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New method for qualitative quantum chemical deductions on organic or inorganic molecules or clusters directly from structural formulas or ORTEP diagrams

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A pictorial "blackboard mnemonic" type method presented allows the molecular orbital level patterns, the numbers of non-bonding, bonding, and anti-bonding orbitals to be figured out from the actual or tentative structural formulas (or ORTEP diagrams) of saturated or unsaturated molecules or intermediates regardless of symmetry. The simple pictorial rules are illustrated on: bicyclo[*p.q.*0] hydrocarbons, pyridine, alkyl groups, quaternium ions, some amines, ethers, water and alcohols, and on some fluorohydrocarbons. The readily obtained MO level patterns, e.g. during rearrangements, give a handle on the qualitative behaviour of various structures or species. The method applies also to metal atom and other clusters.

Key words: Qualitative quantum chemistry — ORTEP — Non-bonding MO's — Clusters

1. Introduction

While large scale computer calculations may provide data on selected molecular species, day-to-day chemical reasoning requires qualitative pictorial tools, sorts of "blackboard mnemonics" easy to use with large numbers and kinds of species. Structural formulas (SF)[1], ball-and-stick models, as well as the Lewis–Langmuir

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[1] *List of abbreviations*: AO: Atomic orbital; ECI: Electron count index; H.F.: Hartree–Fock; LPI: Level pattern indices; MO: Molecular orbital; SC: Structurally covariant; SCF: Self-consistent field; SEF: Structural-electronic formula; SF: Structural formula; VB: Valence-bond; VIF: Valency points interaction formula; VP: Valency point; VL: VP–VP′ interaction line; VSEPR: Valence shell electron pair repulsion

octet rule and the dative pictures [1] which pre-dated quantum mechanics are such mnemonics as are their quantum version, the valence-bond (VB) structures enhanced by the concept of *resonance* [2]. All are of great utility. However, the octet rule does not guarantee the stability of a molecular species. Species with quite similar dative structures may behave very differently. Take e.g. cyclopropane C_3H_6, cyclotriazane, N_3H_3, and ozone O_3. All are isoelectronic (obtained from each other by the isoelectronic replacements $CH_2 \rightarrow NH \rightarrow O$), all could have had similar geometric and Lewis structures, but do not. C_3H_6 is cyclic and stable, N_3H_3 has never been made, O_3 is stable, but not cyclic, though bent.

The valence bond and resonance picture goes a long way, but does not predict anti-aromaticity. The Hückel $4n+2$ rule does, but then it applies only to single rings [3]. In systems where VB leads to a large number of resonance structures (e.g. over 400 in metallocenes) [4] its convenience diminishes.

The molecular orbital (MO) method has been used both as a qualitative device (types of MO's from combinations of atomic orbital (AO) pictures), and for semi-quantitative calculations [5] as well as, in the sense of "energy-best", Hartree–Fock or self-consistent field (SCF) MO's [5], as the essential starting points of many-electron methods [6, 7], which include the electron correlation effects lacking in MO theory.

While VB preserved a close connection with chemical structural formulas, MO's even as a qualitative tool loose this convenience [8] requiring the use of group theory and/or computer calculations and many orbital pictures for the same molecule.

As pictorial tools, both VB and MO depict wave-functions (w.f.), VB an approximate N-electron w.f., MO the independent electron ones, i.e. orbitals. From the nature of the w.f.'s, deduction of qualitative energetics is attempted. For example orbital pictures should tell which energy levels (and MO's) are bonding, non-bonding, or anti-bonding. From VB (ground state VB w.f.'s) which SF are expected to be more stable, and so on. Either way difficulties, as far as pictorial mnemonics are concerned, may be tracable to the fact that it is not the w.f. that is observable. The structure, drawn crudely as an SF, or accurately as an ORTEP diagram that resulted from a crystallographic analysis reflects directly not the w.f., not the orbitals, but the electron density and the energy. So, one might ask, could one have a pictorial quantum tool for chemical reasoning that is closely related to the conventional structural formulas (or even ORTEP) and which would allow deductions directly on energetics and density without the intermediary of orbitals, parameter choices, or computer calculations? Further the method should not depend on any particular symmetry, since most molecules lack it or rapidly loose it upon the slightest substitution or distortion.

In the present paper, we present such a mnemonic. The first crucial electronic property of a molecule is which of its MO's are bonding, which ones non-bonding and which are anti-bonding. In fact, just the two sets of numbers, (i) how many orbitals of each type, and (ii) how many electrons occupy each type, play a major role. The first (i), we might call for short, the *level pattern indices* LPI $=\{n_+, n_0, n_-\}$ where n_+ = number of bonding valence shell MO's; $n_0 = \#$ non-bonding and $n_- = \#$ anti-bonding. Each atom making up a molecule has a valence shell size ($n_a = 1$ for H; $n_a = 4$ for first main group elements, Li, Be, B, C, N, O, F, Ne; and $n_a = 9$ for transition metals with e.g. 4*s*, 4*p*, 3*d* for the Fe series) whose sum for all the atoms of a molecule gives the total number n of valence shell AO's and also of MO's. Thus $n = \sum_a n_a = n_+ + n_0 + n_-$.

The second index (ii) is the *electron count index* ECI $=\{N_+, N_0, N_-\}$ with N_+ = no. of electrons in bonding MO's, N_0 in non-bonding MO's and so on. The sum $N_+ + N_0 + N_- = N$ is the total number of valence electrons in the molecule.

It will be shown that the LPI can be deduced from the structural formula or ORTEP diagram. Then the electrons can be assigned to get the ECI. There have been attempts of course in the past to get at some feature of the LPI especially in the pi-systems by looking at the molecule or its pi molecular diagram. Well known is the alternant hydrocarbon rule [9] that upon labelling every other carbon with a star, if in the π-system no two adjacent carbons turn out to be both starred, or both unstarred, then the bonding and anti-bonding energy levels are symmetrically disposed (so that also $n_+ = n_-$). Lonquet-Higgins [10] attempted to find also the n_0, the all important (for many additional reasons as we shall see below) non-bonding MO's, but only some inequalities could be given for some hydrocarbons. On the other hand, there is the well-known Frost-Musulin [11] algorithm which gives not only the LPI, but the actual energy levels for monocyclic pi-systems with their pi-molecular diagram drawn in a circle. Neither this, nor the Hückel $(4n+2)$-rule [3] apply however to arbitrary pi-systems with say multiple rings, pi-side chains, etc. not to mention heteroatoms.

In the method below (which we might also call the "structural-electronic" method) the LPI of arbitrary organic or inorganic molecules are obtained using two simple pictorial rules on "*structural-electronic formulas*" (SEF) which are like amplified structural formulas drawn from the latter or from ORTEP diagrams. In addition however, one obtains how the LPI would change as one goes from one set of molecules to another of the same total empirical formula thereby getting a guide to the quality of rearrangements, large or small distortions, and reactions.

2. The structural-electronic method and its two rules

We present the method in a way to indicate that it can be used without any quantum mechanics much as the structural formulas and arrows are used by synthetic organic chemists. The quantum and mathematical connection are noted within the text in small type and along with a summary of proofs in the Appendix. Further details of the mathematical theory behind the method will be found in Ref. [12].

