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COMBINATORIAL PATTERNS IN MULTIPHOTON SPECTROSCOPY

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Abstract

Fermion and photon states are formally introduced in set-theoretical framework and further connected by a homomorphism associating transposition of electron/hole pairs with annihilation/creation of photons. Linear incidence of these two sets is identified as a graph and graph-combinatorial formalism is used in representing these interaction processes.

INTRODUCTION

Multiphoton spectroscopies may be roughly divided into two categories. The names of those may differ; one, for example, may be considered as phase-dependent, time-resolved scopy while the other would be phase-independent. The difference is more substantial in the experimental techniques employed in these two categories (Ref. 1). Conceptual difference may be visualized in the representation using time resolved diagrammatic schemes (Ref. 2) where evolution of individual states is well dissected. The measurable phenomena then occur as direct products of those separately evolved states; in the case of phase-dependent methods particular evolution histories essentially influence the measurable effect. Within the phase-independent methods, though, particular time segments are rather irrelevant, all (measured) states are well matched and all representations are canonical. Typical experimentation is perceptibly simpler. Yet this very area is far from being explored. Remarkably, some intuitive and recognizable patterns are pervasive even in the inherent complexity of multiphoton transitions (Ref. 3). Further rationalization is certainly desirable. Here such an attempt is made.

METHOD

The objective of this paper is a common one - interaction of an atom and a photon. More specifically it is an interaction of bound electrons in an atomic-molecular potential and photons at optical frequencies. It is therefore assumed that electrons may occupy a finite number of discrete states and that photons may occupy discrete states in the Fock boson space (Ref. 4). Finitness of the set of atomic states is not a limitation of the present approach nor is assumed nondegeneracy of certain states, these are just small conveniences used in the presentation. The states existing in an atomic system but unoccupied by electrons at certain initial time may be assumed to be formally occupied by holes. The holes may not be considered as physical particles - these are used here as an essential element in the mathematical formulation of the systems and their interaction; the fact that a state is occupied by a hole sets, within this formalism, the preexistence of the state available to an electron. We therefore may talk about distinctly pro-fermion holes. By analogy, the same formalism can be used for the states 'spanning' the photon space. The structure of the photon space is not essential here and will not be pursued in more details.

Therefore at some primeval time there exists the set B of photons and the set F of fermions. The occupancy of the B is formally being controlled by the action of the boson creation and annihilation operators, $\hat{\beta}^{+}$, $\hat{\beta}^{-}$, respectively, (Ref. 5). The set F is of primary concern here and consequently will be more elaborated upon. We define F as an union of the set E of electrons and the set H of holes, that is,

$$\{F\} = \{E\} \bigcup \{H\} \quad ; \text{ where } e_i, h_j \varepsilon \{F\} \tag{1}$$

We need this distinction as the basis for the model we will develop. At this

stage (primeval time) it is essential to understand that there is no overlap of the sets E and H such that it may result from some structural characteristics of these sets. In other words,

$$\{E\} \cap \{H\} = \{0\} \tag{2}$$

The occupancy of the sets E, H, such that $e_i \in E$ and $h_j \in H$, is being formally controlled by the creation and annihilation operators. Here one amendment has to be made. Beside the electron creation and annihilation operators, $\hat{\eta}^+$ and $\hat{\eta}^-$, respectively, we introduce and employ throughout the hole creation and annihilation operators, $\hat{\chi}^+$ and $\hat{\chi}^-$, respectively. Consequently, we can articulate the previous rationale (vide supra) so that an action of the hole creation operator on the (true) vacuum element produces a distinct discrete hole occupying an element of the finite set of states generally available to an electron. This amendment is simple; it is technically a pure replica of the common electron second quantization formalism, yet it is essential for our formalism.

