

The Emergence and Evolution of Life in a “Fatty Acid World” Based on Quantum Mechanics

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Abstract Quantum mechanical based electron correlation interactions among molecules are the source of the weak hydrogen and Van der Waals bonds that are critical to the self-assembly of artificial fatty acid micelles. Life on Earth or elsewhere could have emerged in the form of self-reproducing photoactive fatty acid micelles, which gradually evolved into nucleotide-containing micelles due to the enhanced ability of nucleotide-coupled sensitizer molecules to absorb visible light. Comparison of the calculated absorption spectra of micelles with and without nucleotides confirmed this idea and supports the idea of the emergence and evolution of nucleotides in minimal cells of a so-called Fatty Acid World. Furthermore, the nucleotide-caused wavelength shift and broadening of the absorption pattern potentially gives these molecules an additional valuable role, other than a purely genetic one in the early stages of the development of life. From the information theory point of view, the nucleotide sequences in such micelles carry positional information providing better electron transport along the nucleotide-sensitizer chain and, in addition, providing complimentary copies of that information for the next generation. Nucleotide sequences, which in the first period of evolution of fatty acid molecules were useful just for better absorbance of the light in the longer wavelength region, later in the PNA or RNA World, took on the role of genetic information storage.

Keywords Self-reproducing fatty acid micelles · Fatty acid world · Photoexcited electron tunneling · Quantum mechanical emergence of genetic material · Protocells

Introduction

The solution of basic questions of emergence and evolution of the first living cells or protocells is tightly connected, in several laboratories round the world, with the rapidly developing field of artificial living technologies. The possibility of synthesizing artificial

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self-reproducing minimal cells also impacts the possibility of the emergence of living protocells on the Earth or elsewhere. Due to the rapid development of computers and quantum mechanical methods and program packages (such as quantum molecular dynamics), possibilities also exist to simulate the main processes of self-assembly and photosynthesis of minimal artificial cells consisting of up to 2,000 atoms.

The main developers of such artificial cells are Steen Rasmussen, James Bailey, Hans Ziock (Los Alamos National Laboratory—LANL) (Rasmussen et al. 2003, 2008; DeClue et al. 2009); Liaohai Chen (Argonne National Laboratory), the Center for Fundamental Living Technology at the University of Southern Denmark (Steen Rasmussen). Pier Luigi Luisi's group at RomaTre University, Guenter von Kiedrowski at Ruhr-Universitaet Bochum, John S. McCaskill, Uwe Tangen and Patrick Wagler in Biomolecular Information Processing research group at the same university, and in the European Center for Living Technology, Venice. Newly synthesized programmable artificial cells or nanobiorobots are planned to be used for nanomedicine, nanoecology, and for future emerging new information technologies.

Our research group creates molecular electronics logic gates regulating the photosynthesis, growth and division of artificial living cells and nanobiorobots. Molecular electronics and spintronics logical devices which regulate photosynthesis and self-assemble to mobile computing structures, have been quantum mechanically designed. They can selectively capture and transport nuclear, chemical and microbial pollutants (Tamulis et al. 2003, 2004, 2007; Tamuliene et al. 2004; Rinkevicius et al. 2006; Tamulis and Tamulis 2008; Tamulis 2008a, b). Another variety of device will regulate the photosynthesis and growth of artificial minimal living cells under conditions of external magnetic fields, while also providing a perspective for success in the synthesis of new forms of artificial living organisms (Tamulis et al. 2006, 2008; Tamulis and Tamulis 2007a, b, 2008; Tamulis 2008a, b, c).

The artificial minimal living cells that are synthesized in LANL are only a few (4–6) nanometers in size (Rasmussen et al. 2003, 2008; DeClue et al. 2009). In their simplest form, these cells consist of a micelle which acts as the container, a light driven metabolism, and a genetic system, whose functions are all very tightly coupled. The container consists of amphiphilic fatty acid (FA) molecules that self-assemble into a micelle. The hydrophobic interior of the micelle provides an alternative thermodynamic environment from the aqueous or methanol exterior and acts as a sticking point for the photosensitizer, fatty acid precursors (pFA) (food), and the genetic material. Peptide nucleic acid (PNA) is chosen as the genetic material as it is far less polar than RNA or DNA and therefore should stick to the micelle, especially if hydrophobic chains are added to the PNA backbone. The geometric and electronic structure (without the presence of water and FA molecules) was obtained by the quantum mechanical semiempirical PM3 method implemented in GAMESS-US (Schmidt et al. 1993) or TURBOMOLE (TURBOMOLE V6.0 2009) packages installed in Linux servers cluster of our Theoretical Molecular Electronics and Spintronics research group.

The metabolism involves the photoexcitation of an electron in various photosensitizers which are stabilized by the donation of an electron from non-canonical PNA bases (for example, 8-oxo-guanine). The excited electron is in turn used to cleave a fatty acid precursor to yield another fatty acid molecule, thereby allowing the container to grow until it reaches an unstable size and divides. The artificial minimal cell could be fed PNA monomers or use an essentially identical metabolism to convert a PNA precursor monomer into a true monomer, thereby also providing the material to allow the double-stranded PNA “gene” to replicate when it undergoes a random dehybridization to yield two complementary single-stranded templates (Rasmussen et al. 2003, 2008; DeClue et al. 2009). Finally, as the different nucleobases have different electron donor and electron relay capabilities,

there is also a mechanism for natural selection, with some bases and base orderings being superior to others in their ability to facilitate the metabolism. We can define these self-replicating minimal artificial cells as PNA World life referring to the similar definitions of RNA or DNA World life.

The artificial minimal living cell contains on the order of 10^3 atoms. Due to its small size, all its processes, including its self-assembly from component molecules, its absorption of light, and its metabolism should in principle be investigated using quantum mechanical (wave) theory (Tamulis et al. 2006, 2008; Tamulis and Tamulis 2007a, b, 2008; Tamulis 2008a, b, c).

The main goal of this article is to demonstrate, by quantum mechanical methods which include electron correlation effects, the mechanism of the emergence of the simplest forms of minimal living organisms which might occur in the hot and UV-rich environment of the Earth 3.9–3.6 billion years ago or on other planets of the Universe.

The main idea of this paper is that life on Earth or elsewhere could have emerged in the form of self-reproducing photoactive fatty acid micelles, which step by step evolved to nucleotide containing micelles due to an enhanced ability to absorb visible light.

Procedure/Methodology

The description of the quantum mechanical (QM) electron correlation interaction density functional theory (DFT) methods *i.e.* high precision quantum mechanical simulations are presented in the Appendix of this article. We have successfully used DFT for the investigations of various self-assembled photoactive bioorganic systems of artificial minimal living cells (Tamulis et al. 2006, 2008; Tamulis and Tamulis 2007a, b, 2008; Tamulis 2008a, b, c). The cell systems studied in these articles are based on peptide nucleic acid (PNA) and consist of up to 2,000 atoms (not including the associated water solvent shells) and are about 8.0 nm in diameter.

