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On the algebraic construction of chemistry from quantum mechanics. A fundamental valency vector field defined on the euclidean 3-space and its relation to the Hilbert space

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To obtain from quantum mechanics directly the qualitative deductions of chemistry, a mathematical machinery is set up. A single vector space, and a dyad space relate different molecules or spatial configurations of an isomeric set of atoms to each other. Different electronic Hamiltonians belong to the dyad space and are treated so as to be used directly without the intermediary of orbitals, parameter choices, or variational calculations.

Key words: Valency vector field—qualitative quantum chemistry—Dyad field of electronic Hamiltonians

1. Introduction and motivation

1.1. The gap between quantum mechanics and chemistry

Dirac said in 1929 that "the underlying physical laws necessary for the mathematical theory of chemistry are thus completely known, ..." [1].

However, Todd has recently stated [2] that organic chemistry had developed mainly in terms of a very few, simple, empirical rules pertaining to first 2-Dim, then 3-Dim *structural formulas* based mainly on the tetrahedral nature of the carbon atom. On the inorganic side, that "inert gases" like Xe too, should form chemical compounds was not foretold by quantum mechanics but was experimentally discovered in the sixties [3]. The entire, exciting, new field of organometallic chemistry and the related catalysis by metals show many unusual electronic effects, bonding situations, and structures such as hydrogen bridged and other osmium [4], rhenium, cobalt, platinum... cluster compounds [5], and multiple metal-metal bonds [6]. These phenomena too by and large were not predicted by quantum theory.

In the opinion of this author, the above gap exists, not because quantum mechanics is incapable of leading directly to a derivation of qualitative chemistry or of providing the basis for chemical reasoning. Nor are the intellectual achievements and additional language provided for chemists by the Lewis-Langmuir octet rule (which pre-dated quantum theory) [7], the *valence-bond* (VB) and resonance picture of Pauling [8], and the more spectroscopic then chemical molecular orbital (MO) methodology of Hund, Mulliken, Hückel [9, 10] and Walsh, [11] extended later by Fukui, [12] Woodward and Hoffman [13] and others in ingenious ways to organic chemistry, to be undermined. What nevertheless appears to be needed are additional mathematical tools to unlock the chemistry, and particularly the all crucial *qualitative chemistry* and reasoning of the chemical practitioners from the Schrödinger equation.

1.2. Chemistry as transformation of chemicals

Chemistry basically deals with the spatial, structural transformations of one or several molecules, or an isomeric assembly of atoms. The constitutional, geometric, or stereo-isomers of a molecule differ in the 3-dim spatial arrangements and/or connectivity of a given set of M atoms. In the Born-Oppenheimer [14] or adiabatic approximation, at each set $\{\vec{R}_i\} \equiv \boldsymbol{R}$ of nuclear positions there is a fixed electronic potential energy (P.E.), $E_{\text{elec}}(\{\vec{R}_i\})$ and a total P.E., $U(\{\vec{R}_i\})$ which includes the electrostatic nuclear repulsions.

Chemical transformations take place on the potential energy surface $U(\boldsymbol{R})$ of the given isomeric assembly (atom numbers conserved) of atoms. The sets of reactants, products, isomers, transition states are special points on the $U(\boldsymbol{R})$.

Quantum theory in the past has dealt mainly with individual, static molecular-electronic structures. Both in the one [15] and in the many-electron [16] approximations, the electronic wave function (w.f.), and the energy, $E_{\text{elec}}(\boldsymbol{R})$ are calculated at one or more points $\boldsymbol{R} \in \varepsilon_{3M}$, the Euclidean $3M$-dim space, at a time.

For a derivation of qualitative chemistry however, one needs to figure out the global relationships between the different points of the manifold $E_{\text{elec}}(\boldsymbol{R})$ embedded in ε_{3M}, and/or of $U(\boldsymbol{R})$.

