Journal of Mathematical Chemistry 16 (1994) 285–308

Chemical algebra. IV: "Length" of transformation pathways between skeletal analogs

Remi Chauvin

Laboratoire de Chimie de Coordination du C.N.R.S., Unité 8241, liée par convention à l'Université Paul Sabatier, 205 Route de Narbonne, 31 077 Toulouse Cedex, France

Received 7 July 1994

Even if the eq. ($\mathbb{E}$) of completely G-invariant distance extensions derived from a pairing product is not resolved, a distance is defined by means of a metric obtained by differential resolution. Under specified conditions, the linear element solution $d\sigma^2$ is homogeneous to square coordinate differentials. Integration of $d\sigma$ along a curve of E affords a length relative to $d\sigma^2$. Boundaries of the curve represent skeletal analogs **u** and **v**, whereas inner points represent intermediates in the transformation $\mathbf{u} \to \mathbf{v}$, where the ligand parameters are supposed to vary continuously: a stereogenic pairing equilibrium between infinitesimally close skeletal analogs is assumed. If the curve runs orthogonal to a unit representation space of G, the length is infinite and the curve might be regarded as a "fractal" transformation pathway. The "thermodynamic gap" D_p is always shorter than the "kinetic" distance of the metric $d\sigma^2$.

1. Introduction

In accordance with a previously discussed model [1], molecules are described by a skeletal symmetry G and ligand (atoms or bonds) parameters taking their values in a Hermitian or Euclidean vector space E. The transformation of a molecule **u** into a skeletal analog **v** is considered.

A measure of the thermochemical gap $D_p(\mathbf{u}, \mathbf{v})$ between **u** and **v** has been proposed by considering the stereogenic pairing equilibrium: $2\mathbf{u}/\mathbf{v} \rightleftarrows \mathbf{u}/\mathbf{u} + \mathbf{v}/\mathbf{v}$ [2]. An equation ($\mathbb{E}$) defining D_p from the pairing constant K_p has been constructed [2]. The completely G-invariant solution $D_p(\mathbf{u}, \mathbf{v})$ (it does not depend on the reference orientation arbitrarily selected for the mathematical description of skeletal analogs) has only a thermodynamical meaning. The pathway of the transformation $\mathbf{u} \to \mathbf{v}$ (or $\mathbf{v} \to \mathbf{u}$) is not taken into account in the design of $D_p(\mathbf{u}, \mathbf{v})$. From a mechanistic standpoint, the transformation is partitioned in several steps characterized by thermodynamical functions. The sums of the absolute values of these energy functions are characteristic of the whole transformation, featuring a "length" of the reaction diagram. The partition is supposed to be infinitesimal: the chemical transformation is assumed to be "completely gradual", i.e. it happens as a continuous change of the ligand parameter values in **u** to the ligand parameter values in **v**.

Beside the chemical potential, the thermodynamics of the transformation of an intermediate **w** to a very neighbouring intermediate ($\mathbf{w} + d\mathbf{w}$) can be quantified by the thermochemical gap $D_p(\mathbf{w}, \mathbf{w} + d\mathbf{w})$ calculated by mean of eq. ($\mathbb{E}$). The D_p value of $\mathbf{w} \to \mathbf{w} + d\mathbf{w}$ is formally related (through eq. ($\mathbb{E}$)) to the free energy difference of the stereogenic pairing equilibrium:

$$2\mathbf{w}/(\mathbf{w} + d\mathbf{w}) \rightleftarrows \mathbf{w}/\mathbf{w} + (\mathbf{w} + d\mathbf{w})/(\mathbf{w} + d\mathbf{w})\,.$$

The sum of the solutions $D_p(\mathbf{w}, \mathbf{w} + d\mathbf{w})$ of ($\mathbb{E}$) is in fact an integral representing the "length" of the pathway (defined by the intermediates **w**) leading from **u** to **v**.

2. Definition equation of metrics on sets of skeletal analogs

Let us remind the basic equation providing a definition of completely G-invariant distance candidates $D_p : E \times E \to R_+$ from discriminating pairing products K_p associated with an isometric action of a compact group G on a metric space (E, d) [2]:

$$\Phi_{\mathbf{u},\mathbf{v}}(D_p(\mathbf{u}, \mathbf{v})) = [K_p(\mathbf{u}, \mathbf{v})]^p \qquad (\mathbb{E})$$

with

$$\Phi_{\mathbf{u},\mathbf{v}}(x) = \iiiint_{G^4} \exp\left[\frac{p}{2}\,\frac{d^2(g\mathbf{u}, l\mathbf{v}) + d^2(k\mathbf{u}, h\mathbf{v}) - d^2(g\mathbf{u}, k\mathbf{u}) - d^2(l\mathbf{v}, h\mathbf{v})}{d(g\mathbf{u}, h\mathbf{v}) \cdot d(k\mathbf{u}, l\mathbf{v})}\, x^2\right] \times dg\, dh\, dk\, dl\,,$$

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

Solutions of ($\mathbb{E}$) are examined when the points **u** and **v** are infinitesimally neighbouring. For this purpose, the differential of a point **u** in E must be defined, that is to say the metric space E must be a complete normed vector space. In practice, E is assumed to be G-Hilbert space or its real Euclidean counterpart. The following notations are adopted (($\cdot|\cdot$) denotes the scalar product of E):

$$\forall(\mathbf{a}, \mathbf{b}) \in E^2\,, \quad \cos(\mathbf{a}, \mathbf{b}) = \mathrm{Re}\frac{(\mathbf{a}|\mathbf{b})}{\|\mathbf{a}\| \cdot \|\mathbf{b}\|}\,, \quad d^2(\mathbf{a}, \mathbf{b}) = \|\mathbf{a} - \mathbf{b}\|^2\,.$$

DEFINITION 1

Let G act on a normed vector space E and preserve the norm. Suppose that a pairing product K_p is discriminating. Let D_p be the corresponding completely G-invariant solution of ($\mathbb{E}$). For any points $\mathbf{u}$ and $\mathbf{v}$ in E, D_p is unequivocally defined by the equation

$$\Phi_{\mathbf{u},\mathbf{v}}(D_p(\mathbf{u},\mathbf{v})) = [K_p(\mathbf{u},\mathbf{v})]^p .$$

Even if K_p is not proved to be discriminating, let us consider the function $A_{\mathbf{u}}$ such that

$$A_{\mathbf{u}}(x) = \lim_{\boldsymbol{\varepsilon}\to\mathbf{0}} \Phi_{\mathbf{u},\mathbf{u}+\boldsymbol{\varepsilon}}(x)$$

(in the limit, $\boldsymbol{\varepsilon}$ is supposed to be colinear to some fixed direction).

When $\boldsymbol{\varepsilon}\to\mathbf{0}$, the definition equation of $x(\boldsymbol{\varepsilon}) = D_p^2(\mathbf{u},\mathbf{u}+\boldsymbol{\varepsilon})$ between $\mathbf{u}$ and $\mathbf{v} = \mathbf{u}+\boldsymbol{\varepsilon}$ reduces to

$$A_{\mathbf{u}}(x(\boldsymbol{\varepsilon})) = K_p^p(\mathbf{u},\mathbf{u}+\boldsymbol{\varepsilon}) = K^{\mathbf{u}}(\boldsymbol{\varepsilon}) \quad \text{(definition of } K^{\mathbf{u}}(\boldsymbol{\varepsilon})) .$$

Considering the two members of this equation as functions of $\boldsymbol{\varepsilon}$, successive differentiations at $\boldsymbol{\varepsilon} = \mathbf{0}$ give

$$\left[\frac{dA_{\mathbf{u}}}{dx}\right]_{x=x(\mathbf{0})=0} \cdot dx_0 = dK_{\mathbf{0}}^{\mathbf{u}} ,$$

$$\left[\frac{dA_{\mathbf{u}}}{dx}\right]_{x=0} \cdot d^2x_0 + \left[\frac{d^2A_{\mathbf{u}}}{dx^2}\right]_{x=0} \cdot dx_0^2 = d^2K_{\mathbf{0}}^{\mathbf{u}} .$$

In order to dwell on the spirit of the process, extensive proofs of theorems are reported in the appendix.

THEOREM 1

Let E be a real Euclidean vector space with a finite dimension n. Let G be a finite or compact isometry group of E. Let $K = K_1$ be the corresponding pairing product ($p = 1$ without a loss of generality: for other values of p, vectors $\mathbf{u}$ have to be replaced by $\sqrt{p}\,\mathbf{u}$).

The differential of $K^{\mathbf{u}}$ is zero over $E/G : dK_{\mathbf{0}}^{\mathbf{u}} = 0$. A direct use of the definition of $A_{\mathbf{u}}$ shows that at the same time, $[dA_{\mathbf{u}}/dx]_{x=0} = 0$. It follows that a first differentiation of ($\mathbb{E}$) does not afford a definition of $d\sigma^2$. On the other hand,

$$d^2K_{\mathbf{0}}^{\mathbf{u}} = \frac{2}{\mathbf{I}^2}\left\{\mathbf{I}\int_G (g(d\mathbf{u})|d\mathbf{u})e^{(g\mathbf{u}|\mathbf{u})}\,dg + \mathbf{I}\int_G (g\mathbf{u}|d\mathbf{u})^2 e^{(g\mathbf{u}|\mathbf{u})}\,dg - \left(\int_G (g\mathbf{u}|d\mathbf{u})e^{(g\mathbf{u}|\mathbf{u})}\,dg\right)^2\right\},$$

where $\mathbf{I} = \int_G e^{(g\mathbf{u}|\mathbf{u})}\,dg$.

(Proof is given in the appendix.)

