Dyad algebra and multiplication of graphs. I. Directed graphs

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The ket–bra algebra for quantum mechanics and for the quantum chemistry in valence shells was made by this author fully covariant recently. The resulting "principle of linear covariance" allowed diverse approaches such as molecular orbital, valence bond, localized orbital theories to come out as special cases in particular basis frames not necessarily orthonormal. The principal also led to the pictorial VIF (valency interaction formula) methods for deducing qualitative quantum chemistry directly from the structural formulas of molecules. The present set of two papers (II on undirected graphs) develops graphs and graph rules for abstract linear vector spaces, bras, kets, and abstract operators as ket–bra dyads. Multiplications of such operators are carried out with graphs of two kinds of lines and two kinds of vertices. The theorems are demonstrated on some examples and are useful, e.g., with the recent method of moments and in deriving Lie algebras pertinent to quantum chemistry.

1. Motivation and introduction

Dyad algebras provide a general formulation of quantum chemistry independent of basis set selections when treated in a linearly covariant fashion [1,2]. Qualitative quantum chemistry is constructed on a finite n-dimensional linear vector space V_n, with starting basis vectors $\{|e_i\rangle\}$, n valency orbitals of a molecule. Operators such as the one-electron Hamiltonian h and the electron density operator d are dyads in the $V_n \times V_n^+$ space with V_n^+ the adjoint. A basis for $V_n \times V_n^+$ is $\{|e_i\rangle\langle e_j|\}$. Dirac [3] formulated quantum mechanics in terms of kets $|\,\rangle$ and bras $\langle\,|$. Although abstract and combining the Heisenberg and Schrödinger formulations/representations, Dirac's algebra was not fully covariant under all basis-frame transformations. The recent principle of linear covariance [2] makes quantum-mechanical formulations fully covariant with diverse advantages leading for example to the pictorial VIF (valency interaction formula) rules for qualitative chemical deductions [4]. Quantitative quantum chemistry is obtained using the complements of V_n and $V_n \times V_n^+$ in the infinite dimensional Hilbert space as was done sometime ago in the theory of electron correlation (the "many-electron theory of atoms and molecules", MET [5] for closed shells and NCMET [6] for non-closed shells). Later, these theories were made covariant (ref. [2] and subsequent papers) and thereby directly applicable to molecular orbital, valence bond, or localized orbital starting points.

For valence shell qualitative quantum chemistry we have the vector space V_n and valency atomic orbital (AO) vectors $\{|e_i\rangle\}$ and the one-electron h which is a ρ-term dyad in $V_n \times V_n^+$. To each molecule there corresponds an abstract (and linear invariant [2]) h and its graphs, the VIF, transformable to new VIFs with the pictorial VIF rules [4]. Dyad algebra based graphs tend to yield more general results than matrix based graphs which have been studied extensively [7].

The present set of two papers (II being on undirected graphs) treats the multiplication, in general non-commutative, of abstract operators in $V_n \times V_n^+$ and their corresponding graphs. Such multiplications are needed, e.g., in applying projection operators, symmetry operators, and others, to a molecule and its h, in calculating the total energy as Tr dh with d the density operator, in obtaining the powers of h as in the method of moments [8], and in deriving Lie algebras pertinent to quantum chemistry.

Product graphs $G_P = G \times G'$ involve during their evaluation, new types of graphs of two kinds of vertices and two kinds of lines, reminiscent of, but different than, the "networks" introduced and studied for mechanisms (and/or synthetic pathways) in complex reaction mixtures [9–11].

We first treat directed graphs G and their underlying dyad algebra.

2. Dyads, vectors and their corresponding *G's*

The ket-vector $|e_i\rangle \in V_n$ corresponds to an "out-vertex",

$$|e_i\rangle \sim i \bullet\!\!\longrightarrow\!\!\!-\!\!- \,, \tag{1}$$

a bra $\langle e_j|$ to an "in-vertex"

$$\langle e_j| \sim j \bullet\!\!-\!\!\longleftarrow\!\!- \,. \tag{2}$$

A dyadic $|e_i\rangle\langle e_j|$ results from the multiplication of eqs. (1) and (2). Of the possible products including $|e_i\rangle|e_j\rangle$, $\langle e_i|\langle e_j|$, this is the only one that leads to a new flow from i to j therefore joined to give a directed line (di-line),