A structural formula (SF) or an ORTEP diagram is first amplified into a *structural-electronic formula* (SEF) [which may also be called a "*valency points interaction formula*" (VIF)] this way: Each atom a of valency shell size n_a is represented by n_a *valency points* (VP). If two VP's between two atoms are thought to interact (cf. below) a VP–VP′ *interaction line* (VL) is drawn between them. Nearest neighbor VP's for example will in general interact. In the case of a pi-system this will lead to the familiar "pi-molecular diagram" [13]. It is not crucial whether one includes at first more lines or not. Whether additional lines would alter the LPI can be ascertained later with the two pictorial rules on more elaborate VIF's.

For arbitrary molecules made up of main group elements with $n_a = 4$ (s and p valencies only), if one is not looking just at a pi-system, the four VP's of any given atom are also connected to each other with *intra-atom* VL's. Each such atom therefore looks like a tetrahedron (actual geometry not important in the VIF, cf. below) interestingly as in the 19th century van't Hoff model for carbon, but here not only for carbon but any of the others like B, N, O, F, S, P, etc. (in the second main group elements if the expansion of the valence shell is not at first included) as well.

In the molecule, two neighboring "tetrahedra" may be oriented corner-to-corner, edge-to-edge, face-to-face, ... The required orientation being evident from the structural formula (cf. the examples below). In conjugated systems with *both* the sigma and the pi valencies included in the VIF, this leads to pictures with what look like "banana bonds" (e.g. in C_2H_4, C and C′ are edge-to-edge) rather than sigma and pi bonds. [It should be emphasized however, at the outset, that the lines in a VIF are not "bonds", but depict one-electron interactions (cf. below) which are parts of the one-electron hamiltonian h, as electrons have not been assigned to the MO's or the VIF yet.]

Quantum connection (QC): Each VP represents a valence atomic orbital (AO), either a pure one (s, p_x, d_{xy}, ...) or a hybrid (tetrahedral t, trigonal u, etc.) Each molecular structure corresponds to a one-electron effective hamiltonian, h (such as the usual, or extended Hückel one) which is parametrically dependent on the 3 Dim. atomic positions $\{\boldsymbol{R}\}$. The h is of the form $h = \sum_{i,j}^{n} \beta_{ij} A^{ij}$ with $A^{ij} = |e^i\rangle\langle e^j| + |e^j\rangle\langle e^i|$ and $\beta_{ij} = \langle e_i|h|e_j\rangle$. In fact, the VIF depicts directly this *operator* h with $|e^i\rangle$ being a VP, A^{ij} being a line (of standard unit "strength", i.e. coefficient of A^{ij} unity) between the VP's i and j. In hydrocarbons interatomic β_{ij}'s are roughly of comparable magnitude say β_0. Thus $\beta_{ij}/\beta_0 \approx 1$ are taken as std. unit strength and positive; otherwise the actual relative magnitude $|\beta_{ij}/\beta_0| = |\kappa|$ and the sign of the strength may be written on its line in the VIF.

VP's also have self-energies $\beta_{ii} \equiv \alpha_i$ which are the orbital ionization potentials. Where α's of different atoms or VP's do not differ greatly, an average of all α's in the molecule is taken as the std. α_0. As is usual in Hückel MO's, α_0 may be taken out of the h, i.e. $\bar{h} \equiv h - \alpha_0 I$ so that the std. VP's will be at this reference zero of energy ($\bar{\alpha}_i \equiv \alpha_i - \alpha_0 = 0$). If a $\xi_i \equiv \bar{\alpha}_i/\beta_0$ is not negligible compared to unity, there will also be "*loopline*" ($i \bullet\!\!\bigcirc \xi_i$) of strength ξ_i in the VIF.

The overlaps $\Delta_{ij} = \langle e_i|e_j\rangle$ between AO's need not be assumed zero. By the "covariance theorem" proved in Ref. [12], the LPI of h will be the same with or without overlaps.

With pure AO type VP's there are no intra-atomic lines since $\langle e_{ia}|h|e_{ja}\rangle = 0$ in that case. With hybrid AO's $\{m\}$, $\langle m_{ia}|h|m_{ja}\rangle \neq 0$ in general. Such intra-atom β's were included in the earliest sigma MO theories [14] but often omitted in later semi-empirical MO methods [15]. Recently the importance of intra-atom β's in semi-empirical MO was elegantly demonstrated by Dewar [16], who noted that $\beta_{t_a t_a}$, between the tetrahedral AO's of a carbon should be comparable to the inter-atomic sigma $\beta_{cc'}$. The one center $\beta_{tt'} = \frac{1}{4}(\alpha_s - \alpha_p)$, the coefficient becoming 1/3 for trigonals, 1/2 for diagonal hybrids. One might take [16] roughly $\beta_{tt'} \approx \beta_0$.

The LPI to be deduced pictorially from the VIF below is not dependent on the actual magnitudes of the line strengths ($\xi_i, \kappa_{ij}, \ldots \neq 1$) often over broad ranges of these, or their parent (α_i, β_{ij}) parameters. These ranges can also be found from the VIF by the two VIF-rules given below. There are "critical" values of some of the ξ and κ however where suddenly the LPI changes. These values have a crucial role in determining when a molecule rearranges, changes hybridization type on some of its atoms, etc. Various examples of this "*electronic tuning*" phenomena will be observed in this and subsequent papers.

A stable molecular structure and the observed ground state geometry actually results not so much from only the 3-dimensional Hückel hamiltonian [17], but from an interplay of this "orbital control" or "electronic control factor" (given by the one-electron MO levels) and another well-known effect [18], the VSEPR, "valence shell electron pair repulsion". The latter arises from the N-electron wave function Φ constructed as an anti-symmetrized product of spin MO's, the anti-symmetry of Φ keeping electrons of like spin apart, the effect displaying itself as an "exchange repulsion". The norm, the "energy best" MO's, are the Hartree–Fock (HF) or self-consistent field (SCF) MO's, all the other MO's of various approximate methods [5] approaching these. For stable ground states HF Φ with its full N-electron energy $\langle\Phi|H|\Phi\rangle$ (omitting electron correlation, E_{corr} effects [7, 19, 20] which are however even qualitatively important for highly non-closed shell states such as excited states [19*a*] or on many points of potential energy surfaces [19*b*]) reproduces the ground state geometry fairly well [5, 21]. Unlike the 3-dim. Hückel method, the *HF* has both the "electronic (or orbital) control" *and* the VSEPR built into it [22]. What about the relation of these two effects to the VIF?

If a 3 dim. Hückel full VIF were drawn with all the lines in it with all of the strengths, α_i's and β_{ij}'s in the h, it would not necessarily be a more realistic description of the observed molecular structure than a VIF drawn looking at the SF or the ORTEP and selecting the significant lines. The actual structure reflects the VSEPR as does therefore the mnemonic VIF derived from the SF. If the structure is not known, one can draw some tentative SF's and their VIF's, get the LPI, then assign the N electrons to the MO types as well as/or on the decoupled pieces of VIF's "reduced" by the two SE rules as will be seen later. Then looking at the electrons assigned to the decoupled or reduced VIF's, one can see where large VSEPR effects would want to change the geometry making some VP's mutually further apart and eliminating their substantial lines. In any case, one can also start with a realistic looking SF-based VIF, get its LPI, add more lines, change some strengths, and see if the LPI is changed.