The quantum simulations of single bioorganic molecules possessing closed electronic shells start from a trial geometry (Cartesian coordinates of the nuclei). Using quantum mechanical semiempirical (*e.g.* PM3, PM6), Hartree–Fock (HF) and density functional theory (DFT) approaches in the GAMESS-US (Schmidt et al. 1993), TURBOMOLE (TURBOMOLE V6.0 2009) or ORCA (Neese 2003, 2009) program packages, we obtain the lowest molecular energy which parametrically depends on these coordinates. The subsequent standard geometry optimization procedure (Dreizler and Gross 1990) minimizes the energy with respect to the nuclear positions. Special care is required to verify that the obtained optimal molecular structure is a global minimum in the phase space of the nuclear ($3n-6$, n being the number of atoms) degrees of freedom.

In order to obtain accurate results in investigating supermolecules, two factors need to be accounted for: 1) the quality of the density functional and 2) the quality of the molecular orbitals (extent of the phase space of the single-electron states). For simple covalently bonded molecules we chose Becke’s 3 parameter exchange functional (Becke 1988) with non-local Lee–Yang–Parr electron correlations (Lee et al. 1988) (DFT B3LYP). Currently, B3LYP is considered to be the most appropriate method for taking into account electron correlations in large closed-shell supermolecules in which atoms are linked by covalent bonds *i.e.* there are no Van der Waals or hydrogen bonds between atoms in a single molecule. For simulations of the self-assembly of bioorganic supramolecules in which the separate molecules are associated by hydrogen bonds or Van der Waals forces, the PBELYP (Perdew et al. 1996) in GAMESS-US and PBE (Perdew et al. 1996) in ORCA and

TURBOMOLE methods were used. In these two methods, exchange functionals include some electron correlation effects at larger distances that provide relatively good descriptions of the Van der Waals forces and hydrogen bonds. To obtain accurate optimal molecular geometries for single molecules, we use the 6-311G** basis set which includes (5d, 7f) polarized atomic orbitals. For self-assembly of pairs of bioorganic molecules we add diffusion orbitals of the 6-31++G** basis set (the standard tables ([Basis Set Databases](#)) give an appropriate basis set description). The above-mentioned 6-311++G** basis set convention was adopted by John Pople and coworkers.

Quantum Mechanical Self-Assembly of Photoactive Fatty Acid Micelles

We used quantum mechanical density functional theory methods that included nonlocal gradient electron correlation interactions to investigate various self-assembled photoactive fatty acid micelles. The micelle systems studied are based on a photoactive squaraine sensitizer, a fatty acid and its precursor (pFA). The systems include a water environment and consist of some 400 atoms and are up to about 4.5 nm in diameter. The quantum mechanical based electron correlation interactions are the source of the weak hydrogen and Van der Waals chemical bonds that are critical to the behavior of these systems. Polar solvent molecules such as water increase the strength of these bonds and thus play a central role in the self assembly and functioning of the systems studied. The distances between the separated sensitizer, precursor of fatty acid, and water molecules are comparable to Van der Waals and hydrogen bonding radii. As a result, these nonlinear quantum interactions compress the overall molecular system resulting in a smaller gap between the HOMO and LUMO electron energy levels allowing enhanced tunneling of photoexcited electrons from the sensitizer {either a bis(4-dimethylamine-2-phenyl)-squaraine (see in the Fig. 1 a movie based visualization of the last 1762 steps of the geometry optimization) or a bis(4-diphenylamine-2-phenyl)-squaraine} to pFA molecule and splits it.

The new fatty acid joins the existing micelle, growing it. After reaching some critical size, the micelle divides into two separate smaller micelles. We can define these self-reproducing photoactive fatty acid micelles as Fatty Acid World life referring on the similar definitions of RNA or DNA World life.

The water molecules, which surround the entire photosynthetic complex shown in moving 1762 images were found to stabilize the system. Thereby reducing all the interatomic distances. The water molecules organized into nano ice-like substructures. It is only because of the hydrogen and Van der Waals bonds among the bis(4-dimethylamine-2-phenyl)-squaraine and fatty acid, and pFA molecules, and water molecules that this system with 4.0 nm larger diameter exists. The distances among the separated sensitizer and fatty acid, and pFA molecules, and water molecules are comparable to Van der Waals and hydrogen bonding radii, and therefore we may regard the minimal cell as single electron conjugated supramolecule that we can deal with using an electron correlated model. Since bis(4-dimethylamine-2-phenyl)-squaraine molecule interacts with fatty acid, and pFA molecules and with water molecules through their correlated electrons, intermolecular distances and surface area calculations are critical in understanding the time dependent electron tunneling processes associated with the various excited states of this micelle.

To achieve a better understanding of the quantum mechanical self-assembling process of the photoactive fatty acid micelles, the electronic structure of fatty acid $\text{HO-CO-(CH}_2\text{)}_{10}\text{-CH}_3$ was calculated by the B3LYP method using rather a wide basis set 6-311++G**.

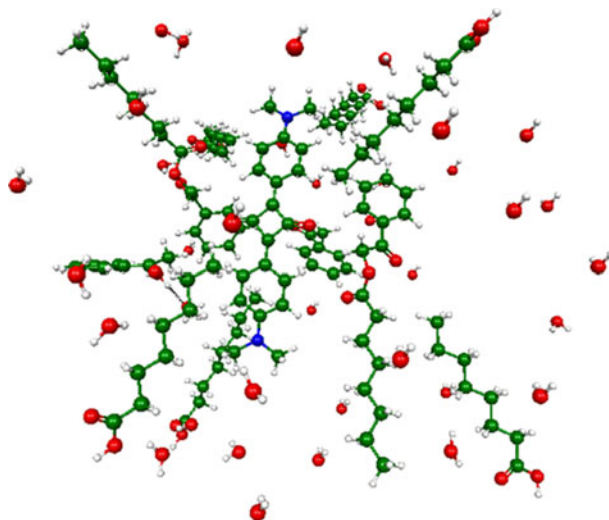


Fig. 1 A movie based visualization of the last 1762 steps of the geometry optimization of a self-reproducing FA based micelle system containing a bis(4-dimethylamino-2-phenyl)-squaraine molecule (*in the center*) that was done using semiempirical quantum mechanical method PM3. This micelle contains also two precursors of a FA, 2 aromatic ends of pFA, 6 FA and 37 water molecules (in total 427 atoms). Carbon atoms and their associated covalent bonds are shown as grey spheres and sticks, hydrogens—light grey, oxygens—red, nitrogens—blue (Fig. 1S)

The sum of Lowdin charges on the hydrophilic head of fatty acid and on the fragment (HO–CO[−]) was equal to -0.14 of electron charge. Since this molecule is neutral (the total sum of Lowdin charges = 0.00), on the rest part of the hydrophobic tail of this fatty acid the charge will be equal to $+0.14$ of electron charge due to a small quantum mechanical internal shift of the whole conjugated valence electron cloud from the electron-donor tail to the electron-acceptor head. An additional factor for the repulsion of fatty acid tails is that the tails are covered by positively charged hydrogen atoms.

