

# von Neumann Entropies Analysis of Nanostructures: PAMAM Dendrimers of Growing Generation

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## ABSTRACT

Quantum Information Theory (QIT) is a new field with potential implications for the conceptual foundations of Quantum Mechanics through density matrices. In particular, information entropies in Hilbert space representation are highly advantageous in contrast with the ones in real space representation since they can be easily calculated for large systems. Quantum information entropies have shown, through quantum mechanics concepts such as entanglement, several interesting critical points which are not present in the energy profile, such as depletion and accumulation of charge, non-nuclear attractors and bond breaking/formation regions. In this work, von Neumann informational entropies are employed to characterize the initial steps (monomer, dimer, trimer, tetramer) towards growing a nanostructured molecule of Polyamidoamine (PAMAM) dendrimer of generation zero (G0). Structures were geometrically optimized at the b3lyp/6311+G\*\* level of theory.

**Keywords:** dendrimers, PAMAM, quantum information theory, an initio calculations, entanglement

## 1 INTRODUCTION

The most interesting technological implications of quantum mechanics are based on the notion of entanglement, which is the essential ingredient for both quantum cryptography, quantum computing, and quantum teleportation [1]. Generally speaking, if two particles are in an entangled state, then even if the particles are physically separated by a great distance, they behave in some respect as a single entity rather than as two separate entities. Entanglement shows up in cases where a former unit dissociates into simpler sub-systems. Corresponding processes are known quite well in chemistry. The real-space partitioning of a molecule into subsystems is still a challenging problem in theoretical chemistry [2-14], because during this process a certain entanglement of the subsystems emerges, and it is very difficult to get rid of it without destroying elementary correlations between the subsystems. So, apart from its evident importance for the

foundations of physics, entanglement plays a role in chemistry too. Although information entropies have been used for a variety of studies in quantum chemistry [15-21], applications of entanglement measures in chemical systems are very scarce. Very recently, marginal and non-marginal information measures in Hilbert space have been proposed [22], and applied to small chemical systems, showing that entanglement can be realized in molecules [23].

It is of great interest in Chemistry to understand molecular systems as combination of atoms and molecular fragments. Thus, the concept of AIM has been the focus of great deal of attention [2-14]. Chemical processes involve small changes between atoms and molecular subsystems and it is crucial to understand the interactions (correlation and entanglement) involved in such chemical changes. The main goal of the present study is to show that marginal entropies of bipartite composite systems in Hilbert space [22,23] are able to reveal the growing behavior of PAMAM towards its generation zero. This is achieved by use of novel measures of conditional, mutual, joint information von Neumann entropies computed by means of the spectral decomposition of the first reduced density matrix in the natural atomic orbital-based representation, assuring rotational invariance, and N and v-representability in the AIM scheme [24].

Dendrimers [25] are nanostructured molecules which are highly branched, star-shaped macromolecules which are defined by three components: a central core, an interior dendritic structure (the branches), and an exterior surface with functional surface groups. Monodisperse dendrimers are synthesized by step-wise chemical methods to give distinct generations (G0, G1, G2, ...) of molecules with narrow molecular weight distribution, uniform size and shape, and multiple (multivalent) surface groups. In particular, Polyamidoamine (PAMAM) dendrimers are the most common class of dendrimers suitable for many materials science and biotechnology applications which consist of alkyl-diamine core and tertiary amine branches. PAMAM dendrimers represent an exciting new class of macromolecular architecture called "dense star" polymers systematically changing the normal dendrimer features (e.g. generation or surface group).

## 2 THEORETICAL FRAMEWORK

The uncertainty in a collection of possible observables  $A_i$  with corresponding probability distribution  $p_i(A)$  is given by its Shannon entropy  $H(A)$  [26]

$$H(A) = -\sum_i p_i(A) \ln p_i(A) \quad (1)$$

This measure is suitable for systems described by classical physics, and is useful to measure uncertainty of observables but it is not suitable for measuring uncertainty of the general state of a quantum system. It is the von Neumann entropy which is appropriate to measure uncertainty of quantum systems since it depends on the density matrix (see below).