We now state the basic result derived from the theorems proved in [12] and with the proofs outlined in the Appendix:

All VIF's *that can be obtained from each other by the two rules given below have the same* LPI. *Conversely, if two* VIF's *have the same* LPI, *they must be transformable into each other by the two rules.* The rules may be applied any number of times, in any desired combination or succession to get from one VIF to the other. (This is so, because any intermediate VIF obtained will also have the same LPI).The two rules are:

Rule 1: Any valency point VP of a VIF may be multiplied by an arbitrary constant κ, positive or negative so long as it is not zero. This changes, distorts, etc. the VIF but does not change its LPI. Multiplying a VP by κ means multiplying the strengths of all the lines emanating from that VP by κ.

Rule 2: Any VP of a VIF may be lifted up, taken over and placed onto any other VP′ carrying along the lines that terminated on VP onto the new VP′ which becomes a terminus for those lines. If in the process two lines superimpose their strengths are added algebraically giving the strength of one new line. The original lines that terminated at the initial VP and that VP are also retained in the resulting VIF′. Then VIF and VIF′ will have the same LPI.

With these rules one can generate all the molecules (or reacting assemblies of molecules) that are iso-LPI, hence of similar energetic quality (if electron occupations, ECI, also do not change, i.e. the rearrangement or reaction is electronically adiabatic). Changing the strengths of some of the interaction lines in a VIF using Rule 1 one or more times may correspond to changing some interatomic distances in the molecular structure (since $\beta_{i_a j_b}$ is a monotonic function of the interatomic distance R_{ab}), or for the intra-atom lines, to changing hybridization, or to changing the values of some of the β parameters as in a semi-empirical MO theory. Thus one can tell whether the qualitative level pattern, i.e. the LPI will be affected or not by any such changes. Using the rules on a VIF one can also obtain the LPI itself. In this case, the aim is to "reduce" the VIF in such a way that more and more lines are eliminated until one ends up with the n-valency points none connected to each other. Such a fully reduced VIF will have n_0 VP's which are just bare, n_+ VP's each with a positive strength loop (i.e. a line that starts and ends on the same VP), and n_- VP's each with a negative strength loop. Thus one reads off from the final picture, the LPI$=\{n_+, n_0, n_-\}$.

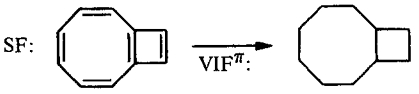
A few simple examples will illustrate the rules and their use.

3. Some examples and applications

3.1. *Conjugated hydrocarbons (their pi parts) and clusters of* uni-VP *atoms*

To draw the pi part only, i.e. VIF$^\pi$, place one pi-VP for each such carbon, then connect all the nearest neighbor pi-VP's (additional interaction lines' possible effects may also be examined if desired). The VIF of a uni-VP atoms' cluster, e.g. hydrogen clusters, or alkali clusters (if p-effects are at first neglected) are similar (even with some 3-dim clusters).

Take e.g. bicyclo[6.2.0]decapentaene. From any one of the Kekule structures, SF, we get the VIF$^\pi$ as in Eq. (1).

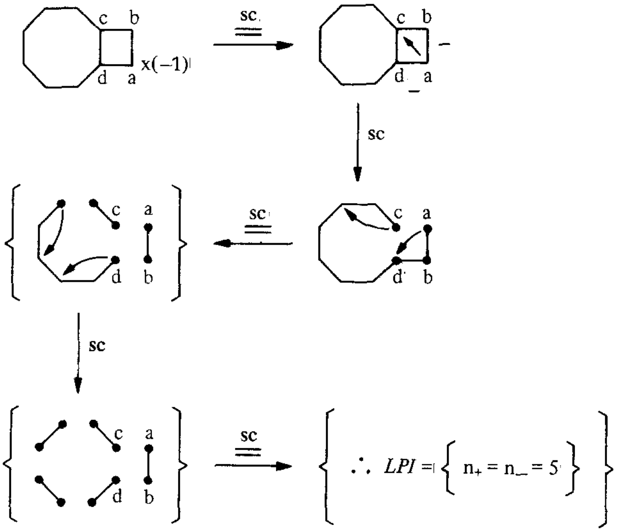


(1)

Where no "strength" is shown on a line it is taken to be $(\beta_{ij}/\beta_0=1)$, i.e. plus 1. All the π-lines in Eq. (1) are assumed to be standard, hence +1.

The strategy in applying the rules to rings to get their LPI is first to try to break the rings. In Eq. (2), multiply first, the VP "a" by $\kappa=-1$. This makes the lines (ab) and (ad) of (-1) strength. Then, by Rule 2, take a onto c. The minus (ab) line cancels the (bc), while (ad) cancels (dc). Both rings are broken. An iso-LPI straight chain π-VIF, that of n-decapentaene results. Such VIF's (or molecules) which have the same LPI, we refer to as being "*structurally covariant*" $(\overset{\mathrm{SC}}{=})$. Conversely, all $(\overset{\mathrm{SC}}{=})$-molecules are in the same mathematical class [1] and will have the same LPI.

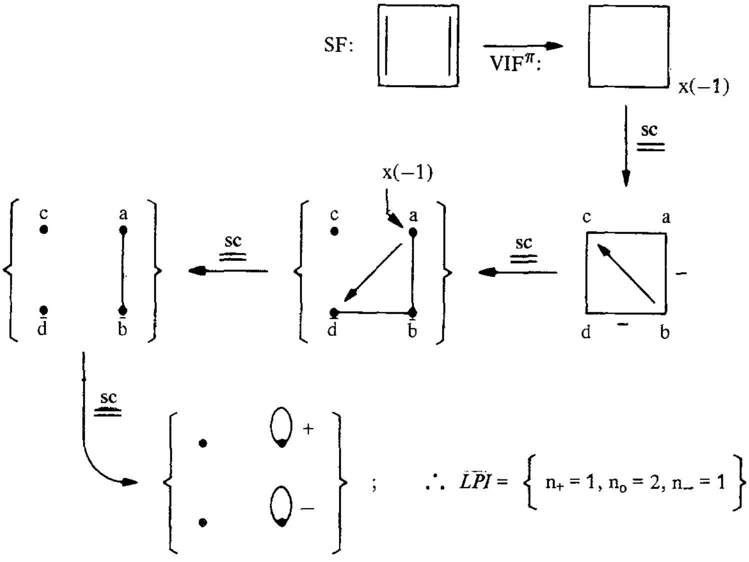
Continuing, one may multiply a by $\kappa=-1$, take it over onto d which is the same as folding (ab) onto (db). The signs now again being opposite, (ab) cancels (db).



(2)

Proceeding similarly one ends up with five single π-lines as seen in Eq. (2). But this is the same as the π-VIF of a collection of five isolated pi-bonds. Thus the pi-parts of a Kekulé SF (as drawn without further delocalization, or as in a simple ball-and-stick model) and of the actual molecule with its pi-delocalization over both rings (for standard geometry) are LPI-equivalent. They both yield zero non-bonding MO's and five bonding-antibonding pairs of MO's. Since the neutral molecule has $N_\pi = 10$ pi-electrons, the ECI $= \{N_+ = 10,\ N_0 = 0,\ N_- = 0\}$, so the pi-system itself is stable. It is interesting that, the individual rings, being of the $(4k)$-type ($k = 1$ for cyclobutadiene, $k = 2$ for the eight ring), are both $4n$-Hückel anti-aromatic, but their edge-fused composite is not.

Had we applied the rules to a std. geometry cyclobutadiene, we would have gotten, Eq. (3).



