ZAGADNIENIA BIOFIZYKI WSPÓŁCZESNEJ

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EXCITATION ENERGY TRANSFER IN BIOLOGICAL SYSTEMS

1 PHYSICAL NATURE OF EXCITATION ENERGY TRANSFER

The notion of excitation energy transfer applies to the exchange of energy between closed physical systems (molecules) excluding mass or charge transfer Thus the exchange is achieved thanks to the electromagnetic field which exists in the surrounding medium In most biological processes, excitation energy transfer involves exchange of quanta which belong to the visible part (or near UV and IR) of the frequency spectrum (i.e. 1.5 do 3.5 eV) These frequencies are associated to the motion of weakly bound electrons (slow electronic subsystem) Let us consider the interaction of an isolated molecule with a pure transverse electromagnetic field (frequency ω) Under the action of the electric field $\vec{E}_0(\omega)$ it appears, within the molecule, a polarization $\vec{P}(\omega)$ which -in the linear approximation is linked to $\vec{E}_0(\omega)$ by means of the complex polarizability tensor $\overline{\overline{\alpha}}(\omega)$

$$\vec{P}(\omega) = \overline{\overline{\alpha}}(\omega)\, \vec{E}_0(\omega) \tag{1}$$

If $\overline{\overline{\alpha}}(\omega)$ is known, it is possible to analyse the optical properties of the molecule For instance the absorption is proportional to the imaginary part of this tensor. For some particular frequencies (ω_0), the induced polarization becomes very large (resonance) and the absorption spectrum exhibits a strong absorption band In the first approximation, this band may be considered as an absorption line, and thus

$$Im\, \overline{\overline{\alpha}}(\omega) = \frac{\pi}{\hbar} d^2\, \vec{s}\, \vec{s}\, \delta(\omega_0 - \omega), \tag{2}$$

where δ denotes the Dirac distribution, $\vec{s}\,d$ is the dipole moment corresponding to the resonance frequency ω_0 (d length and $\vec{s}$ direction of the dipole).

In quantum mechanics it is possible to demonstrate that ω_0 corresponds to the frequency of a stationary state of the molecular electronic system. Concerning our present discussion, equation (2) indicates that the optical properties of a molecule are -near a resonance- similar to those of an oscillating dipole (proper frequency ω_0)

An electric field $\vec{E}_0(\omega)$ induces a polarization $\vec{P}(\omega)$, but an oscillating dipole gives rise to an electromagnetic field (fig. 1). It may be evaluated by means of the Maxwell equations At short distances ($r \ll \lambda = \omega/c$, c velocity of light), the emitted electric field $\vec{E}(\omega)$ may be calculated in the static approximation (Coulomb law) and

$$\vec{E}(\omega) = \vec{E}_c(\omega) = \frac{1}{r^3} \left(\frac{\vec{r}\, \vec{r}}{r^2} \right) \vec{P}(\omega) \tag{3}$$

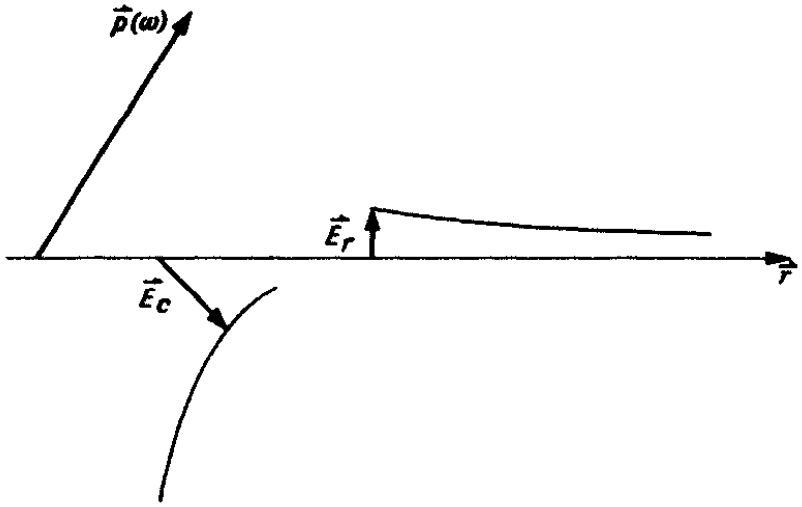

Fig. 1. Electric field emitted by an oscillating dipole $\vec{P}\cdot\vec{E}_c$ Coulomb and $\vec{E}_r$ radiative fields

The corresponding wave is longitudinal.

At large distances ($r \gg \lambda$) the field $\vec{E}$ is transverse and correaponds to the radiative part $\vec{E}_r(\omega)$ of the emitted wave·

$$\vec{E}_r(\omega) = \frac{\omega^2}{c^2}\, e^{i\omega/cr}\left(1 - \frac{\vec{r}\cdot\vec{r}}{r^2}\right)\vec{P}(\omega)\,. \tag{4}$$

In biological systems r is small as compared to the wavelength λ. Thus the exchange of energy between molecules is achieved by means of longitudinal photons At large distances the transverse field represents the radiation scattered by the molecule. (For macroscopic crystals it it necessary to take into account the intermediary distances retardation effect, Agranovitch [1])

