Photon-Induced Biomolecular Sensing and Processing: Towards Engineering, Science and Medical Applications

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ABSTRACT

This paper discusses and researches photon-induced sensing and processing by molecules and biomolecules. Rhodopsin photon receptor functionality and energetics are examined by applying quantum mechanics. We focus on fundamental and experimentally-verified results in order to consistently study mechanisms, processes and transitions in molecules. The solution of the aforementioned long-standing problems will enable one to:

1. Apply the *first principles* and examine biophysics of quantum phenomena exhibited by various vertebrates and invertebrates;
2. Utilize quantum-mechanical transductions and transitions in *microscopic* and *macroscopic* devices and systems;
3. Transfer basic knowledge, engineering solutions and enabling technologies in various areas such biotechnology, medicine, security and other.

This paper quantitatively studies bioenergetics, quantum phenomena, transductions and *state* transitions order to coherently evaluate molecular functionality and capabilities. The solution of these problems will advance knowledge, support engineering and enable technologies. We outline typifying prospects and devise advanced-performance molecular sensing and processing devices. These *engineered* devices can be used in various molecular processing, communication and interfacing applications.

Keywords: Biomolecule, molecule, photon, processing, quantum mechanics, sensing

1. INTRODUCTION

For many decades, the photoreception has being extensively studied as reported in [1-3] and numerous references therein. Rhodopsin is a photosynthetic absorbing (sensing) – interfacing – and – processing transmembrane protein which senses and processes the information on detected photons. The term processing means that some pre-processing and specific processing tasks (coding, communication and other) may be exhibited by rhodopsin. We do not imply that rhodopsin accomplishes overall data or information processing.

It is important to assess conventional concepts and apply quantum mechanics to examine photon-induced transductions and transitions in the cromophore (light-absorbing group) of rhodopsin. Retinal absorbs photon and initiates sensing, communication and other events.

Quantum mechanics allows one to examine energetics of photon absorption with the consequent analysis of photon-electron and photon-biomolecule interactions, charge variations, etc. Based on this analysis, the functionality and mechanisms in the intact photosynthetic assemblies and *engineered* devices can be studied. The experimental studies and fundamental analyses suggest possible use of molecules for sensing, interfacing, networking and processing. We consider possible mechanisms, phenomena, effects, transductions and transitions in the *natural* and *engineered* receptors. Many molecules exhibit photon absorption, photon emission, quantum *state* transitions, charge distributions, etc. The resulting transductions may be utilized in sensing (detection) and processing, while the emitted photons can be used for interfacing, networking and communication.

2. RHODOPSIN

Rhodopsin, represented in Figure 1, is a membrane-intrinsic protein. Rhodopsin is characterized by seven transmembrane α-helices, covalently attached carotenoid chromophore (retinal) which is shown in the center. The rhodopsin complex consists of three units (*rhodonine* which is a liquid crystalline coating exterior surfaces of a passive protein *opsin*, and the *dendritic structure* of the adjacent photoreceptor cell). There are various transductions in rhodopsin which has being intensively studied [1-12].

Consider the photon receptor molecule, e.g., retinal $C_{20}H_{28}O$. During the photo-excitation process, the rhodopsin absorbs light, and, thus, excited to a higher electronic state. The mechanisms of the photon absorption which may include a *cis-trans* isomerization of retinal $C_{20}H_{28}O$, conformational changes, activation of G-protein, enzymatic activities and other alterations are studied in [1-19]. Publications [1-19] and references therein report discrepancies and the fact that some results lead to inconsistencies. Following a conventional hypotheses, Figure 1 illustrates that upon photoexcitation, the retinal chromophore isomerizes around its $C_{11}=C_{12}$ double bond. This leads to conformational changes, H-bond rearrangements, ion-cation formation, intermediate evolutions and stabilization, loss of a molecule of water and other possible events [1-22]. These events trigger the subsequent changes which result in a signal to the brain. Biophysics of these transductions and transitions is insufficiently comprehended [1-22] and not addressed in this paper.
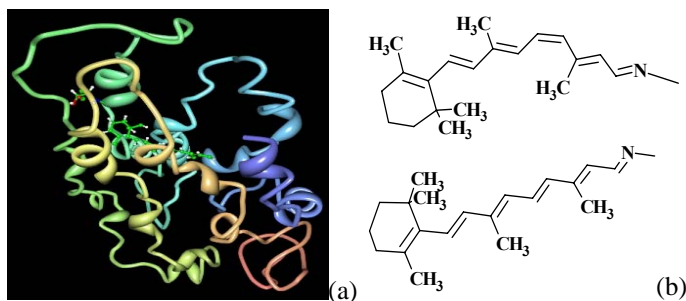
Figure 1. Rhodopsin: (a) 3D-structure of rhodopsin; (b) 11-*cis* and all-*trans* retinal as a part of rhodopsin (bonded through amino group of opsin protein)