Mulliken's separated atoms↔"united atom" orbital correlation diagrams, [17] extended to bent↔linear triatomics by Walsh [11] are steps in that direction as are the works of Woodward and Hoffmann [13]. The latter used orbital correlation diagrams between different organic molecular structures limited mainly to hydrocarbons. These methods are based on the molecular orbital (MO) approach and are dependent on the existence of point groups symmetries [18] But most molecules of chemistry lack spatial symmetry, yet their qualitative chemistry is not of a different nature than their cousins exhibiting high degree of point group symmetries.

The valence-bond method (VB) [8] also dealt with individual static structures. State correlation diagrams as in the Wigner–Witmer rules [19] somehow did not find much popular usage amongst practicing chemists.

In the present set of papers, we derive a quantum mechanical machinery suitable for qualitative deductions of chemistry, but also rigorously extendable and relatable to quantitative methodology. In particular, *a*) we generate a single vector space ($\equiv$the "valency space") from which all molecules are constructed thereby displaying their continuous as well as discrete relationships to each other, *b*) qualitative electronic properties are obtained directly from the conventional *structural formulas* (SF) or from the X-ray crystallographic ORTEP diagrams (3 dim geometric structures) without the intermediary of orbitals, parameter choices, or computer calculations, *c*) the space containing all the molecules of an isomeric assembly of atoms becomes the space containing all the electronic Hamiltonians. It is not necessary to obtain the individual orbitals, or the ground state wave functions first, as required in the MO and VB methods. Deductions follow directly from manifolds of Hamiltonians, *d*) various aspects of molecular electronic quantum theory and diverse mathematical constructs for them, such as Lie algebras, symmetries both in the Hilbert space and in Euclidean 3-space, various groups, many-electron states as higher rank tensors, some new covariance principles are obtained systematically as *algebraic structures built on the valency vector space.*

2. The fundamental valency vector space

Each atom i, infinitely far apart from all others, has a one-electron, Hilbert space $\mathscr{L}_2(\vec{R}_i)$ located at $\vec{R}_i \in \varepsilon_3$. For such a hydrogen atom for example, the hydrogenic eigenvectors at $\vec{R}_i$ would form a complete basis set for the infinite-dim $\mathscr{L}_2(\vec{R}_i)$. (For a many-electron atom, the basis set may start out with the self-consistent field (SCF) orbitals). The Hilbert space for an independent collection of atoms then would be $\mathscr{L}_2(\vec{R}_1) \otimes \mathscr{L}_2(\vec{R}_2) \cdots \otimes \mathscr{L}_2(\vec{R}_M)$. This is the space implied in both the MO and the VB methods as they both use atomic orbitals $\{|e_\mu(\vec{R}_i)\rangle\}$ centered on various $\vec{R}_i$. The MO takes linear combinations of them, then products, the VB starts directly with the products of AO's.

At any interatomic distance of physical, chemical interest however, the basis set as a union for the collection $\{\mathscr{L}_2(\vec{R}_i)\}$ is overcomplete as can be seen from the "overlap matrix",

$$\Delta = \{\langle e_\mu(\vec{R}_i)|e_\nu(\vec{R}_j)\rangle\}.$$

Even if the lowest AO's of neighboring atoms did not overlap much, higher orbitals would do so more and more leading to a singular Δ.

For a set of atoms close to each other, one could indeed take just a single, e.g. $\mathscr{L}_2(\vec{R}_1) = \mathscr{L}_2$ and with the single atomic basis set cover any wave function anywhere in ε_3, not just around $\vec{R}_1$. But this is highly impractical. Expansion of an AO at $\vec{R}_{j\neq 1}$ in terms of a basis for $\mathscr{L}_2(\vec{R}_1)$ is slowly convergent.

A single and not overcomplete basis for any valency shell one-electron wave function for a molecule or isomeric assembly is obtained by taking the n_i *valency* AO's of each atom ($n_i = 1$ for H; $n_i = 4$ for {B, C, N, O, F}; $n_i = 9$ for transition metals, etc. corresponding to $\{1s\}$, $\{2s, 2p\}$, $\{3d4s4p\}$, etc. respectively).

