

Exploration

Water Oxidation & Photosynthesis in TGD Framework

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Abstract

Water oxidation in which water splits into 4 electrons, 4 protons and oxygen molecule O_2 is the first step of photosynthesis. The catalytic mechanism behind water oxidation remains rather poorly understood. The total binding energy of H_2O is about 75 eV and the catalyst should provide this energy to temporarily overcome this barrier. Zero energy ontology (ZEO), which is behind the TGD based quantum measurement theory, predicts that "big" (ordinary) state function reductions (BSFRs) involve time reversal. The time reversal of water oxidation occurs spontaneously in a reversed time direction and second BSFR establishing the original arrow of time makes it possible to achieve water oxidation. This mechanism involving two BSFRs applies quite generally to catalysis. The function of the catalyst is to make possible the BSFR and the natural expectation is that the description of catalysis as a process with apparently standard arrow of time is possible. The reduction of the value of h_{eff} for cyclotron states of dark particles at magnetic flux tube liberates energy assignable to cyclotron states of dark particles and could kick the reactants over the potential wall making the reaction extremely slow otherwise.

1 Introduction

These comments were inspired by an interesting article "Isolating an elusive missing link" (<https://cutt.ly/dng7My6>) about water oxidation. It came as a surprise to me that water oxidation is still a poorly understood piece of biochemistry. Bio-chemists believe that they understand various aspects of the reaction reasonably well with one exception, which is the formation of the O_2 molecule in water oxidation and the article tells about progress in this respect.

The water oxidation reaction (WOR) is one of the most important reactions on the planet since it is a key step in photosynthesis and is also the source of nearly all the atmosphere's oxygen. What is so beautiful is that both photosynthesis as a chemical storage of the solar energy and water oxidation producing oxygen essential for aerobic respiration to utilize the stored energy, are parts of the same process.

Understanding the intricacies of WOR can hold the key to improve the efficiency of the reaction which could be utilized to produce hydrogen. As the article tells, the reaction's chemical mechanisms are complex and the intermediates highly unstable. This makes their isolation and characterisation extremely challenging. To overcome this, scientists are using molecular catalysts as models to understand the fundamental aspects of water oxidation particularly the oxygen-oxygen bond-forming reaction.

WOR (see <https://cutt.ly/Jng72R8> and <https://cutt.ly/Ang781b>) forms an essential part of photosynthesis (<https://cutt.ly/Tng77R4>). What happens in WOR is that two water molecules split $4H^+$, $4e^-$, and O_2 . The reaction mechanism is not completely understood. Somehow the solar radiation induces the process in which two H_2O molecules split to $4H^+$, $4e^-$, and O_2 . The 4 electrons are utilized in photosynthesis in the KOK cycle.

In the sequel a general mechanism of catalysis inspired by zero energy ontology (ZEO) [6] is discussed. In this approach biocatalysis involves two "big" state function reductions (BSFRs) changing the arrow of time. The first BSFR induces time reversed time evolution leading from the final of a sub-reaction kicking the reactants over the potential wall preventing the reaction from occurring. After the second BSFR the time evolution continues from the initial state of time reversed time evolution in standard time

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direction. The catalytic process takes place spontaneously and the role of the catalyst is to make the spontaneous occurrence in the reversed time direction possible and probable enough. Quantum coherence in long scales is necessary and the identification of dark matter as $h_{eff} = nh_0$ phases implied by adelic physics predicts it [4].

2 Basic facts about photosynthesis and water splitting

Photosynthesis involves two parts. The first part does not involve photons and leads to the splitting of water producing from two water molecules 4 protons and 4 electrons plus O_2 molecule. The second part involving photons stores their energy chemically. The first part occurs in oxygen evolving complex (EOC), known also as water splitting complex, and acting as a cofactor of photosystem II enzyme in which the photosynthesis proper takes place.