The summary of the detailed investigations of quantum mechanical self-assembly of various fatty acid micelles and artificial minimal cells models is that fatty acids in the vacuum are not able to perform self-assembly due to the quantum dispersion forces and due to the alternating charge of the different groups $-\text{CH}_2-$ in the tails because really these two kinds of attraction forces are small. Dispersion forces are weak Van der Waals intermolecular forces that arise from the attractive force between quantum multipoles. The more competitive electrostatic repulsion forces which destroy micelles and artificial cells in the vacuum due to the small negative sum of electron charges on the head of fatty acid and the small positive sum of electron charges on the FA tail, and additionally because each hydrogen atom in the tail of FA possesses the slightly positive electron charge.

The electron correlations interactions among polar solvent (*e.g.* water, methanol) molecules, fatty acid, precursor of fatty acid, and waste ends of precursor of fatty acid molecules leads to appearing the additional attraction dispersion forces and hydrogen bonds. A hydrogen bond is a special type of quantum attractive interaction that exists among an electronegative atom and a hydrogen atom bonded to another electronegative atom and this hydrogen atom exist in two quantum states. The hydrogen bonds and Van der Waals weak chemical bonds (dispersion forces) play a critical role in the quantum

mechanical electron correlations interaction based self-assembly of the photosynthetic center and functioning of the photosynthetic processes of the artificial minimal cells.

The best available method to simulate in minimal cells these Van der Waals dispersion forces and hydrogen bonds is to perform quantum mechanical non-local density functional potential calculations (Tamulis et al. 2006, 2008; Tamulis and Tamulis 2007a, b, 2008; Tamulis 2008a, b, c). Other approaches, such as lowest level of correction (MP2) (Jensen 1999), multiconfiguration self consistent field (MCSCF) (Jensen 1999) or complete active space SCF (CASSCF) (Jensen 1999), in principle more suited to model dispersion forces, would not be applicable for micelles and artificial cells due to the huge computational cost.

As one can see in Fig. 1 after geometry optimization these molecules self-organized to the regular structure due to accounting the quantum electron correlations interactions, *i.e.* due to the balance of weak electrostatic, hydrogen bonding and weak dispersion Van der Waals forces:

- 1) the bis(4-dimethylamine-2-phenyl)-squaraine sensitizer molecule is in the center;
- 2) fatty acid molecules are oriented by their hydrophobic ends to the bis(4-dimethylamine-2-phenyl)-squaraine sensitizer molecule;
- 3) precursor of fatty acid molecule is oriented by their hydrophilic end to the bis(4-dimethylamine-2-phenyl)-squaraine sensitizer molecule;
- 4) most of the water molecules self-organize into clusters of nano ice-like substructures. Furthermore, all the interatomic distances between the sensitizer {either a bis(4-dimethylamine-2-phenyl)-squaraine or a bis(4-diphenylamine-2-phenyl)-squaraine} and the pFA molecule become reduced, *i.e.* the photosynthetic system become more compressed due to the presence of the water molecules.

To sum it up, all fatty acid micelles and artificial minimal cells are self-assembling and achieve this based on interactions involving weak electrostatic forces (due to a small internal shift of the whole conjugated valence electron cloud from the electron-donor tail to the electron-acceptor head) and other quantum (dispersion, H-bonding) fine effects. The emergence of artificial or natural life *a priori* relies on the existence of these weak quantum mechanical electron correlation interactions.

Quantum Mechanical Evolution of Photoactive Fatty Acid Micelles

We have performed QM semiempirical PM3 and DFT PBE/6-31G methods for geometry optimization of photoactive fatty acid micelles using two types of squaraine molecules Sq(I) and Sq(II) (see Figs. 2 and 3) and precursor of fatty acid molecule: pFA – $C_6H_5-CO-CH_2-O-CO-(CH_2)_6-CH_3$.

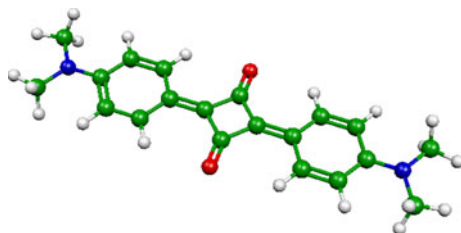


Fig. 2 Image of bis(4-dimethylamine-2-phenyl)-squaraine – Sq(I) molecule

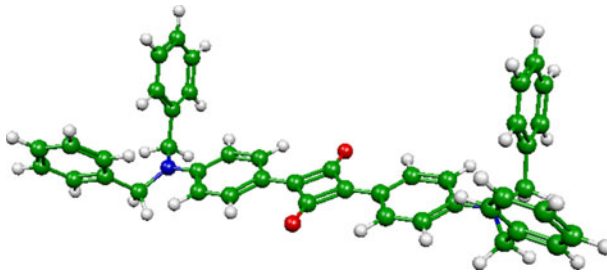


Fig. 3 Image of bis(4-diphenylamine-2-phenyl)-squaraine - Sq(II) molecule

The electron tunneling and associated light absorption of the most intense transitions of self-assembled artificial minimal cells as calculated by the TD DFT method differs from spectroscopic experimental results by only 0.3 or 0.2 nm, which is within the value of experiment errors (Rasmussen et al. 2008; Tamulis and Tamulis 2008; Tamulis 2008a). This agreement implies that the quantum mechanically modeled self-assembled structures of minimal cells very closely approximate the real ones.

Quantum mechanical electron correlation-based simulations of the above described fatty acid micelle drawn in Fig. 5 show it to be complex system, as only the entire ensemble of sensitizer, pFA, FA, and water molecules yields stable systems with a functioning photosynthetic process. Our studies show the importance of modeling as much of the full system as possible in order to obtain realistic results. Already just removing small parts of the FA, or water molecules leads to structural changes, as well as a shift in the spectroscopic values associated with the photoexcited electron tunneling from the photosensitizer {either a bis(4-dimethylamine-2-phenyl)-squaraine or bis(4-diphenylamine-2-phenyl)-squaraine} to the pFA molecules. Removing larger parts, e.g. more FA or water molecules leads to degradation of the fatty acid micelle. Furthermore our results show that inclusion of an ever greater fraction of the true amount of water present, as well as a greater number of fatty acid, pFA, and nucleobase molecules to begin to approach a complete fatty acid micelle or artificial minimal cell, results in a shift of the absorption spectrum to the red for the protocell photosynthetic center, leading to an ever closer approach to the real experimental value (Tamulis et al. 2008). These results indicate that the fatty acid micelle is acting as a single quantum mechanical based system. Trials with different simulation methods also show that only the QM electron correlation TD DFT simulations give results exactly comparable with spectroscopic results and all other more simplified QM methods such as local gradient DFT or *ab initio* Hartree–Fock give structures and spectra that are far from the experimentally measured ones.

Part of the water and aromatic end molecules were removed from the self-assembled fatty acid micelle shown in the Fig. 1. The geometry of this new constructed micelle other micelles in this article were reoptimized by using PBELYP/3-21 method with GAMESS-US package. The reconstructed and self-assembled micelle is shown in the Fig. 4.

