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Chemical algebra.
II: Discriminating pairing products

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The algebra of stereogenic pairing equilibria is presented in a very general context. Starting from the notions of fuzzy subgroup and conjugacy link, chemical pairing constants between molecular species **u** and **v** having a skeletal symmetry group G are formulated as "pairing products" on a G-Hilbert space. "Discriminating pairing products" K are defined by the conditions: "$K \geqslant 1$" and "$K = 1 \Leftrightarrow$ the representative vectors of the paired species are G-equivalent". When G has only two elements, the pairing product is always discriminating. For several skeletal symmetries, if the vectors are "enantiomorphic ($\mathbf{v} = \sigma\mathbf{u}, \sigma^2 = e, \sigma \notin G$), then K is greater than 1 and reaches 1 only if **u** is "achiral": "chirality indexes" and general "permutational indexes" are then defined from $K(\mathbf{u}, \sigma\mathbf{u})$. The general model is illustrated by some examples.

1. Introduction

In preceding papers, chemical hypotheses were specified to represent the constant of pairing equilibria $2\mathbf{u}/\mathbf{v} \rightleftarrows \mathbf{u}/\mathbf{u} + \mathbf{v}/\mathbf{v}$ by an algebraic expression, where **u** and **v** are vectors featuring molecules [1]. These molecules are supposed to be skeletal analogs which pair tightly under the influence of a single interaction of either attractive-type or repulsive-type. Three assumptions were invoked: *skeleton symmetrization, skeleton overlap pairing and scalar product form of the ligand interaction.* Two constants were defined, depending on whether the stereogenicity is regarded as an "enthalpic contribution" (constant K') or as an "entropic contribution" (constant K).

The pairing constant $K'(\mathbf{u}, \mathbf{v})$ was proven to be always greater than 1 for attractive-type interactions, and smaller than 1 for repulsive-type interactions [2]. Nevertheless, $K'(\mathbf{u}, \mathbf{v})$ may equal 1 even if **u** and **v** are not chemically equivalent: that is the reason why our efforts focus on the chemical pairing constant K.

For attractive-type interactions, if G acts by permutation on a two-site skeleton ($G \cong \mathbb{S}_2$), then $K(\mathbf{u}, \mathbf{v})$ was proven to be always positive and it was proven to vanish only when **u** and **v** are equivalent skeletal analogs. The chemical implications of these algebraic speculations were analyzed for some equilibrating stereoselective chemical reactions: olefin metathesis, Diels-Alder reactions and cyclopropanation reactions. When **u** and **v** represent enantiomers, the same statement was proven for various skeletal symmetries, and in particular for tetrahedral symmetry [3].

A very general formulation is now detailed for the sake of mathematical consistency. Beginning with the notion of fuzzy symmetry group, a set-theoretic introduction is first proposed [4]:

DEFINITION 1

Let G be a group. A fuzzy subset $\underline{A}$ of G is called a "fuzzy subgroup of G" if its membership function $\mu_{\underline{A}}: G \to [0, 1]$ satisfies:
(i) $\underline{A}$ contains a trivial element, i.e. $\exists g \in G, \mu_{\underline{A}}(g) = 1$.
(ii) $\forall (g, h) \in G^2, \mu_{\underline{A}}(g) \cdot \mu_{\underline{A}}(h) \leqslant \mu_{\underline{A}}(gh)$.
(iii) $\forall g \in G, \mu_{\underline{A}}(g) = \mu_{\underline{A}}(g^{-1})$.

The definition and its consequences were shown to meet basic definitions of group theory [4]. Throughout the discussion, p denotes a strictly positive real number having the thermodynamical significance $p = -a/r^q kT, a < 0$ (only attractive-type interactions are considered).

2. Pairing products on metric spaces

DEFINITION 2

Let a compact or finite group G act on a metric space (E, d) and preserve the distance ($\forall g \in G, \forall (M, N) \in E^2, d(gM, gN) = d(M, N)$ [5]). For each point M in E, the map

$$\mu_{\underline{A}} = \mu_M: G \to [0, 1]$$
$$g \to \exp[-d(gM, M)/\sqrt{2}]$$

is the membership function of a fuzzy subgroup $\underline{A}$ of G (the requirement (ii) in definition 1 results from the triangular inequality). This fuzzy subgroup is denoted as $\underline{A} = \underline{G}^M$.

PROPOSITION 1

Straight from definition 2, it follows that:
(i) The trivial part of $\underline{G}^M$ is the stabilizator of M: $T(\underline{G}^M) = G^M$.
(ii) If M and N belong to the same orbit (i.e. if $\exists h \in G, N = hM$), then $\underline{G}^M$ and $\underline{G}^N$ are *trivially conjugated*, namely: $\forall g \in G, \mu_N(g) = \mu_M(h^{-1}gh)$ [4].

DEFINITION 3

Under the same conditions as in definition 2, for each couple $(M, N) \in E^2$, the map

$$\mu_M^N : G \to [0, 1]$$
$$g \to \exp[-d(gM, N)/\sqrt{2}]$$

is the membership function of a fuzzy subset of G denoted as $\underline{G}_M^N$.