Since $x(\boldsymbol{\varepsilon}) = D(\mathbf{u}, \mathbf{u} + \boldsymbol{\varepsilon})$, the squared differential of x at zero is denoted: $dx_0^2 = d\sigma^2$. The theorem claims that, providing that $[d^2 A_{\mathbf{u}}/dx^2]_{x=0} \neq 0$, eq. ($\mathbb{E}$) is locally equivalent to a definition equation of $d\sigma^2$:

$$\left[\frac{d^2 A_{\mathbf{u}}}{dx^2}\right]_{x=0} d\sigma^2 = d^2 K_{\mathbf{0}}^{\mathbf{u}} . \tag{$\mathbb{E}'$}$$

This equation has a single solution $d\sigma^2$ if: $d^2 K_{\mathbf{0}}^{\mathbf{u}} \cdot [d^2 A_{\mathbf{u}}/dx^2]_{x=0} \geqslant 0$.

THEOREM 2

Retaining the definitions of the preceding discussion,

$$\left[\frac{d^2 A_{\mathbf{u}}}{dx^2}\right]_{x=0} = \frac{2p}{[G : G^{\mathbf{u}}]^2} \frac{ds_1^2}{ds^2}, \quad \text{where} \quad G^{\mathbf{u}} = \{g \in G; g\mathbf{u} = \mathbf{u}\} \; ([G : G^{\mathbf{u}}] \geqslant 1),$$

where ds^2 denotes the Euclidean metric of E, and ds_1^2 denotes the Euclidean metric of the projection of E onto the unit representation subspace $\mathcal{P}_1(E)$.

(Proof is given in the appendix.)

Therefore, $[d^2 A_{\mathbf{u}}/dx^2]_{x=0} \neq 0$ only if the vector displacement $\boldsymbol{\varepsilon}$ at $\mathbf{u}$ has a non-zero unit component ($d\mathbf{u}_1 \approx \mathcal{P}_1(\boldsymbol{\varepsilon}) \neq \mathbf{0}$).

If, in addition, $d^2 K_{\mathbf{0}}^{\mathbf{u}} \geqslant 0$, then the solution of ($\mathbb{E}'$) is

$$d\sigma^2 = \frac{[G : G^{\mathbf{u}}]^2}{2p} \frac{ds^2}{ds_1^2} d^2 K_{\mathbf{0}}^{\mathbf{u}} .$$

If $[d^2 A_{\mathbf{u}}/dx^2]_{x=0} = 0$, ($\mathbb{E}'$) does not permit to define $d\sigma^2$ (if $d^2 K_{\mathbf{0}}^{\mathbf{u}} \neq 0$, the derived expression does not make sense: $d\sigma^2 = +\infty$!).

Let $B_{\mathbf{u}}$ be the function defined by: $\forall y \in R_+, B_{\mathbf{u}}(y) = A_{\mathbf{u}}(\sqrt{y})$. Then, differentiations of eq. ($\mathbb{E}$) may also be written as

$$\left[\frac{dB_{\mathbf{u}}}{dy}\right]_{y=x^2(0)=0} \cdot dy_0 = dK_{\mathbf{0}}^{\mathbf{u}} (= 0 \text{ from theorem 1})$$

$$\left[\frac{dB_{\mathbf{u}}}{dy}\right]_{y=0} \cdot d^2 y_0 + \left[\frac{d^2 B_{\mathbf{u}}}{dy^2}\right]_{y=0} \cdot dy_0^2 = d^2 K_{\mathbf{0}}^{\mathbf{u}} .$$

It is easily checked that

$$\left[\frac{dB_{\mathbf{u}}}{dy}\right]_{y=0} = \frac{1}{2}\left[\frac{d^2 A_{\mathbf{u}}}{dy^2}\right]_{y=0} = \iiint_{G^3} \lim_{\varepsilon \to \mathbf{0}} \cos(g\mathbf{u} - h(\mathbf{u} + \boldsymbol{\varepsilon}), k\mathbf{u} - \mathbf{u} - \boldsymbol{\varepsilon}) \, dg \, dh \, dk .$$

Since $dx_0 \approx D_p(\mathbf{u}, \mathbf{u} + \boldsymbol{\varepsilon}) - D_p(\mathbf{u}, \mathbf{u})$ and $dy_0 \approx D_p^2(\mathbf{u}, \mathbf{u} + \boldsymbol{\varepsilon}) - D_p^2(\mathbf{u}, \mathbf{u})$ when

$\boldsymbol{\varepsilon} \to \mathbf{0}$, and since $D_p(\mathbf{u}, \mathbf{u}) = 0$, the *formal* writing "$dy_0^2 = dx_0^4 = d\sigma^4$" is consistent. Therefore, if $[d^2 A_{\mathbf{u}}/dx^2]_{x=0} = 0$, then eq. (𝔼) takes the second differential form:

$$\left[\frac{d^2 B_{\mathbf{u}}}{dy^2}\right]_{y=0} d\sigma^4 = d^2 K_0^{\mathbf{u}} . \qquad (\mathbb{E}'')$$

This is a definition equation of $d\sigma^4$ as soon as $[d^2 B_{\mathbf{u}}/dy^2]_{y=0} \neq 0$. The theorem below claims that it has one real solution as soon as $d^2 K_0^{\mathbf{u}} \geqslant 0$.

THEOREM 3

Whatever the compact group G is: $[d^2 B_{\mathbf{u}}/dy^2]_{y=0} \geqslant 0$. And if G is a finite group: $[d^2 B_{\mathbf{u}}/dy^2]_{y=0} > 0$.

Proof

It is easily checked that

$$\left[\frac{d^2 B_{\mathbf{u}}}{dy^2}\right]_{y=0} = \iiint_{G^3} \lim_{\varepsilon \to 0} \cos^2(g\mathbf{u} - h(\mathbf{u} + \boldsymbol{\varepsilon}), k\mathbf{u} - \mathbf{u} - \boldsymbol{\varepsilon})\, dg\, dh\, dk \geqslant 0 .$$

This expression is strictly positive if the set of the members of G^3 satisfying

$$\lim_{\boldsymbol{\varepsilon} \to \mathbf{0}} \cos^2(g\mathbf{u} - h(\mathbf{u} + \boldsymbol{\varepsilon}), k\mathbf{u} - \mathbf{u} - \boldsymbol{\varepsilon}) \neq 0$$

cannot be neglected for the Haar measure of G^3. Since it equals 1 for $g = h = k = e$ (whatever $\boldsymbol{\varepsilon}$ is), this is always true for finite groups. □

We conclude that the existence of a differential solution for the basic equation (𝔼) by means of either eq. (𝔼′) or (𝔼″) depends on whether $d^2 K_0^{\mathbf{u}} \geqslant 0$. Furthermore, the solution is a consistent metric on E/G if $d^2 K_0^{\mathbf{u}}$ has a definite and positive bilinear form.

From the Cauchy–Schwartz inequality,

$$\mathbf{I} \int_G (g\mathbf{u}|d\mathbf{u})^2 e^{(g\mathbf{u}|\mathbf{u})}\, dg - \left(\int_G (g\mathbf{u}|d\mathbf{u}) e^{(g\mathbf{u}|\mathbf{u})}\, dg\right)^2 \geqslant 0 .$$

Thus, theorem 1 provides a sufficient condition ensuring that $d^2 K_0^{\mathbf{u}}$ is positive:

$$\int_G (g(d\mathbf{u})|d\mathbf{u}) e^{(g\mathbf{u}|\mathbf{u})}\, dg \geqslant 0 ,$$

i.e., whatever the value of $\mathbf{a}$ $(= d\mathbf{u})$ is: $\int_G (g\mathbf{a}|\mathbf{a}) e^{(g\mathbf{u}|\mathbf{u})}\, dg \geqslant 0$.

If $\mathbf{u}$ is close enough to the unit representation $(\forall g \in G, g\mathbf{u} \to \mathbf{u})$, $\int_G (g\mathbf{a}|\mathbf{a}) e^{(g\mathbf{u}|\mathbf{u})}\, dg$ tends to $e^{\|\mathbf{u}\|^2} \int_G (g\mathbf{a}|\mathbf{a})\, dg$. From a proposition given in refs. [1a,3], $\int_G (g\mathbf{a}|\mathbf{a})\, dg \geqslant 0$. Thus, $d^2 K_0^{\mathbf{u}}$ is positive for any vector $\mathbf{u}$ in the neighborhood of the unit representation (in particular in the neighborhood of zero).

THEOREM 4

Let G be an *Abelian* compact group acting on an Euclidean space E. Then, $d^2K_0^{\mathbf{u}}$ is *positive* anywhere in E/G.

(Proof is given in the appendix.)

If G is no longer Abelian, it is difficult to determine whether $d^2K_0^{\mathbf{u}}$ is always positive (and/or definite) in E/G. Nonetheless, some examples below validate the relevance of the question.

3. Irreducible representations

From now onwards, the terminology of representations in Hermitian C-vector spaces (G-Hilbert spaces) is adopted.

THEOREM 5

Let G be a compact group realized as an isometry group of the Euclidean plane $E \cong R^2$, such that if R^2 is identified to C, E is a G-Hilbert space of degree one with an irreducible character χ_i ($G = \mathrm{C}_n, \mathrm{D}_n, n = 2, \ldots, \infty$). Then $d^2K_0^{\mathbf{u}}$ is anywhere *positive* and *definite* in E/G.

(Proof is given in the appendix.)

General expressions of $d^2K_0^{\mathbf{u}}$, alternative to the expression given in theorem 1, are proposed when E is considered as a G-Hilbert space.

THEOREM 6

Let $E \cong R^2 \cong C$ be an irreducible representation space of a compact group G, isomorphic to an irreducible representation Γ of degree one, with a character $\chi = e^{i\alpha}$. Then

$$d^2K_0^{\mathbf{u}} = 2[K_1(\mathbf{u}, \mathbf{u} + d\mathbf{u}) - 1 - \mathcal{O}(|d\mathbf{u})^3] = 2\left\{\left(\frac{K}{I} - \frac{J^2}{I^2}\right) \mathrm{Re}^2(\mathbf{u}|d\mathbf{u}) + \frac{J}{I}\|d\mathbf{u}\|^2 - \left(1 - \frac{K}{I}\right) \mathrm{Im}^2(\mathbf{u}|d\mathbf{u})\right\},$$

where

$$I = \int_G e^{r^2 \cos\alpha(g)}\, dg\,, \quad J = \int_G \cos\alpha(g) e^{r^2 \cos\alpha(g)}\, dg\,,$$

$$K = \int_G \cos^2\alpha(g) e^{r^2 \cos\alpha(g)}\, dg\,.$$

In terms of polar coordinates (r, θ):

$$d^2K_0^{\mathbf{u}} = \left(\frac{r^2K}{I} - \frac{r^2J^2}{I^2} + \frac{J}{I}\right) dr^2 + \left(\frac{J - r^2L}{I}\right) r^2\, d\theta^2\,.$$

This results from theorem 1, but a somewhat intuitive proof is given in the appendix.