We can formally define these operators as maps mapping the elements of the common progenitorial set V, $v_n \in V$, (Ref. 6), to the sets E and H. Since there is nothing in the E, H beside fermions (or pro-fermions) one can postulate that the operators $\hat{\eta}^+$, $\hat{\eta}^-$ are surjective. Due to the quantum mechanical restrictions set upon fermions it is obvious that these operators are as well injective (at least $\hat{\eta}^+$ is). The properties of the boson number operators are different; it might be that these produce a surjective map, however due to the general properties of the whole-number-spin particles the operators are generally very noninjective. Consequently, both $\hat{\beta}^+$ and $\hat{\beta}^-$ should be weighted by the factor $[n(b)\ ]^{-1/2}$ where n(b) is the number of photons in the particular photon state. There may exist relations within either E or H or both; we are not concerned with the possibility of the relations within B. It is customary to endow a set of the type E with structure and leave H essentially structureless. It is said that H acquires an induced structure. One of the common forms of relations within the set E is the structure of the Slater orbitals which are, due to the fundamental nature of

the particles, given the determinantal representation for fermions,

$$[N!]^{-1/2} \sum_{i,j=1}^{N!} (-)^{\sigma(p)} P_{ij} \prod_{i=1}^{N} e_{ij} \qquad (3)$$

and permanental representation for bosons,

$$[N! \prod_{i} n_i!]^{-1/2} \sum_{i,j=1}^{N!} P_{ij} \prod_{i=1}^{N} b_{ij} \qquad (4)$$

with the usual meaning of the symbols.

Now the atom and photons are allowed to interact. A possible consequence is that the photon field induces changes in the atom. It happens that a certain number of photons are absorbed and another certain number of electrons occupy different states from those prior to the interaction. Thus an electron can occupy the state previously occupied by a hole; consequently that same hole can occupy the state previously occupied by an electron. In terms of the sets E, H one formally defines a permutation map,

$$T: \{F\} \longrightarrow \{F\} \qquad (5)$$

such that

$$t_{ij}(e_i h_j) \longrightarrow (e_j h_i), \quad t_{ij} \in T \qquad (6)$$

The map T is obviously an automorphism on $\{F\}$ and is composed of products of the elements t_{ij}, $T = \prod_n t_n$. It can as well be redefined in terms of creation operators,

$$t_{ij}: \hat{\eta}_i^+ \hat{\chi}_j^+ | > \longrightarrow \hat{\eta}_j^+ \hat{\chi}_i^+ | > \qquad (7)$$

It may be furthermore useful to articulate the map t_{ij} by endowing it with a

sense preference,

$$t^{+}_{ij}:(\hat{\eta}^{+}_{i}\ \hat{\chi}^{+}_{j})|\ > \longrightarrow \qquad \hat{\eta}^{+}_{j}\ \hat{\chi}^{+}_{i}|\ >$$
$$t^{-}_{ij}:(\hat{\eta}^{+}_{j}\ \hat{\chi}^{+}_{i})|\ > \longrightarrow \qquad \hat{\eta}^{+}_{i}\ \hat{\chi}^{+}_{j}|\ > \qquad (8)$$

If we consider creation of the electron state in the H and a creation of the hole state in the E as a single event then we are formally introducing the Liouville space; consequently, the state $\hat{\eta}^{+}_{i}\ \hat{\chi}^{+}_{j}|\ >$ is the line state (Ref. 7) and will be written as $\hat{\eta}^{+}_{i}\ \hat{\chi}^{+}_{j}|\ >>$. If this process has been energetically contributing to the atom a photon of similar energy should have been absorbed. In the single interaction act the unperturbed energy is approximately conserved (Ref. 4b). There is therefore one photon less in the B, that is,

$$\hat{\beta}_{k}|b_{k}> \longrightarrow \qquad (b_{k})^{1/2}|b_{k}-1> \qquad (9)$$

or more generally,

$$(n!)^{-1/2}(\hat{\beta}^{+}_{k})^{n}|b_{k}> \longrightarrow \qquad \prod_{n=0}^{n(b_{k})-1} (b_{k}-n)^{1/2}|b_{k}-n> \qquad (10)$$

and analogously for a creation,

$$(m!)^{-1/2}(\hat{\beta}^{+}_{k})^{m}|b_{k}> \longrightarrow \qquad \prod_{m=1}^{m(b_{k})} (b_{k}+m)^{1/2}|b_{k}+m> \qquad (11)$$