Another important concept derived from relative entropy concerns the gathering of information. When one system learns something about another, their states become correlated. How correlated they are, or how much information they have about each other, can be quantified by the mutual information. The *Shannon mutual information* between two random variables  $A$  and  $B$ , having a joint probability distribution  $p_{ij}(A,B)$  and marginal probability distributions

$$p_i(A) = \sum_j p_{ij}(A,B) \text{ and } p_j(B) = \sum_i p_{ji}(B,A) \quad (2)$$

defined as

$$\begin{aligned} H(A:B) &= H(A) + H(B) - H(A,B) \\ &= \sum_{ij} p_{ij}(A,B) \ln \frac{p_{ij}(A,B)}{p_i(A)p_j(B)} \end{aligned} \quad (3)$$

Where  $H(A,B)$  is the joint entropy defined as

$$H(A,B) = -\sum_{ij} p_{ij}(A,B) \ln p_{ij}(A,B) \quad (4)$$

which measures the uncertainty about the whole system  $AB$ . The mutual information  $H(A:B)$  can be written in terms of the Shannon relative entropy. In this sense it represents a distance between the distribution  $p(A,B)$  and the product of the marginals  $p(A) \times p(B)$ . Suppose that we wish to know the probability of observing  $b_j$  if  $a_i$  has been observed. This is called a conditional probability and is given by

$$p_{ij}(A|B) = \frac{p_{ij}(A,B)}{p_j(B)} \text{ and } p_{ji}(B|A) = \frac{p_{ji}(B,A)}{p_i(A)} \quad (5)$$

Hence the conditional entropy is,

$$H(A|B) = -\sum_{ij} p_{ij}(A,B) \ln p_{ij}(A|B) \quad (6)$$

This quantity, being positive, tells us how uncertain we are about the value of  $B$  once we have learned about the value of  $A$ . Now the Shannon mutual information can be rewritten as

$$H(A:B) = H(A) - H(A|B) \quad (7)$$

And the joint entropy as

$$H(A,B) = H(B) + H(A|B) \quad (8)$$

The difference between classical and quantum entropies can be seen in the fact that quantum states are described by a density matrix  $\rho$  (and not just probability vectors). The density matrix is a positive semidefinite Hermitian matrix, whose trace is unity. An important class of density matrices is the idempotent one, i.e.,  $\rho = \rho^2$ . The states these matrices represent are called pure states. When there is no uncertainty in the knowledge of the system its state is then pure. Another important concept is that of a composite quantum system, which is one that consists of a number of quantum subsystems. When those subsystems are entangled it is impossible to ascribe a definite state vector to any one of them, unless we deal with a bipartite composite system. The most often cited entangled system is the Einstein-Podolsky-Rosen state (EPR) [27,28], which describes a pair of two photons.

Since the uncertainty in the probability distribution is naturally described by the Shannon entropy, this classical measure can also be applied in quantum theory. In an entangled system this entropy is related to a single observable. The general state of a quantum system, is described by its density matrix  $\rho$ . Let the observables  $a_i$  and  $b_j$ , pertaining to the subsystems  $A$  and  $B$ , respectively, have a discrete and non degenerate spectrum, with probabilities  $p(a_i)$  and  $p(b_j)$ . For simplicity let us define them as  $p_i(A)$  and  $p_j(B)$ . In addition, let the joint probability be  $p_{ij}(A,B)$ . Then

$$\begin{aligned} H(A) &= -\sum_i p_i(A) \ln p_i(A) \\ &= -\sum_{ij} p_{ij}(A,B) \ln \sum_j p_{ij}(A,B) \end{aligned} \quad (9)$$

and similarly for  $H(B)$ .

An indication of correlation is that the sum of the uncertainties in the individual subsystems is greater than the uncertainty in the total state. Hence, the Shannon mutual information is a good indicator of how much the two given observables are correlated. However, this

quantity, as it is inherently classical, describes the correlations between single observables only. The quantity that is related to the correlations in the overall state as a whole is the von Neumann mutual information which depends on the density matrix. The von Neumann entropy [29], may be considered as the proper quantum analog of the Shannon entropy [30] for a system described by a density matrix  $\rho$ , and is defined as

$$S(\rho) = -\text{Tr}(\rho \ln \rho) \quad (10)$$

The Shannon entropy is equal to the von Neumann entropy only when it describes the uncertainties in the values of the observables that commute with the density matrix, i.e., if  $\rho$  is a mixed state composed of orthogonal quantum states, otherwise

$$S(\rho) \leq H(A) \quad (11)$$

where  $A$  is any observable of a system described by  $\rho$ . This means that there is more uncertainty in a single observable than in the whole of the state [31].

We have recently shown [24] that there is an information-theoretic justification for performing Lowdin symmetric transformations [32] on the atomic Hilbert space, to produce orthonormal atomic orbitals of maximal occupancy for the given wavefunction, which are derived in turn from atomic angular symmetry subblocks of the density matrix, localized on a particular atom and transforming to the angular symmetry of the atoms. The advantages of these kind of atoms-in-molecules (AIM) approaches [33,34] are that the resulting natural atomic orbitals are N- and  $\nu$ -representables [24], positively bounded, and rotationally invariant [35,36].