There have being extensive studies of the photoinduced conformations, *cis–trans* conformations of retinal, orientation of the β-ionone ring, charge changes, isomerizations and evolutions of retinal and binding pocket, variations of structures of cytoplasmic region, etc. [4-12]. While several experiments suggest a 6*s-cis* conformation for the chromophore, a 6*s-trans* form is also reported. The structure allows both orientations, and the 6*s-cis* conformation leads to a –72° dihedral angle $C_5=C_6-C_7=C_8$. The salt bridges may play important roles in the activation and stabilization. Several important conformational changes, transitions and adjustments of the β-ionone ring, bridges, helixes, matrix and other structures were observed and identified experimentally. The relative displacement of the helices is also studied.

In situ modeling of retinal isomerization is reported in [9, 13-19] using different models and concepts. In general, these models apply classical mechanics and conventional electrostatics. With the attempt to utilize a complete atomic representation of the rhodopsin, membrane and interacting *natural* environment (lipid bilayer and water under varying temperature, pressure, pH, hydrodynamics, boundary conditions and other conditions), a great number of hypotheses, simplifications, assumptions, parametric approximation, scaling and other assertions were introduced. The equilibrated and scaled structure can be used for the virtual simulation not attempting to coherently examine biomolecular assemblies. Retinal may isomerize around the $C_{11}=C_{12}$ double bond by *switching* the dihedral potential energy function of this bond from the primary equilibrium state to the isomerization state. This results in an all-*trans* retinal transition. After isomerization, the dihedral potential is restored to its original state, and simulations to examine expected ~10 nsec transient dynamics are carried out [9]. Even applying largely simplified models, each simulation run requires weeks. A great number of debatable hypothesis were applied to ensure the mathematical tractability, and, the consistency and accuracy of the results were disputed.

3. PHOTONS AND MOLECULES: QUANTUM-MECHANICAL ANALYSIS

The studied state evolutions are represented as
ground state → exited state → ground state

with various intermediate transitions. The *state* transitions are mathematically described by the Schrödinger and other equations. Experiments and fundamental analysis should result in the physically observable quantities consistent with *microscopic* systems. We consider the following events: photon (multi-photon) absorption → electron excitation → charge or thermal (photon emission) changes → relaxation.

We study the interaction of photons, which is the quanta of the electromagnetic field, with the *microscopic* target (biomolecular assemblies), e.g., rhodopsin receptor. Our goal is to examine the interactions between photons, electrons and atoms within a *microscopic* target molecule. A nonrelativistic approximation is used to describe the motion of electron. Using the conventional notations of quantum mechanics [20], for the interacting field operators, the Hamiltonian operator is found to be

$$H = \frac{1}{2\pi}\int \mathbf{E}^- \cdot \mathbf{E}^+ dv + \frac{1}{2m}\int \psi^*\left(\frac{\hbar}{i}\nabla + \frac{e}{c}\mathbf{A}\right)^2 \psi dv + \int \Pi\psi^*\psi dv, \quad (1)$$

where the Hermitian field operator is $\mathbf{E}(t,\mathbf{r})=\mathbf{E}^+(t,\mathbf{r})+\mathbf{E}^-(t,\mathbf{r})$.