Obviously, creation/annihilation of photons is essentially associated with the transposition within pairs of hole/electron elements. This can be formally stated by defining a map g such that,

$$g:(t^{+}_{ij}) \longrightarrow \hat{\beta}^{-}_{k}$$
$$g:(t^{-}_{ij}) \longrightarrow \hat{\beta}^{+}_{k} \qquad (12)$$

where g is obviously a homomorphism, (Ref. 8), defining a nonempty intersection of sets B and F, that is,

$$\{B\} \quad \{F\} \neq \{0\}$$
$$\{B\} \quad \{F\} = \{G\} \qquad (13)$$

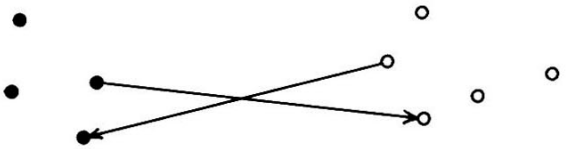
The intersection set G(f,b) is constructed by a linear incidence of the elements b_k, $b_k \in B$, and ordered pairs of the elements f_m, $f_m \in F$. The set G is therefore a graph (Ref. 9). Its single element is depicted in Figure 1a or, given explicitly the sense to the relation, in Figure 1b.

Figure 1a.

Figure 1b.

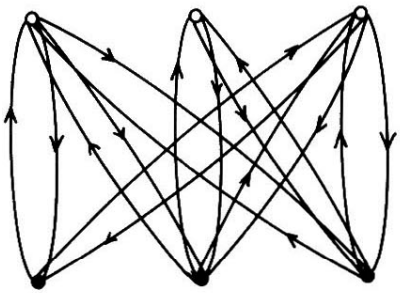
This single element has usually been referred to as the K_2 graph (Ref. 10) or as dimer (Ref. 11). For a more complete scenario we need more elements, as in Figure 2.

Figure 2.



Representing all possible single interactions for such an array one gets Figure 3. which is the well known $K_{3,3}$ graph (Ref. 9).

Figure 3.



APPLICATION

One can easily go on using this elementary graph formalism in representing various interaction schemes. To recapitulate the main steps,

(i) electronic quantum states in an atom are dissected into a set E occupied by electrons and a set H occupied by (pro-fermion) holes,

(ii) electromagnetic field is quantized, divided into discrete nonoverlapping cells (Ref. 4b) and given the occupation number representation, thus creating the set B,

(iii) interaction of two systems, (i) and (ii), is represented as an intersection of the sets E, H and B; an element of this interaction is a graph composed of one vertex defined in the E, the other vertex defined in the H and the incident edge defined in the B.

We may, in principle at least, imagine cascade-type processes with the elements of interaction as given in Figures 4. and 5.

Figure 4.

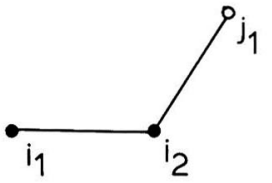
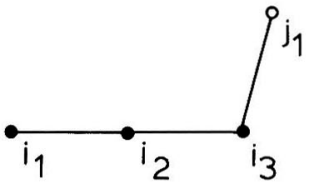


Figure 5.



Algebraic representation of the first scheme, for example, can be dissected into following parts,

$$T{:}\hat{n}^+_{i1}\ \hat{n}^+_{i2}\ \hat{x}^+_{j1}|>\longrightarrow \underset{(a)}{} \quad \hat{n}^+_{i1}\ t_{ij}(\hat{n}^+_{i2}\ \hat{x}^+_{j1})|>>\longrightarrow \underset{(b)}{} \quad t_{ij}(\hat{n}^+_{i1}\ \hat{x}^+_{j1})\hat{n}^+_{i2}|>>$$

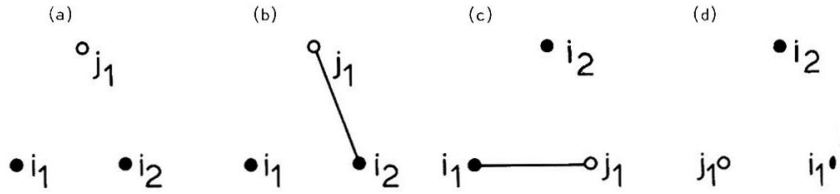
(c)

$$\hat{x}^+_{j1}\ \hat{n}^+_{i1}\ \hat{n}^+_{i2}|> \qquad (14)$$

(d)

To these parts correspond following graphs,

Figure 6.



Analogous expressions - graphs can be easily constructed for the scheme given in Figure 5.