THEOREM 7

Let G be a finite group, and let $E \cong R^2$ be an isotypical G-Hilbert space of an irreducible representation of degree one with a character $\chi = e^{i\alpha}$. If E is not isotypical to the unit representation, then

$$\left[\frac{d^2 B_{\mathbf{u}}}{dy^2}\right]_{y=0} = \tfrac{1}{2} + 2\left(\frac{c}{|G|}\right)^2 \int_G \cos[2\alpha(g)]\, dg\, \frac{dr^2}{ds^2}\,,$$

where c is the number of elements g such that $\chi(g) = 1, ds^2 = \|d\mathbf{u}\|^2, dr^2 = d\|\mathbf{u}\|^2$. c is also the order of the group $C(e) = \{g \in G; \chi(g) = 1\}$, and $c/|G|$ is also the reciprocal of the index of $C(e)$ in G, $[G : C(e)]$.

(Proof is given in the appendix.)

COROLLARY

Under the same general hypothese as in theorem 7, G is supposed to be a cyclic group $C_n, n \geqslant 2$, and its natural representation on $E \cong R^2$ is considered $(\chi(g^k) = \exp[\frac{2ik\pi}{n}])$. Then $[d^2B_{\mathbf{u}}/dy^2]_{y=0}$ depends on dr^2/ds^2 only if $n = 2$. More precisely,

- if $G = C_2$, $\left[\frac{d^2 B_{\mathbf{u}}}{dy^2}\right]_{y=0} = \frac{1}{2}\left(1 + \frac{dr^2}{ds^2}\right)$,
- if $G = C_n, n \geqslant 3$, $\left[\frac{d^2 B_{\mathbf{u}}}{dy^2}\right]_{y=0} = \frac{1}{2}$,

(in polar coordinates in R^2, $ds^2 = dr^2 + r^2 d\theta^2$).

Proof

If $n = 2$,

$$|G| \int_G \cos[2\alpha(g)]\, dg = \cos[0] + \cos[2\pi] = 2\,.$$

If $n \neq 2$,

$$|G| \int_G \cos[2\alpha(g)]\, dg = \mathrm{Re}\left[\sum_{g \in G} e^{2i\alpha(g)}\right] = \mathrm{Re}\left[\sum_{k=0}^{n-1} \exp\left(\frac{4ik\pi}{n}\right)\right]$$

$$= \mathrm{Re}\left[\frac{1 - e^{4i\pi}}{1 - e^{4i\pi/n}}\right] = 0\,.$$

The corollary follows from theorem 7. □

A direct application of theorems 5, 6 and 7 allows the solution $d\sigma^4$ of eq. ($\mathbb{E}''$) to be explicitly calculated when E is a G-Hilbert space of degree one.

$$ds^4 = \frac{d^2 K_0^{\mathbf{u}}}{\left[\dfrac{d^2 B_{\mathbf{u}}}{dy^2}\right]_{y=0}} .$$

This formula is illustrated in the examples below.

(1) $G = C_\infty$

Let $\mathbb{C} \cong R^2$ be the irreducible representation space of C_∞ defined by

$$\forall\, g = e^{i\alpha} \in C_\infty\,, \quad \forall\, z = re^{i\theta} \in \mathbb{C}\,, \quad gz = re^{i(\theta+\alpha)} .$$

Using theorem 6 and the corollary of theorem 7, the solution of eq. ($\mathbb{E}''$) is simply calculated [4]:

$$d\sigma^4 = 4r^2\left(1 - \frac{J^2}{I^2}\right)dr^2 ,$$

with

$$I = \frac{1}{2\pi}\int_0^{2\pi} e^{r^2\cos\alpha}\, d\alpha\,, J = \frac{1}{2\pi}\int_0^{2\pi} e^{r^2\cos\alpha}\cos\alpha\, d\alpha .$$

(2) $G = C_2$

Euclidean pairing products of this group were proved to be discriminating. By a direct calculation or by applying theorem 6 and the corollary of theorem 7, the general expression of the solution of ($\mathbb{E}''$) for the representation "$\sigma\mathbf{u} = -\mathbf{u}$" is calculated:

$$d\sigma^4 = \frac{4}{1 + \dfrac{dr^2}{ds^2}}\left(\tanh r^2\, ds^2 + \frac{r^2}{\cosh^2 r^2}dr^2\right) ,$$

or using the polar coordinates:

$$d\sigma^4 = 4\frac{1 + r^2\dfrac{d\theta^2}{dr^2}}{2 + r^2\dfrac{d\theta^2}{dr^2}}\left[\left(\tanh r^2 + \frac{r^2}{\cosh^2 r^2}\right)dr^2 + r^2\tanh r^2\, d\theta^2\right] .$$

Along real lines ($d\theta = 0$: $F \cong \mathbb{R}$), $dr^2 = ds^2 = dx^2$,

$$\text{for } x \neq 0: \quad d\sigma^4 = 2\left(\tanh x^2 + \frac{x^2}{\cosh^2 x^2}\right) dx^2 ,$$
$$\text{for } x = 0: \quad d\sigma^2 = dx^2 .$$

Along the circle of radius $r > 0$ $(dr = 0)$: $d\sigma^4 = 4r^2 \tanh r^2 \, d\theta^2$.

4. Kinetic distances on E/G

Let E/G be identified to a part of representative vectors of E, and suppose that E contains a unit representation subspace of G. Let us consider curves of E with everywhere a non-zero projection onto the isotypical unit representation ($ds_1 \neq 0$). Theorem 2 suggests that if $d\sigma$ is a positive differential form (especially if K_p is a discriminating pairing product), a distance Δ_p could be defined by

$$\Delta_p(\mathbf{u}, \mathbf{v}) = \underset{\text{curves } C_{\mathbf{u}\to\mathbf{v}}}{\mathrm{Inf}} \int_{C_{\mathbf{u}\to\mathbf{v}}} d\sigma = \frac{[G : G^{\mathbf{u}}]}{\sqrt{2p}} \underset{\text{curves } C_{\mathbf{u}\to\mathbf{v}}}{\mathrm{Inf}} \int_{C_{\mathbf{u}\to\mathbf{v}}} \frac{(ds/dt)}{(ds_1/dt)} \sqrt{\frac{d^2 K_0^{\mathbf{u}}}{dt^2}} \, dt .$$

A curve $C_{\mathbf{u}\to\mathbf{v}}$ with an extremum length for a metric $d\sigma^2$ can be called a "geodesic line" between **u** and **v**. By extension, curves without a projection on the unit representation ($ds_1 = 0$) would have an infinite length. However, an area can be associated with such curves by means of the definition of $d\sigma^2$ from eq. ($\mathbb{E}''$) as soon as $[\frac{d^2 B_{\mathbf{u}}}{dy^2}]_{y=0} \neq 0$ (theorem 3):

$$A(\mathbf{u}, \mathbf{v}) = \underset{\text{curves } C_{\mathbf{u}\to\mathbf{v}}}{\mathrm{Inf}} \int_{C_{\mathbf{u}\to\mathbf{v}}} d\sigma^2 = \underset{\text{curves } C_{\mathbf{u}\to\mathbf{v}}}{\mathrm{Inf}} \int_{C_{\mathbf{u}\to\mathbf{v}}} \sqrt{\frac{1}{\left[\frac{d^2 B_{\mathbf{u}}}{dy^2}\right]_{y=0}}} \sqrt{\frac{d^2 K_0^{\mathbf{u}}}{dt^2}} dt .$$

Metric forms on E have a quadratic expression:

$$ds^2 = \sum_i \sum_j \alpha_{ij} dx_i dx_j ,$$

where the x_i's are curvilinear coordinates of M. The α_{ij}'s are functions of the x_i's, and ds^2 is *heterogenous* and *isotropic* (the α_{ij}'s depend on the position, but not on the "direction" in which the linear element is measured: the α_{ij}'s do not depend on the dx_i's). Metric forms $d\sigma^2$ on E/G depend on both the position $(x_1, \ldots, x_n)$ and on the "relative directions" $(\frac{dx_2}{dx_1}, \ldots, \frac{dx_n}{dx_1})$ with respect to the subspace of the unit representation (where the metric and eventually the interpolating completely G-invariant distance coincide with the Euclidean metric). These metrics are therefore *heterogenous* and *anisotropic*.

5. Comprehensive study of the group $\mathbb{S}_2$

We first give a general result concerning the direct sum of irreducible representations of degree one containing the unit representation.

