Quantum Biology

Earth magnetic field

magnetoreception

vision

photosynthesis

Theoretical and Computational Biophysics group
Beckman Institute
University of Illinois at Urbana-Champaign
Where does QM come into play?

Biology has a knack for using what works. And if that means “quantum hanky-panky”, then quantum hanky-panky it is.

*Seth Lloyd, MIT*


(see the article DawnQuantumBio.pdf on course website!)

(quote notwithstanding) most of biology can be described classically (ignoring for the moment chemistry of reactions, bonding, etc.), with *a few key exceptions*

photosynthesis

vision

magnetoreception
photosynthesis

- converts light to chemical energy
- exists in all domains of life
- first photosynthetic organisms (purple bacteria) evolved ~2.8-3.5 billion years ago (shortly after life 3.8 GYs ago)

Molecular Evidence for the Early Evolution of Photosynthesis

molecules absorb in specific frequency windows
how efficient is photosynthesis?

100% sunlight → non-bioavailable photons waste is 47%, leaving

53% (in the 400–700 nm range) → 30% of photons are lost due to incomplete absorption, leaving

37% (absorbed photon energy) → 24% is lost due to wavelength-mismatch degradation to 700 nm energy, leaving

28.2% (sunlight energy collected by chlorophyll) → 32% efficient conversion of ATP and NADPH to d-glucose, leaving

9% (collected as sugar) → 35–40% of sugar is recycled/consumed by the leaf in dark and photo-respiration, leaving

5.4% net leaf efficiency.
photosynthesis in purple bacteria

(1) light absorbed by LH2/LH1

(2) charge separation at RC

(3) electrons added to quinone (reduced)

(4) protons from cytoplasm added, Q→QH₂

(5) QH₂ migrates to bc₁ complex, gets oxidized; protons released to periplasm

(6) protons drive ATP synthesis and return to cytoplasm

(7) remaining electrons are shuttled back to RC by cytochrome c₂

Photosynthetic Apparatus of Purple Bacteria.
Xiche Hu, Thorsten Ritz, Ana Damjanovic, Felix Autenrieth & Klaus Schulten.
photosynthesis in plants

much more complex, involves multiple systems and additional molecules (NADP, H₂O)

2 H₂O + 2 NADP⁺ + 3 ADP + 3 Pᵢ + light → 2 NADPH + 2 H⁺ + 3 ATP + O₂
What are the products used for?

Calvin-Benson cycle for carbon fixation uses CO$_2$ as a carbon source for making other biomolecules.

- RuBisCO (Ribulose-1,5-bisphosphate carboxylase/oxygenase) - main enzyme
- Most abundant protein on Earth(!), catalyzes primary reaction for converting inorganic carbon into bio-available carbon.
- Structure composed of 8 copies each of large and small subunits.
decay channels

absorbed light energy can decay in a few ways...

charge separation step in photosynthesis
electron transfer in purple bacteria

the reaction center in more detail...

rate-limiting step
pigment molecules

pigments have strong colors in the wavelengths *not absorbed*

pigments have lots of conjugated double bonds

electrons move “freely” within this system, i.e., $V = 0$

can be treated quantum mechanically as spatially constrained in a box

orange

red

green

chlorophyll a

phycoerythrobilin

PBoC 18.2.3
particle in a box

Schrödinger equation

\[ i\hbar \frac{\partial \psi(x, t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x, t)}{\partial x^2} + U(x)\psi(x, t) \]

wavefunction \( \Psi \) is a probability amplitude

\[ \langle \psi | \hat{A} | \psi \rangle = \int_{-\infty}^{\infty} \psi^*(x) \hat{A} \psi(x) \, dx \]

For a particle confined to a box with infinite walls:

\[ -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} = E \psi(x) \]

\[ \psi(0) = \psi(a) = 0 \]

\[ \psi(x) = A \cos kx + B \sin kx \]

energies are quantized due to boundary conditions!

