QUANTUM SELF-ASSEMBLY AND PHOTOINDUCED ELECTRON TUNNELING IN PHOTOSYNTHETIC SYSTEMS OF ARTIFICIAL MINIMAL LIVING CELLS

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Abstract: The natural and artificial living cells and their substructures are self-assembling due to electron correlation interactions among biological and water molecules which leads to appearing the attraction dispersion forces and hydrogen bonds. Dispersion forces are weak intermolecular forces that arise from the attractive force between quantum multipoles. A hydrogen bond is a special type of quantum attractive interaction that exists between an electronegative atom and a hydrogen atom bonded to another electronegative atom and this hydrogen atom exist in two quantum states. The best method to simulate these dispersion forces and hydrogen bonds is to perform quantum mechanical non-local density functional potential calculations of artificial minimal living cells consisting of around 1000 atoms. The cell systems studied are based on peptide nucleic acid and are 3.0 – 4.2 nm in diameter. The electron tunneling and associated light absorption of most intense transitions as calculated by the time dependent density functional theory method differs from spectroscopic experiments by only 0.2 - 0.3 nm, which are within the value of experiment errors. This agreement implies that the quantum mechanically self-assembled structure of artificial minimal living cells very closely approximate the realistic ones.

We used quantum mechanical program packages: GAUSSIAN03, GAMESS-US, ORCA, DALTON, DIRAC, CPMD and molecular dynamics packages: GROMACS, AMBER, CPMD. Visualization of molecules were performed by MOLDEN and MOLEKEL programs.

KEYWORDS: quantum self-assembly of photosynthetic centers, measure of the complexity of artificial minimal living cell

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QUANTUM SELF-ASSEMBLY AND PHOTOINDUCED ELECTRON TUNNELING IN PHOTOSYNTHETIC SYSTEMS OF ARTIFICIAL MINIMAL LIVING CELLS

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The artificial minimal cells that are synthesized in USA Los Alamos National Laboratory [1, 2] are only a few nm in size. 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. It is also capable of undergoing the same Watson-Crick pairing and replication as RNA and DNA. 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 (pFA) to yield another fatty acid molecule, thereby allowing the container to grow until it reaches an unstable size and divides. The protocell 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 [1]. 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.

The minimal protocell 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 (wave) theory [3].

We used quantum mechanical (QM) electron correlation interactions density functional theory (DFT) methods (i.e. high precision quantum mechanical simulations) to investigate various self-assembled photoactive bioorganic systems of artificial minimal living cells [3-7]. The cell systems studied are based on peptide nucleic acid (PNA) and consisted of up to 360 atoms (not including the associated water or methanol solvent shells) and are up to 3.0-4.2 nm in diameter. The electron correlations interactions originating the hydrogen bonds and Van der Waals weak chemical bonds that increase due to the addition of a polar solvent (water or methanol) molecules, and fatty acid (FA) and precursor fatty acid (pFA) molecules play a critical role in the QM interaction based self-assembly of the photosynthetic center and functioning of the photosynthetic processes of the artificial minimal living cells. The distances between the separated sensitizer, precursor fatty acid, and water or methanol molecules are comparable to Van der Waals and hydrogen bonding radii. As a result these nonlinear quantum interactions compress the overall system resulting in a smaller gap between the HOMO and LUMO electron energy levels and photoexcited electron tunneling occurs from the sensitizer (either a 1,4-bis(N,N-dimethylamino) naphthalene or a [Ru(bpy)$_2$(4,4'-Me$_2$-2,2'-bpy)]$^{2+}$) to pFA molecules (notation used: Me = methyl; bpy = bipyridine).

The electron tunneling and associated light absorption of most intense transitions as calculated by the time dependent density functional theory (TD DFT) method differs from spectroscopic experiments by only 0.3 or 0.2 nm, which is within the value of experiment errors [2]. This agreement implies that the quantum mechanically self-assembled structures of minimal living cells very closely approximate the realistic ones.
One of the successful examples: we have performed calculations using TD DFT PBEPBE method with the 6-31G basis set together with COSMO water solvent model installed on our research group dual processor Opteron servers Linux cluster of the difference of electron charge density (excited-state - ground-state) for the photosynthetic center of artificial minimal living cell [1] which consists of conjugated cytosine-1,4-bis(N,N-dimethylamino)naphthalene supermolecule, six fatty acid, two pFA molecules, and two the waste pieces of the pFA molecules and visualized the electron charge tunneling associated with certain excited state transitions (see Figure 1).

Figure 1. Image of the geometric and electronic structure of a photosynthetic system consisting of a cytosine-PNA fragment covalently bonded to a 1,4-bis(N,N-dimethylamino)naphthalene sensitizer molecule (in the center), six 5-carbon fatty acid molecules, two pFA molecules (in the top-left and top-right), and two the waste pieces of the pFA molecules and water molecules that were optimized using the PBEPBE/3-21G model. Visualization of the electron charge tunneling associated with the eighth excited state. The transition is from the conjugated cytosine-PNA fragment-1,4-bis(N,N-dimethylamino)naphthalene supermolecule (in the right) to the one of the pFA molecules (in the top-right). The electron cloud holes are indicated by the blue color while the transferred electron cloud locations are 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.

Electron charge tunneling associated with the eighth excited state shown in Figure 1 exactly correspond to experimental value equal to 450.3 nm of the most intense absorption line [2]. This agreement implies that the quantum mechanically self-assembled structures of minimal living cells
very closely approximate the realistic ones.

Quantum mechanical electron correlation experiments of self-assembly of above described artificial minimal living cells show that these cells are complex systems because only entire ensemble of PNA, and sensitizer, and pFA, and FA and water molecules is stable and perform quantum photosynthetic processes. Removing the small part of nucleobase, FA and water molecules leads to the structural changes in comparison with realistic structures and difference in comparison with the spectroscopic values of photoexcited electron tunneling from sensitizer (1,4-bis(N,N-dimethylamino)naphthalene to pFA molecules. QM electron correlation experiments of self-assembly of artificial minimal living cells removing the main part of nucleobase, and FA and water molecules leads to the degradation of these cells. We can state what the inclusion of ever more water, and fatty acid, and pFA molecules, and waste pieces of the pFA molecules and nucleobase molecules in the different artificial minimal living cells results in a shift of the absorption spectrum to the red for the artificial protocell photosynthetic center, leading to an ever closer approach to the real experimental value and indicates the measure of the complexity of this quantum complex system, i.e. a minimal protocell. It is important to say that only QM electron correlation TD-DFT experiments with minimal living cells gives results exactly comparable with spectroscopic results and all other more simplified QM methods such as local gradient DFT or ab initio Hartree-Fock gives structures and spectra far from the experimentally measured.

The corresponding of experimental absorption spectra peaks and our QM calculated confirm that our chosen method of designing single electron nano photocells might be useful not only for artificial living organisms but also for wide implementation in the nano photodevices, and molecular computers.

Our goals are by using quantum mechanical experiments to predict the possibility of biochemical experimental synthesis of quantum information based artificial living organisms or nanobiorobots for nanomedicine and cleaning of nuclear, chemical and microbial pollutions. We are creating molecular electronics and spintronics logical gates regulating the photosynthesis, growing and dividing of artificial living cells and nanobiorobots [8-11]. Designed of variety of the molecular spintronics devices will regulate photosynthesis and growth of artificial minimal living cells in the conditions of external magnetic fields, while also providing a perspective of the requirements for success in the synthesis of new forms of artificial living organisms:

http://www.daviddarling.info/encyclopedia/M/molecular_quantum_computing_cloud.html

Reference:


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