At the typical distances $|\vec{R}_i - \vec{R}_j|$, the valency overlaps $\langle e_\mu(R_i)|e_\nu(R_j)\rangle < 1$ and the finite dimensional Δ is non-singular [20].

Most of the qualitative chemistry involves the ground and excited valency shell states of a molecule or of a reacting assembly. Thus we can confine ourselves for the qualitative purpose at first, to the finite (n)-dimensional vector field $V_n(\vec{R})$. The m atoms, $i \in \{1, 2, \ldots, m\}$

$$V_n(\vec{R}) = V_{n_1}(\vec{R}_1) \oplus V_{n_2}(\vec{R}_2) \oplus \ldots V_{n_m}(R_m)_1 \tag{1}$$

each with its n_i valency shell AO's constituting a basis for V_{n_i} centered at $\vec{R}_i \in \varepsilon_3$ give a linear vector space $V_n(\vec{R})$ of

$$\text{Dim } V_n(\vec{R}) = n = \sum_{i \geq 1}^{m} n_i$$

defined at the configurational point $R \in \varepsilon_{3m}$. The $\{V_n(R)\}$ for all $\vec{R} \in \varepsilon_{3m}$ and $\vec{R} = \sum_{i \geq 1}^{m} \oplus \vec{R}_i$ define our *fundamental valency vector space field* $\{V_n(\vec{R})\}$.

As the molecule (or reacting assembly) of the spatial configuration $\{\vec{R}_i\}$ changes its shape in ε_3, the Dim $= 3m$ vector $\vec{R} \in \varepsilon_{3m}$ is transformed into another vector $\vec{R}' \in \varepsilon_{3m}$ and $V_n(\vec{R}) \to V_n(\vec{R}')$.

At each such $\vec{R}$, the vector spaces $\{V_n(\vec{R})\}$ are isomorphic to each other,

$$V_n(\vec{R}) \sim V_n(\vec{R}') \sim V_n(\vec{R}'') \ldots \tag{2}$$

and hence to a *standardized linear vector space* $\langle\langle V_n \rangle\rangle$ which is defined irrespective of a particular $\vec{R}$. If we omit the double brackets, or the $(\vec{R})$, i.e. write just V_n, we shall imply $\langle\langle V_n \rangle\rangle$.

3. The one-electron valency shell Hamiltonians and the Dyad space field $\{V_n(\vec{R}) \times V_n^+(\vec{R})\}$

For each spatial configuration $\{\vec{R}_i\} \to \vec{R}$ fixed by the positions of the nuclei, there is a one-electron effective Hamiltonian $h(\vec{R})$ for the molecule or assembly. The h may be e.g. that of the usual 2- or 3-dimensional Hückel method [9, 10], or the h^{eff} of a more complete method.

The representation of h on the valency vector space field is obtained by

$$I = \sum |e_{\mu i}(\vec{R}_i)\rangle\langle e_{\nu j}(\vec{R}_j)| \tag{3}$$

acting on h:

$$h(\vec{R}) = IhI = \sum \beta_{\mu\nu}(\vec{R})|e_\mu\rangle\langle e_\nu| \tag{4}$$

where

$$\beta_{\mu\nu}(\vec{R}) \equiv \langle e_{\mu i}(\vec{R}_i)|h|e_{\mu j}(\vec{R}_j)\rangle \tag{5}$$

We have assumed for now that

$$\langle e_\mu(R_i)|e_\nu(\vec{R}_j)\rangle = \delta_{\mu_i\nu_j} \tag{6}$$

as in the usual version of the Hückel ("HMO") method. In reality, for neighboring interacting atoms, the AO's are not at all mutually orthogonal, although the HMO method (as well as VB) assumes so. However, the formulation can be readily carried out also for non-orthogonal bases for the $V_n(\vec{R})$ and in a most general way as shown in another paper [22].