(3)

The familiar result with two non-bonding orbitals ($n_0 = 2$) is obtained. For the neutral molecule, the ECI $= \{N_+ = 2 \times n_+ = 2;\ N_0 = 2$ in two non-bonding MO's$\}$. Note that since the zero of the energy as the reference point for MO levels is fixed and remains fixed during the application of the rules, $n_0 = 2$ also gives (unlike n_+ or n_-) the actual degeneracy of the energy level at $\varepsilon = 0$. [For the n_+ or n_- on the other hand this is not so, whether e.g. the n_+ MO's are degenerate or not, so long as they are bonding, they are counted in the n_+. Other degeneracies than the $\varepsilon = 0$ levels can also be obtained with the present theory [1] without using group theory. However, the other degeneracies not being as important unless the levels coincide with a highest occupied MO, for qualitative energetics with static molecules that topic is not included here.]

Various classes of polycyclics and other conjugated systems can be treated this way. The cases of the bicylco[*p.q.*0] hydrocarbons for example, are reported in detail in [23]. These pi-systems fall into several classes [23], one of which is the class bicyclo[*p.q.*0] with the two rings of the [4*k*][4*k*′] (with *k*, *k*′ integers) type, Eq. (1) being an example. For these we have from the rules:

$$\begin{aligned} &\mathrm{LPI}^{\pi}(\text{bicyclo}[p.q.0] \text{ with } [4k][4k'] \text{ fusion}) \\ &\quad = \left\{ n_+^{\pi} = \frac{p+q}{2} + 1;\ n_0^{\pi} = 0;\ n_-^{\pi} = \frac{p+q}{2} + 1 \right\}. \end{aligned} \tag{4}$$

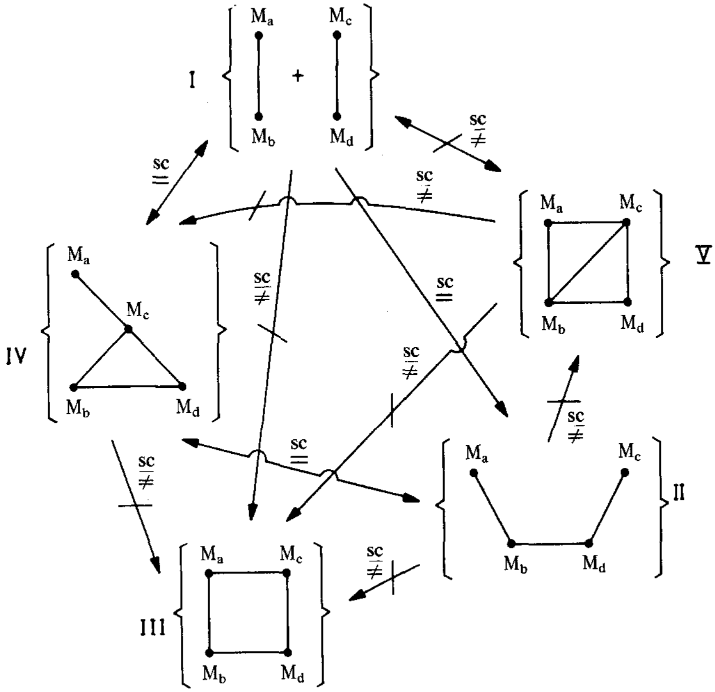


Fig. 1. Some spatial configurations of a cluster of four uni-VP (*s*-type) atoms. The ($\overset{\mathrm{sc}}{=}$) lines between configurations indicate the latter are "structurally covariant", having therefore the same MO level patterns, LPI = {numbers of bonding, non-bonding, antibonding MO's}. If ($\overset{\mathrm{sc}}{\neq}$), the LPI's differ

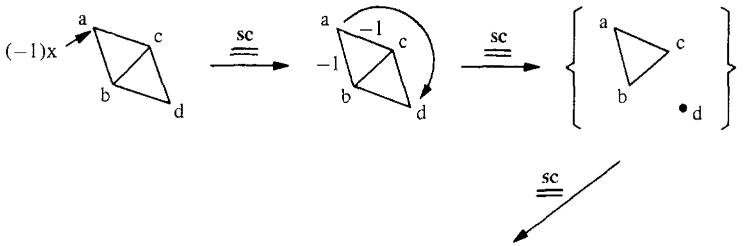
As another example with uni-VP atoms, and related also to the π-cyclobutadiene case, consider several spatial configurations of a cluster of four uni-VP atoms as in Fig. 1. The atoms {M} may be hydrogen, deuterium or Li, Na,... (alkali with s-valencies only; the inclusion of p would make for a more complicated example).

Figure 1 shows all the interatomic distances (and since here one atom means one VP, and $\beta_{ij}(R_{ij})$ is a monotonic function), hence all the line strengths as being equal (unity). Using the rules as in Eq. (3), we readily see Eq. (5).

$$\begin{aligned} &\mathrm{LPI(I)} = \mathrm{LPI(II)} = \mathrm{LPI(IV)} = \{n_+ = 2,\ n_- = 2\} \\ &\mathrm{LPI(III)} = \{n_+ = 1,\ n_0 = 2,\ n_- = 1\} \\ &\mathrm{LPI(V)} = \{n_+ = 1,\ n_0 = 1,\ n_- = 2\}. \end{aligned} \tag{5}$$

E.g. in configuration (IV), multiplication of M_a by $\kappa = -1$, then taking it over first to M_d, then to M_b reduces the VIF (i.e. iso-LPI-wise) into the pieces (ac) and (bd), hence $\{n_+ = n_- = 2\}$.

In (V), one may multiply M_a by (-1) making the (ac) and (ab) lines minus, then take it onto M_d cancelling out (cd) and (bd) yielding one triangle and one bare dot. Thus we have Eq. (6).



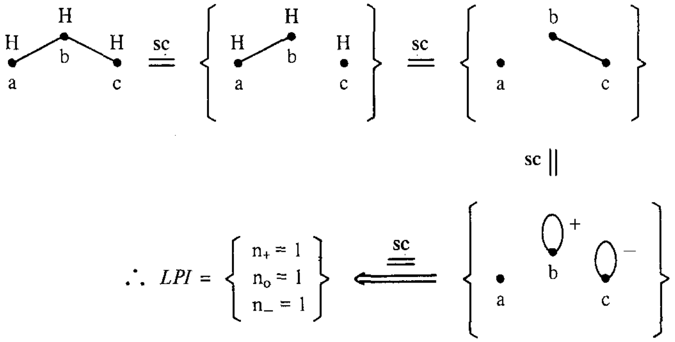
$$\therefore\ LPI = \{n_+ = 1,\ n_o = 1,\ n_- = 2\} \tag{6}$$

The triangle's LPI is well-known (e.g. by the Frost-Musulin algorithm) contributing one bonding, two anti-bonding MO's (note that after the second step in Eq. (6) a is multiplied by (-1) again making all the sides of the triangle positive, i.e. we have a Hückel polygon). [Nevertheless, if the answer were not already known, we could have obtained it with the rules, in this case folding (ab) onto (bc) would fold line (ac) into a loop at c of strength 2 (cf. Appendix B for cases which lead to loops during application of the rules and how to deal with them.]