\[ E = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m} \left( \frac{n\pi}{a} \right)^2 \]
particle in a box

electrons are fermions, obey Pauli principle (two per energy level in the box)

transition energy $\Delta E$ governed by difference between highest occupied molecular orbital (HOMO) and lowest unoccupied (LUMO)

$$\Delta E = E_{N/2+1} - E_{N/2} = \frac{\hbar^2 \pi^2}{2ma^2} \frac{N + 1}{(N - 1)^2}$$

wavelength of absorbed photon:
$$\lambda = \frac{hc}{\Delta E} = \frac{8mc}{\hbar a^2} \frac{(N - 1)^2}{N + 1}$$
particle-in-a-box is a special case

The Schrödinger equation is easily solved for the hydrogen atom. With inclusion of relativistic corrections via the Dirac equation, almost perfect agreement was found with experimental spectroscopic data.

“The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.”

P.A. M. Dirac

“(Dirac’s remark) was a cry both of triumph and of despair.”

need advanced codes (and lots of approximations!) to do QM calculations for molecules still limited to tens of atoms

Georgia Tech is on the list! (thanks to David Sherrill) even Pople is on the list!

www.bannedbygaussian.org
if the wall isn’t infinite, electrons can **tunnel** through *classically* forbidden regions between molecules. Electrons move from one chlorophyll to the next in RC by tunneling.

Total wavefunction $\Psi$ is a linear combination of individual molecular wavefunctions:

$$\psi_{\text{tot}} = a_1 \psi_1 + a_2 \psi_2$$

Transfer rate is a function of well depth and distance between them (*derives from energy minimization and wavefunction overlap*):

$$\text{rate} = \frac{2\pi}{\hbar} V_1^2 F^2 \rho e^{-2\kappa d}$$

requires two molecules to have almost identical potentials.
tunneling

experiments on azurin, a test protein for tunneling

change in distance by $\sim 1$ nm increases rate by four orders of magnitude

protein environment accelerates tunneling process compared to vacuum, water, but how?
tunneling

**Problem:** if the neighboring molecules need to have similar energy levels, how can tunneling occur in practice?

**Solution:** thermal fluctuations of the environment shift the energy levels and spontaneously create a transition state!
Marcus theory (1956)

Free energies of donor (D)/acceptor (A)/solvent system for electron on D or A modified transition rate includes probability of transition state ($p_T$):

$$k_{ET} = kp_T$$

Two state system:

$$p_T = \frac{e^{-\beta \Delta G^*}}{1 + e^{-\beta \Delta G^*}}$$

$$p_T \approx e^{-\beta (\Delta G - \lambda)^2/4\lambda} \quad (\lambda = \kappa q_A^2/2)$$

Theory predicts transfer rate does not simply increase with favorability of the A state.

It took ~30 years for exp. evidence of this inverted region!
absorbed light energy can decay in a few ways...

how energy gets to RC

charge separation step in photosynthesis
quantum antennae

special pair in RC receives direct photons at ~10/sec.
RC can turnover ~10,000/sec.

about 300 chlorophylls needed to produce one O₂ in algae

two rings of chlorophylls in each LH2, one w/9, one w/18
B800s/B850s absorb light in 800/850-nm range

Carotenoids (car) absorb in 500-nm range
excitation transfer

\[ D^* + A \rightarrow D + A^* \]

upon receiving photon, electron in chlorophyll becomes excited
can transfer energy to neighboring molecule through Förster resonance energy transfer (FRET)

excitation energy flows downward
each pigment has two excited states

energy of
Car states > B800 states > B850 states
excitation transfer

\[ H_{ij} = C \left[ \frac{\vec{d}_i \cdot \vec{d}_j}{r_{ij}^3} - \frac{3(\vec{r}_{ij} \cdot \vec{d}_i)(\vec{r}_{ij} \cdot \vec{d}_j)}{r_{ij}^5} \right] \]