PROPOSITION 2

Straight from the definition, it follows:
(i) $\forall (g, h) \in G^2, \mu_M^N(g^{-1}) = \mu_N^M(g)$ and $\mu_{hM}^N(g) = \mu_N^M(h^{-1}g)$.
(ii) The trivial part of $\underline{G}_M^N$ is $T(\underline{G}_M^N) = \{g \in G; N = gM\} = G_M^N$.
(iii) $\underline{G}_M^N$ is a fuzzy subgroup of G, if and only if $G \cdot M = G \cdot N$. Then $\underline{G}_M^N = \underline{G}^M$. Moreover, $T(\underline{G}_M^N) = \varnothing \Leftrightarrow G \cdot M \neq G \cdot N$.
(iv) $\underline{G}_M^N$ is a right class modulo a fuzzy subgroup $\underline{A}$ of G, if and only if M and N belong to the same orbit. Then $\underline{A} = \underline{G}^M$.

THEOREM 1

$\underline{C} = \underline{G}_M^N$ is a conjugacy link between $\underline{A} = \underline{G}^M$ and $\underline{B} = \underline{G}^N$ [4].

Proof

From the inequality $d(gM, N) + d(hM, N) \geqslant d(gM, hM) = d(h^{-1}gM, M)$, it follows that

$$\forall (g, h) \in G^2, \mu_{\underline{C}}(g) \cdot \mu_{\underline{C}}(h) \leqslant \mu_{\underline{A}}(h^{-1}g) = \mu_{h\underline{A}}(g) \leqslant \mu_{\underline{C}}(g)/\mu_{\underline{C}}(h) .$$

From the inequality $d(h^{-1}gM, M) + d(hM, N) \geqslant d(gM, N)$, it follows that

$$\mu_{h\underline{A}}(g) \leqslant \frac{\mu_{\underline{C}}(g)}{\mu_{\underline{C}}(h)} .$$

Analogous inequalities are obtained by permuting M and N. Therefore $\underline{C}$ is a conjugacy link between $\underline{G}^M$ and $\underline{G}^N$. □

DEFINITION 4

Retaining the same notations, the reciprocal of the $1/p$ power of the corresponding conjugacy index X is denoted as $K_p(M, N)$ and is called the "pairing product of M and N":

$$K_p(M, N) = (1/X)^{1/p} = \left[\frac{\#\underline{A}\#\underline{B}}{(\#\underline{C})^2}\right]^{1/p}$$

$$= \frac{\left(\int_G e^{-pd^2(gM,M)/2}\, dg\right)^{1/p} \left(\int_G e^{-pd^2(gN,N)/2}\, dg\right)^{1/p}}{\left(\int_G e^{-pd^2(gM,N)/2}\, dg\right)^{2/p}} .$$

By using the basic properties of the distance d and the isometric character of the action of G on (E, d), the statements below are immediately obtained:

PROPOSITION 3

$\forall (M,N) \in E^2, \forall (g,h) \in G^2$,
(i) $K_p(M,N) = K_p(N,M)$.
(ii) $K_p(gM,hN) = K_p(M,N)$ (K_p is "completely G-invariant").
(iii) $K_p(gM,hM) = 1$.

Replacing the fuzzy subsets $\underline{A}$, $\underline{B}$ and $\underline{C}$ by their trivial parts in the expression of $X = 1/K_p^P(M,N)$, we get: $TX(M,N) = (\#T(\underline{C}))^2/(\#T(\underline{A}) \cdot T(\#\underline{B})) = (\#G_M^N)^2/(\#G^M \cdot \#G^N) = 0$ or 1 (proposition 2). Therefore, for any point M_0, the map

$$TX(M_0, \cdot): E \to [0,1],$$
$$N \to 1, \text{if } N \text{ belongs to orbit of } M_0,$$
$$N \to 0, \text{otherwise}.$$

is the membership function of the orbit of M_0.

Provided that:
(a) $\forall (M,N) \in E^2, 1/K_p(M,N) \leqslant 1$,
(b) $1/K_p(M,N) = 1 \Rightarrow M$ and N belong to the same orbit, TX is the integer part of $X = 1/K_p^p$. The maps $X(M_0, \cdot) = 1/K_p^p(M_0, \cdot): E \to [0,1]$ are interpreted as membership functions of "fuzzy orbits": they indicate "how much M_0 and N belong to the same orbit".

DEFINITION 5

A pairing product satisfying the conditions (a) and (b) is called a "discriminating pairing product".

PROPOSITION 4

When $p \to \infty$, K_p converges to a discriminating pairing product K_∞:

$$K_\infty(\mathbf{u}, \mathbf{v}) = \lim_{p \to \infty} K_p(\mathbf{u}, \mathbf{v}) = \exp\left[\operatorname*{Min}_{g \in G} d^2(g\mathbf{u}, \mathbf{v})\right].$$

Proof

$$K_p(\mathbf{u}, \mathbf{v}) = \frac{\left(\int_G \exp\left[-\frac{p}{2} d^2(g\mathbf{u}, \mathbf{u})\right] dg\right)^{1/p} \left(\int_G \exp\left[-\frac{p}{2} d^2(g\mathbf{v}, \mathbf{v})\right] dg\right)^{1/p}}{\left(\int_G \exp\left[-\frac{p}{2} d^2(g\mathbf{u}, \mathbf{v})\right] dg\right)^{2/p}}.$$

A well-known result claims that when $p \to +\infty$,

$$\left(\int_G \exp\left[-\frac{p}{2}d^2(g\mathbf{u},\mathbf{u})\right]dg\right)^{1/p} \to \operatorname*{Max}_{g\in G}\{\exp[-d^2(g\mathbf{u},\mathbf{u})/2]\} = 1$$

