Physics 550 / Fall 2013

Problem Set September 12
Due: Thursday, September 19 before class

Problem 1: Fluorescent Resonant Energy Transfer

This problem investigates fluorescent resonant energy transfer (FRET) between donor, D, and acceptor, A, described, as derived in class, through the expression of the rate constant

$$k_{\mathrm{FRET}} \;=\; \frac{2\pi}{\hbar}\,|\vec{d}_{\mathrm{D}}|^2\,|\vec{d}_{\mathrm{A}}|^2\,\frac{\kappa^2}{R^6}\times J_{\mathrm{DA}} \tag{1}$$

Here $\vec{d}_{\mathrm{D}}$ ($\vec{d}_{\mathrm{A}}$) are the donor (acceptor) transition dipole moments of the optical transitions involved in the FRET process and R is the center-center distance of donor and acceptor molecules. κ is an orientation factor (unitless) defined through ($\hat{a}$ denotes a unit vector)

$$\kappa \;=\; \hat{d}_{\mathrm{D}}\cdot\hat{d}_{\mathrm{A}} \;-\; 3\,(\hat{d}_{\mathrm{A}}\cdot\hat{R})\,(\hat{d}_{\mathrm{D}}\cdot\hat{R})\;. \tag{2}$$

J_{DA} with unit 1 / energy denotes spectral overlap between donor and acceptor defined through (a factor E^{-4} is "absorbed" in the factors S_{D} and S_{A}

$$J_{\mathrm{DA}} \;=\; \int_{-\infty}^{+\infty} dE\, S_{\mathrm{D}}(E)\; S_{\mathrm{A}}(E) \tag{3}$$

where S_{D} and S_{A} are assumed normalized Gaussians (j =D, A)

$$S_j(E) \;=\; \frac{1}{\sqrt{\pi\sigma_j^2}},\exp\left[-\,(E\,-\,E_j)^2/\sigma_j^2\right] \tag{4}$$

In case of FRET between molecules of chlorophylls involving their so-called Q_y electronic transition, it holds approximately

$$k_{\mathrm{FRET}} \;=\; \kappa^2\,40\,\left(\frac{100\text{Å}}{R}\right)^6 \mathrm{cm}^{-1}\,\frac{1}{\mathrm{ns}}\,J_{\mathrm{DA}} \tag{5}$$

Here and below, cm^{-1} denotes an energy unit often used in molecular spectroscopy.

(a) Show that $|\vec{d}_{\mathrm{D}}|^2\,|\vec{d}_{\mathrm{A}}|^2$ has unit (energy)^2 (length)^6 and, hence, k_{FRET} in (1) has unit 1 / time.

(b) In case of the chlorophyll system holds very approximately for the normalized Gaussian spectra in (4): $\sigma_j = 250$ cm^{-1}, $E_{\mathrm{D}} = \Delta E + 150$ cm^{-1}, and $E_{\mathrm{A}} = \Delta E$. Evaluate $J_{\mathrm{DA}} \approx 0.001/\mathrm{cm}^{-1}$.

(c) What are the smallest and largest possible values of κ^2 in case that the chlorophylls have a fixed orientation?

(d) Assume that during the FRET process the chlorophyll molecules are isotropically distributed. One can choose in this case that $\hat{R}$ points in the direction of the z-axis. Present then the orientation of $\hat{d}_j$ through spherical coordinates θ_j (angle with respect to z-axis) and ϕ_j (azimutal angle), $j =$D, A. Using $d_{\rm D} \cdot \hat{d}_{\rm A} \,=\, \cos\theta_{\rm D}\,\cos\theta_{\rm A} + \sin\theta_{\rm D}\,\sin\theta_{\rm A}\,\cos(\phi_{\rm D} - \phi_{\rm A})$ show that κ is given by $\kappa \,=\, \sin\theta_{\rm D}\,\sin\theta_{\rm A}\,\cos(\phi_{\rm D} \,-\, \phi_{\rm A}) - 2\,\cos\theta_{\rm D}\,\cos\theta_{\rm A}$. Using the distribution function

$$p(\cos\theta_{\rm D},\, \cos\theta_{\rm A}, \phi_{\rm D}, \phi_{\rm A}) \;=\; 1/(4\pi)^2 \tag{6}$$

and values of $\cos\theta_{\rm D}$, $\cos\theta_{\rm A}$ in the interval [-1, 1] and $\phi_{\rm D}, \phi_{\rm A}$ in the interval $[0,\, 2\pi]$ calculate the average $\langle\kappa^2\rangle$ employing

$$\langle\kappa^2\rangle \;=\; \int_{-1}^{+1} d\cos\theta_{\rm D} \int_{-1}^{+1} d\cos\theta_{\rm A} \int_0^{2\pi} d\phi_{\rm D} \int_0^{2\pi} d\phi_{\rm A}\;\; [\,\kappa(\cos\theta_{\rm D},\, \cos\theta_{\rm A}, \phi_{\rm D}, \phi_{\rm A})]^2\;\; p(\cos\theta_{\rm D},\, \cos\theta_{\rm A}, \phi_{\rm D}, \phi_{\rm A}) \tag{7}$$

Hint: The answer is $\langle\kappa^2\rangle \;=\; 2/3$.

(e) The donor-acceptor pair D*A can either engage in fluorescence, i.e., D*A $\rightarrow$ DA, described by a rate $k_{\rm fl}$, or in FRET, i.e., D*A $\rightarrow$ DA*, described by a rate $k_{\rm FRET}$. Assume that the initial concentration of pairs D*A is $c(0)$. Argue why the time-dependence of the concentration of D*A is given by $c(t) \;=\; c(0)\,\exp[-\,(k_{\rm fl} + k_{\rm FRET})\,t\,]$. Argue, why the concentration $c'(t)$ of DA* obeys the differential equation

$$\frac{d}{dt} c'(t) \;=\; k_{\rm FRET}\, c(t) \tag{8}$$

where $c(t)$ is given above as the concentration of D*A. Evaluate $c'(\infty)$, i.e., the total concentration of DA* produced. Show then $q_{\rm FRET} \;\equiv\; c'(\infty)/c(0) \;=\; 1/(1 + (k_{\rm fl}/k_{\rm FRET}))$.

(f) Assuming $k_{\rm fl} \;=\; 1/{\rm ns}$ and $\langle\kappa^2\rangle \;=\; 2/3$, give the distances R at which the total FRET yield $q_{\rm FRET}$ assumes the values 0.01, 0.1, 0.5, 0.9, 0.99.

Problem 2: Case Study Ubiquitin

This case study introduces ubiquitin and the proteasome. You are asked to inspect these molecule in various forms by means of molecular graphics. Please work through the case study and then do as specified below, answering in scholarly English (full, grammatically correct sentences).

The case study material is available at http://www.ks.uiuc.edu/Training/CaseStudies/ (see Ubiquitin). For the exercises below you need to use VMD already employed in earlier homework sets.

(a) Do Exercise 1.
(b) Do Exercise 2.
(c) Do Exercise 3.