In Eq. (3), while I is the unity on $V_n(\vec{R})$, it also is a projector from the full Hilbert space $\mathscr{L}_2(\vec{R})$ onto the valency shell space $V_n \subset \mathscr{L}_2$. Thus IhI in Eq. (4) is actually the full h projected onto $(V_n \times V_n^+)$. The $\{\beta_{\mu\nu}\} \in$ real or complex number field.

The $h(R)$ in Eqs. (4–6) is a mixed tensor, or dyad on $V_n(\vec{R})$,

$$h(\vec{R}) \in V_n(\vec{R}) \times V_n^+(\vec{R}). \tag{7}$$

It is also a vector on $V_{(n^2)}(\vec{R})$ if one views each basis dyad $|e_\mu\rangle\langle e_\nu|$ as a basis vector for $V_{(n^2)}$.

Thus the $\{h(\vec{R})\}$ for various spatial configurations $\{\vec{R}\}$ of our molecule (or reacting assembly) constitute *i*) a dyad field on ε_{3m} and/or *ii*) a vector field on ε_{3m}.

If we map each $h(\vec{R})$ onto the standardized dyad space $\langle\langle V_n\rangle\rangle \times \langle\langle V_n^+\rangle\rangle \equiv V_n \times V_n^+$, *we get all isomeric molecules to belong in the same dyad space.* Alternatively, we can map each $h(\vec{R})$ viewed as a vector in its $V_{(n^2)}(\vec{R})$ vector space (Dim $= n^2$), onto the std. $\langle\langle V_{(n^2)}\rangle\rangle \equiv V_{(n^2)}$.

Thus towards our aim for chemistry to relate different structures and molecules to each other, we have obtained a single linear vector space, (or a single bilinear (dyad) space) containing all the isomeric spatial arrangements of an assembly of atoms along the electronic potential energy surface.

For each molecular structure there is an $h(\vec{R})$ whose AO representation from Eq. (4) is the hermitian matrix $\{\beta_{\mu\nu}\}$ (O.N. AO basis). The elements of β are also the coefficients of the vector ($\equiv$ the β-vector) in $V_{(n^2)} \equiv V_\beta$. The β-coefficients remain unchanged when $h(\vec{R})$ is mapped into the std. $(V_n \times V_n^+)$ or into the std. V_β.

The set of all isomeric structures' $\{h(\vec{R})\}$ does not cover the space $V_n \times V_n^+$, (nor V_β). That is because $R \in \varepsilon_{3m}$ is also embedded in ε_3.

Any set of n^2-numbers from the real or complex fields would define a vector in V_β. But such a vector does not necessarily correspond to an $h(\vec{R})$ or a molecule. First, one must have $\beta_{\mu\nu} = \beta_{\nu\mu}$. Second, $\beta_{\mu_i\nu_j}$ $(i \neq j)$ is a function of the interatomic distance $R_{ij} = |\vec{R}_i - \vec{R}_j|$. The $\beta_{\mu_i\nu_j}$ $(i \neq j)$ numbers can be arbitrary only for $n = 1$, 2, 3, or 4. Beyond a cluster size of four atoms, not all R_{ij} are independent, but are constrained to structures possible in ε_3.

Thus the set of ε_3-compatible β-vectors $(\leftarrow \{h(\vec{R})\};\ (\{\vec{R}_i\} \rightarrow \vec{R}))$ form one or more non-linear manifolds or varieties of $\mathrm{Dim} < n^2$ in $V_{(n^2)} = V_\beta$.

To proceed directly from a molecule's structure (or structural chemical formulas) to its electronic, quantum, and stability properties, we need to classify the β-vectors $(\leftarrow \{h(\vec{R})\})$ with respect to the manifold or variety a given β-vector belongs to. This classification is carried out in Ref. [23] and will form the basis of an *a priori* chemical transformation theory indicating qualitatively which molecules can react or rearrange into other 3-dim. structures.