(reached for $g = e$),

$$\left(\int_G \exp\left[-\frac{p}{2}d^2(g\mathbf{v},\mathbf{v})\right]dg\right)^{1/p} \to \operatorname*{Max}_{g\in G}\{\exp[-d^2(g\mathbf{v},\mathbf{v})/2]\} = 1$$

(reached for $g = e$),

$$\left(\int_G \exp\left[-\frac{p}{2}d^2(g\mathbf{u},\mathbf{v})\right]dg\right)^{2/p} \to \operatorname*{Max}_{g\in G}\{\exp[-d^2(g\mathbf{u},\mathbf{v})/2]\}.$$

Owing to the facts that the exponential is an increasing real function and that $\exp[-X] = 1/\exp[X]$, the result follows. □

This result prompts us to find out whether the discriminating property can be extended to finite p values. It is noteworthy that if E is an Euclidean or Hermitian vector space, then $K_p^p(\mathbf{u},\mathbf{v}) = K_1(\sqrt{p}\mathbf{u}, \sqrt{p}\mathbf{v})$. Thus, as soon as K_1 is a discriminating pairing product, all pairing products K_p are discriminating for $p<\infty$.

3. Pairing product on G-Hilbert spaces

In the sequel, we consider complex vector spaces of finite dimension.

If the compact group G acts on a Hermitian C-vector space E according to a linear representation preserving the Euclidean distance (E is a G-Hilbert space), then, for any vector $\mathbf{u}\in E$, $\underline{G}^{\mathbf{u}}$ is defined by

$$\mu_{\mathbf{u}}: G \to [0,1],$$
$$g \to e^{-\{\|g\mathbf{u}-\mathbf{u}\|/\sqrt{2}\}}.$$

It is easily checked that if $\mathrm{Re}(z)$ denotes the real part of a complex number z, then the pairing product of the vectors $\mathbf{u}$ and $\mathbf{v}$, is given by

$$K_p(\mathbf{u},\mathbf{v}) = \frac{\left(\int_G e^{p\,\mathrm{Re}(g\mathbf{u}|\mathbf{u})}\,dg\right)^{1/p}\left(\int_G e^{p\,\mathrm{Re}(g\mathbf{v}|\mathbf{v})}\,dg\right)^{1/p}}{\left(\int_G e^{p\,\mathrm{Re}(g\mathbf{u}|\mathbf{v})}\,dg\right)^{2/p}}.$$

E is expanded as a direct sum of irreducible representations of G, $V_1, \ldots, V_r$, where V_1 is the unit representation: $E = m_1V_1 \oplus \cdots \oplus m_rV_r, m_i \in \mathbb{N}$. It is easily shown that if u_1 belongs to m_1V_1,

$$\forall(\mathbf{u},\mathbf{v})\in E^2, \quad K_p(\mathbf{u}+\mathbf{u}_1,\mathbf{v}) = e^{\|\mathbf{u}_1\|^2+2\,\mathrm{Re}(\mathbf{u}-\mathbf{v}|\mathbf{u}_1)}K_p(\mathbf{u},\mathbf{v}).$$

Thus, if $m_1 \neq 0$, for any couple of vectors $(\mathbf{u}, \mathbf{v})$, there exist an infinite range of vectors $\mathbf{u} + \mathbf{u}_1$ such that $K_p(\mathbf{u} + \mathbf{u}_1, \mathbf{v}) \geqslant 1$ (since $\mathrm{Re}(\mathbf{u} - \mathbf{v}|\mathbf{u}_1) \leqslant \|\mathbf{u} - \mathbf{v}\| \cdot \|\mathbf{u}_1\|$, it suffices to take $\mathbf{u}_1 \in m_1 V_1$ with a great enough norm: in particular, $\|\mathbf{u}_1\| \geqslant 2\|\mathbf{u} - \mathbf{v}\|$).

In a first approach, discriminating pairing products are sought by means of a minoration.

THEOREM 2

$$\forall h \in G, \quad \forall (\mathbf{u}, \mathbf{v}) \in E^2, \exp\left[\frac{L_{\mathbf{u},\mathbf{v}}(h)}{I(\mathbf{u}, \mathbf{v})}\right] \leqslant K_p(\mathbf{u}, \mathbf{v}),$$

with

$$L_{\mathbf{u},\mathbf{v}}(h) = \int_G e^{p\,\mathrm{Re}(g\mathbf{u}|\mathbf{v})} \cdot \mathrm{Re}(g\mathbf{u} - hg^{-1}\mathbf{v}|h\mathbf{u} - \mathbf{v})\, dg,$$

$$I_{\mathbf{u},\mathbf{v}} = \int_G e^{p\,\mathrm{Re}(g\mathbf{u}|\mathbf{v})}\, dg.$$

Therefore, if there exists an operation h such that $0 \leqslant L_{\mathbf{u},\mathbf{v}}(h)$, then $K_p(\mathbf{u}, \mathbf{v})$ is greater than 1.

The proof is essentially based on the convexity of the exponential and is given in reference [1] for a real Euclidean structure. Since only the real part of the Hermitian product appears in $K_p(\mathbf{u}, \mathbf{v})$, it is easily adapted to the present theorem. The result is now applied to the case $G = \{e, \sigma\}, \sigma^2 = e$.

