Using The Hierarchy Equations of Motion to Simulate Energy Transfer in Photosynthesis

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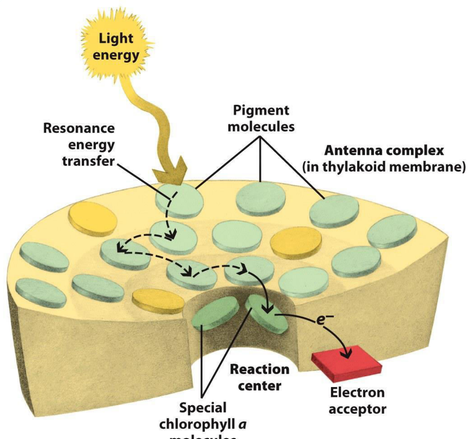
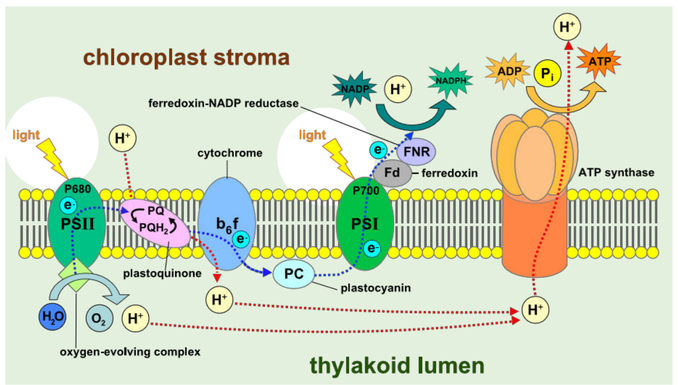
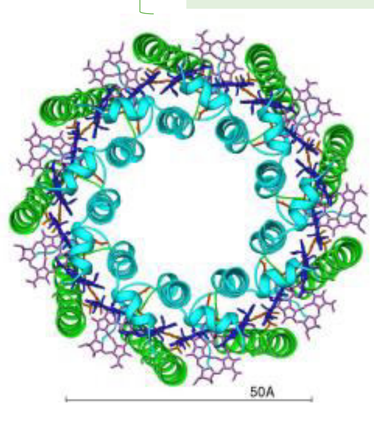
Photosynthesis



Inside the chloroplast, light harvesting **Antenna Pigments** surround **Reaction Centres**.

The **Electron Transport Pathway** in photosynthesis.





Structure of the **LH2 complex** in *Rhodopseudomonas acidophila*.

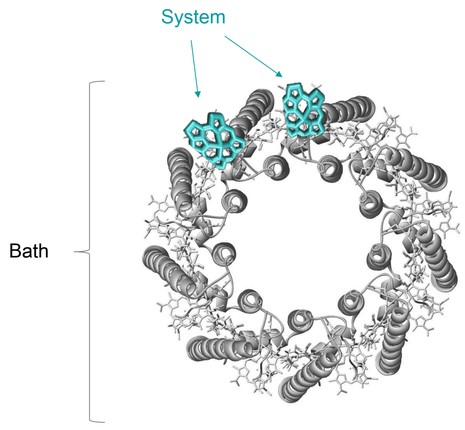
The B800 and B850 pigments are shown in purple and blue respectively, these absorb photons and undergo $\pi \rightarrow \pi^*$ transitions.

The pigments are held in place by proteins, which are shown in green and turquoise.

Quantum Model

The **Schrödinger Equation** can be used to accurately predict the motion of electrons in the system:

$$i\hbar \frac{\partial}{\partial t}\Psi = \hat{H}\Psi$$



The **Hierarchy Equations of Motion** are simply another way of writing the Schrödinger Equation. However, these equations are easier to solve, as they use a **system bath model.**

$$\frac{d}{dt}\hat{\rho}_n = -i\left(\hat{H}_A^{\times} + n\gamma\right)\hat{\rho}_n - ni\hat{\Theta}\hat{\rho}_{n-1} - i\hat{\Phi}\hat{\rho}_{n+1}$$

The **density matrix** ρ, describes the current location of the electrons in the system

$\hat{H}_A$ is the **system Hamiltonian**, it describes the two pigments.