THEOREM 8

Let E be a G-Hilbert space with two isotypical components: $E = m_1 V_1 \oplus m_2 V_2$, where V_1 is a unit representation space of G and V_2 is any irreducible representation space of G: any vectors $\mathbf{u}$ and $\mathbf{v}$ are direct sums of their components $\mathbf{u}_1$ and $\mathbf{v}_1$ in $m_1 V_1$, and $\mathbf{u}_2$ and $\mathbf{v}_2$ in $m_2 V_2$. If K_p is a pairing product of E, then $K_p(\mathbf{u}, \mathbf{v}) = K_p(\mathbf{u}_1 \oplus \mathbf{u}_2, \mathbf{v}_1 \oplus \mathbf{v}_2) = K_p(\mathbf{u}_1, \mathbf{v}_1) K_p(\mathbf{u}_2, \mathbf{v}_2)$, and

$$d^2 K_{\mathbf{0}}^{\mathbf{u}_1 \oplus \mathbf{u}_2} = d^2 K_{\mathbf{0}}^{\mathbf{u}_1} + d^2 K_{\mathbf{0}}^{\mathbf{u}_2} .$$

Proof

For any $\mathbf{u} = \mathbf{u}_1 \oplus \mathbf{u}_2$, with $\mathbf{u}_1 \in m_1 V_1$ and $\mathbf{u}_2 \in m_2 V_2$, the functions $K^{\mathbf{u}}, K^{\mathbf{u}_1}, K^{\mathbf{u}_2}$ are defined in the neighborhood of $\mathbf{0}$ by

$$K^{\mathbf{u}}(\boldsymbol{\varepsilon}) = K_p(\mathbf{u}, \mathbf{u} + \boldsymbol{\varepsilon}) = K_p(\mathbf{u}_1, \mathbf{u}_1 + \boldsymbol{\varepsilon}_1) \cdot K_p(\mathbf{u}_2, \mathbf{u}_2 + \boldsymbol{\varepsilon}_2) = K^{\mathbf{u}_1}(\boldsymbol{\varepsilon}_1) \cdot K^{\mathbf{u}_2}(\boldsymbol{\varepsilon}_2) ,$$

where $\boldsymbol{\varepsilon} = \boldsymbol{\varepsilon}_1 \oplus \boldsymbol{\varepsilon}_2$, with $\boldsymbol{\varepsilon}_1 \in m_1 V_1$ and $\boldsymbol{\varepsilon}_2 \in m_2 V_2$.

By differentiation at $\boldsymbol{\varepsilon} = \mathbf{0}$,

$$dK_{\mathbf{0}}^{\mathbf{u}} = K^{\mathbf{u}_1}(\mathbf{0}) \cdot dK_{\mathbf{0}}^{\mathbf{u}_2} + K^{\mathbf{u}_2}(\mathbf{0}) \cdot dK_{\mathbf{0}}^{\mathbf{u}_1} = 0 \quad \text{(theorem 1)} ,$$

and

$$\begin{aligned} d^2 K_{\mathbf{0}}^{\mathbf{u}} &= K^{\mathbf{u}_1}(\mathbf{0}) d^2 K_{\mathbf{0}}^{\mathbf{u}_2} + K^{\mathbf{u}_2}(\mathbf{0}) d^2 K_{\mathbf{0}}^{\mathbf{u}_1} + dK_{\mathbf{0}}^{\mathbf{u}1} dK_{\mathbf{0}}^{\mathbf{u}_2} + dK_{\mathbf{0}}^{\mathbf{u}_2} dK_{\mathbf{0}}^{\mathbf{u}_1} = 0 \\ &= K^{\mathbf{u}_1}(\mathbf{0}) d^2 K_{\mathbf{0}}^{\mathbf{u}_2} + K^{\mathbf{u}_2}(\mathbf{0}) d^2 K_{\mathbf{0}}^{\mathbf{u}_1} + 0 \quad \text{(theorem 1)} . \end{aligned}$$

Since $K^{\mathbf{u}_1}(\mathbf{0}) = K^{\mathbf{u}_2}(\mathbf{0}) = 1$, the result is proved. □

$\mathcal{S}_2$ has only two irreducible representations: the unit representation V_1 and the representation V_2. Any representation space V of $\mathcal{S}_2$ can be reduced as $V = m_1 V_1 \oplus m_2 V_2$. It has been proved elsewhere that

$$\Phi(x^2) = \Phi_{\mathbf{u},\mathbf{v}}(x) = \frac{1}{8} \sum_{g,h,k=\pm 1} \times \exp\left[p \frac{\|\mathbf{u}_1 - \mathbf{v}_1\|^2 + \mathrm{Re}(g\mathbf{u}_2 - h\mathbf{v}_2 | k\mathbf{u}_2 - \mathbf{v}_2)}{\sqrt{\|\mathbf{u}_1 - \mathbf{v}_1\|^2 + \|g\mathbf{u}_2 - h\mathbf{v}_2\|^2} \sqrt{\|\mathbf{u}_1 - \mathbf{v}_1\|^2 + \|k\mathbf{u}_2 - \mathbf{v}_2\|^2}} x^2 \right] .$$

Thus:

$$\Phi'(0) = \frac{p}{8} \sum_{g,h,k=\pm 1} \frac{\|\mathbf{u}_1 - \mathbf{v}_1\|^2 + \mathrm{Re}(g\mathbf{u}_2 - h\mathbf{v}_2 | k\mathbf{u}_2 - \mathbf{v}_2)}{\sqrt{\|\mathbf{u}_1 - \mathbf{v}_1\|^2 + \|g\mathbf{u}_2 - h\mathbf{v}_2\|^2} \sqrt{\|\mathbf{u}_1 - \mathbf{v}_1\|^2 + \|k\mathbf{u}_2 - \mathbf{v}_2\|^2}} .$$

Setting $\mathbf{u}_1 - \mathbf{v}_1 = \boldsymbol{\varepsilon}_1$ and $\mathbf{u}_2 - \mathbf{v}_2 = \boldsymbol{\varepsilon}_2$, and using the expressions "$\mathrm{Re}(\mathbf{u}_i | d\mathbf{u}_i) = r_i\, dr_i$", "$\|d\mathbf{u}_i\|^2 = ds_i^2$", the values of the eight terms occurring in the sum are collected in the table below for $\mathbf{u}_2 \neq \mathbf{0}$:

g	h	k	
+	+	+	1
+	+	−	dr_2/ds
+	−	+	$-dr_2/ds$
+	−	−	-1

g	h	k	
−	+	+	dr_2/ds
−	+	−	1
−	−	+	$(ds_1^2 - ds_2^2)/(ds_1^2 + ds_2^2)$
−	−	−	$-dr_2/ds$

Therefore,

$$\left[\frac{d^2 A_{\mathbf{u}}}{dx^2}\right]_{x=0} = \lim_{\varepsilon \to 0} \Phi'(0) = \frac{p}{8}\left(1 + \frac{ds_1^2 - ds_2^2}{ds_1^2 + ds_2^2}\right) = \frac{p}{4}\frac{ds_1^2}{ds_1^2 + ds_2^2}\,.$$

If $\mathbf{u} \notin m_1 V_1$ (i.e. $\mathbf{u}_2 \neq \mathbf{0}$) and if $ds_1^2 \neq 0$, the metric $d\sigma^2$ is defined by $[d^2 A_{\mathbf{u}}/dx^2]_{x=0} (\neq 0)$ and by

$$d^2 K_0^{\mathbf{u}} = d^2 K_0^{\mathbf{u}_2} + d^2 K_0^{\mathbf{u}_1} = \tanh r_2^2\, ds_2^2 + \frac{r_2^2}{\cosh^2 r_2^2} dr_2^2 + ds_1^2$$

(see preceding section).

- For $\mathbf{u} \notin m_1 V_1$,

– and $ds_1^2 \neq 0$: $\quad d\sigma^2 = 4\left(1 + \frac{ds_2^2}{ds_1^2}\right)\left(ds_1^2 + \tanh r_2^2 ds_2^2 + \frac{r_2^2}{\cosh^2 r_2^2} dr_2^2\right),$

– and $ds_1^2 = 0$: $\quad d\sigma^4 = \frac{4}{1 + \frac{dr_2^2}{ds_2^2}}\left(\tanh r_2^2 ds_2^2 + \frac{r_2^2}{\cosh^2 r_2^2} dr_2^2\right).$

- For $\mathbf{u} \in m_1 V_1$, $d\sigma^2 = ds_1^2 + ds_2^2 = ds^2$.

The metric is not continuous in the neighborhood of $m_1 V_1$: when $\mathbf{u} \notin m_1 V_1$ but $\mathbf{u} \to m_1 V_1$, r_2 tends to zero and $d\sigma^2 = 4\,(ds_1^2 + ds_2^2)(1+0) \neq ds_1^2 + ds_2^2$, the latter expression being the metric in $m_1 V_1$ [5].

The result is illustrated by the action of $\mathcal{S}_2$ in R^2 by reflection through the y-axis (real projection of the regular representation of $\mathcal{S}_2$). The x-axis is the real projection of the non-unit irreducible representation of $\mathcal{S}_2$ ($dx^2 = dr_2^2 = ds_2^2$), and the y-axis is the real projection of the unit irreducible representation of $\mathcal{S}_2$ ($dy^2 = ds_1^2 = dr_1^2$). The non-differential solution of ($\mathbb{E}$) was already given explicitly. R^2 is now endowed with the corresponding metric $d\sigma^2$, allowing the geodesics of this metric to be calculated.

Let us define the real function $F(x) = \tanh x^2 + x^2/\cosh^2 x^2 \geqslant 0$. We seek for curves $(y = y(t), x = x(t))$ in $R^2/G = R \times R_+$ with extremal lengths for the metric $d\sigma^2$. Setting $T = \frac{1}{2} d\sigma^2/dt^2$, the Euler equations are written as

$$\frac{d}{dt}\left(\frac{\partial\sqrt{T}}{\partial y'}\right) - \frac{\partial\sqrt{T}}{\partial y} = 0\,, \quad \frac{d}{dt}\left(\frac{\partial\sqrt{T}}{\partial x'}\right) - \frac{\partial\sqrt{T}}{\partial x} = 0\,.$$

Excluding both the y-axis and the x-axis from $R \times R_+$, the linear element along curves without any section parallel to the x-axis is:

$$d\sigma^2 = 4\left(1 + \frac{x'^2}{y'^2}\right)(y'^2 + F(x)x'^2)\, dt^2 .$$

Restricting the curves to those given by implicit functions $y = y(x)$, $t = x$:

$$d\sigma^2 = 4\left(1 + \frac{1}{y'^2}\right)(y'^2 + F(x))\, dx^2 .$$

The Euler equation left becomes

$$\frac{\partial}{\partial y'}\sqrt{\left(1 + \frac{1}{y'^2}\right)(y'^2 + F(x))} = k \text{ (constant)} .$$

Simple derivation yields

$$(1 - k^2)y'^8 - k^2(F(x) + 1)y'^6 - (2 + k^2)F(x)y'^4 + F^2(x) = 0 .$$

For $k = 0$, the equation reduces to $y'^8 - 2F(x)y'^4 + F^2(x) = 0$. The geodesic solutions are given by $y_0(x) = c \pm \int_0^x [F(t)]^{1/4}\, dt$, $c =$ constant.