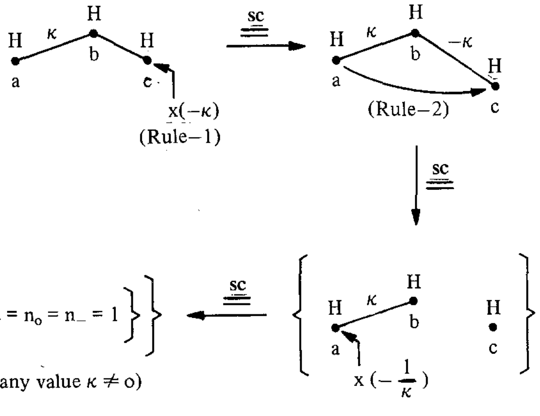
Figure 1 compares the LPI's of the initial and final structures or VIF's for each pair of spatial configurations. If the two have the same LPI (and therefore the same ECI for fixed N), they are "structurally covariant" $(\overset{\mathrm{SC}}{=})$, otherwise not $(\overset{\mathrm{SC}}{\neq})$. This is a very rough guide to the "thermic quality" or "thermicity" of a reaction in the thermochemical, not kinetic sense. Kinetic pathway quality along a deformation or reaction pathway also follows from the present SEF approach with a few additional considerations. It is treated as a separate topic [1, 24] We only note here that with the two rules one examines not only an initial and a final structure or VIF, but also what happens to the LPI (hence adiabatically to the ECI) as one structure or VIF deforms continuously along a certain path to a final structure or VIF. If the LPI remains the same throughout, we call the two structures or VIF's "*deformationally covariant*" [1] $(\overset{DC}{=}p)$ along that path *P*.

The H_3, H_3^+, H_3^- system provides a simple illustration of the deformational principle as well as how the cations and anions of a system may be treated with the same VIF.

Take a linear or quasi-linear (where bending is not sufficient to introduce an end-to-end interaction) H_3 configuration. In Eq. (7) taking the *H-H* (hence line strengths) equal at first ($\beta/\beta_0 = +1$), the familiar LPI with one non-bonding MO is obtained [multiply *a* with (-1), fold it onto *c* cancelling (*bc*).] The VIF's shown in Eq. (7) are structurally covariant $(\overset{SC}{=})$ taken as initial and final states. However, in addition if we multiply (*a*) by an arbitrary $\kappa > 0$ less than or greater than unity, making the (*ab*) line strength equal κ, we get the same LPI $= \{n_+ = n_0 = n_- = 1\}$ regardless of the value of κ as seen in Eq. (8).



(7)



(8)

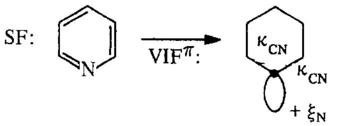
Furthermore in this example κ (hence the (*ab*) distance R_{ab} from the monotonic nature of $\beta(R)$) may vary *continuously* all the way to and including $\kappa = 0$. Thus the VIF which represents either H_3, or H_3^+, or H_3^- (same LPI, different ECI's and *N*'s) is *deformationally covariant* along the quasi-linear path. This indicates why the barrier is small (≈7 kcal/mole) (relative to half a chemical bond energy) in

$$H_2+H \xrightarrow{\text{DC}} H\cdots H\cdots H \xrightarrow{\text{DC}} H+H_2$$

The VIF remains qualitatively the same for the anion and cation giving the same LPI for H_3, H_3^+, and H_3^- with the resulting ECI $(H_3)=\{N_+=2,\ N_0=1\}$, ECI $(H_3^+)=\{N_+=2\}$, ECI $(H_3^-)=\{N_+=2,\ N_0=2\}$. [Beyond this point Pauli exclusion repulsions of like spin electrons (in H_3 and H_3^-) as in VSEPR, electron correlations, details of the nuclear-repulsions-balance, etc. would come into the picture.]

3.2. Heteroatom effect on a heterocyclic

In the pyridine pi-system, as an example of one kind of heteroatom effect, the VIF, Eq. (9) contains a loop-line on the nitrogen pi-VP as the nitrogen *p*-VP self-energy (corresponding to the orbital ionization potential-α_N $(2p)=13.4$ eV) [25] differs from that of carbon $(-\alpha_c(2p)=11.4$ eV) [25]. We examine the effect on *one* heteroatom (several hetero-atoms have a different effect) on pi-aromaticity.



(9)

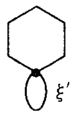
Taking the zero of the energy at the $\alpha_c\equiv\alpha_0$, we have only the nitrogen pi-VP with a non-zero self-energy $(\alpha_N-\alpha_0)$, hence with a loop in Eq. (9) of strength ξ_N relative to the std. line strengths' unity $(\beta_{cc}/\beta_0\equiv 1)$,

$$\xi_N=\frac{\alpha_N-\alpha_c}{\beta_0}>1. \tag{10}$$

Similarly the C–N line strength is changed to $(\beta_{CN}/\beta_{cc})=\kappa_{CN}\neq 1$, relative to C–C lines which were all taken to be of the std. strength $(\beta_{cc}/\beta_0\equiv 1)$.

Dividing the nitrogen π-VP by κ_{CN} in Eq. (9) per Rule 1, we get Eq. (9′) with the same LPI.

$$\text{Eq. (9)} \xRightarrow{\text{SC}}$$

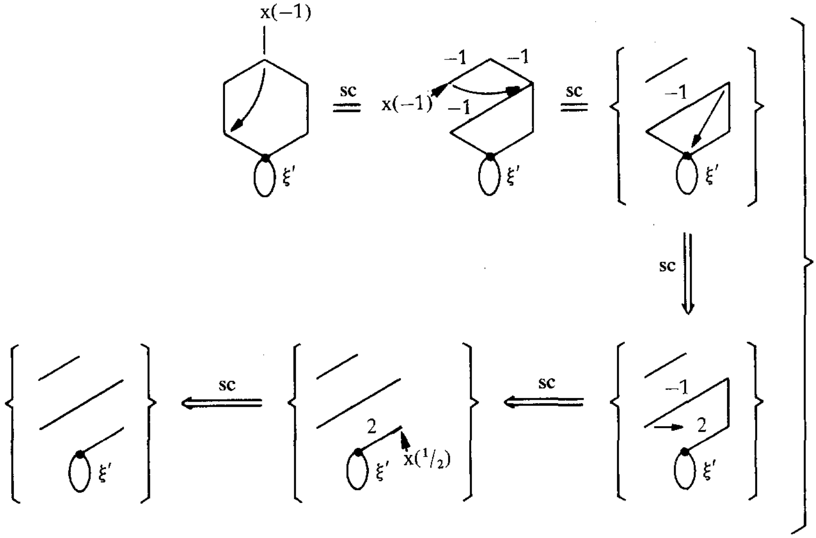


(9′)

where now all lines are of unit strength, and the loop has

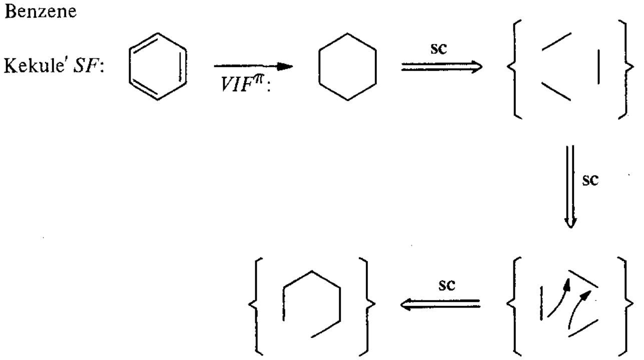
$$\xi'=\xi_N/\kappa_{CN}^2$$

Note that the loop is divided by the *square* of κ as each end of the loop line is divided by κ (cf. Appendix B. for other loop rules). The Eq. (9′) is reduced in Eq. (11), with the two rules.