THEOREM 3

Whatever the Hermitian representation space E of the group $G = \{e, \sigma\}$ ($\sigma^2 = e$) preserving the scalar product, the corresponding pairing product is a discriminating pairing product, i.e. $\forall (\mathbf{u}, \mathbf{v}) \in E^2$,

(i) $$1 \leqslant K_p(\mathbf{u}, \mathbf{v}) = \frac{\left(e^{p\|\mathbf{u}\|^2} + e^{p\,\mathrm{Re}(\sigma\mathbf{u}|\mathbf{u})}\right)^{1/p}\left(e^{p\|\mathbf{v}\|^2} + e^{p\,\mathrm{Re}(\sigma\mathbf{v}|\mathbf{v})}\right)^{1/p}}{\left(e^{p\,\mathrm{Re}(\mathbf{u}|\mathbf{v})} + e^{p\,\mathrm{Re}(\sigma\mathbf{u}|\mathbf{v})}\right)^{2/p}}.$$

(ii) $K_p(\mathbf{u}, \mathbf{v}) = 1 \Rightarrow \mathbf{u} = \mathbf{v}$ or $\sigma\mathbf{u} = \mathbf{v}$.

The proof has been detailed in ref. [1] for an Euclidean structure, and, again, it is easily extended to the Hermitian structure.

For $G = \{e, t, t^2\}, t^3 = e$, the reduction of theorem 2 is not sufficient to prove that the corresponding pairing products are discriminating [6]. Nevertheless, we were not able to prove that the pairing product of any G-vector space is not discriminating.

The pairing product of vectors which are bound to some relationship $\mathbf{v} = f(\mathbf{u})$ can be systematically envisioned:

- $\mathbf{v} = \mathbf{u} + \Delta\mathbf{u}$, $\|\Delta\mathbf{u}\| < \epsilon$. The study of the local (or differential) discriminating character of pairing products will be reported in ref. [7].

• $\mathbf{v} = -\mathbf{u}$. For $p = 1$:

$$K_1(\mathbf{u}, -\mathbf{u}) = \frac{\left(\int_G e^{\mathrm{Re}(g\mathbf{u}|\mathbf{u})}\, dg\right)^2}{\left(\int_G e^{-\mathrm{Re}(g\mathbf{u}|\mathbf{u})}\, dg\right)^2}$$

and therefore,

$$1 \leqslant K_1(\mathbf{u}, -\mathbf{u}) \Leftrightarrow 0 \leqslant \int_G \sinh[p\ \mathrm{Re}(g\mathbf{u}|\mathbf{u})]\, dg\,.$$

It is noteworthy that this inequality is not evidently proven or refuted.

• $\mathbf{v} \perp \mathbf{u}$, *i.e.* $(\mathbf{u}|\mathbf{v}) = 0$. The proposition below holds [8]:

PROPOSITION 5

Suppose that G is an *Abelian* group, and that E is an *irreducible* representation space of G ($\forall \mathbf{u} \in E, \forall g \in G, g\mathbf{u} = \chi(g)\mathbf{u}$, where χ is the character of the representation). Then, if $(\mathbf{u}|\mathbf{v}) = 0$, the corresponding pairing product $K_p(\mathbf{u}, \mathbf{v})$ is greater than 1.

• $\mathbf{v} = \sigma\mathbf{u}$, *with* $\sigma \in \mathrm{O}(E), \sigma^2 = e$. Owing to the chemical importance of the problem, the next part resumes results on $K_p(\mathbf{u}, \sigma\mathbf{u})$: the relevance of propositions below is illustrated by their application for quantifying chiral discrimination [3].

4. Permutational indexes and chirality indexes

DEFINITION 6

Let G be a finite or compact group, let E be a G-Hilbert space, and suppose that G is a subgroup of the isometry group of $E, \mathrm{O}(E) (G^E = \{e\}$ [5]). Suppose that there exists a subgroup of $\mathrm{O}(E), \mathcal{S}_2 \cong \{e, \sigma\}, \sigma^2 = e, G \not\supset \mathcal{S}_2$: the representation of G in E induces a representation of the group $\mathcal{S}_2 \cdot G$ (semi-direct product) in E itself.

Let K_p be a pairing product on E, and let us define the map

$$\chi_p : E \to [-1, +1]\,,$$

$$u \to \chi(\mathbf{u}) = \frac{\sqrt{K_p^p(\mathbf{u}, \sigma\mathbf{u})} - 1}{\sqrt{K_p^p(\mathbf{u}, \sigma\mathbf{u})} + 1}\,.$$

Let E be the n-fold product of a vector space U endowed with a scalar product $\langle \cdot | \cdot \rangle$: $E = (xU)^n$. Then, E is endowed with the scalar product defined by

$$\forall (\mathbf{u}, \mathbf{v}) \in E^2, \quad (\mathbf{u}|\mathbf{v}) = \sum_{k=1}^{n} \langle u_k | v_k \rangle\,,$$

where $\mathbf{u} = (u_1, \ldots, u_n), u_k \in U$ and $\mathbf{v} = (v_1, \ldots, v_n), v_k \in U$.

Assuming that $\mathcal{S}_2 \cdot G$ acts by permutation of the components u_i of $\mathbf{u} = (u_1, \ldots, u_n) \in E$ [9], χ is called a "permutational index of $\mathbf{u}$". This expression does not depend on the choice of $\sigma \in \mathcal{S}_2 \cdot G - G$. When G is isomorphic to a rotation group preserving an achiral skeleton in R^3 and σ acts as a mirror plane, an inversion or an improper rotation, χ has been called the "chirality index of $\mathbf{u}$" [3].

