, n+1, n+2, n+3, \dots\}$ the finite difference approximations of the first f'_n and second f''_n derivatives in the node n , will spectrally depend on the all the nodal values. However, the compact finite differences, or Padé, schemes that mimic this global dependence write as (Lele, 1992):

$$\begin{aligned} & \beta_1 f'_{n-2} + \alpha_1 f'_{n-1} + f'_n + \alpha_1 f'_{n+1} + \beta_1 f'_{n+2} \\ &= c_1 \frac{f_{n+3} - f_{n-3}}{6} + b_1 \frac{f_{n+2} - f_{n-2}}{4} + a_1 \frac{f_{n+1} - f_{n-1}}{2} \end{aligned} \quad (4.350)$$

$$\begin{aligned} & \beta_2 f''_{n-2} + \alpha_2 f''_{n-1} + f''_n + \alpha_2 f''_{n+1} + \beta_2 f''_{n+2} \\ &= c_2 \frac{f_{n+3} - 2f_n + f_{n-3}}{9} + b_2 \frac{f_{n+2} - 2f_n + f_{n-2}}{4} \\ &+ a_2 (f_{n+1} - 2f_n + f_{n-1}) \end{aligned} \quad (4.351)$$

The involved sets of coefficients, $\{a_1, b_1, c_1, \alpha_1, \beta_1\}$ and $\{a_2, b_2, c_2, \alpha_2, \beta_2\}$ are derived by matching Taylor series coefficients of various orders. This way, their particularizations can be reached as the second (2C)-, fourth (4C)- and sixth (6C)-order central differences; standard Pade (SP) schemes; sixth (6T)- and eight (8T)-order tridiagonal schemes; eighth (8P)- and tenth (10P)- order pentadiagonal schemes up to spectral-like resolution (SLR) ones, see Table 4.1.

Assuming that the function $f(n)$ is the total energy $E(N)$ in the actual node that corresponds to the number of electrons, the compact finite difference, the derivatives of Eqs. (4.350) and (4.351) may be accurately evaluated through considering the states with $N-3$, $N-2$, $N-1$, $N+1$, $N+2$, $N+3$ electrons, whereas the derivatives in the neighbor states will be taken only as their most neighboring dependency. This way, the working formulas for electronegativity will be (Putz, 2010a):

$$\begin{aligned} -\chi &= \left. \frac{\partial E}{\partial N} \right|_{|N\rangle} \\ &\cong a_1 \frac{E_{N+1} - E_{N-1}}{2} + b_1 \frac{E_{N+2} - E_{N-2}}{4} + c_1 \frac{E_{N+3} - E_{N-3}}{6} \end{aligned}$$

TABLE 4.1 Numerical Parameters for the Compact Finite Second (2C)-, Fourth (4C)- and Sixth (6C)-Order Central Differences; Standard Padé (SP) Schemes; Sixth (6T)- and Eight (8T)-Order Tridiagonal Schemes; Eighth (8P)- and Tenth (10P)-Order Pentadiagonal Schemes up to Spectral-Like Resolution (SLR) Schemes Unfolding the Numerical Derivatives (4.350) and (4.350) Then Used for the Electronegativity and Chemical Hardness of Eqs. (4.352) and (4.353) and the Subsequent of Their Respective Formulations: Eqs. (4.362) and (4.363); (4.368) and (4.369)