2.1 Oxygen evolving (water splitting) complex (OEC)

OEC is the cofactor of photosystem II enzyme. OEC has an inorganic core obeying the empirical chemical formula $Mn_4Ca_1O_xCl_{12}(HCO_3)_y$ core. Core is surrounded by 4 protein subunits of photosystem II at membrane-lumen interface.

OEC functions as follows.

1. The extraction of 4 electrons and and hydrogen ions from 2 water molecules produces O_2 molecule as a kind of waste.
- 2.
3. OEC transfers 4 electrons, one at a time, to photosystem II via a tyrosine residue in the reaction center. Photosystem II must store the energy of 3 photons before the fourth one provides sufficient energy for water oxidation. Kok theory states that OEC can exist in 5 states S_0, \dots, S_4 . S_4 since OEC has lost 4 electrons. S_0 is the most reduced.
 S_4 is unstable to reset to ground state S_0 and reacts with water producing free oxygen. OEC receives the 4 electrons and returns to state S_0 .
4. After that photons from photosystem II drive the system from S_0 to S_4 . The electrons from OEC are transferred to photosystem II one-by-one. Photons from photosystem II energize electrons which are driven through the a variety of coenzymes and cofactors to reduce plastoquinone to plastoquinol.
5. The 4 hydrogen ions are used to create a proton gradient. This means that they are driven against the membrane potential gradient and gain potential energy liberated later as the protons return back and provide electrostatic energy used to by ATP synthase to transform ADP to ATP.

2.2 The energetics of photosynthesis

Consider first the energetics of photosynthesis (<https://cutt.ly/Tng77R4>).

1. As far the energetics is considered, the process of photosynthesis is equivalent to $CO_2 + 2H_2O + \gamma \rightarrow CH_2O + O_2 + H_2O$. What happens to the 4 electrons and protons produced in the splitting of water?
2. CO_2 loses one O and CO combines with two protons and electrons to form CH_2O . This requires a catalyst to temporarily kick out O from CO_2 . This energy is returned to the catalyst when two electrons and protons combine with O to form H_2O . The binding energy of C=O bond and H=O bond are indeed nearly the same.

3. Water splitting requires energy $E = 4E_B(O - H) + 4E_B(e - p) = 4 \times (5.15 + 13.6) = \text{eV}$. The formation of $O = O$ provides energy $E_B(O = O) = 5.13 \text{ eV}$. In the formation of H_2O $2 \times (5.15 + 13.6) \text{ eV}$ is returned to the catalyst but this energy has been already taken into account and compensates for the energy needed to split CO_2 . Therefore the energy $E_1 = 4(E_B(O - H) + E_B(e - p)) - E_B(O = O) = [4 \times (5.15 + 13.6) - 5.13] \text{ eV}$ needed from catalyst must correspond the energy liberated in the formation of CH_2O . This is true assuming that the binding energy of e and p associated in the O-H valence bond is the sum of atomic binding energy and O-H bond energy.

The formation of CH_2O involves combination of 2 protons and electrons to form two hydrogens, the atomic binding energy $2E_B(e-p) = 2 \times 13.6 \text{ eV}$ is liberated in the formation of CH_2O and compensates the same energy appearing in E_1 . Hence the atomic binding energies can be forgotten in the energy budget and it is enough to compare only the molecular binding energy E_2 in E_1 with E_B . The molecular contribution to E_1 is $E_2 = 4 \times 5.15 - 5.13 \text{ eV} = 15.48 \text{ eV}$.