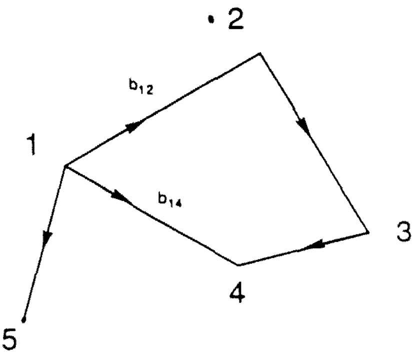
$$B_{ij} = |e_i\rangle\langle e_j| \sim (i \bullet\!\!\longrightarrow\!\!-) \times (-\!\!\longrightarrow\!\!\bullet j) = i \bullet\!\!-\!\!\!-\!\!\!-\!\!\bullet j \,. \tag{3}$$

By contrast to a dyadic product of i and j, a linear combination $\alpha|e_i\rangle + \beta|e_j\rangle$ is simply a disconnected collection of vertices $\left\{ \overset{i}{\underset{\alpha}{\bullet}}\!\!\nearrow \;\; \overset{j}{\underset{\beta}{\bullet}}\!\!\nearrow \right\}$.

B_{ji} in eq. (3) is the reverse line ($i \bullet\!\!\longleftarrow\!\!\bullet j$).

A linear operator $B \in V_n \times V_n^+$, e.g. $B = b_{12}B_{12} + B_{23} + B_{34} + b_{14}B_{14} + B_{15}$ is a di-graph G_B, superposition of di-lines B_{ij} with scalar strengths b_{ij} as in eq. (4).

$\vec{G}_B$:



(4)

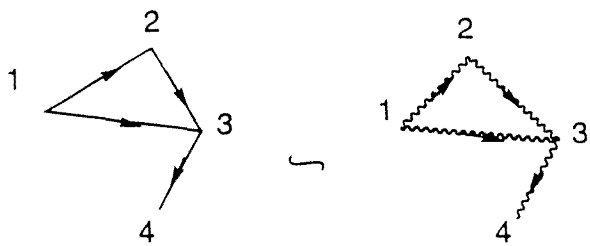
Lines with no b_{kl} indicated are of "standard strength ≡ 1".

3. Product graphs: graphs of two kinds of lines and two types of vertices

A product $P = C \times D = CD$, where, C, D may be vectors or dyads, gives an initial "product graph" $\vec{\mathbb{G}}_P = \vec{G}_C \times \vec{G}_D$, in general non-commutative. It is necessary to distinguish in $\vec{\mathbb{G}}_P$, the lines of the left factor $\vec{G}_C$ from those of the right-factor, $\vec{G}_D$. Draw $\vec{G}_C$ with wiggle lines (•~~~~•), and right factor $\vec{G}_D$ with ordinary lines (•——•). Then $\vec{\mathbb{G}}_P$ is drawn as a di-graph of two kinds of lines superposing $\vec{G}_C$ and $\vec{G}_D$ as in eqs. (5).

Let

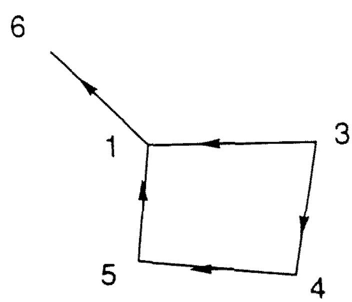
$\vec{G}_C$:



(5a)

and

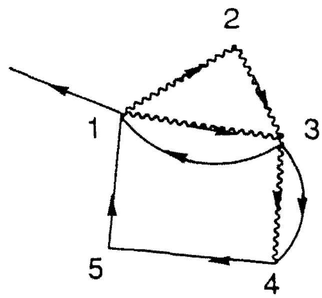
$\vec{G}_D$:



(5b)

then

$\vec{\mathbb{G}}_P$:



(5c)

There are two types of unions of lines in a product graph $\vec{\mathbb{G}}_P$:

(1) Two lines of the same kind, e.g., lines (45) and (51) in eq. (5c), or $(\widetilde{12})$ and $(\widetilde{13})$.

(2) Two lines of differing kind, e.g. $(\widetilde{34})$ and (34) or $(\widetilde{13})$ and (31).

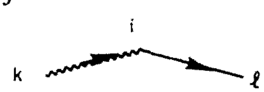
Type (1) union is a superposition, i.e. an algebraic sum of dyadics, e.g. $|e_4\rangle\langle e_5| + |e_5\rangle\langle e_1|$ above, or $|e_1\rangle\langle e_2| + |e_1\rangle\langle e_3|$.

Type (2) union is a product of a wiggle line with an ordinary lines, the product order always being from wiggle to ordinary line with e.g. $|e_3\rangle\langle e_4| \times |e_3\rangle\langle e_4|$ or $|e_1\rangle\langle e_3| \times |e_3\rangle\langle e_1|$ in eq. (5c).