Scheme	Electronegativity					Chemical Hardness				
	a_1	b_1	c_1	α_1	β_1	a_2	b_2	c_2	α_2	β_2
2C	1	0	0	0	0	1	0	0	0	0
4C	$\frac{4}{3}$	$-\frac{1}{3}$	0	0	0	$\frac{4}{3}$	$-\frac{1}{3}$	0	0	0
6C	$\frac{3}{2}$	$-\frac{3}{5}$	$\frac{1}{10}$	0	0	$\frac{12}{11}$	$\frac{3}{11}$	0	$\frac{2}{11}$	0
SP	$\frac{5}{3}$	$\frac{1}{3}$	0	$\frac{1}{2}$	0	$\frac{6}{5}$	0	0	$\frac{1}{10}$	0
6T	$\frac{14}{9}$	$\frac{1}{9}$	0	$\frac{1}{3}$	0	$\frac{3}{2}$	$-\frac{3}{5}$	$\frac{1}{5}$	0	0
8T	$\frac{19}{12}$	$\frac{1}{6}$	0	$\frac{3}{8}$	0	$\frac{147}{152}$	$\frac{51}{95}$	$-\frac{23}{760}$	$\frac{9}{38}$	0
8P	$\frac{40}{27}$	$\frac{25}{54}$	0	$\frac{4}{9}$	$\frac{1}{36}$	$\frac{320}{393}$	$\frac{310}{393}$	0	$\frac{344}{1179}$	$\frac{23}{2358}$
10P	$\frac{17}{12}$	$\frac{101}{150}$	$\frac{1}{100}$	$\frac{1}{2}$	$\frac{1}{20}$	$\frac{1065}{1798}$	$\frac{1038}{899}$	$\frac{79}{1798}$	$\frac{334}{899}$	$\frac{43}{1798}$
SLR	1.303	0.994	0.038	0.577	0.09	0.216	1.723	0.177	0.502	0.056

Adapted from Rubin & Khosla (1977), Putz (2010a, 2011), and Putz et al. (2004).

$$\begin{aligned}
 & -\alpha_1 \left(\frac{\partial E}{\partial N} \Big|_{|N-1)} + \frac{\partial E}{\partial N} \Big|_{|N+1)} \right) - \beta_1 \left(\frac{\partial E}{\partial N} \Big|_{|N-2)} + \frac{\partial E}{\partial N} \Big|_{|N+2)} \right) \\
 & = a_1 \frac{E_{N+1} - E_{N-1}}{2} + b_1 \frac{E_{N+2} - E_{N-2}}{4} + c_1 \frac{E_{N+3} - E_{N-3}}{6} \\
 & -\alpha_1 \left(a_1 \frac{E_N - E_{N-2}}{2} + a_1 \frac{E_{N+2} - E_N}{2} \right) - \beta_1 \left(a_1 \frac{E_{N-1} - E_{N-3}}{2} + a_1 \frac{E_{N+3} - E_{N+1}}{2} \right)
 \end{aligned}$$

$$\begin{aligned}
&= a_1(1 + \beta_1) \frac{E_{N+1} - E_{N-1}}{2} + (b_1 - 2a_1\alpha_1) \frac{E_{N+2} - E_{N-2}}{4} \\
&\quad + (c_1 - 3a_1\beta_1) \frac{E_{N+3} - E_{N-3}}{6} \tag{4.352}
\end{aligned}$$

and respectively for the chemical hardness as (Putz, 2011; Putz, 2010a; Putz et al., 2004):

$$\begin{aligned}
2\eta &= \frac{\partial^2 E}{\partial N^2} \Big|_{|N\rangle} \\
&\cong 2a_2 \frac{E_{N+1} - 2E_N + E_{N-1}}{2} + b_2 \frac{E_{N+2} - 2E_N + E_{N-2}}{4} \\
&\quad + c_2 \frac{E_{N+3} - 2E_N + E_{N-3}}{9} \\
&\quad - \alpha_2 \left(\frac{\partial^2 E}{\partial N^2} \Big|_{|N-1\rangle} + \frac{\partial^2 E}{\partial N^2} \Big|_{|N+1\rangle} \right) - \beta_2 \left(\frac{\partial^2 E}{\partial N^2} \Big|_{|N-2\rangle} + \frac{\partial^2 E}{\partial N^2} \Big|_{|N+2\rangle} \right) \\
&= 2a_2 \frac{E_{N+1} - 2E_N + E_{N-1}}{2} + b_2 \frac{E_{N+2} - 2E_N + E_{N-2}}{4} \\
&\quad + c_2 \frac{E_{N+3} - 2E_N + E_{N-3}}{9} \\
&\quad - \alpha_2 \left(2a_2 \frac{E_N - 2E_{N-1} + E_{N-2}}{2} + 2a_2 \frac{E_{N+2} - 2E_{N+1} + E_N}{2} \right) \\
&\quad - \beta_2 \left(2a_2 \frac{E_{N-1} - 2E_{N-2} + E_{N-3}}{2} + 2a_2 \frac{E_{N+3} - 2E_{N+2} + E_{N+1}}{2} \right) \\
&= 2a_2(1 + 2\alpha_2 - \beta_2) \frac{E_{N+1} + E_{N-1}}{2} + (8a_2\beta_2 + b_2 - 4a_2\alpha_2) \frac{E_{N+2} + E_{N-2}}{4} \\
&\quad + (c_2 - 9a_2\beta_2) \frac{E_{N+3} + E_{N-3}}{9} - \left(2a_2 + \frac{1}{2}b_2 + \frac{2}{9}c_2 + 2a_2\alpha_2 \right) E_N \tag{4.353}
\end{aligned}$$