The first term represents the electromagnetic radiation field. The second term describes the interaction of electrons. The last term describes the external forces, as well as the interactions between the particles, including the Coulomb repulsion between electrons. The remaining terms represent the interaction between radiation and matter fields. From (1), one has

$$H=H_1+H_2,$$

$$H_1 = \frac{1}{2\pi}\int \mathbf{E}^- \cdot \mathbf{E}^+ dv - \frac{\hbar^2}{2m}\int \psi^*\nabla^2\psi dv + \int \Pi\psi^*\psi dv, \quad (2)$$

$$H_2 = \frac{e\hbar}{mci}\int \psi^*\mathbf{A}\cdot\nabla\psi dv + \int \mathbf{A}\cdot\mathbf{A}\psi^*\psi dv,$$

where H_1 is the radiation and matter Hamiltonian terms; H_2 is the interaction Hamiltonian operator.

The dynamics of the *interacting fields*, which depends on the Hamiltonian (1), is described by complex field operators [20]. Assume that the first-order approximation can be applied. The electromagnetic interaction between the radiation field and electrons is weak, and the perturbation theory is used. Our goal is to derive explicit expression for the intensity of *absorption* of photons. We neglect the spin of the electron. The operator H_1 describes the free photons and the target molecular assembly, and, H_1 is the unperturbed Hamiltonian. The interaction is described by H_2 which leads to perturbations. The field operator $\mathbf{A}$ is evaluated, and the first approximation of $\mathbf{A}$ is linear in terms of photon creation and annihilation operators. To describe a single photon absorption in the electron-photon interacting system, we use the electron wave function

$$\langle\Psi_i| = \int \psi_i(\mathbf{r})\psi^*(\mathbf{r})dv\langle 0|\otimes|...n_i^\lambda(\mathbf{k})...\rangle, \quad (3)$$

where $\langle 0|$ denotes the no-electron state; $\langle\ldots n(\mathbf{k})\ldots|$ is the state of the electromagnetic field in terms of photon occupation numbers with the superscript λ which specifies the polarization of a photon with wave vector $\mathbf{k}$.

In the final state, there must be one photon less than in the initial state, and the electron is annihilated and recreated in states $\psi_i(\mathbf{r})$ and $\psi_f(\mathbf{r})$. Examining the perturbation and transition from state *i* to *f*, the field operator $\mathbf{A}$ is evaluated. We have

$$\left\langle \Psi_f \right| = \int \psi_f(\mathbf{r})\psi^*(\mathbf{r})dv\left\langle \mathbf{0}\left|\otimes\right|...n_i^\lambda(\mathbf{k})-1...\right\rangle. \tag{4}$$

From (1)-(4), for the photon absorption and photon emission, one finds

$$\left\langle \Psi_f\left|H\right|\Psi_i\right\rangle = \frac{e\sqrt{4\pi\hbar c^2}}{mcL^{3/2}\sqrt{2\omega_k}}\sqrt{n_i^\lambda}\int\psi_f^*(\mathbf{r})e^{\pm i\mathbf{k}\cdot\mathbf{r}}\mathbf{e}_{\mathbf{k}}^\lambda\cdot\frac{\hbar}{i}\nabla\psi_i(\mathbf{r})dv, \tag{5}$$

$$\left\langle \Psi_f\left|H\right|\Psi_i\right\rangle = \frac{e\sqrt{4\pi\hbar c^2}}{mcL^{3/2}\sqrt{2\omega_k}}\sqrt{n_i^\lambda+1}\int\psi_f^*(\mathbf{r})e^{\pm i\mathbf{k}\cdot\mathbf{r}}\mathbf{e}_{\mathbf{k}}^\lambda\cdot\frac{\hbar}{i}\nabla\psi_i(\mathbf{r})dv,$$

where $\mathbf{e}_k$ is the unit polarization vector.

