

Potential "Missing Link" in Chemistry that Led to Life on Earth Discovered

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Abstract

The phosphorylation of short nucleotide sequences, amino-acid sequences, and lipids making possible formation of small cell membrane like structures is necessary for the formation of larger structures from their building bricks. As noticed, ribozymes catalyze only dephosphorylation. How RNA was phosphorylated during RNA era or were the amino-acids present all the time? It was recently discovered that an organic molecule known as diamidophosphate (DAP) having chemical formula could do the job in presence of water and imidazol. DAP could solve several problems simultaneously: how the short sequences of RNA (later DNA) and amino-acids emerged, and how the predecessors of cell membranes emerged. It is not however whether this process could have been fast enough or whether the slowness only made the first step painful. This problem will be discussed in the sequel.

1 Introduction

In the attempts to understand pre-biology the basic challenge is to understand how the needed short RNA, DNA, and amino-acid sequences managed to form. Phosphorylation (see <http://tinyurl.com/y732fsd3>) is known to be crucial for this process and means energization in standard bio-chemistry. Organic phosphate (see <http://tinyurl.com/cx9ukv9>) possesses somewhat mysterious high energy phosphate bond, which stores energy and makes possible metabolism: in metabolic ATP with three phosphates transforms to ADP with two phosphates by giving one phosphate with high energy phosphate bond to the acceptor molecule, which is therefore phosphorylated.

In the recent biology phosphorylation of various biomolecules such as DNA, RNA, amino-acid sequences is catalyzed by proteins known as enzymes known as phosphorylases. Kinase is one particular enzyme transferring phosphate from ATP to the acceptor molecule. Proteins consist of amino-acids and would not be present in RNA world, which serves almost as a standard model for the prebiotic period. Ribozymes are catalysts formed from RNA but they catalyze typically only the reversal of phosphorylation.

The phosphorylation of short nucleotide sequences and amino-acid sequences, and also lipids making possible formation of small cell membrane like structures is necessary for the formation of larger structures from their building bricks. As noticed, ribozymes catalyze only dephosphorylation. How RNA was phosphorylated during RNA era or were the amino-acid present all the time?

The popular article with the title "*Potential 'missing link' in chemistry that led to life on Earth discovered*" (see <http://tinyurl.com/y9s56xnx>) tells about a mechanism allowing phosphorylation during RNA era in absence of enzymes. The discovery [2] (see <http://tinyurl.com/y9kvgl24>) is that an organic molecule known as diamidophosphate (DAP) (see <http://tinyurl.com/y88vecs2>) having chemical formula $PO_2(NH_2)_2^{-1}$ could do the job in presence of water and imidazol. Imidazol (see <http://tinyurl.com/y8vgfr42>) has chemical formula $C_3N_2H_4$ and is a molecule possessing aromatic hetero-cycle consisting of 3 C atoms and 2 N atoms.

Remark: Pyrimidine (see <http://tinyurl.com/k3vx19b>) in turn is aromatic hetero-6-cycle consisting of 4 C atoms and 2 N atoms and having formula $C_4N_2H_4$. DNA (see <http://tinyurl.com/cpndtse>) has as basic building bricks phosphates PO_4^- having valence bonds with deoxy-ribose (see

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<http://tinyurl.com/qxv9kg8>) molecules (containing 5-rings with 4 C atoms and one O). Each sugar has valence bond with N of nucleoside C, T, A or G. C and T are pyrimidines with single aromatic 6-ring and A and G are purines obtained by fusing imidazol 5-ring and pyrimidine 6-ring to obtain purine double ring. By replacing one OH of de-oxyribose of DNA with H one obtains RNA.

DAP could solve several problems simultaneously: how the short sequences of RNA (later DNA) and amino-acids were formed, and how the predecessors of cell membranes emerged. It is not however clear to me whether this process could have been fast enough or whether the slowness only made the first step painful. This finding will be discussed in TGD framework.