where the involved parameters discriminate between various schemes of computations and the spectral-like resolution (SLR), see Table 4.1 (Rubin & Khosla, 1977; Putz, 2011; Putz, 2010a; Putz et al., 2004).

Next, the Eqs. (4.352) and (4.353) may be rewritten in terms of the observational quantities, as the ionization energy and electronic affinity are with the aid of their basic definitions from the involved eigen-energies of i -th ($i=1,2,3$) order

$$I_i = E_{N-i} - E_{N-i+1} \quad (4.354)$$

$$A_i = E_{N+i-1} - E_{N+i} \quad (4.355)$$

As such they allow the energetic equivalents for the differences

$$E_{N+1} - E_{N-1} = -(I_1 + A_1) \quad (4.356)$$

$$E_{N+2} - E_{N-2} = -(I_1 + A_1) - (I_2 + A_2) \quad (4.357)$$

$$E_{N+3} - E_{N-3} = -(I_1 + A_1) - (I_2 + A_2) - (I_3 + A_3) \quad (4.358)$$

and for the respective sums (Putz, 2011; Putz, 2010a; Putz et al., 2004)

$$E_{N+1} + E_{N-1} = (I_1 - A_1) + 2E_N \quad (4.359)$$

$$E_{N+2} + E_{N-2} = (I_1 - A_1) + (I_2 - A_2) + 2E_N \quad (4.360)$$

$$E_{N+3} + E_{N-3} = (I_1 - A_1) + (I_2 - A_2) + (I_3 - A_3) + 2E_N \quad (4.361)$$

being then implemented to provide the associate “spectral” molecular analytical forms of electronegativity

$$\begin{aligned} \chi_{CFD} = & \left[a_1(1 - \alpha_1) + \frac{1}{2}b_1 + \frac{1}{3}c_1 \right] \frac{I_1 + A_1}{2} \\ & + \left[b_1 + \frac{2}{3}c_1 - 2a_1(\alpha_1 + \beta_1) \right] \frac{I_2 + A_2}{4} \\ & + (c_1 - 3a_1\beta_1) \frac{I_3 + A_3}{6} \end{aligned} \quad (4.362)$$

and for chemical hardness (Putz, 2011; Putz, 2010a; Putz et al., 2004):

$$\begin{aligned} \eta_{CFD} = & \left[a_2(1 - \alpha_2 + 2\beta_2) + \frac{1}{4}b_2 + \frac{1}{9}c_2 \right] \frac{I_1 - A_1}{2} \\ & + \left[\frac{1}{2}b_2 + \frac{2}{9}c_2 + 2a_2(\beta_2 - \alpha_2) \right] \frac{I_2 - A_2}{4} \\ & + \left[\frac{1}{3}c_2 - 3a_2\beta_2 \right] \frac{I_3 - A_3}{6} \end{aligned} \quad (4.363)$$

It is worth remarking that when particularizing these formulas for the fashioned two-point central finite difference, i.e., when having $a_1=1, b_1=c_1=\alpha_1=\beta_1=0$ and $a_2=1, b_2=c_2=\alpha_2=\beta_2=0$ of Table 4.1, one recovers the consecrated Mulliken (spectral) electronegativity (Mulliken, 1934)

$$\chi_{2C} = \frac{I_1 + A_1}{2} \quad (4.364)$$

and the chemical hardness basic form relating with the celebrated Pearson nucleophilic-electrophilic reactivity gap (Parr & Yang, 1989; Pearson, 1997)

$$\eta_{2C} = \frac{I_1 - A_1}{2} \quad (4.365)$$

already used as measuring the aromaticity through the molecular stability against the reaction propensity (Ciesielski et al., 2009; Chattaraj et al., 2007).