$$\hat{\Theta} \equiv -\frac{1}{\beta\hbar}\hat{V}^{\times} + i\hat{V}^{\mathrm{d}}$$

$$\hat{\Phi} \equiv \frac{\eta}{\hbar^2}\hat{V}^{\times}$$

The **relaxation operators** describe how the system is affected by the bath

In the equations above, we are using the hyper operator notation:

$$V^{\times}\rho \equiv V\rho - \rho V$$

$$V^{\mathrm{d}}\rho \equiv V\rho + \rho V$$

My Code

I used the FORTRAN 90 language

```
program mat
    implicit none

    integer i, n
    integer,parameter:: nn=10
    real(8),parameter:: RT=0.223500E+03 , dt=.1, B=1, w1=5
    real(8),parameter:: w2=2, J=-0.42, la=0.25 , g=3
    complex(8),dimension(3,3,nn+3):: p, pdot, k1, k2, k3, k4
    real(8),parameter,dimension(3,3):: V=[-1,0,0,0,1,0,0,0,0]
    complex(8),parameter,dimension(3,3):: u=[0,0,1,0,0,1,1,1,0]
    real(8),dimension(3,3):: H=[w1, J, 0, J, w2, 0, 0, 0, 0]
    real(8):: t, num

    open(1,file='g2.dat')

    !density matrix
    p(:,:,:)=(0.0,0.0)
    p(1,1,2)=1.0

    !Use the Runge-Kutta algorithm
    t=0
    do 1 i=1,RT/dt

    write(1,"(4e23.7)") t, real(p(1,1,2)), real(p(2,2,2))

        call pdott(H, p,           B, V, g, la, nn,  k1)
        call pdott(H, p+0.5*k1*dt, B, V, g, la, nn,  k2)
        call pdott(H, p+0.5*k2*dt, B, V, g, la, nn,  k3)
        call pdott(H, p+k3*dt,     B, V, g, la, nn,  k4)

        p=p+dt*(k1+2*k2+2*k3+k4)/6
        t=t+dt
1   end do

    num=log(RT/dt)/log(2.0)
    print *, 'number of iterations= ',RT/dt,'=2**',num
    stop
end program mat

    !compute the time derivative of the density matrix
subroutine pdott(H, p, B, V, g, la, nn, pdot)
    implicit none
    integer, intent(in) :: nn
    integer :: n
    real(8), intent(in) :: H(3,3), V(3,3), B, g, la
    complex(8), intent(in)  :: p(3,3,nn+3)
    complex(8), intent(out) :: pdot(3,3,nn+3)
    complex(8) :: p2(3,3), p0(3,3), p1(3,3)

    do 2 n=0,nn
        p2(:,:) = p(:,:,n+1)
        p0(:,:) = p(:,:,n+2)
        p1(:,:) = p(:,:,n+3)


        pdot(:,:,n+2) = (0,-1.0)*(matmul(H,p0) &
        - matmul(p0,H)) - n*g*p0 &
        +(0,1.0)*(matmul(V,p1) - matmul(p1,V)) &
        +(0,2.0)*n*la*(matmul(V,p2) - matmul(p2,V))/B&
        +n*la*g*(matmul(V,p2) + matmul(p2,V))

2   continue
end subroutine pdott
```

List all of the variables used later in the program

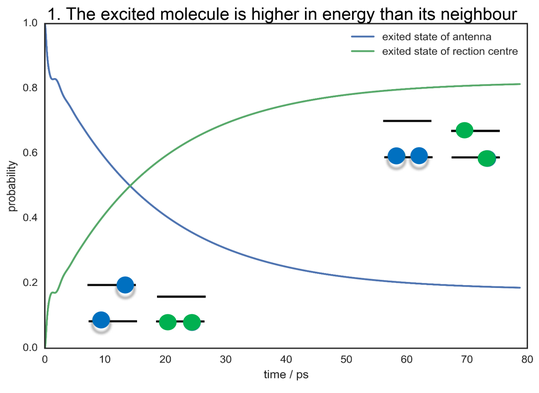
Initially, one of the molecules is excited, the other is in the ground state