The absorption spectra of all micelles in this article are calculated by using TD DFT revPBE method with the 6-31G* basis set together with COSMO water solvent method in the ORCA program package.

Spectrum of micelle given in the Fig. 4 is placed in the Table 1 and in the Fig. 5 (black bar: SQ(I)+pFA).

The most intense electron tunneling transitions of the 10th excited state should not induce metabolic photo dissociation of the pFA molecule because the transferred electron cloud is located on the Sq(I) molecule.

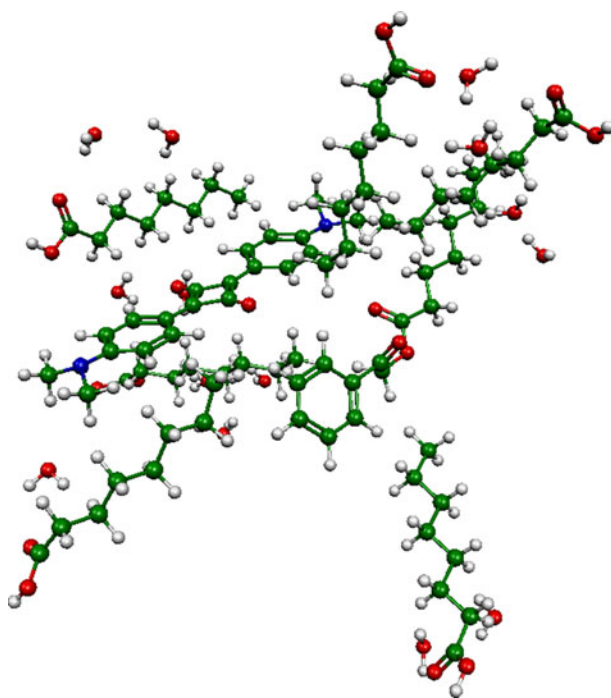


Fig. 4 The last image of reconstructed self-assembled fatty acid micelle contains Sq(I) molecule (*in the center*), pFA molecule (*in the bottom-left*), six fatty acid molecules and 14 water molecules obtained by PBELYP/3-21 method installed in GAMESS-US package

A similar self-assembled fatty acid micelle which contains Sq(II) sensitizer and pFA molecules, six fatty acid molecules and 40 water molecules, was investigated quantum chemically. The expectation was that the additional four aromatic rings will initiate the electron transport from Sq(II) to the pFA molecule in the most intense excited state (see blue bar in the Fig. 5).

Summarizing we can state that such a micelles which possess only Sq(I) or Sq(II) sensitizers should not self-reproduce efficiently because the photosynthetic electron transitions from Sq(I) or Sq(II) to the pFA molecule are not intense.

The geometry optimization of a modified self-assembled fatty acid micelle containing Sq(II) molecule with covalently attached 8-oxo-guanine, pFA molecule and 40 water molecules (see Fig. 6) was done quantum chemically.

Table 1 Excitation transitions energies of a photoactive fatty acid micelle containing Sq(I) molecule, pFA molecule, six fatty acid molecules and 14 water molecules. The weight of the individual excitations are given if larger than 0.01. Arrow \rightarrow indicates the direction of individual electron transition from ground state HOMO- m to certain excited state LUMO+ n

Excited State #	Individual transitions HOMO- m \rightarrow LUMO+ n	Weight of individual transition	Energy (eV)	Wavelength (nm)	Oscillator strength (arbitrary units)
10	HOMO \rightarrow LUMO	0.913	2.7	453.8	2.7235
11	HOMO \rightarrow LUMO+1	0.999	2.8	450.6	0.0001
17	HOMO-1 \rightarrow LUMO+1	0.99	3.0	417.7	0.0001

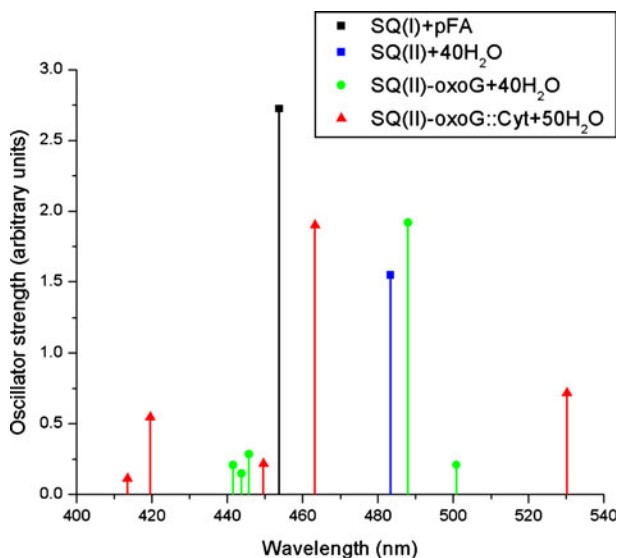


Fig. 5 The intense absorption lines of the investigated squaraine based derivatives: 1) minimal cell based on Sq(I) and pFA (Fig. 4) (*black bar*), 2) minimal cell based on Sq(II) sensitizer and pFA molecules, six fatty acid molecules and 40 water molecules (*blue bar*), 3) micelle based on Sq(II)-8-oxo-guanine+pFA+40 H₂O (Fig. 6) (*green bars*), 4) red bars represents the absorption spectrum lines of Sq(II)-8-oxo-guanine::cytosine+pFA+50 H₂O minimal cell (Fig. 8). Spectra calculated using TD DFT revPBE method with the 6-31G* basis set. The 8-oxo-guanine::cytosine-squaraine supramolecule was observed to have an absorption region that covered more of the visible spectrum than a squaraine-oxo-guanine supermolecule

The most intense excited states of the photoactive fatty acid micelles are partially composed of LUMO+n states located on the fatty acid precursor molecule when the Sq(II) molecule is covalently attached to the 8-oxo-guanine. This coupling also promotes electron hopping (tunneling) to the pFA molecule during the most intense absorption excited state.

The absorption spectrum of the photoactive fatty acid micelle given in the Fig. 6 is detailed placed in the Table 2 and electron charge transfer trajectory in the tenth excited state is shown in the Fig. 7.

The electron tunneling transitions of the 8th and 10th excited states of this micelle should induce metabolic photo dissociation of pFA molecule because the transferred electron cloud is located on the aromatic head of the pFA molecule (see Fig. 7) where it causes this molecule to split due to intense rotation and vibration of the weak chemical bond that joins the aromatic end to the fatty acid section of the pFA molecule.

The difference of electron charge density (certain excited-state - ground-state) for the photosynthetic center of the photoactive fatty acid artificial micelle was taken from TD DFT calculations and the electron charge tunneling associated with certain excited state transitions was visualized (see Figs. 7 and 9).

The most intense 10th excited state is composed mainly from two individual transitions HOMO → LUMO with weight equal to 0.54 (see Table 2), HOMO-12 → LUMO with weight equal to 0.13 and other individual transitions contributions are at most equal to 0.10 therefore it is possible to say that an electron in this excited state most probably will tunnel from HOMO-m to LUMO.