Finally, for computational purposes, Eqs. (4.362) and (4.363) may be once more reconsidered within the Koopmans' frozen core approximation (Koopmans, 1934), in which various orders of ionization potentials and electronic affinities are replaced by the corresponding frontier energies

$$I_i = -\varepsilon_{HOMO(i)} \quad (4.366)$$

$$A_i = -\varepsilon_{LUMO(i)} \quad (4.367)$$

so that the actual working compact finite difference (CFD) orbital molecular electronegativity unfolds as (Putz, 2011; Putz, 2010a; Putz et al., 2004):

$$\begin{aligned} \chi_{CFD} = & - \left[a_1(1 - \alpha_1) + \frac{1}{2}b_1 + \frac{1}{3}c_1 \right] \frac{\varepsilon_{HOMO(1)} + \varepsilon_{LUMO(1)}}{2} \\ & - \left[b_1 + \frac{2}{3}c_1 - 2a_1(\alpha_1 + \beta_1) \right] \frac{\varepsilon_{HOMO(2)} + \varepsilon_{LUMO(2)}}{4} \\ & - (c_1 - 3a_1\beta_1) \frac{\varepsilon_{HOMO(3)} + \varepsilon_{LUMO(3)}}{6} \end{aligned} \quad (4.368)$$

along with the respective chemical hardness formulation

$$\begin{aligned} \eta_{CFD} = & \left[a_2(1 - \alpha_2 + 2\beta_2) + \frac{1}{4}b_2 + \frac{1}{9}c_2 \right] \frac{\varepsilon_{LUMO(1)} - \varepsilon_{HOMO(1)}}{2} \\ & + \left[\frac{1}{2}b_2 + \frac{2}{9}c_2 + 2a_2(\beta_2 - \alpha_2) \right] \frac{\varepsilon_{LUMO(2)} - \varepsilon_{HOMO(2)}}{4} \\ & + \left[\frac{1}{3}c_2 - 3a_2\beta_2 \right] \frac{\varepsilon_{LUMO(3)} - \varepsilon_{HOMO(3)}}{6} \end{aligned} \quad (4.369)$$

Note that the actual CFD electronegativity and chemical hardness expressions do not distinguish for the atoms-in-molecule contributions, while providing post-bonding information and values, i.e., for characterizing the already stabilized/optimized molecular structure towards its further reactive engagements. The difference between the atoms-in-molecule pre-bonding stage and the molecular post-bonding one constitutes the basis of the actual absolute aromaticity as will be elsewhere introduced (see Volume III/Chapter 4 of the present five-volume set).

An illustrative analysis for homologues organic aromatic hydrocarbons regarding how much the second, respectively the third order of the IP-EA or LUMO-HOMO gaps affect the chemical hardness hierarchies, and therefore their ordering aromaticity, will be in the next section exposed and discussed.

4.5.4.5 Testing Koopmans Theorem by Chemical Harness Reactivity Index

It is true Koopmans theorem seems having some limitation for small molecules and for some inorganic complexes (Duke & O'Leary, 1995; Angeli, 1998).

However, one is interested here for testing the Koopmans' superior orders' HOMO-LUMO behavior on the systems that work, such as the aromatic hydrocarbons. Accordingly, in Table 4.2 a short series of paradigmatic organics are considered, with one and two rings and various basic ring substitutions or additions, respectively (Putz, 2010b). For them, the HOMO and LUMO are computed, within semi-empirical AM1 framework (Hypercube, 2002), till the third order of Koopmans frozen spin-orbitals' approximation; they are then combined into the various finite difference forms (from 2C to SLR) of chemical hardness as above, see Table 4.1, grouped also in sequential order respecting chemical hardness gap contributions (i.e., separately for {LUMO1-HOMO1}, {LUMO1-HOMO1, LUMO2-HOMO2}, {LUMO1-HOMO1, LUMO2-HOMO2, LUMO3-HOMO3}): the results are systematically presented in Tables 4.3–4.5.