The quantity $\sqrt{K_p^p(\mathbf{u}, \sigma\mathbf{u})}$ is denoted as $\rho(\mathbf{u})$(K_p, χ and ρ are equivalent data). Then:

(1) if $\exists h \in G, \sigma\mathbf{u} = h\mathbf{u}$, then $\chi(\mathbf{u}) = 0$ $(\rho(\mathbf{u}) = 1)$.

(2) if K_p is discriminating, then $0 \leqslant \chi(\mathbf{u}) \leqslant 1$ $(1 \leqslant \rho(\mathbf{u}))$.

Results that have been proven in a chemical context [3] are now produced in a general context, but the same proofs can be retained.

- $G \cong \mathcal{A}_n$ (alternate group of n symbols), $\mathcal{S}_2 \cdot G \cong \mathcal{S}_n$ (nth symmetric group) [10]

THEOREM 4

Let U be a K-vector space ($K = R$ or C) endowed with a scalar product $\langle \cdot | \cdot \rangle$. Then, the permutational index is the ratio of the determinant to the permanent of the (n, n)-Hermitian matrix $(e^{p\langle u_i|u_j\rangle})_{1 \leqslant i \leqslant n, 1 \leqslant j \leqslant n}$. Moreover,

$$(1) \forall \mathbf{u} \in E = (xU)^n, \quad \chi(\mathbf{u}) = \frac{\begin{vmatrix} e^{p\langle u_1|u_1\rangle} & \cdot & \cdot & e^{p\langle u_1|u_n\rangle} \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ e^{p\langle u_n|u_1\rangle} & \cdot & \cdot & e^{p\langle u_n|u_n\rangle} \end{vmatrix}}{\begin{Vmatrix} e^{p\langle u_1|u_1\rangle} & \cdot & \cdot & e^{p\langle u_1|u_n\rangle} \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ e^{p\langle u_n|u_1\rangle} & \cdot & \cdot & e^{p\langle u_n|u_n\rangle} \end{Vmatrix}} \geqslant 0.$$

(2) $\forall \mathbf{u} \in E = (xU)^n, \chi(\mathbf{u}) = 0 \Leftrightarrow \exists h \in \mathcal{A}_n, h\mathbf{u} = \sigma\mathbf{u}$, where σ belongs to $\mathcal{S}_n - \mathcal{A}_n$.

(3) the corresponding results are also valid for the real symmetric matrix $(e^{\mathrm{Re}\langle u_k|u_l\rangle})$.

- $G \cong \mathcal{C}_4$ (cyclic group with four elements)

THEOREM 5

Suppose $U = R$. The subgroup $\mathcal{C}_4 \cdot \mathcal{S}_2$ of $\mathcal{S}_4$ acts on $E = R^4$ by permutating the four components of the vectors of E. The corresponding permutational index is written as: $\forall \sqrt{p}$ $\mathbf{u} = (x, y, z, t) \in R^4$,

$$\chi(\mathbf{u}) = \frac{e^{x^2+y^2+z^2+t^2}+2e^{xy+yz+zt+tx}+e^{2xz+2yt}-e^{x^2+z^2+2yt}-e^{y^2+t^2+2xz}-e^{2xy+2zt}-e^{2xt+2yz}}{e^{x^2+y^2+z^2+t^2}+e^{xy+yz+zt+tx}+e^{2xz+2yt}+e^{x^2+z^2+2yt}+e^{y^2+t^2+2xz}+e^{2xy+2zt}+e^{2xt+2yz}}$$

and

(1) $\forall \mathbf{u} \in R^4, \chi(\mathbf{u}) \geqslant 0$.

(2) $\forall \mathbf{u} \in R^4, \chi(\mathbf{u}) = 0 \Leftrightarrow \exists h \in \mathcal{C}_4, h\mathbf{u} = \sigma\mathbf{u}$, wherein σ belongs to $\mathcal{C}_4 \cdot \mathcal{S}_2 - \mathcal{C}_4$.

- $G \cong \mathcal{D}_4$ (non-cyclic group with four elements isomorphic to $\mathcal{S}_2 \times \mathcal{S}_2$)

THEOREM 6

Suppose $U = R$. The subgroup $(\mathcal{S}_2 \times \mathcal{S}_2) \cdot \mathcal{S}_2 \cong \mathcal{D}_4 \cdot \mathcal{S}_2$ of $\mathcal{S}_4$ acts by permutating the four components of the vectors of R^4. The corresponding permutational index is written as $\forall \sqrt{p}\ \mathbf{u} = (x, y, z, t) \in R^4$:

$$\chi(\mathbf{u}) = \frac{e^{x^2+y^2+z^2+t^2}+e^{2xy+2zt}+e^{2xt+2yz}+e^{2xz+2yt}-e^{x^2+z^2+yt}-2e^{xy+yz+zt+tx}-e^{y^2+t^2+2xz}}{e^{x^2+y^2+z^2+t^2}+e^{2xy+2zt}+e^{2xt+2yz}+e^{2xz+2yt}+e^{x^2+z^2+2yt}+2e^{xy+yz+zt+tx}+e^{y^2+t^2+2xz}},$$

and

(1) $\forall \mathbf{u} \in R^4, \chi(\mathbf{u}) \geqslant 0$.

(2) $\forall \mathbf{u} \in R^4, \chi(\mathbf{u}) = 0 \Leftrightarrow \exists h \in \mathcal{D}_4, h\mathbf{u} = \sigma\mathbf{u}$, wherein σ belongs to $\mathcal{D}_4 \cdot \mathcal{S}_2 - \mathcal{D}_4$.