The intense absorption lines (see green bars in the Fig. 5) of the squaraine-8-oxo-guanine supermolecule were found to be shifted to the red when these molecules were associated

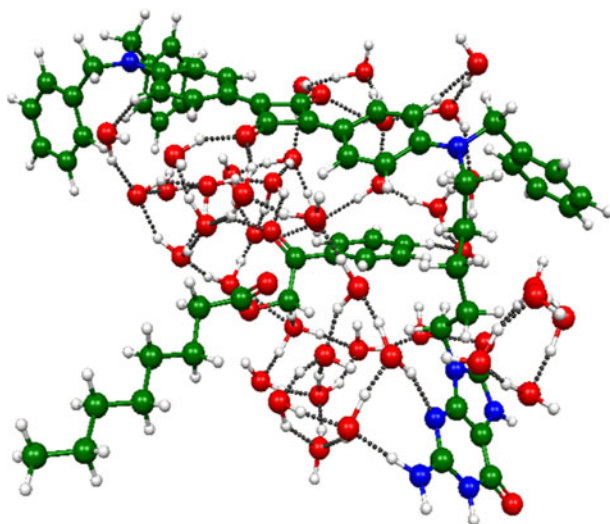


Fig. 6 A movie based visualization of the last steps of the geometry optimization of a self-reproducing FA based micelle system containing a Sq(II) molecule with attached covalently 8-oxo-guanine (*in the bottom-right*), pFA molecule (*in the bottom*) and 40 water molecules. *Dashed lines* show the hydrogen bonds (Fig. 2S)

with simple fatty acid micelles based only on Sq(I) or Sq(II) sensitizer molecules (see black and blue bars in the Fig. 5).

The geometry optimization of a more complex photoactive fatty acid micelle containing Sq(II) attached covalently to 8-oxo-guanine::cytosine supramolecule, pFA and 50 water molecules (see Fig. 8), was performed by using quantum chemical methods.

Part of the absorption spectrum of the photoactive fatty acid micelle shown in Fig. 8 is summarized in Table 3 and electron charge transfer trajectory in 32nd excited state are shown in Fig. 9.

The electron tunneling transitions of the 14th and 32nd excited states of this micelle should induce metabolic photo dissociation of the pFA molecule because the transferred electron cloud is located on the head of the pFA molecule (see Fig. 9). In these excited states it causes the molecule to split and the aromatic portion is ejected due to intense rotation and vibration of the weak chemical bond that joins it to the fatty acid section of the pFA molecule.

The most intense 32nd excited state is composed mainly from two individual transitions HOMO \rightarrow LUMO with weight equal to 0.36 (see Table 2), HOMO-14 \rightarrow LUMO with weight equal to 0.28 and other individual transitions contributions are at most equal to 0.09

Table 2 Excitation transition energies of a fatty acid micelle, containing Sq(II) molecule with attached covalently 8-oxo-guanine and pFA molecule and 40 water molecules. The weight of the individual excitations are given if larger than 0.1

Excited State #	Individual transitions HOMO-m \rightarrow LUMO+n	Weight of individual transition	Energy (eV)	Wavelength (nm)	Oscillator strength (arbitrary units)
8	HOMO-7 \rightarrow LUMO	0.88	2.48	500.8	0.21
10	HOMO \rightarrow LUMO	0.54	2.54	488.0	1.92
	HOMO-12 \rightarrow LUMO	0.13			

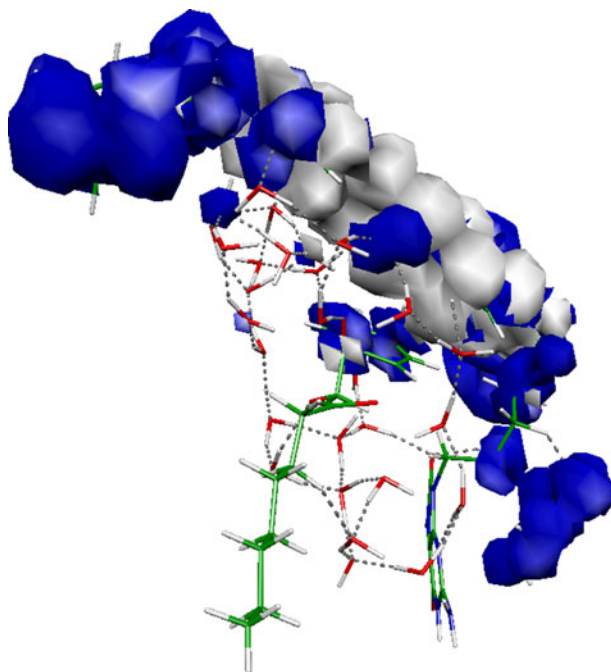


Fig. 7 Visualization of the electron charge tunneling associated with the tenth excited state. The transition is from the Sq(II) (*in the top*) to the same Sq(II) molecule and partially to the pFA molecule (*in the bottom*). The electron cloud hole is indicated by the *dark blue color* while the transferred electron cloud location is designated by the *grey color*. Carbon atoms and their associated covalent bonds are shown as *green sticks*, hydrogens are in *light grey*, oxygens—*red*, nitrogens—*blue*

therefore it is possible to say that electron in this excited state most probably will tunneling from HOMO-m to LUMO.

In order to understand the process of photodissociation of the pFA molecule (see Figs. 7 and 9) but reduce expenses of computations, the electronic structure of a single neutral pFA

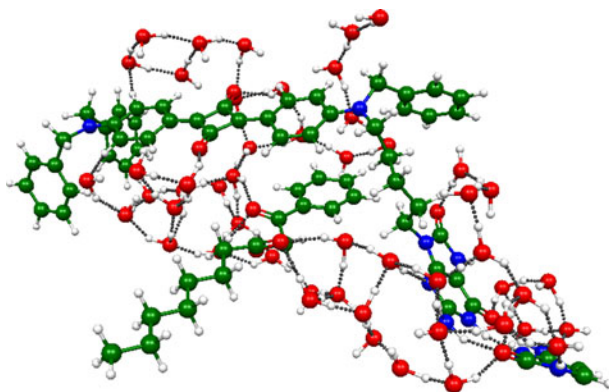


Fig. 8 A movie based visualization of the last steps of the geometry optimization of a self-reproducing FA based micelle system containing a Sq(II) molecule with attached covalently 8-oxo-guanine::cytosine supramolecule (*the bottom-right*), pFA molecule (*extending to the bottom-left*) and 50 water molecules (Fig. 3S)

Table 3 Excitation transition energies of a fatty acid micelle containing Sq(II) molecule with covalently attached 8-oxo-guanine::cytosine supramolecule and pFA molecule, and 50 water molecules. The weight of the individual excitations are given if larger than 0.09

Excited State #	Individual transitions HOMO-m \rightarrow LUMO+n	Weight of individual transition	Energy (eV)	Wavelength (nm)	Oscillator strength (arbitrary units)
14	HOMO-9 \rightarrow LUMO	0.23	2.34	530.2	0.72
	HOMO-3 \rightarrow LUMO	0.2			
	HOMO \rightarrow LUMO	0.19			
	HOMO-11 \rightarrow LUMO	0.17			
32	HOMO \rightarrow LUMO	0.36	2.68	463.3	1.9
	HOMO-14 \rightarrow LUMO	0.28			

molecule was investigated (see Fig. 10) by using the B3LYP/6-311++G** method. After the geometry reoptimization procedure, the electronic structure of the negative ion of this molecule was obtained using the unrestricted B3LYP/6-311++G** method.