The results of Tables 4.3-4.5 reveals very interesting features, in the light of considering the aromaticity as being reliably measured by chemical hardness alone, sine both associate with chemical resistance to reactivity or the terminus of a chemical reaction according with the maximum chemical hardness principle (Chattaraj et al., 1991,1995).

Moreover, the benchmark ordering hierarchy was chosen as produced by Hückel theory (since being an approximate approach for quantum chemical modeling of chemical bonding is let to be exposed in the Volume III of this work (Putz, 2016a), dedicated to quantum molecule and chemical reactivity) and approximation since closely related with pi-electrons delocalized at the ring level as the main source of the experimentally recorded aromaticity of organic compounds under study (Putz et al., 2010).

Note that although computational method used here is of low level it nevertheless responds to present desiderate having an non (orbitalic) basis dependent computational output and discussion, whereas further (Hartree-Fock) ab initio, (Møller–Plesset) perturbation methods and basis set dependency considerations, as HF, MP2, and DFT, respectively, for instance, can be further considered for comparative analysis.

TABLE 4.2 Molecular Structures of Paradigmatic Aromatic Hydrocarbons (Putz, 2010b), Ordered Downwards According with Their Hückel First Order HOMO-LUMO Gap (Putz et al., 2010), along Their First Three Highest Occupied (HOMOs) and Lowest Unoccupied (LUMOs) (in electron-volts, eV) Computationally Recorded Levels Within Semi-Empirical AM1 Method (Hypercube, 2002)

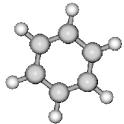
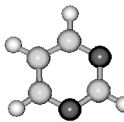
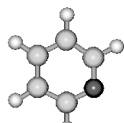
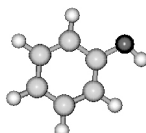
Formula Name CAS Index (mw[g/mol])	Molecular Structure	HOMO (1)	HOMO (2)	HOMO (3)	LUMO (1)	LUMO (2)	LUMO (3)
C ₆ H ₆ Benzene 71-43-2 I (78.11)		-9.652904	-9.653568	-11.887457	0.554835	0.555246	2.978299
C ₄ H ₄ N ₂ Pyrimidine 289-95-2 II (80.088)		-10.578436	-10.614932	-11.602985	-0.234993	-0.081421	2.543489
C ₅ H ₅ N Pyridine 110-86-1 III (79.10)		-9.932324	-10.642881	-10.716373	0.138705	0.278273	2.791518
C ₆ H ₆ O Phenol 108-95-2 IV (94.11)		-9.114937	-9.851116	-11.940266	0.397517	0.507986	2.839472

TABLE 4.2 Continued

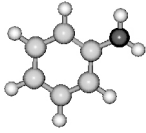
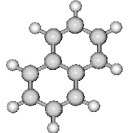
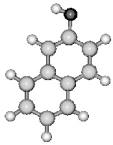
Formula Name CAS Index (mw[g/mol])	Molecular Structure	HOMO (1)	HOMO (2)	HOMO (3)	LUMO (1)	LUMO (2)	LUMO (3)
C ₆ H ₇ N Aniline 62-53-3 V (93.13)		-8.213677	-9.550989	-11.501620	0.758436	0.888921	2.828224
C ₁₀ H ₈ Naphthalene 91-20-3 VI (128.17)		-8.710653	-9.340973	-10.658237	-0.265649	0.180618	1.210350
C ₁₀ H ₈ O 2-Naphthol 135-19-3 VII (144.17)		-8.641139	-9.194596	-10.673578	-0.348490	0.141728	1.117961