Suppose that E is the direct sum $E = V_1 \oplus \cdots \oplus V_r$, where $V_i = (xU)^{n_i}$. Suppose that G is the direct product of permutation groups $G_1, \ldots, G_r$, and that each G_i acts on V_i by permutation of the n_i components of orbit-vectors $u^i = (u_1^i, \ldots, u_{n_i}^i)$. Let $\chi_1, \ldots, \chi_r$ be permutational indexes of respectively $G_1, \ldots, G_r$. Then χ is the product of the χ_i's:

$$\chi(\mathbf{u} = u^1 \oplus \ldots \oplus u^r) = \prod_{i=1}^{r} \chi_i(u^i) = \chi(\mathbf{u}).$$

Consequently, if the properties $\forall u^i \in V_i, \chi_i(u^i) \geqslant 0$ and $\chi_i(u^i) = 0 \Leftrightarrow \exists h \in G_i$, $hu^i = \sigma u^i$ are satisfied by all the V_i's, the corresponding property is also satisfied in E.

THEOREM 7

If ligand parameters are real numbers, the differential equation below holds [11]:

$$\sum_{i=1}^{n} \frac{\partial \Delta}{\partial x_i} = 2\left(\sum_{i=1}^{n} x_i\right) \cdot \Delta,$$

where $\sqrt{p}\ \mathbf{u} = (x_1, \ldots, x_n)$, and Δ is the numerator of χ:

$$\Delta(\mathbf{u}) = \int_G \exp\left[\sum_{k=1}^{n} x_{g(k)} x_k\right] dg - \int_G \exp\left[\sum_{k=1}^{n} x_{g(k)} x_{\sigma(k)}\right] dg .$$

(Proof is given in ref. [3].)

Finally, in order to dwell on the consistency of the algebraic model, the definitions can be applied to situations without a direct chemical interpretation. Let a group G act on a Hermitian vector space E and preserve the scalar product. Suppose that S is a part of E endowded with a measure $d\tau$. The set $\mathsf{H}(S)$ of the maps $\mathbf{v}: S \to E$ satisfying $\int_S \|\mathbf{v}(u)\|^2 \, d\tau_u < \infty$ is a Hilbert space for the scalar product defined by

$$\forall(\mathbf{v}, \mathbf{v}') \in \mathsf{H}(S)^2, \quad \langle \mathbf{v}|\mathbf{v}'\rangle = \int_S (\mathbf{v}(u)|\mathbf{v}'(u)) \, d\tau_u .$$

Then, G naturally acts on $\mathsf{H}(S)$ by: $\forall \mathbf{v} \in \mathsf{H}(S), \forall g \in G, g \cdot \mathbf{v}: S \to E, u \to \mathbf{v}(gu)$.

The pairing product of two maps $\mathbf{v}$ and $\mathbf{v}'$ of $\mathsf{H}(S)$ is therefore defined.

If S is a part of R^m, let G_S denote the isometry group of S. Considering the subduced representation of the rotation subgroup $G = G_S^+$ of G_S, the chirality index of any element in $\mathsf{H}(S)$ (for $p = 1$) is defined. In particular, the chirality index of the canonical map Id_S: $S \to E, u \to u$, is a "vectorial chirality index" of S. Several calculations performed without an intent of chemical interpretation always afford vectorial chirality indexes which are strictly greater than 1 [12]: they support the relevance of the questions asked by the model.

5. Conclusion

The discriminating character of other pairing products is under current investigation, and among our calculations performed to date, no pairing product was found to be greater than 1, nor to match 1 for non-G-equivalent vectors. Nonetheless, the preceding prerequisites have been set out in view of further developments concerning the design of "completely G-invariant distances" associated with discriminating pairing products [13].

References and notes

[1] R. Chauvin, J. Phys. Chem. 96 (1992) 4701.

[2] In ref. [1], it was shown that the equilibrium constant is written as

$$K'(\mathbf{u}, \mathbf{v}) = \frac{\prod_{g\in G}[gu/u] \prod_{g\in G}[gv/v]}{\left(\prod_{g\in G}[gu/v]\right)^2} = \exp\left[\frac{-a}{r^q kT}\sum_{g\in G}(g(u-v)|(u-v))\right] .$$

The following proposition was proven in Supplementary Material of ref. [1]:

Theorem. Let G be a compact group, endowed with its Haar measure dg (if G is a finite group $dg = 1/|G|$, wherein $|G|$ is the order of G, and the integral symbol $\int$ is replaced by the sum symbol $\sum$). Let $V = m_1 V_1 \oplus \ldots \oplus m_r V_r$ be the splitting of V into irreductibles representations. The character of V_i is noted as χ_i and its degree is denoted as n_i. Let $\mathcal{P}_i: V \to m_i V_i$ be the projector of V onto the isotypical representation $m_i V_i$. Then

$$\forall g \in G, \forall (u,v) \in V^2, \int_G (ghu|hv)\, dh = \sum_{i=1}^{r} \frac{(\mathcal{P}_i u|\mathcal{P}_i v)}{n_i} \cdot \chi_i(g)\,.$$

If $u = v$, then $\int_G (ghu|hu)\, dh = \sum_{i=1}^{r} \frac{\|\mathcal{P}_i u\|^2}{n_i} \cdot \chi_i(g)$. By integration over g, if $u = u_1 - u_2$: $\int_G (g(u_1 - u_2)|(u_1 - u_2))\, dg = \|\mathcal{P}_1(u_1 - u_2)\|^2 \geqslant 0$. $K'(u,v)$ is therefore greater than 1 for attractive-type interaction ($a<0$), and always smaller than 1 for a repulsive-type interaction ($a>0$).