2 How could the discovery relate to TGD inspired quantum biology?

It is interesting to interpret the discovery in TGD framework. The basic question is whether the presence of dark atoms and electrons in bio-molecule distinguish between atomic physics, in-organic chemistry, and organic chemistry. Usually organic chemistry is defined to be chemistry of carbon compounds, typically hydrocarbons. Could it be that the formation of hydrocarbons involves dark variants of proton and electron identified as $h_{eff} = n \times h$ variants of ordinary proton and electron?

2.1 From atomic physics to chemistry

How could one proceed from atomic physics to atomic physics to chemistry in TGD framework. The basic question is how to understand valence bond: it is not at all clear whether mere Schrödinger equation allows to understand it. Could the emergence of dark electrons allow their delocalization and formation of valence bonds? It has been known for decades that the heating of rare-earth metals leads to a mysterious loss of some valence electrons and the explanation would be the energy provided by heating kicks them to higher energy states by making some valence electrons dark [9]. The explanation would be in terms of dark electron orbitals for valence electrons which have radii scaled up by factor n^2 and are analogous to Rydberg states identified as orbitals with large value of principal quantum number and having very large radius.

The dark variants of atoms have binding energy scale reduced by factor $1/n^2$ so that their formation requires energy feed (perhaps radiation at required frequencies). One or more valence electrons of ordinary atom could be dark so that the size of the orbital is scaled up by factor n^2 . The valence bond central for chemistry in general and in particular for basic biopolymers could contain dark electrons delocalized because of larger value of n than for the non-valence electrons. Note that one could be $n = n_0 > 1$ for ordinary atoms making in principle possible atoms with $n < n_0$ with anomalous large binding energy also for the filled shells as the findings of Randel Mills indeed suggest [6].

Surprisingly, dark electrons would be essential in ordinary chemistry thought to reduce to standard model physics! The increase of n reduces binding energy scale and requires energy feed. This would allow to understand why anabolism (see <http://tinyurl.com/c8x8avz>) - that is generation of biopolymers from their building blocks by generating valence bonds - requires energy feed and why catabolism (see <http://tinyurl.com/cbx99fv>) - the splitting of biopolymers to their building blocks by splitting the valence bonds liberates energy.

The valence bonds would be classified by the value of n and it is quite possible that in organic chemistry the values of n are larger than in in-organic chemistry. Could this mean that valence bonds H and C and N and O have higher values in bio-chemistry? Also the valence bonds between O and H in water could have larger value of n .

To sum up, the transition from atomic physics to ordinary chemistry involved generation of dark electrons associated with valence bonds. The value of n for dark electrons can vary and allow hierarchy of evolutionary steps with increasingly delocalized valence electrons.

2.2 From chemistry to bio-chemistry

What about the step leading to a genuine bio-chemistry involving genetic code? Magnetic body (MB) is the basic aspect of biochemistry according to TGD. Pollack effect [1] (see <http://tinyurl.com/y8uxocch>) leading to the formation of negatively charged regions - exclusion zones (EZs) - would involve generation of dark protons at magnetic flux tubes of MB with electrons left to the EZ - possible as ordinary particles [4]. Also Pollack effect requires feeding of energy, say as irradiation by photons.

DNA is stable against spontaneous hydration only inside cell membrane. This suggests that the EZs of Pollack containing partially dark water molecules satisfying effectively the stoichiometry $H_{3/2}O$ allowed to stabilize DNA. Therefore EZs are excellent candidates for the predecessors of cell.

The TGD inspired proposal is that DNA strand for which each phosphate has negative unit charge is accompanied by dark analog of DNA consisting of dark protons such that the states of 3-proton units are in one-one correspondence with DNA, RNA, tRNA and amino-acids and the degeneracies of the vertebrate genetic code (number of codons coding for given amino-acid) come out correctly [5] (see <http://tinyurl.com/jgfjlbe>). A more general picture is that ordinary chemistry is kind of shadow for the dynamics of dark matter at magnetic flux tubes doing its best to emulate it. This would explain also why genetic code has also other variants.