Denoting the initial and final energy of the unperturbed atom as E_i and E_f, the photon energy is $\hbar\omega_k=E_f-E_i$, where $\omega_k=ck=c|\mathbf{k}|$. The incident photon flux dI_0 is the number of photons incident to the target per unit area and unit time in the frequency interval $d\omega$. For photons in the polarization mode λ and momentum $\hbar\mathbf{k}$ pointing with a solid angle $d\Omega_{\mathbf{k}}$, we have

$$dI_0 = \frac{n_i c\hbar\rho(\hbar\omega)}{L^3}d\omega = \frac{n_i\omega^2}{8\pi^3 c^2}d\omega d\Omega_{\mathbf{k}}. \tag{6}$$

The photon flux provides one with the energetics estimates of the transition in rhodopsin. It also illustrates that the frequency interval and angle should be used.

For the monochromatic orthogonal plane-wave modes, we have

$$\mathbf{u}_{\mathbf{k},o}(\mathbf{r})=\mathbf{e}_{\mathbf{k},o}e^{i\mathbf{k}\cdot\mathbf{r}}, \; \sigma=\pm 1. \tag{7}$$

The electromagnetic field Hamiltonian operator is given using the monochromatic annihilation and creation operators $a_{\mathbf{k},\sigma}$ and $a^+{}_{\mathbf{k},\sigma}$ as

$$H_{em} = \sum_o\int\frac{\hbar\omega_{\mathbf{k}}}{(2\pi)^3}a_{\mathbf{k},o}a_{\mathbf{k},o}^+ d^3k. \tag{8}$$

The energy-momentum equation $E=\sqrt{c^2|\mathbf{p}|^2+m^2c^4}$ yields $E=c\sqrt{\mathbf{p}\cdot\mathbf{p}}$ because for photons $m=0$.

The multi-photon transitions can be examined. An n-photon wave function is a tensor product over the n different single-photon states. We have

$$\Psi^{(n)}(t,\mathbf{r}_1,..,\mathbf{r}_n) = \sum_{[a]}L_{[a]}\bigotimes_{j=1}^n\psi_{[a]_j}^{(1)}(t,\mathbf{r}), \tag{9}$$

where $\psi_{[a]_j}^{(1)}$ is the set of single-photon basis states; $L_{[a]}$ is the system-label exchange matrix, and $[a]=[a_1,\ldots,a_n]$.

The partial differential equation in the tensor form is

$$i\hbar\frac{\partial\Psi^{(n)}(t,\mathbf{r}_1,..,\mathbf{r}_n)}{\partial t} \tag{10}$$

$$=\sum_{j=1}^n\hbar c\left(\begin{bmatrix}\mathbf{I}&\cdots&\mathbf{0}\\\vdots&\ddots&\vdots\\\mathbf{0}&\cdots&-\mathbf{I}\end{bmatrix}\otimes\begin{bmatrix}\mathbf{I}&\cdots&\mathbf{0}\\\vdots&\ddots&\vdots\\\mathbf{0}&\cdots&\mathbf{I}\end{bmatrix}+\begin{bmatrix}\mathbf{I}&\cdots&\mathbf{0}\\\vdots&\ddots&\vdots\\\mathbf{0}&\cdots&\mathbf{I}\end{bmatrix}\otimes\begin{bmatrix}\mathbf{I}&\cdots&\mathbf{0}\\\vdots&\ddots&\vdots\\\mathbf{0}&\cdots&-\mathbf{I}\end{bmatrix}\right)\nabla_j\times\Psi^{(n)}(t,\mathbf{r}_1,..,\mathbf{r}_n),$$

where $\mathbf{I}\in\mathbb{R}^{3\times3}$ is the identity matrix.

