Problems

1. a. It was stated in lecture that if the rate of Förster transfer is proportional to \( r^{-6} \) (where \( r \) is the donor-acceptor distance), then the FRET efficiency is

\[
E_T = \frac{1}{1 + (r / R_0)^6}
\]

where \( R_0 \) is a constant. Prove it.

The donor excited state \( D^* \) can decay both by the Förster pathway (energy transfer to acceptor) and by non-Förster pathways:

\[
\begin{align*}
D^* & \xrightarrow{k_F} D \\
& \xrightarrow{k_{NF}} \text{(emission + non-rad. decay)}
\end{align*}
\]

Given \( k_F = a r^{-6} \), we have:

\[
E_T = \frac{k_F}{k_F + k_{NF}}
\]

\[
E_T = \frac{a r^{-6}}{a r^{-6} + k_{NF}} = \frac{a}{a + k_{NF} r^{-6}} = \frac{1}{1 + (r / R_0)^6}
\]

where \( R_0 = \left(\frac{a}{k_{NF}}\right)^{1/6} \)
b. The quantum yield of a dye "D" is 50%. The quantum yield of D is decreased to 30% when a dye "A" with an absorption spectrum that overlaps the emission of D is positioned 7 nm away from D. What is the expected quantum yield of D if A is moved to a position 3 nm away from D?

Here, because we are concerned with the quantum yield of D, we need to consider radiative and non-radiative decay individually:

\[
\begin{align*}
&\text{(energy trans.)} \\
&\text{(emission)} \\
&\text{(non-radiative decay)} \\
&k_F \\
&k_R \rightarrow k_{NR}
\end{align*}
\]

Quantum yield \( q = \frac{k_F}{k_R + k_F + k_{NR}} \)

Since \( q = 0.5 \) when \( k_F = 0 \) (no acceptor present)

we have \( 0.5 = \frac{k_F}{k_R + k_{NR}} \) \( \Rightarrow \) \( k_F = k_{NR} \equiv k' \)

At \( r = 7 \text{ nm} \), we have \( q = 0.3 = \frac{k}{2k + k_{F,7}} \)

since \( k_F = a r^{-6} \) (as above),

\[ 0.6 k + 0.3 k_{F,7} = k \Rightarrow 0.3 a (7 \text{ nm})^{-6} = 0.4 k \]
\[ a = \frac{4}{3} (7 \text{ nm})^6 \quad k = 1.6 \times 10^5 \text{ nm}^6 \]

At 3 nm,

\[ k_B = a r^{-6} = \left( \frac{1.6 \times 10^5}{(3 \text{ nm})^6} \right) k = 2.2 \times 10^2 k \]

Therefore,

\[ \frac{q}{b} = \frac{k}{2k + 220k} = 4.5 \times 10^{-3} \]

2. In a laser, a monochromatic light pulse of frequency \( v = \Delta E / h \) corresponding to an electronic transition in the lasing medium is amplified by stimulated emission from the excited state to the ground state. A requirement for this amplification is that the number of molecules in the excited state be greater than the number in the ground state. Explain why this “population inversion” is necessary to get light amplification. Can the population inversion be achieved by irradiating the lasing medium with light of frequency \( v \)?

Since the rate constants for absorption and stimulated emission are equal, \( (\# \text{ photons emitted}) - (\# \text{ absorbed}) \) cannot be \( > 0 \) unless \( \# \) molecules in the excited state is greater than \( \# \) in the ground state

\[ N_2 \quad \uparrow \quad k \quad \downarrow \quad N_1 \]

\[ \text{(emitted)} - \text{(absorbed)} = p k N_2 - p k N_1 \]

where \( p \) = radiation density

Population inversion cannot be achieved by simply irradiating the transition, because this can at best produce \( N_2 = N_1 \), and that only at large \( p \) when spontaneous emission is negligible.
3. At what magnetic field strength will an $^1$H nucleus resonate at 600 MHz? In this magnetic field, what is the ratio of the population of protons in the $m_s = +1/2$ and $m_s = -1/2$ states?

$$\Delta E = 8 \frac{h}{2\pi} \frac{H}{1} = h\nu$$

$$\Rightarrow \left[ H = \frac{2\pi \nu}{\gamma} = \frac{(2\pi)(6 \times 10^8 \text{ s}^{-1})}{2\pi \times 10^7 \text{ T s}^{-1}} = 13.09 \text{ T} \right]$$

$$\Delta E = h\nu = \left(6.6 \times 10^{-34} \text{ J s}\right) \left(6 \times 10^8 \text{ s}^{-1}\right) = 4.00 \times 10^{-25} \text{ J}$$

$$\frac{N_2}{N_1} = e^{-\frac{\Delta E}{kT}} = e^{-\frac{4 \times 10^{-25}}{4 \times 10^{-21}}} = 0.999$$

4. An organic dye molecule shows the following absorbance (left curve) and fluorescence emission (right curve) spectra:
a. The spectrum shows that the dye absorbs light over a range of wavelengths, for example, it absorbs approximately equally well at 480 nm and 505 nm. Explain how it is possible for the single dye molecule to absorb light at these two different wavelengths.

b. The spectra show a shift between the peak absorption wavelength (~490 nm) and peak emission wavelength (~515 nm). Explain what causes these two peaks to be at different wavelengths.

c. Explain why the two peaks must overlap.

1-6 are examples of the various absorption - non-radiative decay - emission sequences that contribute to the spectral peaks shown.

(a) different sequences have a range of absorption wavelengths (for example, $\lambda_{abs}$ 4 < $\lambda_{abs}$ 0)

(b) for all sequences $\lambda_{abs}$ < $\lambda_{emiss}$ because of non-radiative decay to the lowest vibrational level of the electronic ES. Therefore, the average emission wavelength is longer than the average absorption wavelength.

(c) sequence 1 will always exist. For it, $\lambda_{emiss}$ = $\lambda_{abs}$