Atomic Lowdin charges in Table 5 are with hydrogens summed into carbon atoms, i.e. the atomic charges of hydrogens are already added to the atomic charge of neighboring carbon atom. The sum of Lowdin charges of atoms from No 1 to 9 of neutral pFA molecule are equal to 0.274 of electron charge (e) while the sum on the same atoms in anion pFA molecule is equal to -0.620 e (see Table 4). This means that almost the entire (-0.894 e) additional electron after self-consistent field procedure localizes on the aromatic end of the pFA molecule while only -0.106 e charge of additional electron localizes on the FA fragment of this molecule.

Data of bond orders of selected chemical bonds of neutral and anion pFA molecules are presented in Table 5.

Analysis of selected bond orders of neutral and anion pFA molecules shows that the weakest chemical bond order is between the 9th and 10th atoms in the neutral pFA molecule. The additional electron which is placed on the aromatic end of the pFA molecule

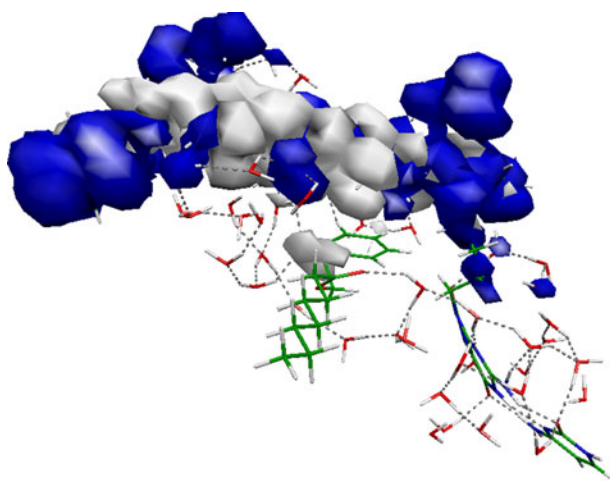


Fig. 9 Visualization of the electron charge tunneling associated with the 32nd excited state. The transition is from the Sq(II) (*in the top*) to the same Sq(II) molecule and partially to the pFA molecule (*in the bottom*)

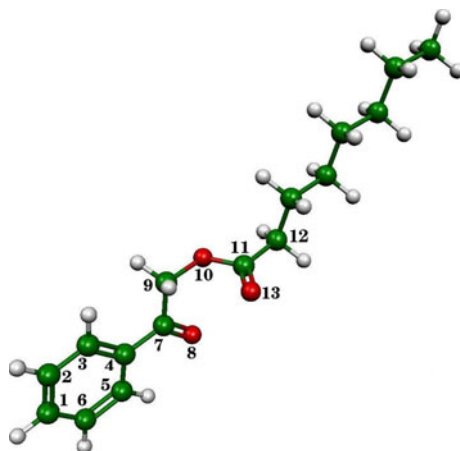


Fig. 10 Geometrical structure of pFA molecule. The aromatic end of the molecule which is ejected is shown by the numbered atoms from 1 to 9

(see Figs. 7 and 9) decreases the bond order from 0.772 to 0.734 between the 9th and 10th atoms.

It is known in molecular physics that additional electrons which are hopping on the molecular fragment initiate the vibrations and rotations of all chemical bonds in this fragment and there is a large probability that the weakest chemical bond between 9th and 10th atoms will be broken. The new released fatty acid from the dissociated pFA molecule will join to the minimal cell, therefore resulting in growth and later spontaneously breaking into two new minimal cells, and so forth. Similar photoinduced autocatalytic bioorganic systems were experimentally created by Rasmussen et al. (2003; 2008) and DeClue et al. (2009), and called in LANL “Protocell Assembly” project as minimal artificial living cells or protocells.

Table 4 Atomic Lowdin charges with hydrogens summed into carbon atoms of neutral and anion pFA molecules calculated by B3LYP/6-311++G** method

Number of atom	Neutral pFA	Anion of pFA
1 C	0.035	-0.130
2 C	0.021	-0.047
3 C	0.091	0.002
4 C	-0.119	-0.146
5 C	0.035	-0.063
6 C	0.017	-0.047
7 C	0.196	0.045
8 O	-0.308	-0.490
9 C	0.307	0.257
10 O	-0.380	-0.385
11 C	0.299	0.291
12 C	0.087	0.069
13 O	-0.342	-0.370
Sum of charges on 1–9 atoms	0.274	-0.620

Table 5 Bond orders of selected chemical bonds of neutral and anion pFA molecules calculated by B3LYP/6-311++G** method

Chemical bonds	Neutral pFA	Anion of pFA
9–10 C–O	0.772	0.734
7–8 C–O	1.980	2.143
10–11 O–C	1.295	1.332

The most intense absorption lines of the squarine-8-oxo-guanine supermolecule were found to be shifted to the red when these molecules were associated with fatty acid micelles (see green bars situated from left to right in the Fig. 8). Red bars represents the absorption spectrum lines of Sq(II)-8-oxo-guanine::cytosine+pFA+50 H₂O minimal cell calculated using TD DFT revPBE method with the 6-31G* basis set. In addition, the 8-oxo-guanine::cytosine-squarine supramolecule was observed to have an absorption region that covered more of the visible spectrum than a squarine-oxo-guanine supermolecule.

The redward shift of the intense absorption lines would allow a self reproducing micelle to absorb the light in the longer wavelength region, which may have been important in the environment where life might have developed, in addition to extending the photoactive period into the earlier morning and later evening hours. Furthermore, the nucleotide-caused wavelength shift and broadening of the absorption pattern potentially gives the nucleotides an additional valuable role, other than just a purely genetic one in the early stages of the development of life.

Most probably, that appearance of the simplest self-reproducing photoactive fatty acid micelles were in the period of 3.9–3.8 billion years before, *i.e.* just after formation of stable core in the Earth. Later these photoactive fatty acid micelles evolved incorporating nucleotide molecules (most probably in the period of 3.8–3.7 billion years before).