4. The formation of CH_2O means a generation of molecular binding energy which is approximately the sum of $O=CH_2$ binding energy and C-H binding energies. Besides this atomic binding energy of two hydrogen atoms is liberated. The liberated molecular binding energy is $E_B(CH_2O) = E_B(O = CH_2) + 2 \times E_B(C - H) = (7.75 + 2 \times 4.28) \text{ eV} = 16.31 \text{ eV}$. The amount of the liberated molecular binding energy is $E_B(CH_2O) = 16.31 \text{ eV}$ and is by .83 eV larger than $E_2 = 15.48 \text{ eV}$. One must drive 4 protons against a potential gradient and this requires energy $4 \times .07 \text{ eV} = .28 \text{ eV}$ which is smaller than this energy. 4 photons are used and if their energies are about 2 eV they provide 8 eV.
5. This estimate does not take thermodynamics and second law into account. Since pressure and temperature can be assumed to stay constant in the process, the thermodynamical approach using Gibbs free energy $G = E + pV - TS$ as thermodynamical function is natural. $dG = VdP - SdT + \sum_i \mu_i dN_i$ reduces to $dG = \sum_i \mu_i dN_i$ if pressure and temperature are constant.
6. The overall process can be written as $6CO_2 + 6H_2O + \text{light} \rightarrow C_6H_{12}O_6 + 6O_2$. This form corresponds to a polymerization of 6 CH_2O molecules to form sugar $C_6H_{12}O_6$.
7. Several separate steps are involved with photosynthesis besides the splitting of water; there are 4 steps corresponding to the transfer of electron decomposing to substeps related to the photosynthesis proper. Each of this steps involves catalysis.

That two water molecules are involved in the basic process, could also be essential. The hydrogen bond between the water molecules or its dark variant could play some role.

3 TGD view about water photosynthesis and water oxidation

TGD provides a new view about bio-catalysis in which the magnetic body (MB) acts as a controller. One might hope that at this level the description of the biocatalysis is much simpler than at the level of biochemistry. Therefore one can ask whether a simple overall view based on the energetics and the notion of MB carrying dark matter at its flux tubes could help. Since 5 different kinds of valence bonds must be temporarily split in the overall reaction, a catalyst providing the needed energy to temporarily break the valence bonds is needed.

There are many other steps involving catalysis and the actual situation taking into account reactions involving photons is extremely complex. From the foregoing it is clear that the splitting of water requires 75 eV energy. Most of this energy is related to the ionization of hydrogen atoms. Note however that valence electrons in the valence bonds are approximated as ordinary atomic electrons. Unless quantum tunnelling is involved, this energy must be provided by some source.

3.1 Does time reversal provide a general mechanism of bio-catalysis?

In the TGD framework one can consider 3 general mechanisms of biocatalysis and both mechanisms could be involved.

The basic problem in the understanding of catalysis is to identify the mechanism kicking the reactants over the potential wall making the reaction extremely slow. How to get over this potential wall is even rid of it?

Zero energy ontology (ZEO) [6, 4, 8] suggests a completely general mechanism of biocatalysis.

1. ZEO is behind the TGD inspired quantum measurement theory and makes it possible to resolve the basic paradox of standard quantum measurement theory and gives rise to a quantum theory of consciousness. The new element is that the arrow of time changes in ordinary ("big") state function reduction (BSFR), whereas it remains unchanged in "weak" measurements, "small" state function reductions (SSFR).

In ZEO, BSFR creates a superposition of time reversed deterministic classical time evolutions analogous to Bohr orbits and leading from the final state to the geometric past. The findings of Mineev et al [1] support the notion of BSFR [3].

2. BSFR has far reaching implications. Since water splitting has turned out to be very difficult to understand, a natural question is whether BSFR could explain it. If water splitting occurs as BSFR, it would correspond to a spontaneously occurring process $4e+4p+O_2 \rightarrow H_2O$ in reversed time direction requiring no catalysis. Second BSFR would mean a return to a moment of geometric time where one has $4e+4p+O_2$.
3. BSFRs could be involved also with the other steps involving the splitting of chemical bonds and make it possible to kick the reactants over the potential wall. In a reversed time direction this process would take place spontaneously and lead from free atoms to their bound states by generation of atomic and molecular bonds.
4. BSFR is especially natural in the situations in which the reverse process occurs spontaneously meaning that only the process but not its reversal involves potential wall. This seems to be the case in bio-catalysis. In nuclear reactions the situation is different since both the process and its reversal involve overcoming of a Coulomb wall.