Eq. (11a)

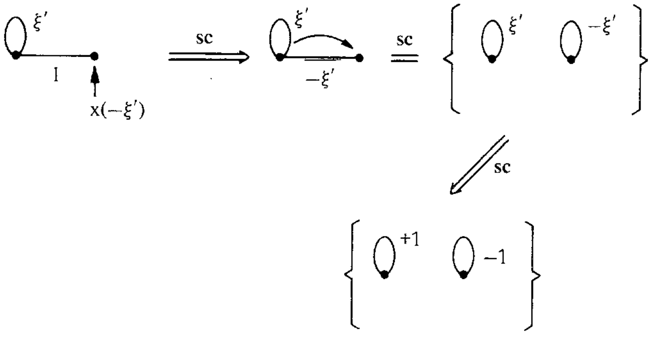
Had we done pi-benzene with the very same steps as in Eq. (11a), we would have gotten three unity line segments yielding the known LPI (benzene-π) = $\{n_+ = n_- = 3\}$ (and ECI = $\{N_+ = 6\}$). In that case we would have also observed that the full π-VIF of benzene is iso-LPI and structurally covariant with its Kekulé structures as well as with its cut-open 6-pi VP chain version, Eq. (12).



(12)

The last part follows from Rule 2 as indicated with the two arrows. In fact, this gives us a qualitative criterion for pi-aromaticity: If the pi-system is pi-aromatic (necessary condition) [26], the full pi-VIF is iso-LPI i.e. structurally covariant with the VIF$^\pi$ of the actual standard Kekule structures. This is consistent with Dewar's [27] definition of aromaticity as seen from the last part of Eq. (12) as the cut-open straight chain case used by Dewar and also has the same LPI.

In the pyridine case, any change in the LPI$^\pi$ from benzene is reduced to the behavior of the looped piece in the last picture in Eq. (11a). One might think that the LPI$^\pi$ and pi-aromaticity will depend on the value of ξ' which differs from heteroatom to heteroatom. However, we find in Eq. (11b) that the loop-piece contributes one to n_+ and one to n_- no matter what the value [26] of ξ'.



(11b)

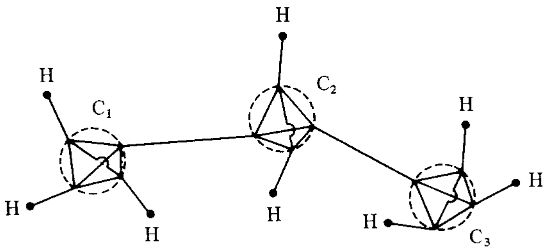
[For the looped VIF reductions see Appendix B. Also a caution: Zero limits of variables like ξ or κ should not be taken during a VIF reduction. The constants used in Rule 1 for example can be any value, but not zero].

Thus Eqs. (11a, 11b) have proved that the LPI$^\pi$ of a single heteroatom pi-hexagon is the same, $\{n_+ = 3,\ n_- = 3\}$, as π-benzene, no matter what the heteroatom or ion is. The pi-aromaticity is unaffected as is known to be so in pyridine and e.g. in the pyrylium cation. [With more than one heteroatom, different and interesting things happen [26]. Further, the role of the sigma framework even on the aromaticity of benzenoids traditionally viewed as a π-only problem, need be considered [26].

3.3. *Some saturated molecules*

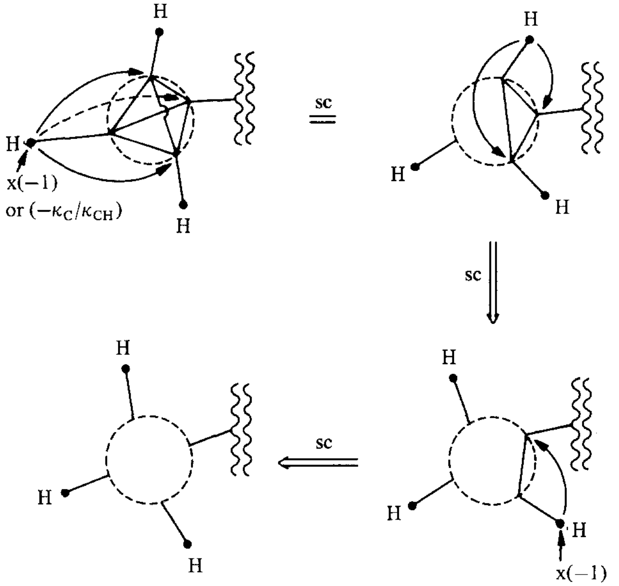
(i) Alkanes, alkyl groups, quaternium ions. For each carbon (or nitrogen,...) a tetra-VP atomic VIF is drawn as mentioned in Sect. 1. Ordinarily interatomic VP-VP' lines will be drawn from the structural formula. [More refined molecular VIF's may also be drawn by adding lines ($|\kappa| < 1$) between atoms which are further apart to study e.g. conformational effects (omitted here).]

For any straight or branched chain alkane, the VIF reduces ($\overset{\mathrm{SC}}{=}$) with the rules into a set of isolated CH and CC line segments as demonstrated for propane in Eq. (13).



(13a)

The intra-carbon, inter-carbon, and C–H line strengths are of comparable magnitudes. But even if their differences are put in, the reduction procedure in Eq. (13b) by the two rules shows that the LPI is unaffected.



(13b)

Each simple line segment contributes a $n_+ = 1$ and a $n_- = 1$, so that LPI $= \{n_+ = n_- = 10\}$ for propane or for any such alkane $n_+ = n_- =$ (no. of C–C and C–H bonds). As there is one electron per VP in alkanes, ECI $= \{N_+ = 20,\ N_0 = 0,\ N_- = 0\}$ in propane or $N_+ = 2n_+$. These electrons may be assigned not only to the n_+ MO's, but in the reduced VIF to each VP–VP′ one electron (β) interaction line segment as well, which only in saturated systems *looks like* the SF or the valence bond structure. [Note however that, a bond-line in the SF or in the Pauling VB theory is an electron-pair bond *wave function*. Here, in the VIF, a C–H or C–C′ line is a piece of the *one-electron hamiltonian h*. Thus the VIF single line, giving rise to two MO's (bonding-anti-bonding couplet), can accommodate up to 4 electrons charge repulsions permitting. Thus H_2 and He_2 have the same VIF, but not the same SF or valence bond diagram.]

In any alkane or alkyl group one starts the VIF reduction from the terminal methyl group as in Eq. (13b). The C_1–C_2 line that remains connected to the rest of the molecule, in e.g. Eq. (13a) is treated then the way a C–H line was treated (multiply by -1 or $-\kappa$, fold it onto three *intra*-carbon lines one at a time).

A tetraalkyl ammonium ion will have the same VIF as the corresponding alkane branched at the carbon that replaced the nitrogen. One advantage of the VIF-method is that molecules are classified with respect to their similar VIF's rather than by their iso-electronic aspect. There are sets of molecules which are chemically very different even though iso-electronic (like the ozone series cited in Sect. (1)), while molecules with similar VIF's have similar behavior given similar electron occupations.

Equations (13) did not show any loops implying the self-energies of H($\alpha_H = -13.6$ eV) and tetrahedral carbon VP ($\alpha_t = [\alpha_C(s) + 3\alpha_C(P)]/4 = -13.9$ eV) do not deviate much from their average (13.75 eV) where the zero of energy is taken.