LEMMA

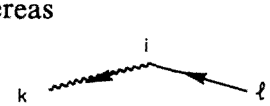
A non-zero product results only when there is a net flow at a type (2)-vertex from wiggle to ordinary lines.

Proof



$$|e_k\rangle\langle e_i|e_i\rangle\langle e_l| \neq 0\,,$$

whereas

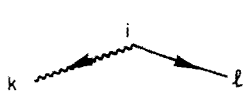


$$|e_i\rangle\langle e_k|e_l\rangle\langle e_i| = 0\,,$$

and

$$|e_k\rangle\langle e_i|e_l\rangle\langle e_i| = 0\,,$$

or



$$|e_i\rangle\langle e_k|e_i\rangle\langle e_l| = 0\,. \tag{6}$$

Comment

We have taken the vectors $\{|e_i\rangle\}$ to be an orthonormal (ON) set, $\langle e_i|e_j\rangle = \delta_{ij}$. If the set is non-ON we can use the linearly covariant formulation and the resulting dual ON sets between contravariant and covariant indices, $\langle ei|ej\rangle \neq \delta ij$, but $\langle e^i|ej\rangle = \delta^i_j$ as shown in ref. [2]. The graph results then remain the same as in the ON case discussion of this paper. In the general case, an out-vertex (i •—>—) is $|e_i\rangle$, whereas an in-vertex (—>—• j) becomes $\langle e^j|$, index raised with the metric tensor Δ^{mn} (cf. ref. [2]).

THEOREM

In a product graph $\vec{\mathbb{G}}_P$ non-zero product type vertices contract out. The $\vec{\mathbb{G}}_P$, which had two kinds of lines and two types of vertices, then contracts to (is "reduced" to) an ordinary di-graph $\vec{G}_P$ with only ordinary di-lines and one type of (ordinary) vertices.

Proof

From the lemma above, non-zero terms in $\vec{\mathbb{G}}_P = \vec{G}_C \times \vec{G}_D$ result only from type (2) vertices (~~~•—>—) with a net flow *from wiggle lines to* ordinary lines as in eq. (6). With an ON set $\{|e_i\rangle\}$ (or for non-ON using the dual ON set [2]), vertex (i) is eliminated by

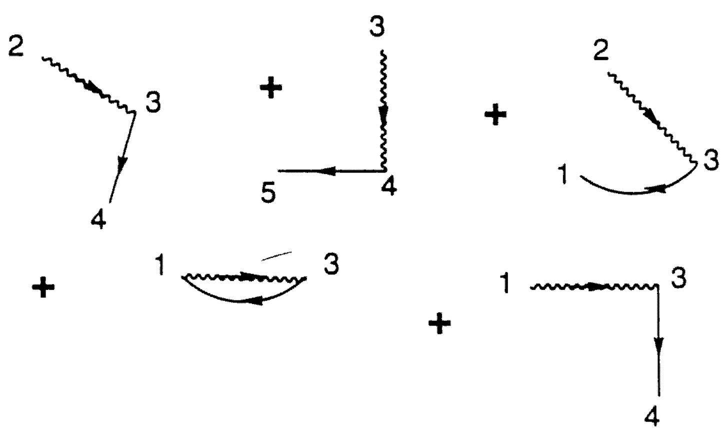
$$|e_k\rangle\langle e_i|e_i\rangle\langle e_l| = |e_k\rangle\langle e_l|$$

(7)

Thus $\vec{\mathbb{G}}_P$ is reduced into a final $\vec{G}_P = \vec{G}_C \times \vec{G}_D$ with no wiggle lines, the resulting ordinary di-graph.

Example

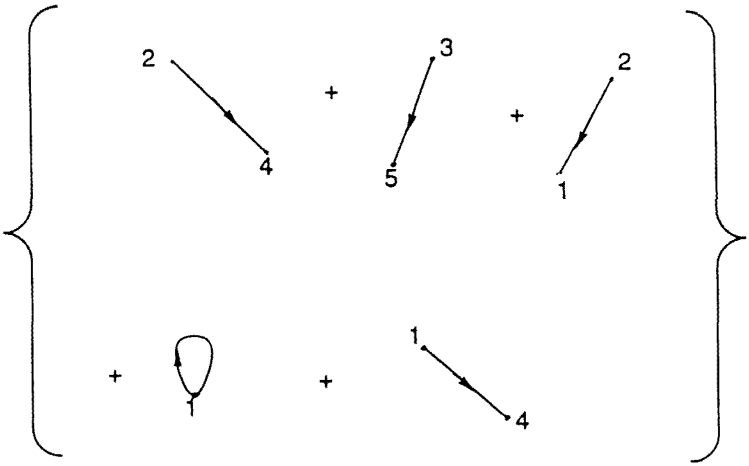
In eq. (5c) consider all type (2) vertices with the proper (wiggle to ordinary) net flows. These are



(8)

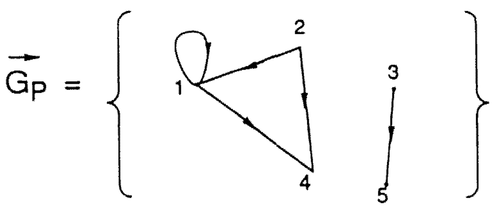
They are found readily by taking one wiggle line at a time and looking at flows from it.