For $k = 1$, setting $Y(x) = [F(x) + 1]y'^2(x) + F(x)$, the equation is easily proved to be equivalent to $Y^3 - 3F^2(x)Y - F^2(x)[1 + F^2(x)] = 0$. The discriminant of this equation equals $\Delta = 4[-3F^2]^3 + 27[F^2(1 + F^2)]^2 = 27F^4[F^2 - 1]^2 \geqslant 0$, and a Cardan's solution is $Y_1 = F^{2/3} + F^{4/3}$

The equation is therefore

$$(Y - Y_1)\left(Y^2 + [F^{2/3} + F^{4/3}]Y + \frac{F^2(F^2 + 1)}{F^{4/3} + F^{2/3}}\right) .$$

The discriminant of the equation of degree two is:

$$\Delta = -3F^{4/3}(1 - F^{2/3})^2 \leqslant 0 .$$

Thus, there is only one geodesic left for $k = 1$:

$$y_1(x) = c \pm \int_0^x \sqrt{\frac{F^{2/3}(t) + F^{4/3}(t) - F(t)}{1 + F(t)}}\, dt .$$

All the lines parallel to the y-axis are also geodesics: along these lines, $ds^2 = 4ds_1^2$ ($ds_2^2 = 0$) is of Euclidean type. Geodesic lines in R^2 for some k values are plotted in fig. 1. Intuitive graphical speculations suggest that the shortest pathway $\Delta_p(\mathbf{u}, \mathbf{v})$ joining to points $\mathbf{u}$ and $\mathbf{v}$ with the same y coordinate does not exist: the series of the *lengths* of pathways drawing nearer to the segment $[\mathbf{u}, \mathbf{v}]$ seems to tend toward a lower limit, but the limit *pathway* (segment $[\mathbf{u}, \mathbf{v}]$) is discontinuously associated with an infinite length [6].

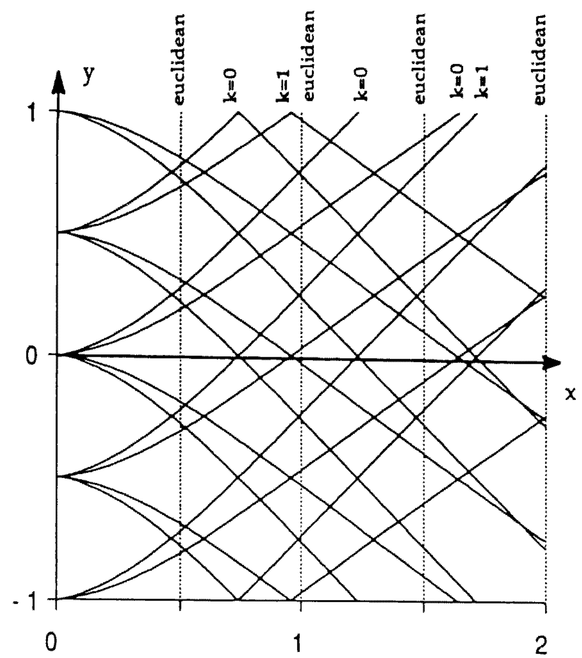

Fig. 1.

6. Concluding remarks

Two kinds of distance are *possibly* defined on E/G: a distance extension D_p and the distance Δ_p of the metric $d\sigma^2$. The former is derived from a thermodynamical interpretation, while the latter gives the length of the "shortest pathway" between skeletal analogs. Since $D_p < \Delta_p$, "the shortest transformation pathway is always longer than the thermodynamic gap". In other words, some kind of non-zero "activation energy function" is needed to transform a molecule into a skeletal analog: this activation energy function lengthens the ideal thermodynamic gap between them. When none of the ligand parameters is constant, this activation energy does not rapidly tend to zero when the skeletal analogs draw nearer to each other, so that the curve lengths are infinite: these transformation pathways may be compared to "fractal" pathways. Differential geometry is a tool serving the analysis of chemically reacting systems [7]. Modeling of chemical transformation pathways by geodesics of simple Hilbert spaces ($G = \{e\}$) has been proposed [8]. In view of reproducing the Woodward–Hoffmann rules, the geodesic lines of the Hilbert space of the electron states of a reacting system (endowed with its natural metric), were shown to satisfy the Least Motion Principle of minimal structural changes which is itself expressed by a maximization condition of a scalar product. This is related to our formalism where geodesic lines correspond to the requirement of stereogenic pairing equilibria between infinitesimally close intermediates (equations ($\mathbb{E}'$) and ($\mathbb{E}''$)). The mathematics that have been elaborated so far aim at describing the very conceptual chemistry of stereogenic pairing equilibria. Many questions are still open: the discriminating character of general pairing products, the explicit and differential resolutions of eq. ($\mathbb{E}$), the triangular inequality of the solutions and the comparison of distances D_p and Δ_p. The ultimate design of new completely G-invariant distances might find applications in all problems of recognition between symmetrized systems, and these preliminary results and speculations will give rise to further investigations.

Acknowledgement

I thank Pr. H.B. Kagan for stimulating discussions.

Appendix

Proof of theorem 1

Let $(\varepsilon_1, \ldots, \varepsilon_n)$ and $(u_1, \ldots, u_n)$ be the respective coordinates of vectors ε and u in an orthonormal basis set $(e_1, \ldots, e_n)$ of E.

By differentiation,

$$dK_0^u = \sum_{i=1}^{n} \left[\frac{\partial K^u}{\partial \varepsilon_i}\right]_{\varepsilon=0} d\varepsilon_i\,;$$

$$d^2K_0^u = \sum_{i=1}^{n} \sum_{k=1}^{n} \left[\frac{\partial^2 K^u}{\partial \varepsilon_i \partial \varepsilon_j}\right]_{\varepsilon=0} d\varepsilon_i\, d\varepsilon_k\,.$$

By definition,

$$K^u(\varepsilon) = \frac{\left(\int_G e^{(gu|u)}\, dg\right)\left(\int_G e^{(g(u+\varepsilon)|u+\varepsilon)}\, dg\right)}{\left(\int_G e^{(gu|u+\varepsilon)}\, dg\right)^2}\,,$$

$$\frac{\partial K^u}{\partial \varepsilon_i} = \frac{\mathrm{I}}{\left(\int_G e^{(gu|u+\varepsilon)}\, dg\right)^4} \left\{ \left(\int_G A_i(g) e^{(g(u+\varepsilon)|u+\varepsilon)}\, dg\right)\left(\int_G e^{(gu|u+\varepsilon)}\, dg\right)^2 \right.$$

$$\left. - \left(\int_G e^{(g(u+\varepsilon)|u+\varepsilon)}\, dg\right)\left(\int_G e^{(gu|u+\varepsilon)}\, dg\right)\left(\int_G 2B_i(g) e^{(gu|u+\varepsilon)}\, dg\right) \right\}.$$

With:

$$\mathbf{I} = \int_G e^{(gu|u)}\, dg\,,$$

$$A_i(g) = \frac{\partial}{\partial \varepsilon_i}(g(u+\varepsilon)|u+\varepsilon)(= A_i)\,,$$

$$B_i(g) = \frac{\partial}{\partial \varepsilon_i}(gu|u+\varepsilon)(= (gu|e_i) = B_i)\,.$$

Since $e^{(gu|u)} = e^{(g^{-1}u|u)}$, the term $2B_i(g)$ occurring in the sums can be replaced by $B_i(g) + B_i(g^{-1})$.

Let $u = (u_1, \ldots, u_n), \varepsilon = (\varepsilon_1, \ldots, \varepsilon_n)$ in an orthonormal basis of E. The matrix coefficients of the isometry g in the same basis are denoted as $a_{rs}(g), 1 \leqslant r \leqslant n$, $1 < s \leqslant n$.

$$\begin{aligned} A_i(g) - B_i(g) - B_i(g^{-1}) &= \frac{\partial}{\partial \varepsilon_i}[(g(u+\varepsilon)|u+\varepsilon) - (gu|u+\varepsilon) \\ &\quad - (g^{-1}u|u+\varepsilon)] = \frac{\partial}{\partial \varepsilon_i}[(g\varepsilon|\varepsilon) - (gu|u)] \\ &= \frac{\partial}{\partial \varepsilon_i}(g\varepsilon|\varepsilon) = \frac{\partial}{\partial \varepsilon_i}\sum_{r=1}^{n}\sum_{s=1}^{n} a_{rs}(g)\varepsilon_r\varepsilon_s \\ &= \sum_{r=1}^{n}(a_{ir}(g) + a_{ri}(g))\varepsilon_r\,. \end{aligned}$$

At $\varepsilon = 0$: $A_i(g) - B_i(g) - B_i(g^{-1}) = 0$, i.e. $A_i(g) = B_i(g) + B_i(g^{-1})$. But at $\varepsilon = 0$, we calculate

$$\left[\frac{\partial K^u}{\partial \varepsilon_i}\right]_{\varepsilon=0} = \frac{1}{\mathbf{I}^2}\int_G [A_i(g) - 2B_i(g)]e^{(gu|u)}\, dg\,.$$

Consequently, $[\partial K^u/\partial \varepsilon_i]_{\varepsilon=0} = 0$, and $dK_0^u = 0$.