But the rules show that even if ξ_{H} or ξ_{tc} loops are added, the LPI is unaffected. If the reference zero is taken at α_{H}, a ξ-loop occurs on each carbon VP, but then the $(\overset{\mathrm{SC}}{=})$-reduction proceeds just the same as in Eq. (13b). At the end, instead of the $({}^{\mathrm{H}}\bullet\!\!-\!\!-\!\!-\!\!\bullet^{tC})$ lines, a segment $({}_{\mathrm{H}}\bullet\!\!-\!\!-\!\!-\!\!\bullet\!\!\bigcirc\ \xi)$ will remain. But this piece was shown to have the same $(n_+=1,\ n_-=1)$ LPI contribution for any value of ξ in Eq. (11*b*). For the line connected to the rest of the molecule that will remain in Eq. (13b), one must proceed from another methyl terminus. Thus in a X-substituted alkane, the line connecting to X need be treated with care. In any larger straight or branched chain alkane the VIF splits into isolated C–H lines and a carbons-only continuous chain with loops on each carbon VP.

This chain is still split into isolated C_t–C'_t lines with a separate LPI of its own and with its own reference zero at the $\alpha_t(\mathrm{c})$ slightly displaced from the hydrogen zero.

(ii) *Alkylamines and ammonia.* Primary, secondary, or tertiary alkylamines lead to similar VIF reductions and LPI's. The zero of energy is taken at the H, C average $(\tilde{\alpha}_0=[\alpha_{\mathrm{H}}+\alpha_t(\mathrm{c})]/2)$ leaving only tetra-VP loops on nitrogen (if $\alpha_{\mathrm{N}}-\tilde{\alpha}_0/\tilde{\alpha}_0$ is not neglected). Alkyls split into G–H and C–C lines as in alkanes. The N–C and N–H isolated lines similarly result in addition to a nitrogen lone VP. Thus alkyl-amines have LPI $=\{n_+=n_-=$ no. of H–C, C–C, and N–C bonds and $n_0=1$ (at the nitrogen tetra-VP self energy).

As in alkanes, any differences in the H–C, C–C and C–N line strengths (κ's relative to say $(\beta_{\mathrm{cc}}/\beta_0\equiv 1)$ do not affect the VIF-reductions, nor the LPI (as seen by Rule 1).

Thus in the alkylamines too the numbers of the bonding, non-bonding, and anti-bonding MO's in the delocalized description of electronic structure can be figured out directly from the structural formula (SF). The VIF's i.e. the structural-electronic formula (SEF) also gives the structurally covariant localized descriptions. Into either form electrons can be assigned noting that an SEF line can get up to four electrons $(n_+=1,\ n_-=1;\ N_+=2,\ N_-=2)$ it representing the unoccupied orbitals as well as the occupied ones unlike the SF which depicted only the ground state.

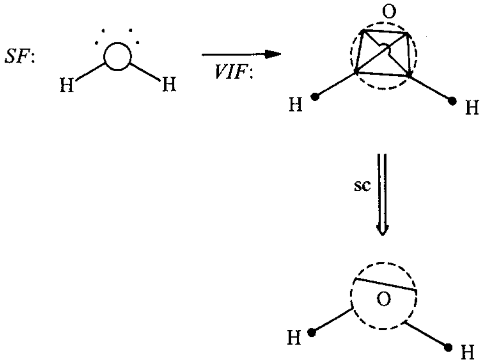
Note that the use of the rules above provides a far stronger statement about the MO LPI coming out as simply related to the number of single bonds and lone pairs of the SF VB picture, than an intuitive guess would surmise. As all the atomic orbitals overlap with each other, in general it is not possible to assert just from the SF or VB that MO's will have so many bonding, non-bonding, ... types intuitively. The theorems of the new method in particular "structural covariance" (cf. Ref. [12]) show that with or without overlaps the LPI is the same. Thus a rigorous deduction is made by the VIF-rules as to the MO–LPI. In fact, there are many cases where one could not have guessed the correct MO LPI intuitively from the numbers of "bonds" or "lone pairs" indicated by the octet rule or a SF VB: e.g. in H_2O, there are two single bonds and two octet-type "lone pairs", but the MO LPI is different than {2, 2, 2}; rather one has from the VIF-rules: LPI $=\{n_+=3;\ n_-=3\}$.

(iii). *Dialkyl ethers, alkylalcohols, and the water molecule.* The alkyl groups' VIF's are drawn from the SF as in Eqs. (13) and each one $\overset{SC}{=}$ reduced that way until the oxygen is reached. The oxygen atomic VIF is also tetra-VP (possibly with ξ-loops included relative to the std. carbon tetra-VP, hydrogen VP average reference energy;

$$\alpha_t(\text{oxy.}) = (32.3 + 3 \times 14.8\ \text{eV})/4;$$

$$\xi(\text{oxy.}) = \frac{\alpha_t(\text{oxy}) - \tilde{\alpha}_0}{\beta} \approx \left(\frac{-5.4}{-2.5} \approx 2\right).$$

Thus the VIF of the oxy-vicinity in the said ethers, alcohols, or water is as in Eq. (14).

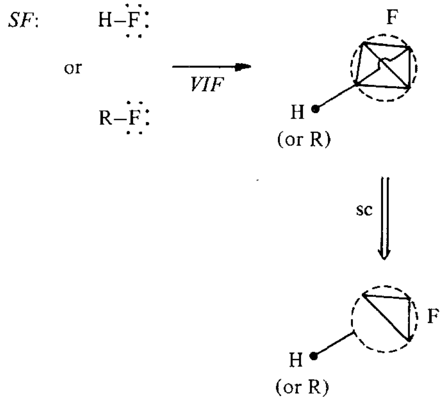


(14)

That the O-H line strengths may be different than the intra-oxygen ones ($\beta_{oo} = (\alpha_S(\text{oxy}) - \alpha_P(\text{oxy})]/4 = -4.4$ eV) does not affect the LPI, since by Rule 1 the O-H line from the H-end may be multiplied by any $\kappa \neq 0$ to make it the same as the intra-oxygen line. Any oxygen VP's-loops too are ineffectual when H-VP's after being multiplied by minus one are folded onto oxygen lines cancelling them. Thus Eq. (14a) shows two decoupled C-H lines and an oxygen "lone" VP-"lone" VP′ line. The LPI = $\{n_+ = n_- = 3\}$. This has covariantly [1], two meanings at the same time: i) there are 3 bonding MO's and 3 anti-bonding ones going over the whole molecule, or ii) providing an equivalent description as far as the LPI is concerned (not the actual magnitudes of the energy levels, since covariance is in-general non-unitary [1] in the mathematical sense) [1] as: local (not necessarily orthogonal) [1] MO's, a bonding-antibonding pair for each O-H and a bonding-antibonding pair for the oxygen "double lone pairs" ("lone" VP's become "lone pairs" if they are doubly occupied by electrons after the ECI assignment to the LPI.)

The oxygen vicinity is the same in the above ethers and alcohols, the LPI consisting of $\{n_+ = n_- =$ no. of C-H, C-C and O-C or O-H bonds +2). In the reduced VIF's, the intra-oxygen lone VP's line gets four electrons in the ECI leading to the slight repulsion between the resulting two lone pairs as anti-bonding is more anti-bonding [28] then bonding is bonding (when arising from a VP-VP′ line; compare e.g. H_2 and He_2).