The ZEO based vision provides only a general idea about what is involved with a given catalytic step of a given step of say photosynthesis but tells nothing of its chemical details, in particular of the role of MB and dark particles at it. The chemistry of water oxidation catalyst - oxygen evolving complex - is extremely complex but a general principle might considerably facilitate its understanding.

3.2 How to model the reverse time evolution behind catalysis as ordinary time evolution?

The most plausible option is that water oxidation and also other steps involving liberation of atoms from bound states take place via BSFR. The ZEO based view about biocatalysis does not however exclude the modelling of the time reversed process as occurring in the standard direction of time and being based on some catalytic mechanism. The presence of the catalyst would make the BSFR possible. This kind of modelling would help to characterize the catalyst and the superposition of time reversed time evolutions leading to the final state as time evolutions with standard time direction.

1. The first mechanism involves a reduction of h_{eff} for a magnetic flux tube liberating energy temporarily kicking the system over the potential wall. That energy is liberated follows from the fact that energies in general increase with h_{eff} . The reduction of the cyclotron energy proportional to h_{eff} of the charged particles at the flux tube would liberate the needed energy.

This mechanism might make sense in the case of molecular binding energies of order few eV which is the energy scale for the cyclotron energies in the magnetic field $B_{end} = .25$ eV for $\hbar_{eff} = \hbar_{gr} = GMm/v_0$.

This mechanism could apply to the catalytic steps of photosynthesis separately. If it applies to water oxidation, the energy 75 eV provided by flux tubes would be returned gradually to the catalyst (shortened magnetic flux tube) during photosynthesis proper as electrons and protons bind to the hydrogen atoms of COH_2 and H_2O during the process.

2. Second, much more speculative (even in TGD framework), mechanism would be a phase transition increasing the thickness of a magnetic flux tube liberating magnetic and volume energy [9] suggested to be behind the proposed rather rapid expansion of the Earth increasing its radius by factor 2 and leading to Cambrian explosion. This transition would scale up the value of \hbar_{eff} for valence electrons by factor of 2 and reduce the bond energies by factor 1/4 and also the energy of electron of hydrogen atom.

This mechanism could be behind the proposed model of quantum tunneling innuclear reactions [5]. The quantum tunnelling would involve BSFR as a phase transition increasing the value of \hbar_{eff} and size scale of the colliding nuclear strings. These dark nuclei would have dramatically reduced binding energy and increased spatial scale making it possible to overcome the Coulomb barrier. The reactions would proceed fast in the dark phase and the second BSFR would transform dark nuclei to ordinary nuclei.

”Cold fusion” would rely on this mechanism except that now the protons would be transformed to dark protons by the analog of Pollack effect, and there is no need to break nuclear bonds as in ordinary nuclear reactions [2, 7]. Also in the case of nuclear quantum tunnelling the phase transition would be scaling of flux tubes.

The basic objection is that the phase transition would reduce the energy scale of valence electrons of all atoms involved. This does not look realistic.

3.2.1 Shortening of flux tubes by a reduction of \hbar_{eff}

How could the bio-catalysis assisted by MB proceed? MB should provide the energy needed to split the bonds of various molecules. Could the reduction of \hbar_{eff} for cyclotron states at dark magnetic flux tubes liberate cyclotron energy of charged particles at them proportional to \hbar_{eff} ?

1. The magnetic cyclotron energy $E_c = \hbar_{eff}ZeB/m$ is large for large \hbar_{eff} . Magnetic energies for $\hbar_{eff} = \hbar$ are rather small. Also for relatively small values of $\hbar_{eff} > \hbar$ assignable to valence bonds, the cyclotron energies for proton and electron are much smaller than atomic binding energies for reasonable values of the magnetic field.
2. The basic proposal which led to the \hbar_{eff} vision is that in TGD framework large values of \hbar_{eff} allowing cyclotron energy in an endogenous magnetic field $B_{end} \simeq .2$ Gauss to be in visible and UV range are possible. The value of \hbar_{eff}/\hbar of order 10^{14} is needed. Nottale hypothesis

$$\hbar_{eff} = \hbar_{gr} = \frac{GMm}{v_0} ,$$

One has $v_0 = 1/2$ in the simplest model - implying that gravitational Compton length equals to the Schwarzschild radius $r_S \simeq 1$ cm of the Earth - implies that cyclotron energies do not depend on the mass of small particle, in particular they are same for all charged particle with given charge if the value of B is same.