[3] R. Chauvin, J. Phys. Chem. 96 (1992) 4706.
[4] R. Chauvin, Paper I of this series, J. Math. Chem. 16 (1994) 245.

[5] For example, G may be a subgroup of the isometry group of E. But in general, let G^E be the normal subgroup of G stabilizing all points in E: $G^E = \{g \in G; \forall M \in E, gM = M\}$. Then G/G^E is isomorphic to a subgroup of the isometry group of E.

[6] The following proposition is proven without difficulties:
Proposition. If $G = \{e, t, t^2\}$, let E be a G-Hilbert space.
Setting: $\forall h \in G, \forall (u,v) \in V^2, L_{u,v}(h) = \int_G e^{p\,\mathrm{Re}(gu|v)} \mathrm{Re}(gu - hg^{-1}v|hu - v)\, dg$,
then: $L_{u,v}(h) = \frac{1}{3}[a_{u,v} e^{p\,\mathrm{Re}(hu|v)} + b_{u,v}]$,
with: $a_{u,v} = \|u\|^2 + \|u\|^2 - \mathrm{Re}(tu|u) - \mathrm{Re}(tv|v)$; $b_{u,v} = \sum_{k=0}^{2} e^{p\,\mathrm{Re}(t^k u|v)}(\|t^k u - v\|^2 - a_{u,v})$.
When $E = \mathbb{C}^3$, $G = \{e, t, t^2\}$ acts by even permutations of the three coordinates of vectors $u = (x, y, z) \in E$ ($G \cong \mathcal{A}_3$, alternate group of three symbols). $K_1(u,v)$ denotes the pairing product of u and v ($p = 1$). It is possible to find vectors u and v fulfilling: $\forall h \in G, L_{u,v}(h) \leqslant 0$. Indeed, for $u = (0, \frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}})$ and $v = (0, 1, 0)$, we calculate: $a_{u,v} = 3/2$, $b_{u,v} \approx -3.208\ldots$ and: $L_{u,v}(e) = L_{u,v}(t^2) \approx -0.166\ldots$ and $L_{u,v}(t) \approx -0.569\ldots$
However, $1 \leqslant K_1(u,v) \approx 1.1102\ldots$

[7] R. Chauvin, Paper IV of this series, J. Math. Chem. 16 (1994) 285.

[8] In theorem 1 the quantity $L_{u,v}(h)$, $h \in G$, has been defined, and for $h = e$:

$$L_{u,v}(e) = \int_G e^{p\,\mathrm{Re}[\chi(g)(u|v)]} \mathrm{Re}(\chi(g)u - \chi^*(g)v|u - v)\, dg$$

$$= \int_G e^{p\,[\mathrm{Re}\chi(g)(u|v)]} \mathrm{Re}(\chi(g)u - \chi^*(g)v - \chi(g)v + \chi(g)v|u - v)\, dg$$

$$= \int_G e^{p\,\mathrm{Re}[\chi(g)(u|v)]} \{\mathrm{Re}\,\chi(g)\|u - v\|^2 + \mathrm{Re}[(\chi(g) - \chi^*(g))(v|u - v)]\}\, dg$$

$$= \int_G e^{p\,\mathrm{Re}[\chi(g)(u|v)]} \{\mathrm{Re}\,\chi(g)\|u - v\|^2 + \mathrm{Re}[2i\,\mathrm{Im}\,\chi(g)(v|u - v)]\}\, dg$$

$$= \int_G e^{p\,\mathrm{Re}[\chi(g)(u|v)]} \{\mathrm{Re}\,\chi(g)\|u - v\|^2 + \mathrm{Re}[2i\,\mathrm{Im}\,\chi(g)(v|u - v)]\}\, dg$$

$$= \int_G e^{p\,\mathrm{Re}[\chi(g)(u|v)]} \{\mathrm{Re}\,\chi(g)\|u - v\|^2 + 2\,\mathrm{Im}\,\chi(g)\,\mathrm{Re}[i(v|u) - i\|v\|^2]\}\, dg$$

$$= \int_G e^{p\,\mathrm{Re}[\chi(g)(u|v)]} \{\mathrm{Re}\,\chi(g)\|u - v\|^2 + 2\,\mathrm{Im}\,\chi(g)\,\mathrm{Im}(u|v)\}\, dg\,.$$

Since $(u|v) = 0$: $L_{u,v}(e) = \|u - v\|^2 \int_G \mathrm{Re}\,\chi(g)\, dg = \|u - v\|^2\, \mathrm{Re}\{\int_G \chi(g)\, dg\} = 0$ or $\|u - v\|^2$, the latter value being obtained only if E is a unit representation space of G. Thus, applying theorem 2, $K_p(u,v) \geqslant 1$. Proposition 5 follows.

[9] That means that: $\forall u \in E, \forall g \in G \cdot \mathcal{S}_2, \forall k \in \{1, \ldots, n\}, (gu)_k = u_{g(k)}$.

[10] The detailed proof is given in Supplementary Material of ref. [3]. For 1), all the eigenvalues of the matrix prove to be positive; the result is based on the fact that all the coefficients of the McLaurin expansion of the exponential function are positive. For 2), the properties of van der Mond determinants are used.

[11] A condensed formulation is given: if $u_0 = (1, \ldots, 1)$, then: $(2\Delta(u)u - \overrightarrow{\mathrm{grad}}\Delta(u)|u_0) = 0$.