It would be the emergence of dark protons with large enough value of n , which would distinguish between ordinary chemistry and bio-chemistry. Water is basic element of life and hydrogen bonding is responsible for the formation of water clusters - certainly one of the key aspects of bio-chemistry. Hydrogen bonds (see <http://tinyurl.com/bntn28n>) appear between highly electronegative (see <http://tinyurl.com/pbh6r6c>) atoms such as O, N, and F (electronegativity is roughly the tendency to attract electrons). What distinguishes hydrogen bond from valence bond is that it is proton rather than electron, which is delocalized. This suggests that the delocalized proton is dark proton at magnetic flux tube connecting the hydrogen bonded molecules.

2.3 The emergence of metabolism

In the proposed framework the first basic aspect of life would be the generation of dark electrons and protons using energy feed and their transfer between molecules and their generation by providing the needed energy.

1. Metabolism (anabolism) would provide the energy needed to transform ordinary atom (that is electron bound to it) to a dark atom with large value of $h_{eff}/h = n$. This requires energy since the binding energy is proportional to $1/n^2$ and reduced in the process. This is quite generally true for all dark variants of quantum states. One can say that the increase of the complexity of the system by increasing n characterizing its "IQ" requires metabolic energy (in adelic physics [10, 11] "IQ" has a concrete interpretation as cognitive resources). Therefore the first steps of prebiotic life was the emergence of energy feed mechanism making possible the increase of n .
2. I have considered the possibility that the period of prebiotic life preceding the the emergence of chemical storage of energy used dark nucleosynthesis [7] (see <http://tinyurl.com/y7u5v7j4>) as the source of metabolic energy. The recently discovered life-like properties [3] in a very simple system consisting of negatively charged plastic balls in the plasma of Ar^+ ions allows to develop rather detailed ideas about this phase of life [8] (see <http://tinyurl.com/yassnhzb>).
3. A fundamental question is about the step leading to the chemical storage of metabolic energy to valence bonds with non-standard value of n . Solar radiation could have generated both negatively charged EZs identifiable as possible predecessors of cell membrane and valence bonded molecules storing metabolic energy.

2.4 About bio-catalysis

Without bio-catalysis biochemical reactions leading to the formation of biopolymers and cell membrane would be quite too slow. Here phosphorylation enters the game.

1. The TGD based model for bio-catalysis relies on the temporary reduction of $h_{eff} = n \times h$ liberating energy kicking the reactants over potential wall. After this step the catalyst - at least in the ideal situation - receives the energy and the atom becomes dark again.
2. Acid catalyst gives a proton and base catalyst gives an electron. Most bio-catalysts are acid catalysts. The TGD based interpretation should rely on the possibility of dark valence electrons and dark protons at flux tubes. Since base catalysts are associated with non-organic chemistry, the identification of the electron given by base catalyst as dark electron looks natural. Acid catalysts would give dark proton.

Bio-catalysts are usually activated by phosphorylation and de-activated by de-phosphorylation but there are exceptions to this rule. This can be understood if the catalyst activates a molecule acting as a switch for a reaction. Catalysts related to phosphorylation are known as phosphotransferases (see <http://tinyurl.com/y87crqad>) and contain kinases transferring phosphate from ATP to the acceptor molecules.

Phosphatases (see <http://tinyurl.com/ybf9onba>) remove phosphate from the target molecule: they are hydrolases (see <http://tinyurl.com/y88zayj7>) and use water to remove the phosphate and to hydrate the molecule.

2.4.1 The difference between organic and inorganic phosphates

Phosphate appears as two variants: organic and inorganic.