Let us calculate the second derivatives at zero:

$$\begin{aligned} \left[\frac{\partial^2 K^u}{\partial \varepsilon_k \partial \varepsilon_i}\right]_{\varepsilon=0} = \frac{I}{\mathbf{I}^8}\Bigg\{\mathbf{I}^4\Bigg[&\left(\int_G \left(\frac{\partial A_i}{\partial \varepsilon_k} + A_i A_k\right) e^{(gu|u)}\, dg\right)\mathbf{I}^2 + \left(\int_G A_i e^{(gu|u)}\, dg\right) \\ &\times \left(2\mathbf{I}\int_G B_k e^{(gu|u)}\, dg\right) \\ &- \mathbf{I}\left(\int_G A_k e^{(gu|u)}\, dg\right)\left(\int_G 2B_i e^{(gu|u)}\, dg\right) - \mathbf{I}\left(\int_G B_k e^{(gu|u)}\, dg\right) \end{aligned}$$

$$\times \left(\int_G 2B_i e^{(gu|u)}\, dg\right) - \mathbf{I}^2\left(\int_G \left(2\frac{\partial B_i}{\partial \varepsilon_k} + 2B_iB_k\right)e^{(gu|u)}\, dg\right)\Bigg]$$

$$- 4\mathbf{I}^3\left(\int_G B_k e^{(gu|u)}\, dg\right)\left[\left(\int_G A_i e^{(gu|u)}\, dg\right)\mathbf{I}^2 - \mathbf{I}^2\left(\int_G 2B_i e^{(gu|u)}\, dg\right)\right]\Bigg\}$$

$$= \frac{1}{\mathbf{I}^2}\Bigg\{\mathbf{I}\int_G \left(\frac{\partial A_i}{\partial \varepsilon_k} + A_iA_k\right)e^{(gu|u)}\, dg + 2\int_G A_i e^{(gu|u)}\, dg \int_G B_k e^{(gu|u)}\, dg$$

$$- 2\int_G A_k e^{(gu|u)}\, dg \int_G B_i e^{(gu|u)}\, dg - 2\int_G B_k e^{(gu|u)}\, dg \int_G B_i e^{(gu|u)}\, dg$$

$$- 2\mathbf{I}\int_G \left(\frac{\partial B_i}{\partial \varepsilon_k} + B_iB_k\right)e^{(gu|u)}\, dg - 4\int_G B_k e^{(gu|u)}\, dg \int_G A_i e^{(gu|u)}\, dg$$

$$+ 8\int_G B_k e^{(gu|u)}\, dg \int_G B_i e^{(gu|u)}\, dg\Bigg\}$$

$$= \frac{1}{\mathbf{I}^2}\Bigg\{\mathbf{I}\int_G \left(\frac{\partial A_i}{\partial \varepsilon_k} + A_iA_k\right)e^{(gu|u)}\, dg - 2\int_G A_i e^{(gu|u)}\, dg \int_G B_k e^{(gu|u)}\, dg$$

$$- 2\int_G A_k e^{(gu|u)}\, dg \int_G B_i e^{(gu|u)}\, dg + 6\int_G B_k e^{(gu|u)}\, dg \int_G B_i e^{(gu|u)}\, dg$$

$$- 2\mathbf{I}\int_G \left(\frac{\partial B_i}{\partial \varepsilon_k} + B_iB_k\right)e^{(gu|u)}\, dg\Bigg\}$$

$$= \frac{1}{\mathbf{I}^2}\Bigg\{\mathbf{I}\int_G \left(\frac{\partial (A_i - 2B_i)}{\partial \varepsilon_k} + A_iA_k - 2B_iB_k\right)e^{(gu|u)}\, dg$$

$$- 2\int_G A_i e^{(gu|u)}\, dg \int_G B_k e^{(gu|u)}\, dg$$

$$- 2\int_G A_k e^{(gu|u)}\, dg \int_G B_i e^{(gu|u)}\, dg + 6\int_G B_k e^{(gu|u)}\, dg \int_G B_i e^{(gu|u)}\, dg\Bigg\}.$$

Again, the terms $2B_i(g)$ and $2B_k(g)$ occurring in the sums can be replaced by $B_i(g) + B_i(g^{-1})$ and $B_k(g) + B_k(g^{-1})$.

It has been shown above that:

$$A_i(g) - B_i(g) - B_i(g^{-1}) = \sum_{r=1}^{n}(a_{ir}(g) + a_{ri}(g))\varepsilon_r .$$

Therefore,

$$\left[\frac{\partial}{\partial \varepsilon_k}[A_i(g) - B_i(g) - B_i(g^{-1})]\right]_{\varepsilon=0} = a_{ik}(g) + a_{ki}(g) .$$

Using again the fact that at $\varepsilon = 0$, $A_i(g) = B_i(g) + B_i(g^{-1})$, we get

$$\left[\frac{\partial^2 K^u}{\partial\varepsilon_k\partial\varepsilon_i}\right]_{\varepsilon=0} = \frac{1}{\mathbf{I}^2}\left\{\mathbf{I}\int_G (a_{ik}(g)+a_{ki}(g))e^{(gu|u)}\,dg + 2\mathbf{I}\int_G B_iB_k e^{(gu|u)}\,dg \right.$$
$$\left. - 2\int_G B_k e^{(gu|u)}\,dg \int_G B_i e^{(gu|u)}\,dg\right\},$$

where

$$B_i(g) = \frac{\partial}{\partial\varepsilon_i}(gu|u+\varepsilon) = \frac{\partial}{\partial\varepsilon_i}(gu|\varepsilon) = \sum_{r=1}^{n} a_{ir}(g)u_r = (gu|e_i)\,.$$

$$d^2K_0^u = \frac{1}{\mathbf{I}^2}\left\{\mathbf{I}\int_G \sum_{i=1}^{n}\sum_{k=1}^{n}(a_{ik}(g)+a_{ki}(g))d\varepsilon_i d\varepsilon_k e^{(gu|u)}\,dg\right.$$
$$+ 2\mathbf{I}\int_G \sum_{i=1}^{n}\sum_{k=1}^{n} B_iB_k d\varepsilon_i d\varepsilon_k e^{(gu|u)}\,dg$$
$$\left. - 2\int_G \sum_{k=1}^{n} B_k\, d\varepsilon_k e^{(gu|u)}\,dg \int_G \sum_{i=1}^{n} B_i d\varepsilon_i e^{(gu|u)}\,dg\right\}$$
$$= \frac{1}{\mathbf{I}^2}\left\{2\mathbf{I}\int_G \sum_{i=1}^{n}\sum_{k=1}^{n} a_{ik}(g)\,d\varepsilon_i\,d\varepsilon_k\,e^{(gu|u)}\,dg + 2\mathbf{I}\int_G\left(\sum_{i=1}^{n} B_i d\varepsilon_i\right)^2 e^{(gu|u)}\,dg\right.$$
$$\left. - 2\left(\int_G \sum_{i=1}^{n} B_i\,d\varepsilon_i\,e^{(gu|u)}\,dg\right)^2\right\}.$$

But from the definition of the $d\varepsilon_i$'s,

$$\sum_{i=1}^{n} B_i\,d\varepsilon_i = (gu|du)\,,\quad \sum_{i=1}^{n}\sum_{k=1}^{n} a_{ik}(g)\,d\varepsilon_i\,d\varepsilon_k = (g(du)|du)\,.$$

In conclusion,

$$d^2K_0^u = \frac{2}{\mathbf{I}^2}\left\{\mathbf{I}\int_G (g(du)|du)e^{(gu|u)}\,dg + \mathbf{I}\int_G (gu|du)^2 e^{(gu|u)}\,dg\right.$$
$$\left. - \left(\int_G (gu|du)e^{(gu|u)}\,dg\right)^2\right\}.$$

□

Proof of theorem 2

Retaining the prerequisites of the proof of theorem 1, for $v = u+\varepsilon$:

$$\left[\frac{d\Phi_{u,u+\varepsilon}}{dx}\right]_{x=0} = 0\,,\ \left[\frac{d^2\Phi_{u,u+\varepsilon}}{dx^2}\right]_{x=0} = 2\Phi'(0)\,.$$

Let $\mathcal{P}_1$ denote the projector onto the unit representation.

Since $A_u(x) = \lim_{\varepsilon\to 0} \Phi_{u,u+\varepsilon}(x)$:

$$\left[\frac{d^2 A_u}{dx^2}\right]_{x=0} = 2\lim_{\varepsilon\to 0}\Phi'(0) = 2\lim_{\varepsilon\to 0} p\|\mathcal{P}_1(u)-\mathcal{P}_1(u+\varepsilon)\|^2\left(\int_G \frac{dg}{\|gu-u-\varepsilon\|}\right)^2$$

$$= 2\lim_{\varepsilon\to 0} p\|\mathcal{P}_1(\varepsilon)\|^2\left(\int_{G,gu\neq u}\frac{dg}{\|gu-u\|}\right)^2 + 2\lim_{\varepsilon\to 0} p\|\mathcal{P}_1(\varepsilon)\|^2\left(\int_{G,gu=u}\frac{dg}{\|\varepsilon\|}\right)^2$$

$$= 0 + 2\lim_{\varepsilon\to 0} p\|\mathcal{P}_1(\varepsilon)\|^2\left(\int_{G^u}\frac{dg}{\|\varepsilon\|}\right)^2 \quad (G^u \text{ is the stabilizator group of } u)$$

$$= \frac{2p}{[G:G^u]^2}\lim_{\varepsilon\to 0}\frac{\|\mathcal{P}_1(\varepsilon)\|^2}{\|\varepsilon\|^2}.$$

The result is proved, by setting $ds_1^2 \approx \|\mathcal{P}_1(\varepsilon)\|^2$ and $ds^2 \approx \|\varepsilon\|^2$. □

Proof of theorem 4

From theorem 1, it is sufficient to show that

$$\forall (a,u)\in E^2, \quad \int_G (ga|a)e^{(gu|u)}\,dg \geqslant 0.$$

$$\int_G (ga|a)e^{(gu|u)}\,dg = \sum_{p=0}^{\infty}\frac{1}{p!}\int_G (ga|a)(gu|u)^p\,dg.$$

The representation in E is naturally extended to a representation in the complex space $C\times E$ endowed with the Hermitian form $\langle\cdot|\cdot\rangle$ coinciding with $(\cdot|\cdot)$ on E. If $\chi_1,\ldots,\chi_r$ are the irreducible characters of G, then

$$\int_G \langle ga|a\rangle\langle gu|u\rangle^p\,dg = \sum_{i=1}^{r}\xi_i\eta_{p,i}^*$$

with

$$\langle ga|a\rangle = \sum_{i=1}^{r}\xi_i\chi_i(g) \quad\text{and}\quad \langle gu|u\rangle^p = \sum_{i=1}^{r}\eta_{p,i}\chi_i(g)$$

(expansions of the central functions $g\to\langle ga|a\rangle$ and $g\to\langle gu|u\rangle^p$ on the basis of the irreducible characters of G). We aim at proving that the ξ_i's and the $\eta_{p,i}$'s are real and positive numbers.