TABLE 4.2 Continued

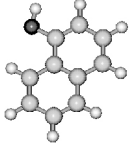
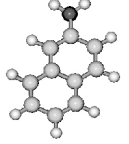
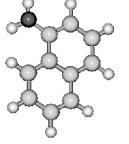
Formula Name CAS Index (mw[g/mol])	Molecular Structure	HOMO (1)	HOMO (2)	HOMO (3)	LUMO (1)	LUMO (2)	LUMO (3)
C ₁₀ H ₈ O 1-Naphthol 90-15-3 VIII (144.17)		-8.455599	-9.454717	-10.294406	-0.247171	0.100644	1.184179
C ₁₀ H ₉ N 2-Naphthalenamine 91-59-8 IX (143.19)		-8.230714	-8.984826	-10.346699	-0.177722	0.278785	1.298534
C ₁₀ H ₉ N 1-Naphthalenamine 134-32-7 X (143.19)		-8.109827	-9.343444	-9.940875	-0.176331	0.230424	1.235745

TABLE 4.3 Chemical Hardness Values (in eV) as Computed for Molecules of Table 4.2 with First LUMO(1)–HOMO(1) Gap Order of Eq. (4.326) with Parameters of Table 4.1 (Putz, 2013)

Molecule	η_{2C}	η_{4C}	η_{6C}	η_{SP}	η_{6T}	η_{8T}	η_{8P}	η_{10P}	η_{SLR}
I	5.10387	6.379837	4.903511	5.512179	7.003643	4.434762	4.030827	3.542746	2.971354
II	5.171722	6.464652	4.968699	5.585459	7.096751	4.493719	4.084414	3.589844	3.010856
III	5.035515	6.294393	4.837839	5.438356	6.909845	4.375368	3.976843	3.495299	2.931559
IV	4.756227	5.945284	4.569516	5.136725	6.5266	4.132695	3.756273	3.301437	2.768964
V	4.486057	5.607571	4.309951	4.844941	6.155866	3.897943	3.542904	3.113904	2.611677
VI	4.222502	5.278128	4.056743	4.560302	5.794211	3.66894	3.334759	2.930963	2.458242
VII	4.146325	5.182906	3.983556	4.47803	5.689679	3.60275	3.274597	2.878086	2.413893
VIII	4.104214	5.130268	3.943098	4.432551	5.631894	3.56616	3.24134	2.848856	2.389378
IX	4.026496	5.03312	3.868431	4.348616	5.525247	3.49863	3.179962	2.794909	2.344132
X	3.966748	4.958435	3.811029	4.284088	5.44326	3.446715	3.132775	2.753437	2.309348

TABLE 4.4 Chemical Hardness Values (in eV) as Computed for Molecules of Table 4.2 with First LUMO(1)–HOMO(1) and Second Order LUMO(2)–HOMO(2) Gaps of Eq. (4.326) with Parameters of Table 4.1 (Putz, 2013)

Molecule	η_{2C}	η_{4C}	η_{6C}	η_{SP}	η_{6T}	η_{8T}	η_{8P}	η_{10P}	η_{SLR}
I	5.10387	5.95447	4.239094	4.89965	6.351413	3.933493	3.865279	3.990091	4.778726
II	5.171722	6.025756	4.283151	4.953449	6.423777	3.976506	3.9136	4.051417	4.875712
III	5.035515	5.839345	4.127062	4.783086	6.212105	3.839122	3.799743	3.973858	4.865044
IV	4.756227	5.513655	3.895318	4.515179	5.864769	3.624046	3.588288	3.755367	4.602943
V	4.486057	5.172574	3.630494	4.218546	5.488872	3.385327	3.373608	3.571375	4.459963
VI	4.222502	4.881395	3.437052	3.989007	5.185887	3.201415	3.180355	3.348194	4.143948
VII	4.146325	4.793892	3.375923	3.917851	5.093191	3.144321	3.123197	3.287199	4.066799
VIII	4.104214	4.732127	3.32121	3.859229	5.021412	3.096976	3.086388	3.267567	4.081062
IX	4.026496	4.647136	3.265531	3.792799	4.933405	3.043772	3.029741	3.200836	3.984165
X	3.966748	4.559524	3.187936	3.709656	4.831596	2.976622	2.977523	3.172958	4.004309