It should be clear at this stage that, (i) representing elements i1, i2, ..., etc, with full circles and elements j1, j2, ..., etc, with empty circles, (ii) writing these elements in certain order, and (iii) placing different kinds of vertices either up or down , is by no means essential to the model. These are just esthetical conventions employed in order to present the model as simply as possible. The essential part of the method is the combinatorial structure of the discrete elements entering into an interaction and here represented by graphs. Thus, the totality of these cascade-type processes on a given set E, $e_i \in E$, i = 1, 2, . . . , z, is given by an expression for counting the number of polygons in the complete graph K_z (Ref. 9). To remind a reader, a complete graph is that where all vertices are mutually connected. For example, in the case z = 6, the first few terms are,

$$Z = \sum_i \sum_j t_{ij} (\hat{n}_i^+ \hat{x}_j^+) \mid >> \; + 15 \sum_{i1\, i2} \sum_j t_{i1\, j} t_{i2\, j} (\hat{n}_{i1}^+ (\hat{n}_{i2}^+ \hat{x}_j^+)) \mid >> \; + \tag{15}$$

$$+ 18 \sum_{i1\, i2\, i3} \sum_j t_{i1\, j} t_{i2\, j} t_{i3\, j} (\hat{n}_{i1}^+ (\hat{n}_{i2}^+ (\hat{n}_{i3}^+ \hat{x}_j^+))) \mid >> \; + \text{higher terms}$$

It should be noted that, from the combinatorial point of view, the size of the set H is unimportant. Summation over indices can be factored out as the weight on a particular vertex of the graph. In a mixed representation the previous expression looks like (16), where weights on particular vertices are represented by (self) loops,

$$Z = \left[\ \right] t_{ij}(\hat{n}_i^+ \hat{x}_j^+)| >> + \left[\ \right] t_{i1\,j} t_{i2\,j} (\hat{n}_{i1}^+ (\hat{n}_{i2}^+ \hat{x}_j^+))| >> +$$

$$- \quad + \quad + \quad + \quad +$$

$$+ \left[\ \right] t_{i1\,j} t_{i2\,j} t_{i3\,j} (\hat{n}_{i1}^+ (\hat{n}_{i2}^+ (\hat{n}_{i3}^+ \hat{x}_j^+)))| >>$$

$$+ \text{ higher terms} \qquad (16)$$

where subscripts K_1, K_2, etc, mean that one enumerates K_1 polygons, K_2 polygons, etc, or, vertices, edges, etc, respectively, in a particular graph.

We can as well construct schemes which appear to be mirror images of those given in Figures 4. and 5.

Figure 7.

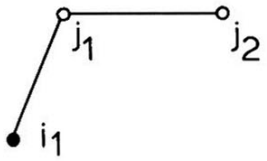
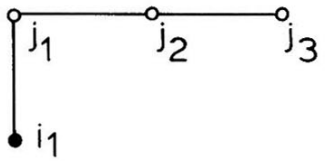


Figure 8.



Algebraic expression corresponding to the scheme given in Figure 7. is,

$$T:\hat{n}^{+}_{i1}\hat{x}^{+}_{j1}\hat{x}^{+}_{j2}|> \longrightarrow \quad t_{ij}(\hat{n}^{+}_{i1}\hat{x}^{+}_{j1})\hat{x}^{+}_{j2}|>> \longrightarrow \quad \hat{x}^{+}_{j1}t_{ij}(\hat{n}^{+}_{i1}\hat{x}^{+}_{j2})|>> \qquad \text{etc.}$$

and analogously for the other scheme. The processes depicted in Figures 7. and 8. may be identified as the two-photon absorption and the three-photon absorption, respectively.

We can express the character of the intersection of the sets B and F by postulating the following proposition:

Proposition: The linear incidence of boson states with fermion line states is a bipartite graph.

To remind a reader, bipartite graph is composed of two sets of vertices with restriction that only vertices from different sets are connected. The proposition is therefore obvious for the schemes represented by the bicolored graphs like $K_{3,3}$ in Figure 3. or by any graph of the type $K_{n,m}$. It is perhaps not so obvious for the schemes represented by graphs given in Figures 4,5 and 7,8, for example. One should understand that those are but condensed representation of the interaction schemes as depicted in Figure 6. Formal description would invoke the notion of the split-vertex graph (Ref. 12). Hence the proposition.