It has been proved above that $\xi_i = \|\mathcal{P}_i a\|^2$ and $\eta_{1,i} = \|\mathcal{P}_i u\|^2$.

Suppose that the $\eta_{p-1,i}$'s are positive real numbers. $\eta_{p,i}$ is expressed by

$$\eta_{p,i} = \int_G \langle gu|u\rangle^p \chi_i^*(g)\, dg = \int_G \langle gu|u\rangle^{p-1}\langle gu|u\rangle \chi_i^*(g)\, dg$$
$$= \sum_{h=1}^{r}\sum_{k=1}^{r} \eta_{p-1,h}\eta_{1,k} \int_G \chi_h(g)\chi_k(g)\chi_i^*(g)\, dg\,,$$

$\int_G \chi_h(g)\chi_k(g)\chi_i^*(g)\, dg = \int_G \chi_{h\otimes k}(g)\chi_i^*(g)\, dg =$ the number of times the ith irreducible representation of G occurs in the tensorial product of the hth by the kth irreducible representations = a positive integer. Since $\eta_{p-1,h}$ and $\eta_{1,k}$ are positive real numbers, the same statement is true for all the $\eta_{p,i}$'s. Thus $\int_G \langle ga|a\rangle\langle gu|u\rangle^p\, dg$ and hence $\int_G \langle ga|a\rangle e^{\langle gu|u\rangle}\, dg$, are positive real numbers. When u and a are restricted to vectors with real components, $\langle\cdot|\cdot\rangle$ can be replaced by $(\cdot|\cdot)$ and $d^2K_0^u$ is positive. □

Proof of theorem 5

The Hermitian form of E is denoted as $\langle\cdot|\cdot\rangle$: its real component is the scalar product of R^2, $(\cdot|\cdot) = \mathrm{Re}\langle\cdot|\cdot\rangle$. Since

$$\langle ga|a\rangle = \chi_i(g)\|a\|^2 \quad\text{and}\quad \langle gu|u\rangle = \chi_i(g)\|u\|^2\,,$$

we get

$$\int_G \mathrm{Re}\langle ga|a\rangle\, e^{\mathrm{Re}\langle gu|u\rangle}\, dg = \|a\|^2 \int_G \mathrm{Re}[\chi_i(g)]\, e^{\mathrm{Re}[\chi_i(g)]\|u\|^2}\, dg\,.$$

Let us define the function on R^+:

$$f\colon R_+ \to R\,,\quad f(x) = \int_G \mathrm{Re}[\chi_i(g)]\, e^{\mathrm{Re}[\chi_i(g)]x}\, dg\,.$$

We get $f(0) = 0$ (the trivial case $G = \{e\}$, where $f'(0) = 1$, is not considered). But

$$f'(x) = \int_G \mathrm{Re}^2[\chi_i(g)]\, e^{\mathrm{Re}[\chi_i(g)]\|u\|^2}\, dg > 0\,.$$

Thus, f strictly increases and remains strictly positive over $R_+ - \{0\}$. Taking $x = \|u\|^2$, it follows that $d^2K_0^u$ is positive. Since $d^2K_0^u = 0$ implies $\|a\|^2 = 0$, i.e. $a = 0$, $d^2K_0^u$ is also definite.

Proof of theorem 6

We proceed intuitively by expanding $K_p(u, u+du)$ to the terms du of order 2.

$$K_1(u, u+du) \sim [I[I + (\|du\|^2 + 2\,\mathrm{Re}(u|du))J + 2K\,\mathrm{Re}^2(u|du)]]/$$
$$[I + J\,\mathrm{Re}(u|du) - J'\,\mathrm{Im}(u|du) + (K/2)\,\mathrm{Re}^2(u|du) + (L/2)\,\mathrm{Im}^2(u|du)$$
$$- M\,\mathrm{Re}(u|du)\,\mathrm{Im}(u|du)]^2]\,,$$

where

$$I = \int_G e^{r^2\mathrm{Re}\,\chi(g)}\, dg\,,$$

$$J = \int_G \text{Re}\,\chi(g)\, e^{r^2 \text{Re}\chi(g)}\, dg\,, \quad J' = \int_G \text{Im}\,\chi(g)\, e^{r^2 \text{Re}\chi(g)}\, dg\,,$$

$$K = \int_G \text{Re}^2\chi(g)\, e^{r^2 \text{Re}\chi(g)}\, dg\,, \quad L = \int_G \text{Im}^2\chi(g)\, e^{r^2 \text{Re}\chi(g)}\, dg\,,$$

$$M = \int_G \text{Re}\,\chi(g)\, \text{Im}\,\chi(g)\, e^{r^2 \text{Re}\chi(g)}\, dg\,.$$

Since $\chi(g) = \chi^*(g^{-1})$, it is evident that $J' = M = 0$. Further expansion to the terms du of order 2 gives

$$1 + \tfrac{1}{2}d^2K_0^u \approx K_1(u, u+du) = 1 + \left(\frac{K}{I} - \frac{J^2}{I^2}\right) \text{Re}^2(u|du) + \frac{J}{I}\|du\|^2$$

$$- \frac{L}{I}\text{Im}^2(u|du) + \mathcal{O}(|du)^3)\,.$$

On the other hand, $K + L = I$, and the theorem is proved.

Considering E as a complex line: $u = re^{i\theta}, du = dr\, e^{i\theta} + ir\, \text{d}\theta\, e^{i\theta}$. Thus, $(u|du) = u\, du^* = r\, dr - ir^2\, d\theta$. Substituting the imaginary and real parts by their expressions in the former equality, the theorem is proved. □

Proof of theorem 7

Since E is an isotypical representation of degree one: $\forall a \in E, ga = \chi(g)a$.

From theorem 3,

$$\left[\frac{d^2B_u}{dy^2}\right]_{y=0} = \iiint_{G^3} \lim_{\varepsilon \to 0} \cos^2(gu - h(u+\varepsilon), ku - u - \varepsilon)\, dg\, dh\, dk \geqslant 0\,.$$

- For g, h, k satisfying $\chi(g) \neq \chi(h)$ and $\chi(k) \neq 1$ ($|G| \times (|G| - c)^2$ triplets):

$$\cos(gu - h(u+\varepsilon), ku - u - \varepsilon) \underset{\varepsilon \to 0}{\longrightarrow} \text{Re}\left\{\frac{\chi(g)\chi^*(k) + \chi(h) - \chi(g) - \chi(h)\chi^*(k)}{|\chi(h) - \chi(g)||\chi(k) - 1|}\right\}.$$

Setting $\chi(g) = e^{i\alpha(g)}$, standard trigonometric calculations lead to

$$\cos(gu - h(u+\varepsilon), ku - u - \varepsilon) \underset{\varepsilon \to 0}{\longrightarrow} \pm\cos\left[\frac{\alpha(g) + \alpha(h) - \alpha(k)}{2}\right] = \pm\cos\frac{\alpha(ghk^{-1})}{2}\,.$$

- For g, h, k satisfying $\chi(g) \neq \chi(h)$ and $\chi(k) = 1$ ($|G| \times (|G| - c) \times c$ triplets):

$$\cos(gu - h(u+\varepsilon), ku - u - \varepsilon)$$
$$\underset{\varepsilon\to 0}{\sim} \mathrm{Re}\{[[\chi(g)\chi^*(k) + \chi(h) - \chi(g) - \chi(h)\chi^*(k)]\|u\|^2 + (\chi(h) - \chi(g))(u|\varepsilon)$$
$$+ \chi(h)(1 - \chi^*(k))(\varepsilon|u) + \chi(h)\cdot\|\varepsilon\|^2]/[|\chi(h) - \chi(g)|\cdot\|u\|\cdot\|\varepsilon\|]\}$$
$$\underset{\varepsilon\to 0}{\sim} \mathrm{Re}\left\{\frac{(\chi(h) - \chi(g))(u|\varepsilon)}{|\chi(h) - \chi(g)|\cdot\|u\|\cdot\|\varepsilon\|}\right\}$$
$$\underset{\varepsilon\to 0}{\sim} [-2\sin(\alpha(hg)/2)\sin(\alpha(hg^{-1})/2)\cos(u,\varepsilon)$$
$$- 2\cos(\alpha(hg)/2)\sin(\alpha(hg^{-1})/2)\sin(u,\varepsilon)]/[2|\sin(\alpha(hg^{-1})/2)|]$$
$$\underset{\varepsilon\to 0}{\sim} \pm\sin\left[\frac{\alpha(hg)}{2} + (u,\varepsilon)\right] = \pm\mathrm{Im}[e^{i\alpha(g)/2}e^{i(u,\varepsilon)}].$$

- For g, h, k satisfying $\chi(g) = \chi(h)$ and $\chi(k) \neq 1$ ($|G| \times c \times (|G| - c)$ triplets):

$$\cos(gu - h(u+\varepsilon), ku - u - \varepsilon) \underset{\varepsilon\to 0}{\sim} \mathrm{Re}\left\{\frac{\chi(h)(1 - \chi^*(k))(\varepsilon|u)}{|\chi(k) - 1|\cdot\|u\|\cdot\|\varepsilon\|}\right\}$$
$$\underset{\varepsilon\to 0}{\sim} [-2\sin(\alpha(k)/2)\sin(\alpha(h) - \alpha(k)/2)\cos(u,\varepsilon) - 2\cos(\alpha(h)$$
$$- \alpha(k)/2)\sin(\alpha(k)/2)\sin(u,\varepsilon)]/[2|\sin(\alpha(k)/2)|]$$
$$\underset{\varepsilon\to 0}{\sim} \pm\sin\left[\frac{\alpha(h^2k^{-1})}{2} + (\varepsilon,u)\right] = \pm\mathrm{Im}[e^{i\alpha(h^2k^{-1})/2}e^{i(\varepsilon,u)}].$$