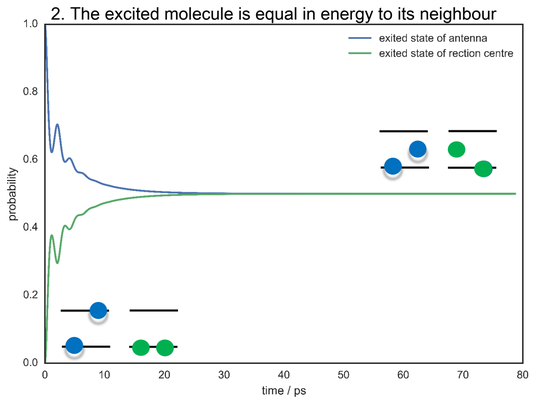
This is the main body of the program, here the wavefunction is moved forward in time, step by step

The subroutine can be called from anywhere inside the main function

This is the HEOM

Exciton transfer Between Molecules

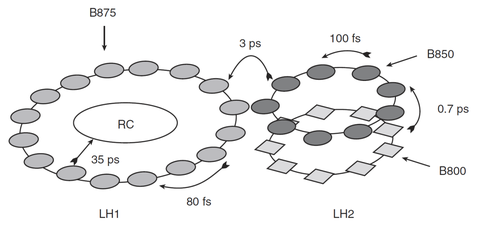




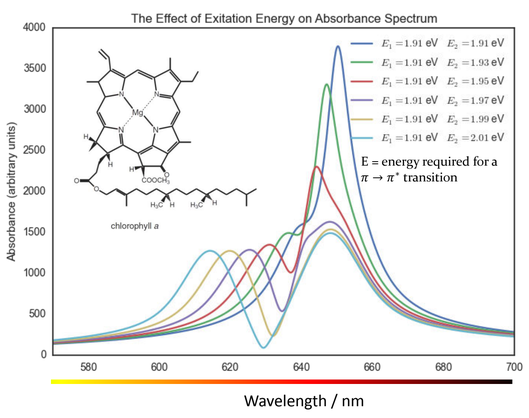
An excitation is passed from the **B850 pigment (blue)** to the **reaction centre (green).**

My simulation shows that this transfer is most effective when the excited state of the reaction centre **is lower in energy** than the pigment.

Hence, the pigments furthest from the reaction centre have the highest energy exited states.

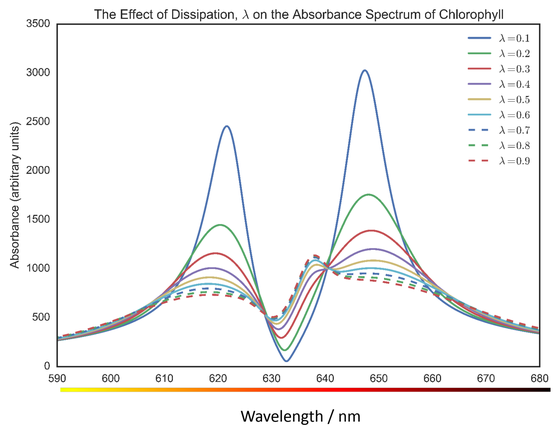


Absorption Spectrum of Chlorophyll



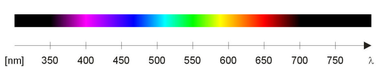
When the two molecules have the **same excitation energy**, they produce a **narrow** absorption peak.

The **range** over which absorption occurs is increased if the two molecules have different excitation energies.



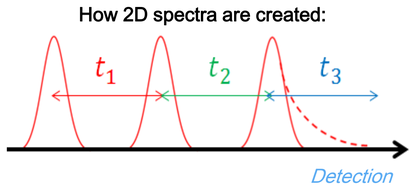
A similar effect is observed when the **dissipation parameter λ** is increased.

This would occur if the surrounding molecules are moved closer to the chlorophylls.