By the theorem, each flow vertex in eq. (8) is taken out yielding

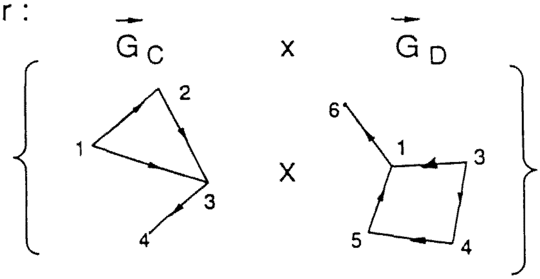


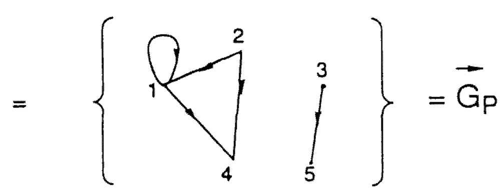
(9)

Thus $\vec{G}_P = \vec{G}_C \times \vec{G}_D$ is the superposition of the surviving lines in eq. (9) out of all the lines in $\vec{G}_C$ and $\vec{G}_D$; i.e.,



or :

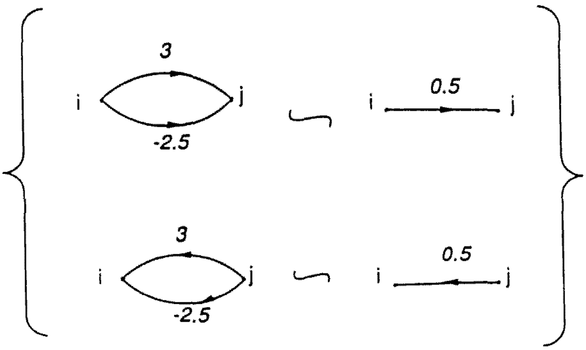




(10)

The treatment above has been for general di-graphs, i.e. graphs which may contain loop and/or multi-lines. As in the example above, loops and multi-lines may also arise even if the initial G's did not contain any.

Note that if a $\vec{G}$ depicts multi-lines between two vertices, the di-lines with the same direction are algebraically added to result in one same-direction-line of some net strength, e.g.,



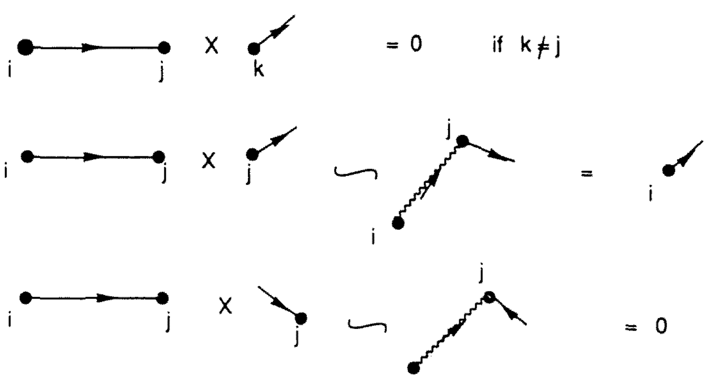
(11)

but multi-lines remain in, e.g.,

The directions of lines are unrelated to the algebraic signs of their strengths.
For convenience, we summarize below, the products of some algebraic objects.

4. Products of elementary algebraic objects and their graphs

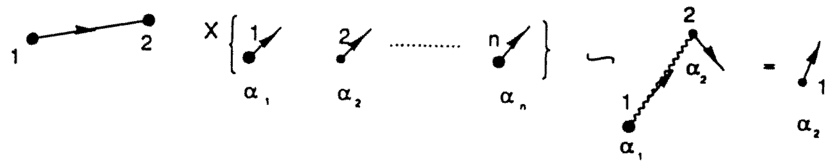
The cases below, useful in carrying out the multiplication of larger digraphs follow from the lemma and the theorem given above (or directly from dyad algebra):
(1) Product of di-line with in- or out-vertex:



(12)

COROLLARY

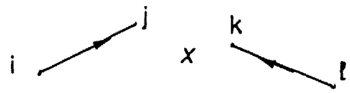
Di-line acting on vector $|u\rangle - \alpha_1|e_1\rangle + \alpha_2|e_2\rangle + \dots \alpha_n|e_n\rangle$ gives, e.g.,



The line out of (2) comes unto (1) eliminating the (12) along with its coefficient.