- For g, h, k satisfying $\chi(g) = \chi(h)$ and $\chi(k) = 1$ ($|G| \times c^2$ triplets):

$$\cos(gu - h(u+\varepsilon), ku - u - \varepsilon) \underset{\varepsilon\to 0}{\sim} \mathrm{Re}\left\{\frac{\chi(h)\|\varepsilon\|^2}{\|\varepsilon\|^2}\right\} = \cos\alpha(h).$$

If G is a finite group, let us define for any element g of G the subset of G: $C(g) = \{h \in G; \chi(g) = \chi(h)\}$. The number of elements in $C(g)$ is denoted as $\#C(g) = \#C(e) = c$. It follows that $[d^2B_u/dy^2]_{y=0}$ equals

$$\frac{1}{|G|^3}\left\{\sum_{g\in G}\sum_{\substack{h\in G\\ \chi(h)\neq\chi(g)}}\sum_{\substack{k\in G\\ \chi(k)\neq 1}}\cos^2\frac{\alpha(ghk^{-1})}{2} + \sum_{g\in G}\sum_{\substack{h\in G\\ \chi(h)\neq\chi(g)}}\sum_{\substack{k\in G\\ \chi(k)=1}}\sin^2\left[\frac{\alpha(hg)}{2} + (u,\varepsilon)\right]\right.$$
$$\left. + \sum_{g\in G}\sum_{\substack{h\in G\\ \chi(h)=\chi(g)}}\sum_{\substack{k\in G\\ \chi(k)\neq 1}}\sin^2\left[\frac{\alpha(h^2k^{-1})}{2} + (\varepsilon,u)\right] + \sum_{g\in G}\sum_{\substack{h\in G\\ \chi(h)=\chi(g)}}\sum_{\substack{k\in G\\ \chi(k)=1}}\cos^2\alpha(h)\right\}.$$

Let us calculate each term of the sum.

(a) The first one is denoted as

$$A=\sum_{g\in G}\sum_{\substack{h\in G\\ \chi(h)\neq\chi(g)}}\sum_{\substack{k\in G\\ \chi(k)\neq 1}}\cos^2\frac{\alpha(ghk^{-1})}{2}\,.$$

Then

$$A=\sum_{g\in G}\left\{\sum_{h\in G}\left[\sum_{k\in G}\cos^2\frac{\alpha(ghk^{-1})}{2}-\sum_{k\in C(e)}\cos^2\frac{\alpha(ghk^{-1})}{2}\right]\right.$$

$$\left.-\sum_{h\in C(g)}\left[\sum_{k\in G}\cos^2\frac{\alpha(ghk^{-1})}{2}-\sum_{k\in C(e)}\cos^2\frac{\alpha(ghk^{-1})}{2}\right]\right\}$$

$$A=\sum_{g\in G}\left\{\sum_{h\in G}\left[\sum_{k\in G}\cos^2\frac{\alpha(k)}{2}-\sum_{k\in C(e)}\cos^2\frac{\alpha(gh)}{2}\right]\right.$$

$$\left.-\sum_{h\in C(g)}\left[\sum_{k\in G}\cos^2\frac{\alpha(k)}{2}-\sum_{k\in C(e)}\cos^2\frac{\alpha(g^2)}{2}\right]\right\}$$

$$A=\sum_{g\in G}\left\{\sum_{h\in G}\left[\sum_{k\in G}\cos^2\frac{\alpha(k)}{2}-c\cos^2\frac{\alpha(gh)}{2}\right]\right.$$

$$\left.-\sum_{h\in C(g)}\left[\sum_{k\in G}\cos^2\frac{\alpha(k)}{2}-c\cos^2\frac{\alpha(g^2)}{2}\right]\right\}.$$

Setting $S=\sum_{k\in G}\cos^2(\alpha(k)/2)$ and $T=\sum_{k\in G}\cos^2\alpha(k)$, we get $(\#C(g)=\#C(e) = c)$

$$A=(|G|^2-2c|G|)S+c^2T$$

(b) The last term is simply

$$D=\sum_{g\in G}\sum_{\substack{h\in G\\ \chi(h)=\chi(g)}}\sum_{\substack{k\in G\\ \chi(k)=1}}\cos^2\alpha(h)=c^2T\,.$$

(c) The second term is denoted as

$$B=\sum_{g\in G}\sum_{\substack{h\in G\\ \chi(h)\neq\chi(g)}}\sum_{\substack{k\in G\\ \chi(k)=1}}\sin^2\left[\frac{\alpha(hg)}{2}+(u,\varepsilon)\right]\ :$$

$$B = c\sum_{g\in G}\left\{\sum_{h\in G}\sin^2\left[\frac{\alpha(gh)}{2} + (u,\varepsilon)\right] - \sum_{h\in C(g)}\sin^2\left[\frac{\alpha(hg)}{2} + (u,\varepsilon)\right]\right\},$$

$$B = c\left\{|G|\sum_{g\in G}\sin^2\left[\frac{\alpha(g)}{2} + (u,\varepsilon)\right] - c\sum_{g\in G}\sin^2[\alpha(g) + (u,\varepsilon)]\right\}$$

(indeed $\alpha(g^2) = 2\alpha(g)$).

(d) The third term is denoted as

$$C = \sum_{g\in G}\ \sum_{\substack{h\in G\\ \chi(h)=\chi(g)}}\ \sum_{\substack{k\in G\\ \chi(k)\neq 1}}\sin^2\left[\frac{\alpha(h^2k^{-1})}{2} + (\varepsilon,u)\right] :$$

$$C = c\left\{|G|\sum_{g\in G}\sin^2\left[\frac{\alpha(g)}{2} + (\varepsilon,u)\right] - c\sum_{g\in G}\sin^2[\alpha(g) + (\varepsilon,u)]\right\}.$$

Using the equality $(\varepsilon,u) = -(u,\varepsilon)$, the sum $B + C$ is calculated by standard trigonometry:

$$B + C = c\left\{2|G|S - 2|G|\cos^2(u,\varepsilon)\sum_{g\in G}\cos\alpha(g)\right.$$

$$\left. - 2cT + 2c\cos^2(u,\varepsilon)\sum_{g\in G}\cos[2\alpha(g)]\right\}.$$

But if E is not the unit representation,

$$\sum_{g\in G}\cos\alpha(g) = \mathrm{Re}\left\{\sum_{g\in G}\chi(g)\right\} = 0.$$

Thus

$$\left[\frac{d^2B_u}{dy^2}\right]_{y=0} = \frac{1}{|G|^3}[A + (B + C) + D]$$

$$= \frac{1}{|G|}S + 2\left(\frac{c}{|G|}\right)^2\cos^2(u,\varepsilon)\frac{1}{|G|}\sum_{g\in G}\cos[2\alpha(g)].$$

(The coefficient of the sum T vanishes.)

Notice that

$$S = \sum_{k \in G} \cos^2 \frac{\alpha(k)}{2} = \sum_{k \in G} \frac{\cos \alpha(k) + 1}{2} = \tfrac{1}{2} + \tfrac{1}{2} \sum_{g \in G} \cos \alpha(g) = \tfrac{1}{2} + 0 .$$

If ε is identified to the differential du,

$$\cos^2(u, \varepsilon) = \left(\frac{\mathrm{Re}(u|du)}{\|u\| \|du\|} \right)^2 .$$

If $r = \|u\|$, then $\mathrm{Re}(u|du) = r\,dr$. On the other hand, $\|du\|^2 = ds^2$. The theorem follows. □

References and notes

[1] (a) R. Chauvin, J. Phys. Chem. 96 (1992) 4701. (b) ibid, 4706.

[2] R. Chauvin, Paper III of this series, J. Math. Chem. 16 (1994) 269.

[3] R. Chauvin, Paper II of this series, J. Math. Chem. 16 (1994) 257.

[4] $I = J_0(ir^2)$ and $J = iJ_0'(ir^2)$, where J_0 is the Bessel function of the first kind satisfying the differential equation $xy'' + y' + xy = 0$. Setting $r^2 = x, I(x)$ satisfies the differential equation $xy'' + y' - xy = 0$.

[5] To render the metric of E continuous at $m_1 V_1$, it has to be divided by 4 outside $m_1 V_1$. This phenomenon will be clarified later.

[6] Let $s_k(x)$ be a curvilinear abscissa on the map in R^2 of a geodesic k. The Euclidean length of a segment $C[a,b], a<b$, is $\int_{C[a,b]} ds_k = \int_a^b (ds_k/dx)dx$, where $ds_k/dx = \sqrt{1 + y'^2(x)}$. The length of this segment for the metric $d\sigma^2$ is $\int_{C[a,b]} d\sigma = \int_a^b (d\sigma/dx)dx$, where

$$\frac{d\sigma}{dx} = 2\sqrt{\left(1 + \frac{1}{y'^2(x)}\right)(y'(x)^2 + F(x))} = 2\frac{ds_k}{dx}\sqrt{1 + \frac{F(x)}{y'^2(x)}} .$$

However, none of the curves with the form $y'^2(x) = \text{cste } F(x)$ satisfies the Euler equation: the metric $d\sigma^2$ is not equivalent to the Euclidean metric upon such a simple change of curvilinear coordinates. For example, a geodesic line of type $k = 0$ is defined by $y'^2 = [F(x)]^{1/2}$, and $d\sigma/dx = 2(ds_0/dx)^2$.

[7] See for example: A. Tachibana, K. Fukui, Theoret. Chim. Acta (Berl.) 49 (1978) 321.

[8] M. Strnad and R. Ponec, Collect. Czech. Chem. Commun. 57 (1992) 232, and references cited therein.