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Non-unitary classification of molecular electronic structures and other atom clusters

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Molecules or reacting assemblies of an isomeric set of atoms become related to each other regardless of any spatial symmetry by the principle of linear covariance and the valency dyad field introduced in two previous papers by the author. Crucial electronic indices characterize certain equivalence classes into which molecules get classified under transformations which are in general non-unitary.

Key words: Non-unitary transformations—Classification of molecules—Equivalence classes of molecules

1. Introduction

Our object is to relate different molecules to each other. We need to deduce directly from quantum mechanics how qualitative quantum electronic properties change as one or more molecules, made of the same isomeric assembly of atoms, change their three dimensional spatial configuration in $\mathscr{E}_3$ (Euclidean 3-space), isomerize, react, or rearrange into other molecules.

To this end, we introduced two notions in the previous two papers of this series: i) the fundamental valency dyad space field [1], and ii) a principle of linear covariance [2] for quantum mechanics in general and for the quantum theory of molecules and other mixed atom clusters in particular.

Previously, the basic staple of molecular quantum mechanics has been point group theory [3], spatial symmetry [4]. But this is more suited to the properties of individual molecules. Computational methods too deal with one geometry at a time.

The present paper will show that the molecules or reacting assemblies (RA) of an isomeric set of atoms become related to each other by the principle of linear covariance [2] and the valency dyad space field [1] regardless of any spatial symmetry. Crucial electronic indices characterize certain equivalence classes into which molecules get classified under transformations which are in general non-unitary.

2. The crucial electronic indices of a molecule are symmetry independent invariants

To each $\{\vec{R}_m\} \equiv \{\vec{R}\}$ in $\mathscr{E}_3$, a spatial configuration of an isomeric assembly of m-atoms, i.e. a particular atom cluster or a molecule, M, there corresponds a full electronic Hamiltonian, $H_{\text{electr}}(\{\vec{R}\})$ which in turn is mapped into the independent electrons approximation $h_{\text{HMO}}(\{\vec{R}\})$. [We shall treat the $\{h\}$ here which display the key qualitative features. The results are extended to the many-electron $\{H\}$ in another paper.]

The covariant form of the $h(\{\vec{R}\})$ of a particular M is [2]

$$h = \beta_{ij} |e^i\rangle\langle e^j| \equiv \beta_{ij} A^{ij} \tag{1}$$

with the starting linear basis frame $\{|e_i\rangle\}$ consists of the in general non-orthonormal (non-O.N.), but linearly independent [5] valency space [1] atomic orbitals, $\{\text{AO}(\vec{R})\}$. On the basis $\boldsymbol{\beta}$ is the conventional $2D$ or $3D$ Hückel matrix. However, Eq. (1) here, also holds for any other linear frame, [2] *though the actual* $\boldsymbol{\beta}$ *will change with the frame.*

Under any $S \in L(n)$, the general linear group (let us take it over the real field), $n = \#\{|e_i\rangle\}$, (the $n \geq m$ in general with many-electron atoms. With uni-valency point atoms $n = m$).

$$S: \{\beta_{ij}\} \to \{\bar{\beta}_{kl} = S_{k}^{\cdot i} \beta_{ij} S^{j}_{\cdot l}\}, \tag{2a}$$

$\boldsymbol{\beta}$ transforms covariantly, while $\{A^{ij}\}$ does so contravariantly:

$$S: \{A^{ij}\} \to \{\bar{A}^{kl} = S^{k}_{\cdot i} A^{ij} S_{j}^{\cdot l}\}. \tag{2b}$$

The h itself in Eq. (1) remains invariant under any such transformation, as it should by the newly stated principle of linear covariance which was shown [2] to be dictated by the "superposition principle" of quantum mechanics.

We see in Eq. (2a) that *a molecule or other* M (its $h(\{\vec{R}\})$) *is represented by many different* $\boldsymbol{\beta}$*-matrices depending on the linear frame used.*

In the conventional quantum theory of molecules, only a single $\boldsymbol{\beta}$, that on the $\{AO(\vec{R})\}$ frame represents an M. This non-covariant, frame specific $\boldsymbol{\beta} \equiv \boldsymbol{\beta}^{\text{AO}}$ is placed so much emphasis on that only those transformations which leave $\boldsymbol{\beta}^{\text{AO}}$ the same, singled out as "symmetry operations", have received attention. These are of course the $\{\vec{R}\}$-fixed, point group symmetries [3, 4], $\mathscr{G}$.

Elements $S_g \in \mathcal{G}$, give

$$S_g : \boldsymbol{\beta}^{\mathrm{AO}} \to \boldsymbol{\beta}^{\mathrm{AO}} \tag{3}$$

(i.e. $[\boldsymbol{\beta}^{\mathrm{AO}}, \mathcal{G}] = 0$, since $S_g^{-1} = S_g^{+}$) while with the more general $S \in L(n)$, the $\boldsymbol{\beta}$ changes along an "orbit" (mathematics sense) of $L(n)$, while the h itself is invariant.