1. Organic phosphates bound to biomolecules have charge -1. Some electrons of organic phosphate ion have transformed to valence electrons and are therefore dark. Also some protons - one dark proton per dark electron to not affect the observed charge in short scales - would be dark and at the magnetic body of the organic phosphate. Both dark protons and dark electrons would be present and give rise to somewhat mysterious high energy phosphate bond.
2. Free phosphate in water environment appears in ionized variants $H_nPO_4^{n-4}$ and is regarded as in-organic and have negative charge 4-n. In inorganic phosphate some dark protons and ordinary electrons giving rise to the negative charge have combined to hydrogen atoms. The larger the number of hydrogens is, the higher the level of inorganicity is.

The fractions of variants of free phosphate in water depend on pH characterizing the density of protons present. Could pH in fact characterize the fraction of dark protons at magnetic flux tubes? Or could it also characterize the fraction of dark hydrogen atoms present. Similar question applies to the counterparts of pH for other biologically important ions.

2.4.2 About phosphorylation and the interpretation of DAP

At chemical level phosphorylation attaches phosphate ion to the hydroxyl group (R-OH) of the acceptor molecule. At deeper level phosphorylation would give dark electron to the acceptor molecule and dark proton to its MB. Phosphorylation would increase the quantum coherence length: the formation of short RNA, amino-acid sequences and of cell membrane like structures would be a basic example of this.

What about the interpretation of the role of DAP in this framework? DAP has charge -1 as also the phosphate bound to DNA and RNA have (in ATP the outermost phosphate has charge -2). DAP is very similar to the phosphate in DNA and RNA and expected to carry high energy phosphate bond. In TGD framework it would possess both dark valence electrons and dark protons at magnetic flux tubes with

only one ordinary electron responsible for the charge of DAP. Due to the properties of phosphatase the phosphorylation would be very simple process at the level of dark electron and proton. Hence DAP and imidazole could make possible the phosphorylation.

2.4.3 About dephosphorylation and phosphoryl transfer

The scanning of web shows that some sources talk of dephosphorylation and some sources about phosphoryl transfer reactions and it remained unclear to me whether the two terms really have the same meaning. In any case, in TGD framework one can distinguish between these notions. Dephosphorylation could mean either phosphoryl transfer (transfer of phosphate between donor and acceptor molecules) or "dropping" of organic phosphate to water environment and giving it negative additional negative charge (the transfer would be now to water environment) and making it inorganic.

1. Phosphoryl would transfer removes PO_4^- group and presumably also the associated dark proton from the target and transfers them to the acceptor molecule and its MB. I have proposed that reconnection of flux tubes transforms the flux tubes entering to the donor molecule to that associated with the acceptor molecule so that dark proton is automatically transferred. In ATP-ADP process the phosphate group and presumably also the dark proton and electron would be transferred to the acceptor molecule from ATP. ADP is dephosphorylated and acceptor phosphorylated.
2. In "dropping" the outcome would be inorganic phosphate denoted by P_i , which is a mixture of HPO_4^{2-} and $H_2PO_4^-$. One interpretation is that 1 or 2 dark protons from magnetic flux tubes have transformed to ordinary protons and combined with electrons to form hydrogen atoms. This operation would reduce the number of dark particles and thus the "evolutionary level" of the system.

Dephosphorylation is known to lead to a decomposition of the donor molecule to smaller structures, indicating the reduction of $h_{eff}/h = n$ and thus of quantum coherence length. In RNA world dephosphorylation would be catalyzed by ribozymes and in some important cases also in the recent biology. Dephosphorylation would reduce quantum coherence length and lead to the decomposition of structures to smaller ones: mRNA splicing is one example of this. Catabolism of nutrients and the decay process of dead organic matter provide further basic examples.

Catabolism (see <http://tinyurl.com/cbx99fv>) of nutrients and the decay process of dead organic matter suggest what happens. In the first preliminary step of catabolism catalysts are involved. At the second step of catabolism inorganic phosphate is formed, which suggests that the number of dark protons is reduced in the process. This conforms with the reduction of the value of $h_{eff}/h = n$.

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