(iv) *Monofluoroalkanes and the HF molecule.*



(15)

Any straight or branched alkyl R after its reduction has the same effect as a hydrogen in the $\overset{\text{SC}}{=}$ reduction with the two rules of the fluorine atomic VIF. (Similar remarks as in (i)–(iii) apply concerning F-self-energy and line strengths).

The three fluorine "lone-VP's" remain triangularly coupled in Eq. (15) contributing one bonding and two antibonding MO's (or local MO's) to the LPI. The triangle accommodates six electrons of the ECI forming three coupled "lone pairs". The full MO LPI is $= \{n_+ =$ no. of C–H, C–C, C–F bonds $+1$, $n_- =$ no. of all bonds $+2\}$.

The examples above illustrated some of the basic methodology of the structural-electronic method and how the SE formulas are drawn and the rules applied. Various classes of compounds may be treated in these ways for making deductions concerning their qualitative chemistry.

Appendix A. Quantum mechanical proof of the rules

It was shown in the text that the "structural electronic formula" (SEF) (or VIF) directly depicts the effective one-electron hamiltonian $h=\sum_{i,j}^{n}\beta_{ij}A^{ij}$ of the molecule, where $A^{ij}=1/2\{|e^i\rangle\langle e^j|+|e^j\rangle\langle e^i|\}$ with the abstract kets of the atomic orbitals which may be orthonormal or non-orthonormal. Each A^{ij} is a line in the SEF whose "strength" is the scalar β_{ij}/β_0 (often + or − unity).

Multiplying a valency point i in the SEF by a number κ, multiplies all the lines out of i by that κ, since each $|e^i\rangle$ or $\langle e^i|$ in h is multiplied by κ, i.e. (Rule 1),

$$\begin{aligned}\kappa\sum_{j(\neq i)}^{n}\beta_{ij}A^{ij}&=\sum_{j}\beta_{ij}\{\kappa|e^i\rangle\langle e^j|+|e^j\rangle\langle e^i|\kappa\}\\&=\sum_{j}(\kappa\beta_{ij})A^{ij}.\end{aligned}$$

Rule 2 amounts to adding an initial $|e^i\rangle$ to an end-point $|e^j\rangle$, i.e. $|e^i\rangle\to[|e^i\rangle+|e^j\rangle]$. Thus any combinations or successions of Rule 1 and Rule 2 applied to an SEF, is tantamount to making a bilinear transformation on the $\{A^{ij}\}$, and therefore of the $h \rightarrow h'$. These transformations have inverses, but do not have to be orthogonal, or unitary. Thus, the non-unitary ones do not preserve the eigenvalues, the spectrum of h, but only their $\{n_0, n_+, n_-\}$ types of the eigenvalues, hence the LPI. Since transformation from non-orthornormal (non-O.N.) AO-bases to orthonormal (O.N.) ones are also of the same type as the general, non-unitary transformations mentioned, the LPI is unaffected whether the initial AO's were non-O.N. or O.N.

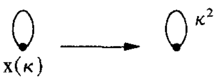
The two rules allow one to quasi-diagnonalize an h by cutting out more and more lines (as in the examples in text) so as to get the LPI pictorially (with practice this gets easier and easier).

In relating different molecules (isomers) to each other however, one more theoretical foundation is needed (derived in detail in Paper I of Ref. [12]) which we outline here. For a fixed geometry of a given molecule, the $\{|e^i\rangle\}$ are vectors in the Hilbert subspace V_n which however are also located in the 3 dim. Euclidean 3-space, ε_3. Thus an $|e^i\rangle$'s location $3D$ vector $\boldsymbol{R}_i$ should also be specified, $|e^i(\boldsymbol{R}_i)\rangle$. In a different geometry or different isomer, that nominally same $|e^i\rangle$ is mapped onto a different location, $|e^i(\boldsymbol{R}_i')\rangle$. These new kets are in a new Hilbert subspace V_n, not in the initial one. Thus the h of one isomer cannot be just transformed onto the h' of another one linearly. However it is shown that [12] one may define a $V_n(\boldsymbol{R}^{(n)})$ *field*, and a dyad space field $(V_n \times V_n^+)_{\boldsymbol{R}^{(n)}}$, each space of each $\boldsymbol{R}^n$ then being mapped onto a single $\boldsymbol{R}$-independent abstract, standardized dyad space $V_n \times V_n^+$. The hamiltonians of each isomer (constitutional, stereo, geometric...) are also mapped onto this standardized dyad space. It is in this new space that transformations given by the two Rules may be carried out. One thereby deduces if two different molecules (same empirical formula) are of the same LPI or not.

Appendix B. Electrononegativity difference loop-rules

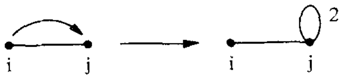
A loop in the SEF (as in some of the examples on the text), is a line starting and ending on the same valency point. Thus it depicts a term in h, such as $A^{ii} = |e^i\rangle\langle e^i|$. Rule 1 now multiplies by κ both ends of the line, so that the new "strength" becomes not $\kappa \times \xi_i$, but $\kappa^2 \times \xi_i$ (since $\kappa|e^i\rangle\langle e^i|\kappa = \kappa^2 A^{ii}$). Rule 2 becomes special "loop-subrules" as listed below.

(i) *Loop-rule 1.*



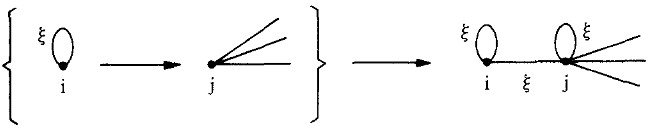
(A1)

(ii) *Loop-rule 2a.* If the initial VP, i, and the end point j to which Rule 2 is being applied are directly connected (by the line (ij)), then j acquires a loop of twice the strength of the (ij)-line.



(A2)

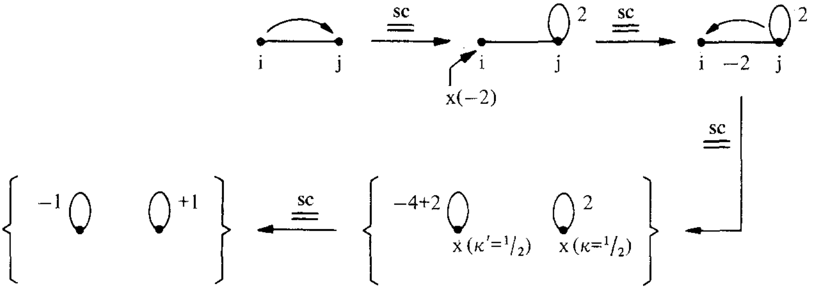
(iii) *Loop-rule 2b.* In using Rule 2, if the initial point i has a loop on it of strength ξ, that loop gets transferred onto the end point j, while at the same time, a line between i and j of strength ξ forms. The initial loop on i is also retained.



(A3)

The proof of these sub-rules follow from the general one in Appendix A. It is convenient nevertheless to remember the loop-rules separately rather than deducing them from the general Rules 1 and 2 each time.

As a simple illustration of the use of the loop-subrules, Eq. (A4) reduces a single line SEF, such as that of H_2 or of π-C_2H_4 into the expected result of a bonding-antibonding pair of MO's.



(A4)

$$\therefore\ LPI = \left\{ n_+ = n_- = 1 \right\}$$

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