The Eq. (3) is a special case of Eq. (2a), since

$$\mathcal{G} \subset L(n). \tag{4}$$

The $\mathcal{G}$-operations are actually symmetries of the geometric object $\{\vec{R}\}$ in ε_3. As $\{\vec{R}\}$ is unchanged under $\mathcal{G}$, so is the $\boldsymbol{\beta}^{\mathrm{AO}}$ which is in a direct relation to, and determined by $\{\vec{R}\}$.

the $\mathcal{S}_n$ being the symmetric group [6] (permutation group) on n-objects (here the n-AO's if $n = m$ as in alkali clusters). So there are further special cases of Eq. (2):

a) If under some S such that S is not a point group operation ($S \notin \mathcal{G}$), but

$$\left.\begin{array}{l} S \in \mathcal{O}(n) \text{ or } U(n) \\ \text{and} \\ S : \boldsymbol{\beta}^{\mathrm{AO}} \to \boldsymbol{\beta}^{\mathrm{AO}}, \end{array}\right\} \tag{6}$$

it will appear that there is a "hidden" symmetry leading to "accidental" degeneracies in the spectrum $\{\lambda_i\}$ of β^{AO}. We might call these "*Hilbert space symmetries*" as opposed to the $\mathcal{G}$ on ε_3, spatial symmetries.

b) If for some S such that

$$\left.\begin{array}{l} S \in \mathcal{O}(n) \text{ or } U(n) \\ \text{but} \\ S : \boldsymbol{\beta}^{\mathrm{AO}} \to \boldsymbol{\beta}' \end{array}\right\} \tag{7a}$$

we have with $S = S_U \in U(n)$, therefore $S_U^{-1} = S_U^{+}$,

$$\left.\begin{array}{l} \boldsymbol{\beta}' = \mathbf{S}_U \boldsymbol{\beta}^{\mathrm{AO}} \mathbf{S}_U^{+} \\ \text{and} \\ \mathbf{A}' = (\mathbf{S}_U^{+})^{-1} \mathbf{A} \mathbf{S}_U^{-1} \end{array}\right\} \tag{7b}$$

Hence h itself, Eq. (1), is "unitarily invariant" as a special case of our "linear invariance".

From Eq. (7b), $\boldsymbol{\beta}' \mathbf{S}_U = \mathbf{S}_U \boldsymbol{\beta}^{\mathrm{AO}}$, for this case (b), as compared to the $[\boldsymbol{\beta}^{\mathrm{AO}}, \mathbf{S}_U] = 0$ of case (a).

In either case the spectrum of $\boldsymbol{\beta}$, $\{\lambda_i\}$ remains unchanged under Eqs. (7a) or (b). [For the relation of Eq. (7) to the rare case of the "iso-spectrality" of different isomers, cf. below.]

The S∈ subgroups of $L(n)$ in Eq. (5), transform O.N. frames to other O.N. frames. Then also, we saw that, whether $\boldsymbol{\beta}^{\mathrm{AO}}$ remained or (rarely) changed, the $\{\lambda_i\}$, eigenvalues (e.v.) of $\boldsymbol{\beta}$ are unchanged.

By the principle of linear covariance [2], non-O.N. frames will do just as well. Under arbitrary non-unitary $S \in L(n)$, by Eqs. (1) and (2), h and *its* eigenvalues are invariant. These are the physically significant objects. The $\boldsymbol{\beta}$'s and the spectrum of a particular $\boldsymbol{\beta}$, on the other hand, are frame dependent.

A $\boldsymbol{\beta}$ resulting after an $S \in L(n)$ so that $\boldsymbol{\beta} \neq \boldsymbol{\beta}^{\mathrm{AO}}$, is the covariant *representation* of h on a contravariant frame which is usually non-O.N.

Given an arbitrary $\boldsymbol{\beta}$ could one determine whether it represents h albeit on a non-O.N. frame? The rest of this section shows the answer is yes.

The principle of linear covariance [2] puts all frames related by $\{S\} \in L(n, C)$ over the complex field on the same footing. Results of the foremost practical importance are obtained however if we confine ourselves here to $L(n, \mathcal{R})$ over the real field (additional features with $L(n, C)$ will be treated in another publication).

The h and its e.v.'s are invariants of $L(n, \mathcal{R}) \equiv L(n)$ frame changes, while $\{\beta_{ij}\}$ are covariant.

While the eigenvalues $\{\lambda_i^{\beta}\}$ of a $\boldsymbol{\beta}$ change as β changes with the frame, the LPI ≡ "*level pattern indices*" ≡ $\{n_+, n_0, n_-\}$, *the numbers of positive, zero, and negative eigenvalues* of any $\{\boldsymbol{\beta}\}$ (hence also equal to those of h itself) are $L(n)$-frame independent.

Any two $\boldsymbol{\beta}$'s representing the same h on some $L(n)$-frames will be called "*L*-equivalent", or "$\overset{\mathrm{L}}{=}$".