References

1. Dirac, P. A. M.:Principles of quantum mechanics, 3rd Ed., Oxford: At the Clarendon Press 1958
2. Todd, A.: Wesleyan Symposium on Chemistry (Middlefield, Conn.: Wesleyan University, May 1982
3. Bartlett, N.: Chemistry of the Noble Gases, Holland: Elsevier, 1971
4. See e.g. Adams, R. D., Seleque, J.P.: in Comprehensive organometallic chemistry, Abel, E. W., Wilkinson, G., Stone, F. G., Eds., London: Pergamon Press, 1983
5. See e.g. a) Cotton, F. A., Wilkinson, G.,: Adv. Inorganic Chemistry, 4th Ed., New York; J. Wiley 1980; b) Johnson, B. F. G., Benfield, R. E.: in *Topics in Inorg. and Stereochem* Geoffroy, G. Ed.. N. Y.: Wiley, 1981; c) Muetterties, E. L.: Chem. Eng. News, **60**, No. 35 (1982)
6. Cotton, F. A., Chisholm, M. H.: Chem. Eng. News, **60**, No. 26, pp. 40–54 (1982)
7. Lewis, G. N.: a) Valence and the structure of atoms and molecules, Chemical Catalog Co., New York 1923; b) J. Amer. Chem. Soc. **38**, 762 (1916)
8. Pauling, L.: The Nature of the Chemical Bond, 3rd Ed., Ithaca, New York: Cornell Univ. Press, 1960
9. Hückel, E. Z. Physik **70**, 204 (1931)
10. cf. also the interesting comments of Feynman, R. P.: Lectures in Physics (1960)
11. Walsh, A. D. J.: Chem. Soc. 2260 (1953)
12. Fukui, K.: in Modern Quantum Chemistry: Vol. I-Orbitals, Sinanoğlu, O. Ed., N.Y.: Academic Press, 1965
13. Woodward, R. B., Hoffman, R.: J. Amer. Chem. Soc. **87**, 395 (1965)
14. Born, M., Oppenheimer, J. R.: Ann. Physik **84**, 457 (1927)
15. See e.g. a) Daudel, R., Sandorfy, C.: Semi-empirical wave-mechanical calens. and polyatomic molecules New Haven & London; Yale Press 1971; b) Sinanoğlu, O., Wiberg, K. B.: Sigma MO theory, Yale Press, 1971
16. See e.g. a) Hurley, A. C.: Electron correlation in small molecules. New York; Academic Press, 1976; b) Sinanoğlu, O.: Proc. Natl. Acad. Sci. USA **47**, 1217 (1961); J. Mol. Struc. **19A**, 81 (1973); c) Sinanoğlu, O., Brueckner, K. A.: Three approaches to electron correlation, New Haven & London; Yale Press, 1970
17. Mulliken, R. S.: Rev. Mod. Phys. **4**, 1 (1932)
18. See e.g. a) Wigner, E: Gruppentheorie und ihre Anwendung auf die Quantenmechanik der Atomspektren. Braunschweig: Vieweg & Sohn 1931; b) Cotton, F. A.: Chemical Applications of Group Theory, 2nd Ed., New York: Wiley-Interscience, 1971
19. Wigner, E., Witmer, E. E.: Z. Physik **51**, 859 (1928)
20. At the united atom limit the finite dim. Δ too becomes singular. This "Δ-catastrophe" pointed out in Ref. [21], apparently was overlooked in the early developments of the MO notions
21. Sinanoğlu, O.: in Chemical Spectroscopy and Photochemistry in the Vacuum Ultraviolet, Sandorfy, C. et al., Eds. Dordrecht; D. Reidel, pp. 337–384 1974
22. Sinanoğlu, O.: A principle of linear covariance for quantum mechanics and the electronic structure theory of molecules; Theoret. Chim. Acta (Berl.), in press
23. Sinanoğlu, O.: Non-unitary classification of molecular electronic structures and other atom clusters Theoret. Chim. Acta (Berl.), in press

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