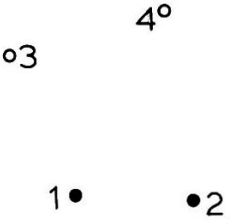
It is useful at this stage to introduce the concept of the adjacency matrix of a graph (Ref. 9). In case of our interaction graphs it would have the general structure,

$$\underset{\sim}{A} = \begin{pmatrix} t_{11} & t_{12} & t_{13} & \cdot & \cdot & \cdot \\ t_{21} & t_{22} & \cdot & \cdot & \cdot & \cdot \\ t_{31} & \cdot & \cdot & \cdot & & \\ \cdot & & & & & \\ \cdot & & & & & \end{pmatrix} \qquad (17)$$

where t_{ab} are transposition operators. Adjacency matrices have one property useful for our consideration - they clearly depict all single and multiple incidences in a graph. Furthermore if a particular interaction is given a representation of a directed graph the adjacency matrix preserves the sense of interaction to all orders.

An example will illustrate this model: within the set of SCF MO's of the benzene molecule, for example, we single out the degenerate pair of Π HOMO's and the subset of unoccupied Π MO's (UMO's) and give these graph representation G_a in Figure 9.

Figure 9.



With a little formulism from the standard graph theory (Ref. 9) one can write the following relations:

$$G_a = G(2\ K_1) \oplus G(3\ K_1) \qquad (18)$$

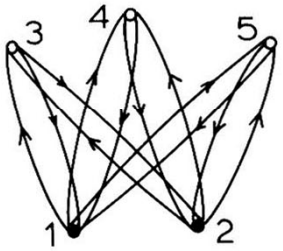
$$\underset{\sim}{A}(G_a) = \underset{\sim}{A}(G(2K_1)) + \underset{\sim}{A}(G(3K_1)) \qquad (19)$$

Here K_1, as usual, stands for vertices or, more correct, nonconnected vertices. Adjacency matrices of graphs composed of such vertices, $\underset{\sim}{A}(n K_1)$, are trivially nilpotent to all orders. In the next step of our example we construct all possible single-type interactions,

$$\sum_{i,j} t_{ij} : \hat{n}_i^+ \hat{x}_j^+ | >> \approx \sum_k \hat{\beta}_k^- | b_k > \qquad (20)$$

and get the scheme represented by the graph G_b in Figure 10.

Figure 10.



Using the same standard formulism one can derive following relations by inspecting the graph G_b;

$$G = G(2K_1) \oplus G(3K_1) \qquad (21)$$

$$\underset{\sim}{A}(G) = \underset{\sim}{A}(G(2K_1)) \oplus \underset{\sim}{A}(G(3K_1)) \qquad (22)$$

The adjacency matrix of the interacting system has the hypermatrix construction, common to the adjacency matrices of bicolored graphs. The diagonal entries $\underset{\sim}{A}(11)$, $\underset{\sim}{A}(22)$, with obvious meaning of the labels 11 and 22 are in this particular case the $\underset{\sim}{A}(2K_1)$ and $\underset{\sim}{A}(3K_1)$, respectively, and are therefore nilpotent. The 'contact' matrices $\underset{\sim}{J}_{ij}$, $\underset{\sim}{J}_{ji}$ with the property defined in complex field as $\underset{\sim}{J}_{ij} = \underset{\sim}{J}^{\dagger}_{ji}$ obviously represent all incidence relations between the two, differently 'colored' sets of vertices, and for our example are given by the rectangular scheme,

$$\underset{\sim}{A}(G) = \begin{pmatrix} \underset{\sim}{A}(11) & \underset{\sim}{J}(12) \\ \underset{\sim}{J}(21) & \underset{\sim}{A}(22) \end{pmatrix} \qquad (23)$$

$$\underset{\sim}{J}(2K_1, 3K_1) = \begin{array}{c} \\ |e_1\rangle \\ |e_2\rangle \end{array} \begin{array}{c} \begin{array}{ccc} |h_1\rangle & |h_2\rangle & |h_3\rangle \end{array} \\ \begin{pmatrix} t_{11} & t_{12} & t_{13} \\ t_{21} & t_{22} & t_{23} \end{pmatrix} \end{array} \tag{24}$$