[12] Some numerical results obtained without difficulties are produced (with $p = 1$).

(a) S is a sphere of unit radius of R^m.

• $m = 1$: $S = \{-1, +1\}$; $G_S^+ = \{e\}$; $d\tau_u = \frac{1}{2}$; $dg = 1: \rho = e^2 (\geqslant 1)$.

• $m = 2$: $S = \{(\cos\theta, \sin\theta);\ \theta \in [0, 2\pi[\}$; $d\tau_u = \frac{1}{2\pi} d\theta$; $G_S^+ = \{$rotations centered at O, of angle $\alpha \in [0, 2\pi[\}$;

$dg = \frac{1}{2\pi} d\alpha: \rho = \frac{1}{2\pi}\int_0^{2\pi} e^{\cos\alpha} d\alpha (1.266\ldots \geqslant 1)$.

• $m = 3$: $S = \{(\sin\theta\cos\phi, \cos\theta\sin\phi, \cos\theta); \theta \in [0, \pi], \phi \in [0, 2\pi[\}; d\tau_u = \frac{1}{4\pi}\sin\theta\, d\theta\, d\phi$.

$G_S^+ = \{$rotations centered at O, of Euler angles $\alpha \in [0, 2\pi[, \beta \in [0, \pi], \gamma \in [0, 2\pi[\}$;

$$dg = \frac{1}{8\pi^3}\sin\beta\, d\alpha\, d\beta\, d\gamma: \rho = \frac{\displaystyle\int_0^{2\pi} \frac{e^{2\cos\alpha+1} - e^{-1}}{\cos\alpha + 1} d\alpha}{\displaystyle\int_0^{2\pi} \frac{e^{2\cos\alpha-1} - e}{\cos\alpha - 1} d\alpha} (\approx 1.16\ldots \geqslant 1).$$

(b) S is a full sphere of unit radius of R^m.

• $m = 1$: $S = [-1, +1]$; $G_S^+ = \{e\}$; $d\tau_u = \frac{1}{2}$; $dg = 1: \rho = e^{2/3} (\geqslant 1)$.

• $m = 2$: $S = \{(r\cos\theta, r\sin\theta);\ \theta \in [0, 2\pi[, r \in [0, 1]\}$; $d\tau_u = \frac{1}{\pi} r\, d\theta\, dr$; $G_S^+ = \{$rotations centered at O, of angle $\alpha \in [0, 2\pi[\}$; $dg = \frac{1}{2\pi} d\alpha: \rho = \frac{1}{2\pi}\int_0^{2\pi} e^{(\cos\alpha)/2} d\alpha (\approx 1.063\ldots \geqslant 1)$.

• $m = 3$: $S = \{(\rho\sin\theta\cos\phi,\ \rho\cos\theta\sin\phi, \rho\cos\theta);\ \rho \in [0, 1];\ \theta \in [0, \theta],\ \phi \in [0, 2\pi[\}$; $d\tau_u = \frac{3}{4\pi}\rho^2 \sin\theta\, d\rho\, d\theta\, d\phi$; $G_S^+ = \{$rotations centered at O, of Euler angles $\alpha \in [0, 2\pi[, \beta \in [0, \pi], \gamma \in [0, 2\pi[\}$;

$$dg = \frac{1}{8\pi^3}\sin\beta\, d\alpha\, d\beta\, d\gamma: \rho = \frac{\displaystyle\int_0^{2\pi} \frac{e^{3(2\cos\alpha+1)/5} - e^{-3/5}}{\cos\alpha + 1} d\alpha}{\displaystyle\int_0^{2\pi} \frac{e^{3(2\cos\alpha-1)/5} - e^{3/5}}{\cos\alpha - 1} d\alpha}.$$

(c) S is constituted by the four vertice of a tetrahedron of unit radius in R^3.

$$G_S = \mathrm{T}_d, G_S^+ = \mathrm{T}: \rho = \frac{e^1 + 3e^{-1/3} + 8e^0}{6e^{1/3} + 6e^{-1/3}} (\approx 1.015\ldots \geqslant 1).$$

(d) S is constituted by the five vertice of trigonal bipyramid of unit radius in R^3.

$$G_S = \mathrm{D}_{3h}, G_S^+ = \mathrm{D}_3: \rho = \frac{e^1 + 2e^{1/10} + 3e^{-2/5}}{e^{1/5} + 3e^{2/5} + 2e^{-7/10}} (\approx 1.037\ldots \geqslant 1).$$

(e) S is constituted by the six vertice of an octahedron of unit radius in R^3.

$$G_S = \mathrm{O}_h, G_S^+ = \mathrm{O}: \rho = \frac{e^1 + 8e^0 + 6e^{1/3} + 9e^{-1/3}}{e^{-1} + 8e^0 + 6e^{-1/3} + 9e^{1/3}} (\approx 1.012\ldots \geqslant 1).$$

(f) S is constituted by the eight vertice of a cube of unit radius in R^3.

Here again: $G_S = \mathrm{O}_h, G_S^+ = \mathrm{O}: \rho = \dfrac{e^1 + 8e^{1/4} + 6e^{-1/2} + 9e^0}{e^{-1} + 8e^{-1/4} + 6e^{1/2} + 9e^0} (\approx 1.005\ldots \geqslant 1)$.

[13] R. Chauvin, Papers III and IV of this series, J. Math. Chem. 16 (1994) 269, 285.