For a two-photon case, the Schrödinger equation is

$$i\hbar\frac{\partial\Psi^{(2)}(t,\mathbf{r}_1,\mathbf{r}_2)}{\partial t}=\hbar c\left(\begin{bmatrix}\mathbf{I}&0\\0&-\mathbf{I}\end{bmatrix}\otimes\begin{bmatrix}\mathbf{I}&0\\0&\mathbf{I}\end{bmatrix}+\begin{bmatrix}\mathbf{I}&0\\0&\mathbf{I}\end{bmatrix}\otimes\begin{bmatrix}\mathbf{I}&0\\0&-\mathbf{I}\end{bmatrix}\right)\nabla_j\times\Psi^{(2)}(t,\mathbf{r}_1,\mathbf{r}_2) \tag{11}$$

4. QUANTUM-MECHANICAL ANALYSIS OF RETINAL

We quantum-mechanically examine retinal $C_{20}H_{28}O$ which is a receptor molecule of our interest. We solve the Schrödinger equations for a single-photon and multiple-photon cases. To make the problem mathematically tractable, consider only electrons on the outer shells which have the largest probability to be exited. In the spherical coordinate system, the wave function $\Psi(t,\mathbf{r})$ is

$$\Psi(t,\mathbf{r})= \Psi(t,r)\,\Psi(t,\theta,\phi).$$

That is, the radial and angular equations are solved considering all atoms with motionless protons with charges q_i. The radial Coulomb potentials are $\Pi_i(r)=-\dfrac{Z_{eff\,i}q_i^2}{4\pi\varepsilon_0 r}$, where for carbon $Z_{eff\,C}=3.14$.

For different photon wavelength λ and photon pointing angle $\Omega_{\mathbf{k}}$, the probability of the photon absorption is reported in Figure 3. The numerical results were performed for $\lambda\in[300\;\;800]$ nm and $\Omega_{\mathbf{k}}\in[-\frac{1}{2}\pi\;\;\frac{1}{2}\pi]$ rad. The maximum probability is observed at $\lambda=555$ nm, and, the photon energy is 3.6×10^{-19} J. We documented the results in a practical wavelength λ and pointing angle $\Omega_{\mathbf{k}}$ envelopes. Our results substantiate:

1. Consistency and coherence of the fundamental results reported with experimental findings;
2. Overall correctness of our fundamental, analytical and numerical results;
3. Accuracy of assumptions and simplifications;
4. Mathematical tractability and consistency;
5. Practicality and applicability of our concept.

For various *engineered* sensing and processing devices, our findings can be straightforwardly applied. For example, different molecules and biomolecules can be studied in the specified λ and $\Omega_{\mathbf{k}}$ envelopes. The results are applicable for numerous *microscopic* sensors, molecular detectors (which are found to be very selective to the activation energy), processing devices, etc.
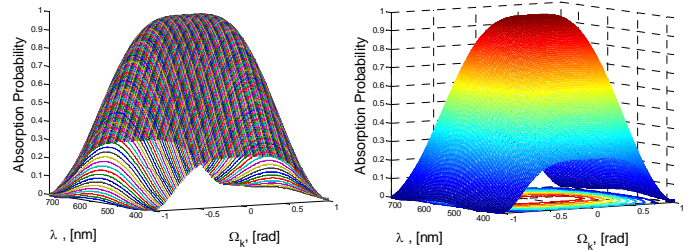

Figure 3. Probability of absorption, $\lambda\in[300\;800]$ nm and $\Omega_{\mathbf{k}}\in[-\frac{1}{2}\pi\;\;\frac{1}{2}\pi]$

5. CONCLUSIONS

We studied rhodopsin, which is a photoactive protein. The photoreceptor molecules were examined quantum-mechanically. The *engineered* molecular phototoreceptors can be used in optical, holographic, memory and processing applications. They may serve as active components in reusable holographic materials, photodiodes, light harvesting systems, input-output devices, interconnect, etc. The ability to examine *natural* rhodopsins and their photoreceptor molecular assemblies (chromophores) with possible engineering modification is very important from fundamental, applied, experimental and technological

prospects. We enable the theory by performing quantum-mechanical quantitative analyses. The performed data-intensive analysis led to studies of complex phenomena with assessment of characteristics, performance and capabilities. Our studies of molecular sensing-and-processing units advance knowledge as well as enable engineering inroads and technologies. The research in molecular photoreceptors is expected to lead towards the development of superior optical, processing and memory devices and systems.

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