Now, if we write the adjacency matrix for the system composed of two elements from the set E, three elements of the set H and all incidences between these two subsets we clearly get the following array,

$$\underset{\sim}{A}(G_b) = \begin{pmatrix} 0 & 0 & t_{13} & t_{14} & t_{15} \\ 0 & 0 & t_{23} & t_{24} & t_{25} \\ t_{31} & t_{32} & 0 & 0 & 0 \\ t_{41} & t_{42} & 0 & 0 & 0 \\ t_{51} & t_{52} & 0 & 0 & 0 \end{pmatrix} \tag{25}$$

It is easy to visualize this scheme as a composition of two 'main set' matrices and two contact matrices. The diagonal matrices are composed by the operation of direct sum $\oplus$ while contact matrices can be imagined as composed by some analogous operation of 'off-diagonal' sum. There is no operator for such an operation but for descriptive purposes of this text and with the obvious meaning we use the symbol ' Θ '. We can consequently decompose the $\underset{\sim}{A}(G_b)$ as,

$$\underset{\sim}{A}(G_i \oplus G_j) = \underset{\sim}{A}_i \oplus \underset{\sim}{A}_j + \underset{\sim}{J}_{ij} \Theta \underset{\sim}{J}_{ji} \tag{26}$$

We shal next exploit the well known property that higher orders of the adjacency matrix of a graph, $\underset{\sim}{A}^n$, contain information on the number of trails (Ref. 9) of the length n and starting at each vertex. The n-trail, $n > 1$, may be visualized either as n-sequence of consecutive single edges

between two vertices (not necessarily different) or as a bundle of m edges, $m < n$, between the same pair of vertices. The number of n-trails in the n-th power of the adjacency matrix of a graph is generally somewhat tricky subject due to the property of repetitivness of trails but this difficulty does not affect specific graphs we are considering. The multiply connected vertices are given in Figure 11.

Figure 11.

The automorphic map $(t^{+}_{ij})^{n}$ of the line state $\hat{n}^{+}_{i}\,\hat{x}^{+}_{j}|\,>>$ represented in these two graphs is induced by multiple changes of the occupancy number in the boson state and are given the following formulism,

$$n = 2 \qquad \langle b'_k\, b'_l|\hat{\beta}^{-}_{l}\,\hat{\beta}^{-}_{k}\,|b_k\, b_l\rangle = (b'_k)^{1/2}(b'_l)^{1/2} \tag{27}$$

$$n = 3 \qquad \langle b'_k b'_l b'_m|\hat{\beta}^{-}_{m}\hat{\beta}^{-}_{l}\hat{\beta}^{-}_{k}|b_k b_l b_m\rangle = (b'_k)^{1/2}(b'_l)^{1/2}(b'_m)^{1/2} \tag{28}$$

or, in case of a single-frequency three-photon interaction,

$$\langle b'_k|\ (3!)^{-1/2}(\hat{\beta}^{-}_{k})^{3}\ |b_k\rangle = (b'_k)^{1/2}(b'_k-1)^{1/2}(b'_k-2)^{1/2} \tag{29}$$

This last event occurs in so-called three-photon homochromatic absorption (Ref. 13). The scheme given by (27) corresponds to two-photon heterochromatic absorption (Ref. 14). Enumerating trails of length one, two, etc. on an interaction graph is extremely simple primarily due to the fact that these are nonrepetitive trails and therefore - paths. The adjacency matrix (25)

contains all the informations on paths of length one. Square of the adjacency matrix should give similar information on paths of length two. Square of the $\underset{\sim}{A}(G_b)$ however, will not produce much of the information we are looking for. There are simply no multiple interactions in it. Adding result in a better model.

Figure 13 a.

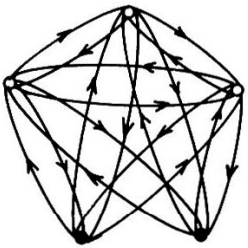
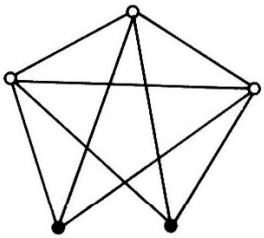


Figure 13 b.