Conclusions

We have modeled three quantum mechanical processes which might have led to the emergence of photoactive fatty acid micelles with potentially genetic material (8-oxo-guanine::cytosine base pair) at the early stages of the emergence of life on Earth (Fatty Acid World):

- 1) All macromolecular systems, including photoactive fatty acid micelles, are self-assembling and achieve this based on interactions involving weak electrostatic forces (due to a small internal shift of the whole conjugated valence electron cloud from the electron-donor tail to the electron-acceptor head) and other quantum (dispersion, H-bonding) fine effects. The emergence of natural or artificial life a priori relies on the existence of these weak quantum mechanical electron correlation interactions.
- 2) The most intense excited states of the photoactive fatty acid micelles are partially composed of LUMO+n states located on the fatty acid precursors when the bis(4-diphenylamine-2-phenyl)-squarine molecule is covalently attached to the 8-oxo-guanine. This coupling also promotes electron hopping (tunneling) to the pFA molecules during the most intense absorption excited state. The photoexcited electron tunnels to the aromatic part of the pFA molecule, where it causes these molecules to split due to intense rotation and vibration of the weak chemical bond that joins this portion of the molecule to the fatty acid section of the pFA molecule;

- 3) The most intense absorption lines of the squaraine-8-oxo-guanine supermolecule were found to be shifted to the red when these molecules were associated with fatty acid micelles. In addition, the 8-oxo-guanine::cytosine-squaraine supramolecule was observed to have an absorption region that covered more of the visible spectrum than a squaraine-8-oxo-guanine supermolecule. The redward shift of the intense absorption lines would allow a self-reproducing micelle to absorb the light in the longer wavelength region, which may have been important in the environment in which life might have developed.

We suggest that nucleotide molecules and their sequences which, in the first period of evolution of fatty acid molecules were useful just for better absorbency of the light in the longer wavelength region, later were used for genetic information storage. From the information theory point of view, the nucleotide sequences in the Fatty Acid World micelles carry positionally information on how to directly provide better electron transport along the nucleotide-sensitizer chain and, in addition, would have been capable of providing complementary copies of that information for the next generation.

Appendix

Quantum chemical calculations methodology

Biological molecules, supermolecules or supramolecules (micelles) are the quantum systems composed of quantum particles: nuclei (with Z charges) and surrounding electrons possessing elementary charge $e = -1.602176487(40) \times 10^{-19}$ Coulomb. Elementary charge is the universal constant. The electromagnetic interaction of two particles consequences on the interaction of all other quantum particles therefore we are dealing with the complex quantum many-body system. The exact many-particle hamiltonian (Jensen 1999) for this system is:

$$\hat{H} = -\frac{\hbar^2}{2} \sum_i \frac{\nabla_{\vec{R}_i}^2}{M_i} - \frac{\hbar^2}{2} \sum_i \frac{\nabla_{\vec{r}_i}^2}{m_e} - \frac{1}{4\pi\epsilon_0} \sum_{i \neq j} \frac{e^2 Z_i}{|\vec{R}_i - \vec{r}_i|} + \frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{e^2 Z_i Z_j}{|\vec{R}_i - \vec{R}_j|} \quad (1.1)$$

The masses of the nuclei M_i , at the distances \vec{R}_i and the electrons possess the elementary mass m_e which are at the distances \vec{r}_i . The reduced Planck constant is the universal constant:

$$\hbar = \frac{h}{2\pi} = 1,054571628(53) \times 10^{-34} \text{ J} \cdot \text{s} = 6,58211899(16) \times 10^{-16} \text{ eV} \cdot \text{s}$$

The first term of the equation 1.1 is the kinetic energy operator for the nuclei, and the second for the electrons.

The last three terms in the equation 1.1 describe the Coulomb interaction between electrons and nuclei, between electrons and other electrons, and between nuclei and other nuclei. The force between two separated electric charges is given by Coulomb's law:

$$F_C = \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r^2}$$

where q_1 and q_2 are the charges, and r is the distance between them. Likewise, ε_0 appears in Maxwell's equations, which describe the properties of electric and magnetic fields and electromagnetic radiation, and relate them to their sources.

The value of ε_0 is defined by the formula:

$$\varepsilon_0 = \frac{1}{\mu_0 c_0^2} = 8,854187817... \times 10^{-12} \text{ A} \cdot \text{s}/(\text{V} \cdot \text{m}) = 8,854187817... \times 10^{-12} \text{ F/m}$$

where c_0 is the speed of light in vacuum and μ_0 is the magnetic constant or vacuum permeability.

All above mentioned constants: elementary charge e , reduced Planck constant, c_0 and μ_0 are universal and according to most of scientists did not changed from the beginning of the Universe.

Unfortunately quantum mechanics Schrödinger equation mathematically is not available to solve exactly (Jensen 1999). In order to find acceptable approximate eigenstates, we will need to make approximations least at two different levels.

Level 1: The Born-Oppenheimer approximation

The nuclei are much heavier and therefore move much slower than the electrons. We can hence 'freeze' them at fixed positions and assume the electrons to be in instantaneous equilibrium with them. In other words: only the electrons are kept as players in our quantum many body problem. The nuclei are deprived from this status, and reduced to a given source of positive charge, they become 'external' to the electron cloud. The nuclei do not move any more, their kinetic energy is zero and the first term on the hamiltonian 1.1 disappears. The last term reduces to a constant. We are left with the kinetic energy of the electron gas, the potential energy due to electron-electron interactions and the potential energy of the electrons in the (now external) potential of the nuclei. We write this formally as:

$$\hat{H} = \hat{T} + \hat{V} + \hat{V}_{ext} \quad (1.2)$$

The kinetic and electron-electron terms of 1.2 depend only on the fact that we are dealing with a quantum many-electron system (Jensen 1999). This part is universal. The system-specific information (which nuclei, and on which positions) is given entirely by \hat{V}_{ext} .

Level 2: Density Functional Theory

The quantum many body problem obtained after the first level approximation (Born-Oppenheimer) is much simpler than the original one, but still far too difficult to solve. Several methods exist to reduce equation 1.2 to an approximate but tractable form. Very important one is the Hartree-Fock method (HF). Modern and powerful method is Density Functional Theory (DFT) (Dreizler and Gross 1990; Jensen 1999).

2.1 The theorems of Hohenberg and Kohn

First theorem: There is a one-to-one correspondence between the ground-state density $\rho(\vec{r})$ of a many-electron system and the external potential \hat{V}_{ext} . An immediate consequence is that

the ground-state expectation value of any observable \widehat{O} is a unique functional of the exact ground-state electron density:

$$\langle \Psi | \widehat{O} | \Psi \rangle = O[\rho] \tag{1.3}$$

Second theorem: For being the hamiltonian, the ground-state total energy functional is of the form

$$E_{V_{ext}}[\rho] = \underbrace{\langle \Psi | \widehat{T} + \widehat{V} | \Psi \rangle + \langle \Psi | \widehat{V}_{ext} | \Psi \rangle}_{F_{HK}[\rho]} \tag{1.4}$$

$$= F_{HK}[\rho] + \int \rho(\vec{r}) V_{ext}(\vec{r}) d\vec{r} \tag{1.5}$$

where the Hohenberg-Kohn density functional $F_{HK}[\rho]$ is universal for any many-electron system. reaches its minimal value (equal to the ground-state total energy) for the ground-state density corresponding to V_{ext} .