According to the preliminaries above we have recently proposed new measures of correlation and entanglement through marginal (H-type) and non-marginal (R-type) von Neumann entropies [22,23]. In Hilbert space we may define a measure of quantum correlations between molecular fragments for a bipartite system through natural atomic probabilities and their joint probability. In the natural atomic decomposition scheme we employ there are  $m$  states pertaining to molecular fragment  $A$ , i.e.,  $\{p_i(A); i=1 \text{ to } m\}$  with  $n$  states corresponding to molecular fragment  $B$ :  $\{p_j(B); j=1 \text{ to } n\}$ , thus, we may define the joint entropy through global operations by correlating  $m \times n$  states providing that the following constraints are met:

$$\sum_i \sum_j P_{ij}(A, B) = \sum_i P_i(A) = \sum_j P_j(B) = \sum_i P_{ij}(A/B) = 1 \quad (12)$$

We are now in position of using definitions above related to the von Neumann entropies, taking into account that in our natural atomic scheme of probabilities, equality in Eq. (11)

holds, and instead of referring to observables we deal with subsystems (molecular fragments), that is why von Neumann entropies are adequate for our study, though we keep the H-terminology to emphasize the orthogonal and commuting properties of the subspaces we are dealing with.

### 3 RESULTS AND CONCLUSION

In the present study we analyze novel von Neumann marginal entropies of bipartite composite systems in Hilbert space (Sec 2) to assess their utility for revealing the growing behavior of recently, ethylenediamine-core (EDA) PAMAM which have a 4-fold multiplicity, i.e., a four branched growing structure. The typical end-groups are primary amines or carboxylate functions depending on if these are full or half-generation PAMAMs. In this work we have calculated several conformations for the monomer, dimer, trimer towards the G0 structure at the b3lyp/6311+G\*\* level of theory, except for the G0 geometry which was obtained from Maiti et al [39]. The electronic structure calculations performed in this study were carried out with the NWchem suite of programs [37] and the natural atomic probabilities were obtained by use of the NBO 5.G program [38].

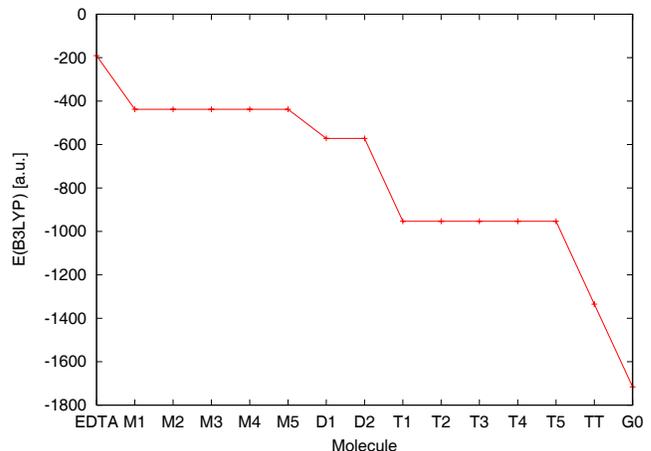


Figure 1: Energies for the monomers M1 through M5, dimers D1 and D2, trimers T1 through T5, tetramer and the G0 structure for PAMAM

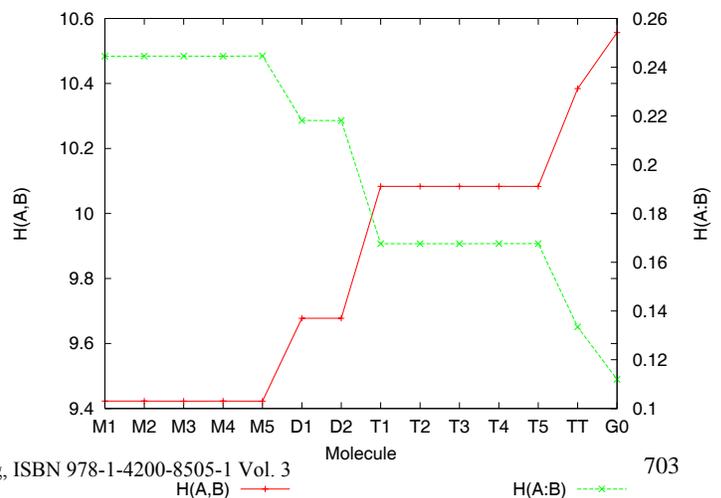


Figure 2: Mutual and joint von Neumann entropies  $H(A:B)$  and  $H(A,B)$  for the monomers M1 through M5, dimers D1 and D2, trimers T1 through T5, tetramer and the G0 structure for PAMAM

From Figures 1 and 2, wherein the energy and the mutual and joint von Neumann entropies are depicted for all the calculated structures it is clear that QIT entropies describe well the growing behavior of PAMAM dendrimer of G0 type. Ongoing research is currently performed in our laboratory to extend the study to G1-G11 PAMAMs and to incorporate descriptors from statistical complexity theory.

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