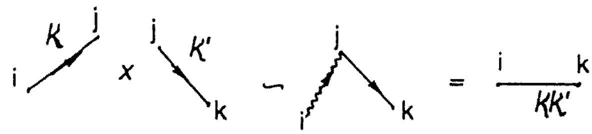
(2) Product of two di-lines:

a)

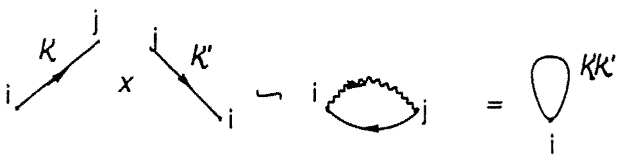


$= 0$
$(i, j \neq k, l)$ (disconnected lines)

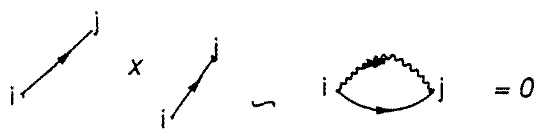
b)



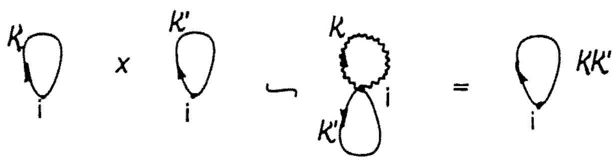
c)

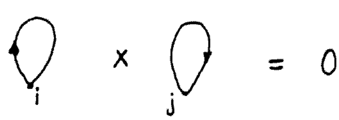


d)



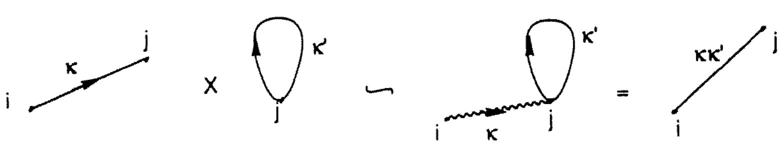
(3) Product of loops:



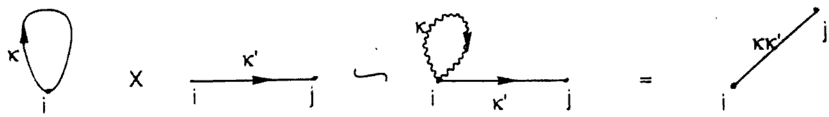


for $i \neq j$

(4) Product of di-line with loop:



(5) Product of loop with di-line:



5. Trace of a di-graph

$(\mathrm{Tr}\,\vec{G})$ is given by the sum of the strengths of its loop only, since

$$\vec{G} \sim \sum_{i \neq j}^{\vec{G}} \kappa_{ij} B_{ij} + \sum_{i}^{n} \xi_i B_{ii} ,$$

$$\mathrm{Tr}\,\vec{G} = \sum_{i \neq j} \underbrace{\kappa_{ij} \mathrm{Tr}\, B_{ij}}_{\text{lines}} + \sum_{i}^{n} \underbrace{\xi_i \mathrm{Tr}\, B_{ii}}_{\text{loops}} .$$

But,

$$\mathrm{Tr}\, B_{ij} = \mathrm{Tr}[|e_i\rangle\langle e_j|] = \langle e_i|e_j\rangle = 0 \quad (i \neq j)$$

and

$$\mathrm{Tr}\, B_{ii} = \mathrm{Tr}|e_i\rangle\langle e_i| = \langle e_i|e_i\rangle = 1$$

for ON $\{|e_j\rangle\}$ or for non-ON with the dual ON sets [2].

Thus

$$\mathrm{Tr}\,\vec{G} = \sum_{i \geqslant 1}^{n} \xi_i = \text{sum of loop strengths} .$$

In computing $\mathrm{Tr}\,\vec{G}_C \times \vec{G}_D$ one need look only at $\vec{\mathbb{G}}_P$ segments that would yield loops per previous section above.

In the next paper II, the results of this paper I are used to obtain the products of undirected or line graphs, G with or without loops. Such G may correspond to Hermitian operators such as the one-electron Hamiltonian or the electron density operator.

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