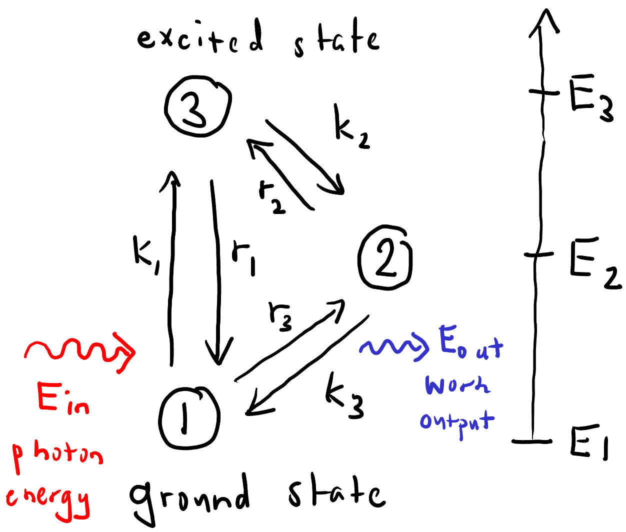
Simple model of light-sensitive protein



$$\frac{\Omega_{nm}}{\Omega_{mn}} = e^{-\beta(E_n - E_m - W_{nm})}$$

work done on sys

$W_{31} = E_{in}$

$$\frac{k_1}{r_1} = e^{-\beta(E_3 - E_1 - E_{in})}$$

$W_{23} = 0$ no work coupling

$$\frac{k_2}{r_2} = e^{-\beta(E_2 - E_3)}$$

$$\frac{k_3}{r_3} = e^{-\beta(E_1 - E_2 + E_{out})}$$

$W_{13} = -E_{out}$

$$\beta = \frac{1}{k_B T}$$

r_1 = spontaneous fluorescence: typically fast $\sim [\text{ps}-\text{ns}]^{-1}$

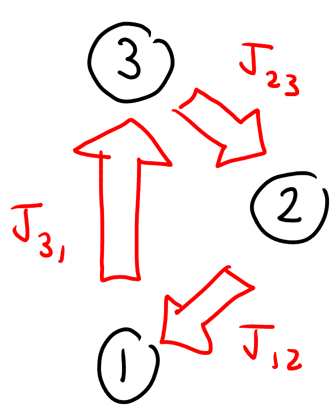
k_2 = rearrangement of protein after photon absorption (lose some energy to heat $E_3 \to E_2$)

$$\frac{k_2}{r_1} \sim 0.1 - 0.7$$

"quantum yield"

fraction of absorptions that are detected:

$$= \frac{k_2}{r_1 + k_2} < \frac{1}{2}$$



stationary: $$0 = \sum_m J^s_{nm}$$

$$\left.\begin{aligned} 0 &= J^s_{12} - J^s_{31} \\ 0 &= J^s_{23} - J^s_{12} \\ 0 &= J^s_{31} - J^s_{23} \end{aligned}\right\} \quad J^s_{12} = J^s_{23} = J^s_{31} = J$$

$$J = J_{12}^s = k_3 p_2^s - r_3 p_1^s$$
$$J = J_{23}^s = k_2 p_3^s - r_2 p_2^s \qquad p_1 + p_2 + p_3 = 1$$
$$J = J_{31}^s = k_1 p_1^s - r_1 p_3^s$$

algebra: $J = \dfrac{k_1 k_2 k_3 - r_1 r_2 r_3}{F}$

F → denominator: > 0 always

$$J = \frac{k_1 k_2 k_3}{F}\left(1 - \frac{r_1 r_2 r_3}{k_1 k_2 k_3}\right)$$

$$= \frac{k_1 k_2 k_3}{F}\left(1 - e^{-\beta(E_{in} - E_{out})}\right)$$

$E_{in} > E_{out}$: $J > 0$ NESS w/ clockwise current (working detector)

earlier: $E_{in} = E_{out} = 0 \Rightarrow J = 0$

(no work, only thermal energy exchange) ESS

if $E_{in} = E_{out} \neq 0 \Rightarrow J = 0$

(perfect conv. of photon energy ⇒ output work) next step: introduce a thermodynamic formalism to keep track of sys. properties, relate them to currents + derive general laws

state n $\ni$ energy E_n

subscript: state prop.

mean energy at time t $\quad \langle E \rangle_t = \sum_n p_n(t) E_n$

simpler notation $\quad E(t) = \langle E \rangle_t$

no subscript: avg

$$\frac{d}{dt} E(t) = \sum_n \underbrace{\frac{dp_n}{dt}}_{\sum_m J_{nm}(t)} E_n = \sum_{n,m} J_{nm}(t) E_n$$

$J_{mn}(t)$
$= - J_{nm}(t)$

$n \to m \quad m \to n$

$$= \frac{1}{2} \sum_{n,m} J_{nm}(t) E_n + \frac{1}{2} \sum_{n,m} J_{mn}(t) E_m$$

$$\frac{d}{dt} E(t) = \frac{1}{2} \sum_{n,m} \underbrace{J_{nm}(t)}_{\text{"current"}} \underbrace{(E_n - E_m)}_{\text{"potential diff." b/t } n + m}$$

power

take care of double counting edges

in general: state property A_n

avg. $A(t) = \sum_n p_n(t) A_n$

rate of change $\dfrac{dA(t)}{dt} = \dfrac{1}{2} \sum_{n,m} J_{nm}(t)(A_n - A_m)$

$\equiv \dot{A}(t)$