We thus get a slightly more complex interaction graph G_c with describing relations,

$$G_c = 2\,K_1 \oplus K_3 \tag{30}$$

and

$$\underset{\sim}{A}(G_c) = \underset{\sim}{A}(2K_1) \oplus \underset{\sim}{A}(K_3) + \underset{\sim}{A}(2K_1, K_3) \otimes \underset{\sim}{A}(K_3, 2K_1) \tag{31}$$

where,

$$\underset{\sim}{A}(G_c) = \begin{pmatrix} 0 & 0 & t_{ij} & t_{ij} & t_{ij} \\ 0 & 0 & t_{ij} & t_{ij} & t_{ij} \\ \bar{t}_{ij} & \bar{t}_{ij} & 0 & t_{jj} & t_{jj} \\ \bar{t}_{ij} & \bar{t}_{ij} & t_{jj} & 0 & t_{jj} \\ \bar{t}_{ij} & \bar{t}_{ij} & t_{jj} & t_{jj} & 0 \end{pmatrix} \tag{32}$$

$\underset{\sim}{A}^2$ and $\underset{\sim}{A}^3$ are rather complex structures with apparently little information of use. Thus, for instance,

$$\underset{\sim}{A}^2 = \begin{pmatrix} t_{ij}t_{ij}^- + t_{ij}t_{ij}^- + t_{ij}t_{ij}^- & \cdot & \cdot & \cdot & t_{ij}t_{jj} + t_{ij}t_{jj} \\ \cdot & 3(t_{ij}t_{ij}^-) & \cdot & \cdot & \cdot \\ \cdot & \cdot & 4(t_{ij}t_{ij}^-) & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ t_{jj}t_{ij}^- + t_{jj}t_{ij}^- & \cdot & \cdot & \cdot & 4(t_{ij}t_{ij}^-) \end{pmatrix} \tag{33}$$

while, for example, the a_{11} element of the $\underset{\sim}{A}^3$ is composed as,

$$a_{11}^{(3)} = t_{ij}t_{jj}t_{ij}^- + t_{ij}t_{jj}t_{ij}^- + \ldots \text{ etc, (eight such terms)} \tag{34}$$

As was stressed earlier these matrices do faithfully represent all the interaction, however, if we evaluate only the specific type of interaction we are concerned with, the complexity of higher order matrices, $\underset{\sim}{A}^n$, $n > 1$ is reduced. If we evaluate two-photon and three-photon interactions given by (27) and (28) we get for the $\underset{\sim}{A}^2(G)$,

$$\underset{\sim}{A}^2(G_c) = \begin{pmatrix} 0 & 0 & 2t_{ij}t_{jj} & 2t_{ij}t_{jj} & 2t_{ij}t_{jj} \\ 0 & 0 & 2t_{ij}t_{jj} & 2t_{ij}t_{jj} & 2t_{ij}t_{jj} \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix} \tag{35}$$

and for the $\underset{\sim}{A}^3(G)$,

$$\underset{\sim}{A}^3(G_c) \begin{pmatrix} 0 & 0 & 2t_{ij}t_{jj}t_{jj} & 2t_{ij}t_{jj}t_{jj} & \text{etc.} \\ 0 & 0 & 2t_{ij}t_{jj}t_{jj} & \text{etc.} & \text{etc.} \\ 0 & \text{etc.} & \text{etc.} & . & . \\ . & . & . & . & . \\ . & . & & & 0 \end{pmatrix} \tag{36}$$

with obvious information on the number of specific interactions. For simple systems all these data can be arrived at by inspecting the interaction graphs.

We could, for a moment, step back and recollect how the interaction graph was defined - as an incidence of boson states with fermion line states. Formally, therefore, such a graph is created as an intersection of two boson sets. A pair of adjacent vertices in that graph forms a boson particle , (Ref. 15). Totality of such pairs is the totality of bosons in the interacting system. Since each such pair exists essentially in the process of a transposition of vertices, evaluating elements in the adjacency matrix of a graph we actually enumerate the number of permutations. One may therefore consider these graphs as purely permutational objects and apply the standard formulism of the symmetric group (Ref. 16). Thus, for example, our system is a 5-center one, however, due to the bipartiteness of the interaction graph the order of the group S(G) is reduced and can be more appropriately described as,

$$S(G) \subset S(4) \cup S(4) \tag{37}$$

which can be understood in such a way that, in case of undirected edges, the symmetry number of the system is 48 rather than 120. One may therefore describe the graphs G_a and G_b by relations,