Two Dimensional Spectra

How 2D spectra are created:

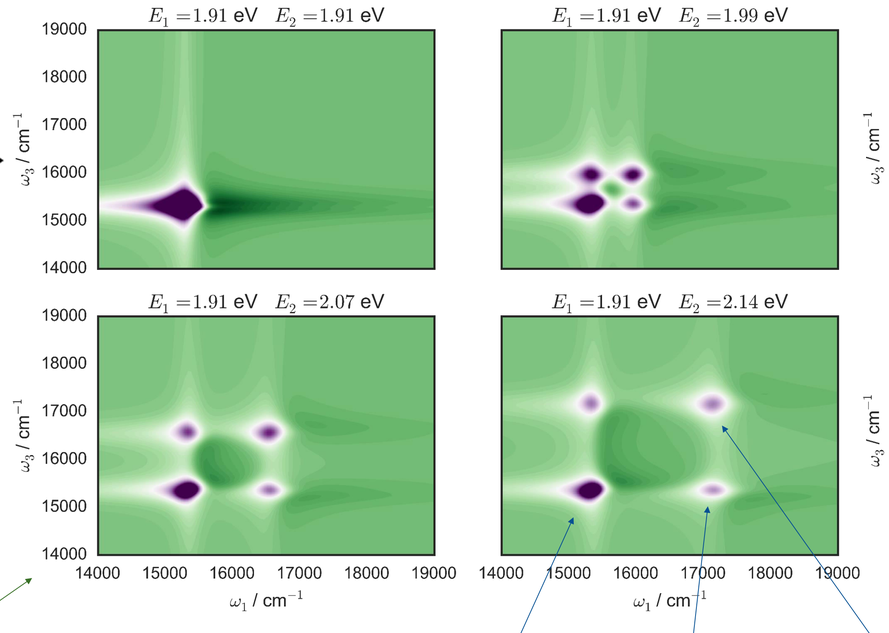


2D spectra can be used to understand **vibrational coupling** and **anharmonicities** within the molecules.

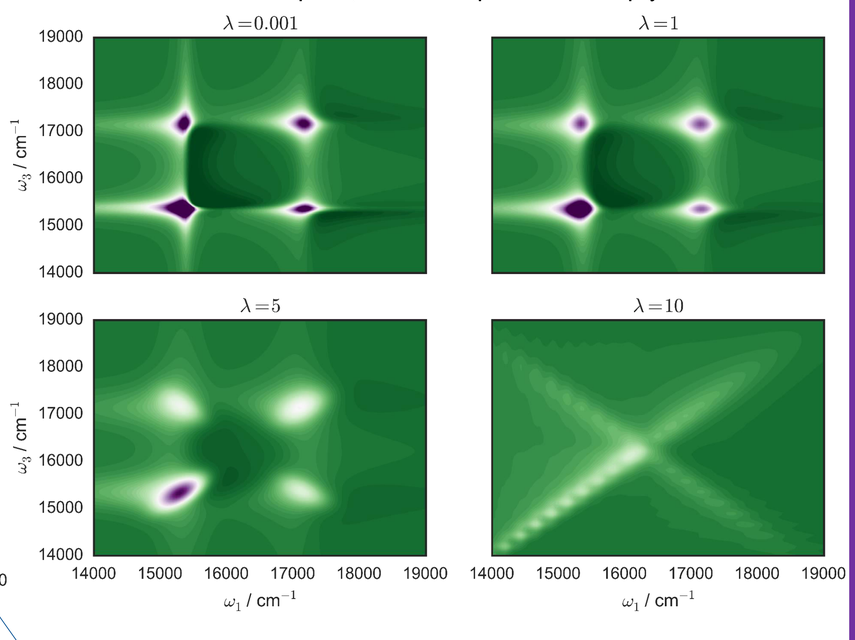
The sample is injected with 3 pulses from a femtosecond laser. Next, the light emitted by the relaxation of the molecule is observed.

This process is repeated several times, with different values of t_1 and t_2.

1. The effect of excitation energy E_2, on the 2D spectrum of chlorophyll



2. The effect of dissipation, λ on the 2D spectrum of chlorophyll



Similarly to the 1 dimensional spectra above, these 4 figures show how the **excitation energy** of the antenna affects the wavelengths that the system can absorb

Response from the **reaction centre**

Coupling

Response from the **antenna pigment**

As the dissipation parameter increases, the peaks become more circular, as the molecules' "memory" of its first excitation is lost.

Acknowledgements

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References

My molecular structure figures were taken from *Molecular Mechanisms of Photosynthesis* by R. E. Blakenship.

The graphs were created using Pyplot.

The other figures were taken from Wikipedia.