TABLE 4.5 Chemical Hardness Values (in eV) as Computed for Molecules of Table 4.2 with First LUMO(1)–HOMO(1), Second LUMO(2)–HOMO(2) and Third Order LUMO(3)–HOMO(3) Gaps of Eq. (4.326) with Parameters of Table 4.1 (Putz, 2013)

Molecule	η_{2C}	η_{4C}	η_{6C}	η_{SP}	η_{6T}	η_{8T}	η_{8P}	η_{10P}	η_{SLR}
I	5.10387	5.95447	4.239094	4.89965	6.516588	3.908499	3.806245	3.921086	4.834997
II	5.171722	6.025756	4.283151	4.953449	6.58096	3.952722	3.857423	3.985751	4.929261
III	5.035515	5.839345	4.127062	4.783086	6.362192	3.816411	3.746102	3.911156	4.916176
IV	4.756227	5.513655	3.895318	4.515179	6.028988	3.599197	3.529596	3.686762	4.658889
V	4.486057	5.172574	3.630494	4.218546	5.648093	3.361234	3.316702	3.504858	4.514206
VI	4.222502	4.881395	3.437052	3.989007	5.31776	3.18146	3.133223	3.293101	4.188874
VII	4.146325	4.793892	3.375923	3.917851	5.224208	3.124496	3.076372	3.232464	4.111434
VIII	4.104214	4.732127	3.32121	3.859229	5.148952	3.077677	3.040805	3.214284	4.124512
IX	4.026496	4.647136	3.265531	3.792799	5.062797	3.024193	2.983496	3.14678	4.028246
X	3.966748	4.559524	3.187936	3.709656	4.955781	2.957831	2.933139	3.121078	4.046616

In these conditions, the main Koopmans' analysis of chemical hardness or aromaticity behavior for the envisaged molecules leaves with relevant observations:

- In absolutely all cases, analytical or computational, the first two molecules, Benzene (I) and Pyrimidine (II) are inverted for their chemical hardness/aromaticity hierarchies respecting the benchmarking Hückel one, meaning that even in the most simple case, say $2C/\{LUMO1-HOMO1\}$, double substitution of carbon with nitrogen increases the ring stability, most probably due to the additional pairing of electrons entering the pi-system as coming from the free valence of N atoms (equivalently with N pi-valence electrons) in molecular ring. This additional pair of electrons eventually affects by shielding also the core of the hydrocarbon rings, i.e., the sigma-system of Pyrimidine (II), in a specific quantum way, not clearly accounted by the Hückel theory.
- The same behavior is recorded also for the couple of molecules I and III (Pyridine), however, only for the SLR of chemical hardness computed with second and the third orders of Koopmans frozen spin-orbitals; this suggest the necessary insight the spectral like resolution analysis may provide respecting the other forms of finite compact differences in chemical hardness computation – yet only when it is combined with higher Koopmans HOMO and LUMO orbitals.
- In the same line of discussion, only for the second and the third Koopmans order and only for the SLR chemical hardness development, i.e., the last columns of Tables 4.4 and 4.5, one record similar reserve order of the molecules 2-Naphtol (VII) and 1-Naphtol (VIII), with the more aromatic character for the last case when having the OH group more closely to the middy of the naphthalene structure; it is explained as previously, due to the electronic pair of chemical bonding contribution more close to the “core” of the system with direct influence to increase the shielding electrons of the sigma systems, while leading with smoothly increased stabilization contribution (enlarging also the sigma-pi chemical gap); yet this is manifested when all the spectral like resolution complexity is considered in chemical hardness expression and only in superior Koopmans orders (second and third), otherwise not being recorded.

However, this result advocates the meaningful of considering of the SLR coupled with superior Koopmans analysis in revealing subtle effects in sigma-pi aromatic systems.

- In the rest of cases the Hückel downward hierarchy of Table 4.2 is recovered in Tables 4.3–4.5 in a systematic way.
- When going from 2C to SLR chemical hardness analytical forms of any of Koopmans orders, on the horizontal axis through the Tables 4.3–4.5, one systematically record an increasing of the average chemical hardness/aromaticity values from 2C to 6T schemes of computations while going again down towards SLR scheme of Table 4.1.