3. Dark protons at magnetic flux tube are a basic building brick of TGD inspired quantum biology. Could the liberation of cyclotron energy for dark protons (or for dark ions) allow to break O-H bonds and ionize hydrogens? Could some dark protons (or ions) transform temporarily to ordinary protons and liberate their cyclotron energy propto h_{gr} so that MB could act as a bio-catalyst.
4. The general view of bio-catalysis suggests that the eventual formation of the final state molecules liberates energy, which increases the value of h_{eff} of dark flux tubes to its original value. Note that the energy of the final state is by .83 eV smaller than that of the initial state so that dissipative losses are possible even if the entire energy of the photon is stored as metabolic energy.

3.2.2 Could the thickening of flux tubes liberate energy and reduce atomic binding energy scale?

Although this option does not look realistic, it deserves a more detailed treatment.

1. The phase transition, which increases the radius of magnetic flux tubes by a power of 2 (by p-adic length scale hypothesis), liberates energy and could induce an increase of h_{eff} at the level of valence electrons and reduce the binding energy scale of the valence electrons proportional to $1/h_{eff}^2$ by a factor $1/2^{2k}$. This mechanism was discussed in [9].
2. The energy of 75 eV would be reduced to about $75/2^{2k}$ eV. $k = 1$ would give 18.8 eV and $k = 2$ would give 4.7 eV. The reduction of the binding energy would be due to the energy liberated in the thickening of the magnetic flux tubes. Water would be special in the sense that these phase transitions could occur for the magnetic flux tubes assignable to water and explain its multiphase character responsible for its numerous thermodynamic anomalies.
3. What is the scale of the flux tubes involved? Suppose that a flux tube portion of radius L and roughly the same length is involved. If the energy E of is of order $E \sim \hbar_{eff}/L$, the length scale would be about $L = (\hbar/h_{eff} \times 1.6 \text{ nm})$. For $h_{eff} = h$, the length scale corresponds to cell membrane thickness. The outcome of this process would be a reduction of the scale of valence electron binding energies and of bond energies. In this phase the required reactions could proceed easily.

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References

- [1] Minev ZK et al. To catch and reverse a quantum jump mid-flight, 2019. Available at: <https://arxiv.org/abs/1803.00545>.
- [2] Pitkänen M. Cold fusion, low energy nuclear reactions, or dark nuclear synthesis? Available at: http://tgdtheory.fi/public_html/articles/krivit.pdf, 2017.
- [3] Pitkänen M. Copenhagen interpretation dead: long live ZEO based quantum measurement theory! Available at: http://tgdtheory.fi/public_html/articles/Bohrdead.pdf, 2019.
- [4] Pitkänen M. Quantum self-organization by h_{eff} changing phase transitions. Available at: http://tgdtheory.fi/public_html/articles/heffselforg.pdf, 2019.
- [5] Pitkänen M. Solar Metallicity Problem from TGD Perspective. Available at: http://tgdtheory.fi/public_html/articles/darkcore.pdf, 2019.
- [6] Pitkänen M. Some comments related to Zero Energy Ontology (ZEO). Available at: http://tgdtheory.fi/public_html/articles/zeoquestions.pdf, 2019.

- [7] Pitkänen M. Could TGD provide new solutions to the energy problem? Available at: http://tgdtheory.fi/public_html/articles/proposal.pdf., 2020.
- [8] Pitkänen M. Negentropy Maximization Principle and Second Law. Available at: https://tgdtheory.fi/public_html/articles/nmpsecondlaw.pdf., 2021.
- [9] Pitkänen M. Updated version of Expanding Earth model. https://tgdtheory.fi/public_html/articles/expearth2021.pdf., 2021.