Equation 1.5 is easily written down by using the density operator, which for an N-particle system is defined as

$$\widehat{\rho}(\vec{r}) = \sum_{i=1}^N \delta(\vec{r}_i - \vec{r}) \tag{1.6}$$

such that its evaluation for a many body wave function Ψ yields the density:

$$\rho(\vec{r}) = \langle \Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) | \widehat{\rho}(\vec{r}) | \Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \rangle \tag{1.7}$$

2.2 The Kohn-Sham equations

Exist the practical procedure to obtain the ground state density. The correlation energy is defined as this part of the total energy which is present in the exact solution, but absent in the Hartree-Fock solution. The total energy functionals $E_e[\rho]$ and $E_{HF}[\rho]$ corresponding to the exact and Hartree-Fock Hamiltonians respectively, are:

$$E_e = T + V \tag{1.8}$$

$$E_{HF} = T_0 + \underbrace{(V_H + V_x)}_V \tag{1.9}$$

Here T and V are the exact kinetic and electron-electron potential energy functionals, T_0 is the functional for the kinetic energy of a non-interacting electron gas, V_H stands for the

Hartree contribution and V_x for the exchange contribution. By subtracting 1.8 from 1.9, the functional for the correlation contribution appears to be:

$$V_c = T - T_0 \quad (1.10)$$

The exchange contribution to the total energy is defined as the part which is present in the Hartree-Fock solution, but absent in the Hartree solution. Obviously, with the Hartree functional given by

$$E_H = T_0 + V_H \quad (1.11)$$

It can be defined as

$$V_x = V - V_H \quad (1.12)$$

With this knowledge, we can rewrite the Hohenberg-Kohn functional in the following way:

$$\begin{aligned} F_{HK} &= T + V + T_0 - T_0 = T_0 + V + \underbrace{(T - T_0)}_{V_c} \\ &= T_0 + V + V_c + V_H - V_H = T_0 + V_H + V_c + \underbrace{(V - V_H)}_{V_x} \\ &= T_0 + V_H + \underbrace{(V_x + V_c)}_{V_{xc}} \end{aligned}$$

We can write explicitly the energy functional:

$$E_{V_{ext}}[\rho] = T_0[\rho] + V_H[\rho] + V_{xc}[\rho] + V_{ext}[\rho] \quad (1.13)$$

We can interpret the above expression also as the energy functional of a *non-interacting* classical electron gas, subject to two external potentials: one due to the nuclei, and one due to exchange and correlation effects. The corresponding Hamiltonian- called the Kohn-Sham Hamiltonian- is

$$\hat{H}_{KS} = \hat{T}_0 + \hat{V}_H + \hat{V}_{xc} + \hat{V}_{ext} \quad (1.14)$$

$$= -\frac{\hbar^2}{2m_e} \nabla_i^2 + \frac{e^2}{4\pi\epsilon_0} \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + V_{xc} + V_{ext} \quad (1.15)$$

where the exchange-correlation potential is given by the functional derivative

$$\hat{V}_{ext} = \frac{\delta V_{xc}[\rho]}{\delta \rho} \quad (1.16)$$

Kohn-Sham exact ground-state density $\rho(\vec{r})$ of an N- electron system is

$$\rho(\vec{r}) = \sum_{i=1}^N \phi_i(\vec{r})^* \phi_i(\vec{r}) \quad (1.17)$$

where the single-particle wave functions are the N lowest-energy solutions of the Kohn-Sham equation

$$\hat{H}_{KS}\phi_i = \varepsilon_i\phi_i \tag{1.18}$$

Be aware that the single-particle wave functions φ_i are not the wave functions of electrons. They describe mathematical quasi-particles, without a direct physical meaning. ε_i - are the single-particle energies (not the single-electron energies).

2.3 Exchange -correlation functional

A widely used approximation- called the *Local Density Approximation* (LDA) - is to postulate that the exchange-correlation functional has the following form:

$$E_{xc}^{LDA} = \int \rho(\vec{r})\varepsilon_{xc}^{LDA}(\rho(\vec{r}))d\vec{r} \tag{1.19}$$

$\rho(\vec{r})\varepsilon_{xc}^{LDA}(\rho(\vec{r}))$ is the local exchange-correlation energy density from the LDA. It means that the exchange-correlation energy due to a particular density $\rho(\vec{r})$ could be found by dividing the material in infinitesimally small volumes with a constant density. Logical step to improve on LDA, is to make the exchange-correlation contribution of every infinitesimal volume not only dependent on the local density in that volume, but also on the density in the neighboring volumes. In other words, the *gradient* of the density will play a role. This approximation is therefore called the *Generalized Gradient Approximation* (GGA). For example, for spectra calculations we used “pure” GGA revPBE (revised Perdew-Burke-Ernzerhof (Perdew et al. 1996)) functional with exchange scaling, which has the following form:

$$E_{xc}^{revPBE} = a_x E_x^{HF} + (1 - a_x) E_x^{revPBE} \tag{1.20}$$

Coefficient a_x in the PBE method might be varied from 0 (pure PBE approximation) to 0.25 (PBE0) or 0.5 (PBEHandH).

The revPBE, i.e. “pure” GGA exchange energy functional E_x^{GGA} can be written

$$E_x^{GGA} = \int \rho(\vec{r})\varepsilon_x^{LDA}(\rho(\vec{r}))F_x(s(\vec{r}))d\vec{r} \tag{1.21}$$

E_x^{HF} - means the Hartree-Fock exact exchange functional, $\rho(\vec{r})\varepsilon_x^{LDA}(\rho(\vec{r}))$ is the local exchange energy density from the LDA, $s(\vec{r})$ is the reduced density gradient:

$$s(\vec{r}) = |\nabla\rho(\vec{r})|/\left[2(3\pi^2)^{1/3}\rho(\vec{r})^{4/3}\right] \tag{1.22}$$

and F_x is a local exchange enhancement factor in the PBE and revPBE:

$$F_x(s) = 1 + \kappa - \frac{\kappa}{1 + \mu s^2/\kappa} \tag{1.23}$$

with $\kappa=0,804$ in PBE and $\kappa=1,245$ in our used revPBE.

We used the functional PBELYP (Perdew et al. 1996; Lee et al. 1988) for all micelle geometry optimization procedure. PBELYP possesses the similar form as revPBE on the 1.20:

$$E_{xc}^{PBELYP} = a_x E_x^{HF} + (1 - a_x) E_x^{PBE} + E_c^{LYP} = E_x^{PBE} + E_c^{LYP} \quad (1.24)$$

where E_c^{LYP} is Lee-Yang-Parr correlation energy (Lee et al. 1988).

We used the hybrid functional B3LYP for the individual molecules calculations. B3LYP means three-parameter hybrid functional with Becke'88 exchange (Becke 1988) and Lee-Yang-Parr correlation:

$$E_{xc}^{B3LYP} = E_{xc}^{LDA} + a_0 (E_x^{HF} + E_x^{LDA}) + a_x (E_x^{GGA} + E_x^{LDA}) + a_c (E_c^{GGA} + E_c^{LDA}) \quad (1.25)$$

Where $a_0=0,20$, $a_x=0,72$, and $a_c=0,81$ are the three empirical parameters determined by fitting the predicted values to a set of atomization energies, ionization potentials, proton affinities, and total atomic energies. and are generalized gradient approximations: the Becke 88 exchange functional and the correlation functional of LYP, and is the VWN LDA approximation (Vosko et al. 1980) to the correlation functional.

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