All in all, one may compare the extreme 2C and SLR outputs of Tables 4.3–4.5 for a global view for the Koopmans' behavior respecting various orders and chemical hardness schemes of (compact finite forms) computations: the result is graphically presented in Figure 4.4. The analysis of Figure 4.4 yields a fundamental result for the present study, i.e., the practical identity among:

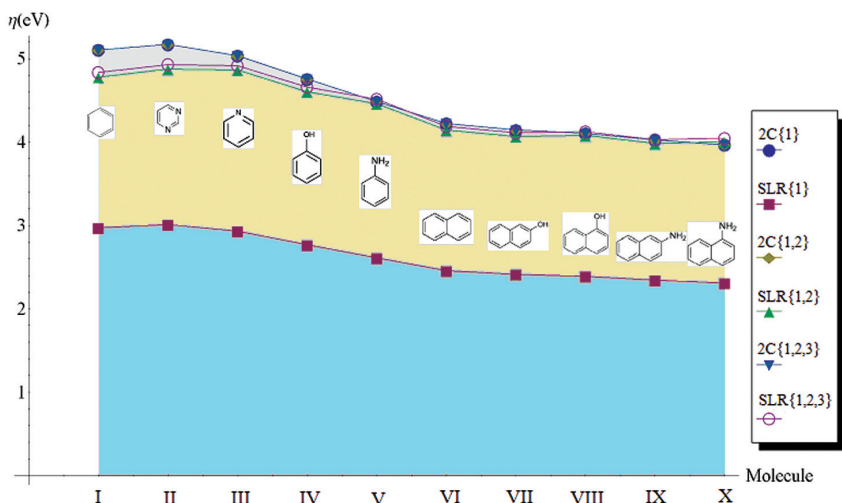


FIGURE 4.4 Representation of the 2C and SLR chemical hardness hierarchies for the set of molecules of Table 4.2 upon the first, second and third order of the Koopmans' theorem applications as presented in Tables 4.3–4.5, respectively (Putz, 2013).

- All Koopmans superior orbitals based chemical hardness computations;
- The simplest 2C and the complex SLR analytical forms for compact finite difference schemes of chemical hardness for the superior HOMO-LUMO gap extensions;

By contrary to someone expecting the first order of Koopmans theorem being more systematic, only in this order 2C result is practically doubled respecting SLR counterpart; such double behavior becomes convergent when superior Koopmans orders of valence orbitals are considered either in simpler or complex forms of 2C and SLR, respectively.

Despite the debating context in which Koopmans theorem is valid, or associates with a physical-chemical sense, the present work give some insight in this matter by clarifying upon some key features of Koopmans analysis, namely:

- The Hartree-Fock spin-orbitals involved in Koopmans' theorem are of computational nature, emerged through solving an eigen-problem in a given basis set so that being characterized by a sort of "quantum shift" related with quantum uncertainty when the free system is affected by observation – here by computation; so this behavior is at its turn computationally naturally and not viewed as a conceptual error in structurally assessing a many-electronic structure;
- The Koopmans' theorem not restrictedly refers to the first ionization potential and may be extended to successive ionization potentials (and electronic affinities) as far the valence shell is not exhausted by the pi-collective electrons, such that the sigma-pi separation may be kept reliable and the "frozen spin-orbitals" may be considered as such through cancellation of the relaxation effects with the electronic correlations, both explicitly escaping to Hartree-Fock formalism; this was however here emphasized by the appearance of the quantum terms of type $\langle HOMO_1 HOMO_2 | HOMO_1 HOMO_2 \rangle$ in Eq. (4.328) and $\langle LUMO_1 LUMO_2 | LUMO_1 LUMO_2 \rangle$ in Eq. (4.329) which were considered as reciprocal annihilating in chemical hardness' IP-EA differences in Eq. (4.330) due to symmetrical bonding vs. anti-bonding spectra displacements in molecular orbital theory – as a simplified version of Hartree-Fock theory;

- 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