FRET via Coulombic mechanism (2-5 nm separation)
interaction energy given by dipole-dipole coupling term
dipoles of two excited states of BChl

transfer rate given by Fermi’s Golden Rule from QM

\[ T_{ij} = \frac{2\pi}{\hbar} |H_{ij}|^2 \int S_i^D(E)S_j^A(E)dE \]

spectral overlap integral (same as density of states in FGR)

transfer time for B800-B800: 1.5 ps
B800-B850: 0.8-0.9 ps
B850-B850: 0.1-0.2 ps (due to tighter packing, dipole-dipole no longer applies)
role of carotenoids

if excitation is transferred to O$_2$, produces reactive **singlet** oxygen

$3\text{BChl}^* + 3\text{O}_2 \rightarrow 1\text{BChl} + 1\text{O}_2^*$

singlet O$_2$ oxidizes nearby double bonds, leads to cell **death**

triplet state is two electrons with total spin $S = 1$ (three $S_z$ states: -1, 0, 1)
singlet state has total spin $S = 0$ (thus only one $S_z$ state)

$3\text{BChl}^* + 1\text{Car} \rightarrow 1\text{BChl} + 3\text{Car}^*$

carotenoid can absorb excitation from BChl via **electron exchange** thanks to close proximity

retinal used in vision produced from ingested carotene, a carotenoid
coherent excitations

electronic excitation becomes delocalized in LH2 rings, forms so-called excitons

quantum coherence increases transfer probabilities

thermal effects between protein and chlorophylls enhance coherence lifetime! (environment usually causes decoherence)

see also: http://www.ks.uiuc.edu/Research/exciton_dynamics/
tissue-level vision

macroscopic eye geometry for animals (left) and insects (right)

resolving power based on aperture size due to diffraction

\[
\sin \theta = 1.22 \frac{\lambda}{D}
\]

rod/cone spacing corresponds well with maximum resolution (coincidence? evolution?)
to maximize photon collection, rod/cone cells have stacks of membrane discs (instead of antennae)

**rods** are most sensitive (can detect even a single photon!)

three types of **cones** detect specific color ranges
the GPCR rhodopsin is activated by light retinal isomerization causes rhodopsin to transition through a series of intermediate states before reaching the signaling state.
atomic-level vision

chromophore retinal is tightly bound in rhodopsin, cis state is lower in energy
photon induces cis→trans isomerization

after isomerization, all-trans-retinal must be cleaved off and replaced with a fresh 11-cis-retinal
replacement can come from recycling by enzyme or derived from β-carotene or vitamin A (retinol)

β-carotene + O₂ → 2 retinal
electron-level vision

if the chromophore is identical, how to change the absorption spectra?

small changes in the protein alter retinal’s electrostatic environment


just a few differences between medium and long cones

subtle twist of one group can notably affect the HOMO-LUMO gap due to different electronic states
Signaling initiates a cascade

One photon → 1 million Na⁺ ions → 1 mV change

Significant energy expended to amplify signal
bacteria “see” too

bacteriorhodopsin, an archaeal protein, absorbs light to pump protons for making ATP

forms a dense, almost crystalline lattice in so-called “purple membranes”

some bacteria have eye-spots to detect light and move towards it

Ex: channel-rhodopsins, which open to $\text{Na}^+$ and $\text{K}^+$ in response to light-driven isomerization
bird navigation

many birds migrate over thousands of miles each year

experiments have shown birds can sense Earth’s magnetic field, a true sixth sense

but how do they sense the very weak (25-65 μT) magnetic field and then interpret it?
magnetoreception

we first need a chemical process that can be altered by a magnetic field

only (known) solution is a radical pair mechanism

magnetic field changes balance between singlet, triplet states, which decay at different rates

Schulten was the first to extrapolate this to a magnetic sense (1978), but it was not initially well received

“A less bold scientist would have designed this piece of work for the wastepaper basket.” - review from original Science submission

http://www.ks.uiuc.edu/History/magnetoreception/
magnetoreception in cells

cryptochrome, a protein found in the eye (among other places!), was proposed to hold the key, a chromophore FAD

not only could it contain the radical pair mechanism, it could influence vision


**proposed reaction process**

arrows denote migration of electron hole, i.e., electron goes in opposite direction to fill vacancy due to excitation

back transfer of extra electron from FADH to a Trp occurs only in singlet state

magnetoreception in eyes

surprisingly, cryptochrome’s orientation only needs to be moderately constrained to function as a magnetic sensor

may be tethered to membranes in the retina, or between discs in rod cells

net effect is expected to be a filter function, applied to incoming light

“a bird’s eye view”