$$G_a: \qquad [S(G_a)] = [1^4] \cup [1^4] \tag{38}$$

and

$$G_b: \qquad [S(G_b)] \subset [2,1^2] \cup [2,1^2] \tag{39}$$

For the G_c interaction equivalent to that given in (27) can be embedded into following sets,

$$[S(G_c)] \subset [3,1] \cup [3,1] \tag{40}$$

while those interactions given by (28) and (29) may be described as,

$$[S(G_c)] \subset [4^1] \cup [4^1] \tag{41}$$

The obviousness of these expression fades away quickly with an increase in the size of the system under consideration and combinatorial relations derived either on the adjacency matrix or taken from the formulism of the symmetric group become indispensable.

One should not neglect a probabilistic aspect in all these. For example, an evaluation of single or double interactions requires covering of the representative bipartite graph by a single dimer or by a pair of disjoint dimers, respectively (Ref. 11). Singular probabilities in the latter case are given by,

$$p_{ik} = p(t_{i_i j_j}) \times p(t_{j_j j_k}) \tag{42}$$

while the total probability in the process of covering the graph with a pair of disjoint dimers is,

$$P(t_{ik}) = \sum_{i,k} p(t_{i_i j_j}) \times p(t_{j_j j_k}) \tag{43}$$

where the operation which connects the composition of separate probabilities is simple multiplication. Using this procedure one can straightforwardly compute, for instance, combinatorial entropy of the two-photon interaction,

(Ref. 17). It is clear that the expressions (42) and (43) imply nonmetric evaluation of the interaction graph. It is also known that interaction processes are inherently quite complex. Thus, for example, to answer the question whether the entries in the matrix $\underset{\sim}{A}^2(G_c)$ given by (35) correspond to a single two-photon interaction or to two consecutive (however short the intermediate time be) one-photon processes one ought to consider probabilities of different types than those given in (42) and (43). Measuring the final state arrived at through some intermediate state necessarily includes amplitudes of those intermediate states and the overall probability for such interaction would rather be,

$$P(t_{ij}) = \sum_{j} p(t_{i_i j_j}) p(t_{j_j j_k}) + \sum_{j} \sum_{j'} p(t_{i_i j_j}) p(t_{j_j j_k}) p(t^{*}_{i_i j_{j'}}) p(t^{*}_{j_{j'} j_k}) \qquad (42)$$

or, in the density operator formulism, exploiting the commutativity property of projectors and idempotency of density operator, Π and ρ, respectively, the previous expression would read,

$$P(t_{ik}) = \mathrm{Tr}\{\rho \Pi_{i_i} \Pi_{j_k}\} + \sum_{j'} \mathrm{Tr}\{\rho \Pi_{j_j} \Pi_{j_{j'}} \Pi_{j_k}\} \qquad (43)$$

Evaluation of a given combinatorial expression within a certain metric would require endowing the codomain of the sets E and H with a proper algebraic structure. A logical candidate for that would be the structure of the point group of the molecule. In the next step one may exploit the structure of the complete permutation inversion group (Ref. 18) or the point group can be mediated by appropriate perturbative procedures. It may appear that the presented discrete formalism will be lost in these considerations. Not so if we recollect the linear, dissected structure underlying most of our approaches; the problem though is how to define our interacting elements. This, however, will be the topic of a separate communication.

CONCLUSION

Using elementary set theory bound fermion states and discretized photon states were formally defined. Fermion states were further divided into electron and hole states. By exploiting this elementary formalism transposition of electrons and holes was formally associated with creation and annihilation of photons. Thus a set created as an intersection of two boson sets was defined and shown to posses properties of a graph. Consequently, graph formalism and formulism were exploited to describe simple, elementary interactions. Combinatorial character of these interactions was derived in terms of the adjacency matrix formalism. Some elements of the symmetric group formulism were also indicated. The elementary, nonmetric character of these schemes was stressed in mentioning probabilistic aspect of these interactions. It is hoped that this, rather elementary formalism, can be used as a basis for elaborating on interaction processes within specific metric structures. It is also hoped that thus dissected interaction structure may be helpful in constructing an algorithm for a general mechanical evaluation (Ref. 19) of interaction processes.

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