The "$\overset{\mathrm{L}}{=}$" is an equivalence relation: [a), $\beta \overset{\mathrm{L}}{=} \beta'$, $\beta' \overset{\mathrm{L}}{=} \beta$; b) $\beta \overset{\mathrm{L}}{=} \beta'$, $\beta \overset{\mathrm{L}}{=} \beta''$, $\beta' \overset{\mathrm{L}}{=} \beta''$; c) $\beta \overset{\mathrm{L}}{=} \beta$]. Proof follows from Eq. (2a) and that $SS' = S'' \in L(n)$ form a group.

Therefore, *all the* $\{\beta\}$ *representing the same h on* O.N. *or non-*O.N. *linear frames fall into one and only one L-equivalence class.*

Any one of the specific $\boldsymbol{\beta}$'s, e.g. the $\boldsymbol{\beta}^{\mathrm{AO}}$ can characterize this class, but a particularly convenient characterization is with $\boldsymbol{\beta}^{\mathrm{LPI}}$, diagonal with plus or minus ones and zeros on the diagonal, i.e. with the LPI.

As far as β's are concerned, the LPI are more fundamental and crucial indices for a molecule than the actual eigenvalues of $\boldsymbol{\beta}^{\mathrm{AO}}$ which would differ from those of h unless the AO's were O.N. (which they are not), and with bases changes.

This is just as well since in practice most conventional MO-theory tools used qualitatively by the chemist are in reality ways to determine not the numerical values of e.v.'s—which depend on parameter choices, etc.—but the types of "orbitals" which are bonding $(\alpha + \beta)$. Non-bonding $(\lambda_{\beta}^{\mathrm{AO}} = 0)$, and anti-bonding $(\alpha - \beta)$, i.e. the $\{n_+, n_0, n_-\} \equiv$ LPI.

Conversely, coming back to the question posed, an arbitrary $\boldsymbol{\beta}$, which is $n \times n$ over $\mathcal{R}$, represents h if it has the same LPI as the h.

3. Different molecules or clusters classified into equivalence classes

Let M_I and M_{II} be two isomeric molecules or clusters with fixed geometries and with their h_I and h_{II}.

All the $n \times n\{\beta\}$ over $\mathfrak{R}$ representing M_I (or h_I) fall in one L-equivalence class C_I. (They are on the same "L-orbit".)

Similarly for $\{\beta;\, h_{II}\}$ and C_{II}.

In the relation between M_I and M_{II} only two cases can arise: a) If $(\mathrm{LPI})_I \neq (\mathrm{LPI})_{II}$ then $C_I \neq C_{II}$ and conversely. Then *no* β_I in any frame can equal any of the $\boldsymbol{\beta}_{II}$ in any frame. b) Suppose there is one $\boldsymbol{\beta}_I$ in some frame that is the same as some $\boldsymbol{\beta}_{II}$ in one of its frames. Then $(\mathrm{LPI})_I = (\mathrm{LPI})_{II}$; $C_I = C_{II}$ and the two molecules M_I and M_{II} will be in the same equivalence class: $M_I \overset{L}{=} M_{II}$; $h_I \overset{L}{=} h_{II}$. (Either two elements are in distinct equivalence classes, or if the two orbits intersect at a $\boldsymbol{\beta}$, then the orbits are one and the same, because each $\boldsymbol{\beta}$ can belong in one and only one L-class.)

Consequences: The members $\{M\}$ of an isomeric assembly get classified into distinct L-equivalence classes $\{C_i\}$. Each M (its h) belongs in one and only one C_i. Each class is characterized by a distinct LPI. Molecules (or chemically unstable clusters) with the same LPI are in the same class in any linear basis frame.

Let M_I and M_{II} be in the same L-class ($M_I \overset{L}{=} M_{II}$), and $\boldsymbol{\beta}_I^{\mathrm{AO}}$ be the conventional Hückel matrix of M_I. In general $\boldsymbol{\beta}_{II}^{\mathrm{AO}}$, but since $\boldsymbol{\beta}_I^{\mathrm{AO}} \overset{L}{=} \boldsymbol{\beta}_{II}^{\mathrm{AO}}$, there will be some in general non-O.N. basis frame for M_{II}, such that the representation of h_{II} in that frame $\bar{\boldsymbol{\beta}}_{II} = \boldsymbol{\beta}_I^{\mathrm{AO}}$. In other words one can find a linear frame for II, such that the graph which depicts $\bar{\boldsymbol{\beta}}_{II}$ will look the same as the $2D$ or $3D$ Hückel graph of M_I, i.e. of $\boldsymbol{\beta}_I^{\mathrm{AO}}$.

One might call M_I and M_{II} if they are $\overset{L}{=}$ to each other, "*iso*-LPI" or "*isonomic*" molecules (or clusters).

Thus the members of an isomeric assembly of reacting atoms or molecules, or of static molecules each with its fixed geometry, become classified by their LPI's into equivalence classes. The qualitative chemistry of molecules can be deduced directly from this class structure without the intermediary of detailed quantum calculations on the computer, parameter choices, *etc.* The considerations of Refs. [1, 2] and above will be supplemented by practical techniques introduced in the next two papers of this series, then enabling various applications.

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