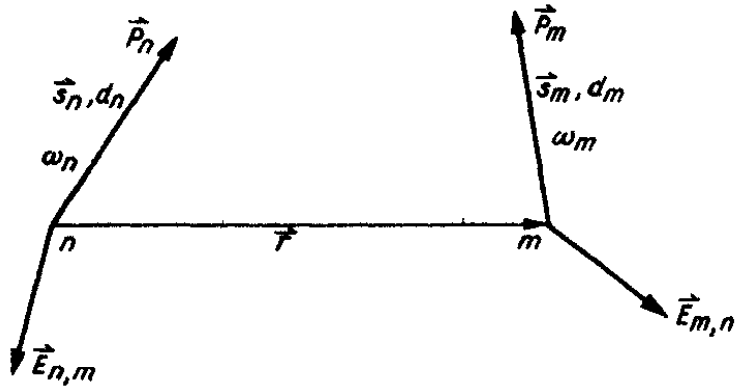

Fig. 2. Coulomb interaction between two oscillating dipoles

Now we consider a system (dimer) with two oscillating dipoles ($\vec{P}_n$ and $\vec{P}_m$ at the apart distance r (fig. 2) (proper frequencies ω_n and ω_m, dipole moments $\vec{s}_n d_n$ and $\vec{s}_m d_m$). The interaction between the dipoles takes place through the Coulomb field given by equation (3). Then for instance the field $\vec{E}_{nm}$ acting upon $\vec{P}_n$ is

$$\vec{E}_{nm}(\omega) = \overline{\overline{T}}_{nm}\, \vec{P}_m(\omega), \tag{4a}$$

where

$$\overline{\overline{T}}_{nm} = \left(3\frac{\vec{r}:\vec{r}}{r^2} - 1\right)\frac{1}{r^3}\vec{P}_m\,. \tag{4b}$$

The motion of $\vec{P}_n$ is described by the equation

$$\frac{d^2\vec{P}_n}{dt^2} + \omega_n^2\,\vec{P}_n = 2\,\omega_n\frac{d_n^2}{\hbar}\vec{s}_n\,(\vec{s}_n\ \vec{E}_{nm}) \tag{5}$$

Let us introduce the two complex amplitudes q_n and q_m defined in the following way

$$\vec{P}_n = d_n\vec{s}_n\, Re\, q_n\,,\ \vec{P}_m = d_m\vec{s}_m\ Re\ q_m\ (Re = \text{real part}), \tag{6}$$

we find from (5)

$$\dot{q}_n = -\,\iota\omega_n q_n - \iota M_{nm}\, q_m\,, \tag{7}$$

where

$$M_{nm} = -\frac{1}{\hbar}d_n\vec{s}_n\ \overline{\overline{T}}_{nm}\vec{s}_m\, d_m\,, \tag{8}$$

and

$$\dot{q}_n = \frac{d\,q_n}{dt}\,.$$

[In quantum mechanics analogous equations are obtained in the frame of the second quantization Starting from equation (7) it is necessary to replace q_n by b_n and q_n^* (conjugated of q_n) by b_n^+, where b_n and b_n^+ are the annihilation and creation operators for an excitation [1]]

From equation (7) it appears that the coupling of two molecules through longitudinal electromagnetic waves is formally equivalent to a linear coupling of two oscillating dipoles.

2 COUPLING OF ELECTRONIC AND NUCLEAR MOTIONS

As yet we have supposed that the electronic motion was not disturbed by the nuclear one. Thus to the proper frequencies were assigned discrete and well defined values But the molecules of biological interest are made of many nuclei and consquently present a large number of vibrational modes. To some of these modes correspond large frequencies ($\hbar\omega > kT$). One, or a few number of these modes and an electronic excitation may be created at once This case is very similar to the one analysed before. The proper frequency of the associated oscillating dipole is equal to the sum of the pure electronic and vibrational modes frequencies (vibronic mode). On the other hand, the low frequency modes ($\hbar\omega < kT$)

give rise to multi-phonon processes. They introduce a statistical modulation of the proper frequencies. This kind of "nuclear noise" plays an important part in the process of excitation energy transfer

Let us return to the case of an isolated molecule In the absence of any coupling with nuclear motion, the time evolution of the amplitude of the polarization is governed by the equation (see equation 7)

$$\dot{q}_n = -\imath\omega_n q_n \quad (M_{nm} = 0),$$

and (equation 2) the imaginary part of $\bar{\bar{\alpha}}$ (i e. the absorption) is proportional to

$$Im\,\bar{\bar{\alpha}} \sim \delta(\omega_n - \omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{\imath(\omega - \omega_n)t}\, dt,$$

By the mere fact of the low frequency vibrational modes, ω_n is a stochastic function of the time $\omega_n(t)$ Then·

$$\dot{q}_n = -\imath\omega_n(t)\, q_n,$$

$$q_n = \exp -\imath \int_0^t \omega_n(t')\, dt'\; q_n(0), \tag{9}$$

and

$$Im\,\bar{\bar{\alpha}} \sim \frac{1}{2\pi} \int_{-\infty}^{+\infty} < \exp(\imath\omega t - \imath \int_0^t \omega_n(t')\, dt' > dt, \tag{10}$$

where $< .. >$ denotes a mean value over the frequencies

Since the value of ω_n is not well defined, the absorption band has a finite band width w, and its shape is given by equation (10) The explicit solution of such an equation was obtained by K u b o [3].

Let us introduce the fluctuating part $\omega_n'(t)$ of the proper frequency,

$$\omega_n'(t) = \omega_n(t) - <\omega_n(t)>, \tag{11}$$

and the correlation time τ_c of ω_n'

$$\tau_c = \int_0^\infty <\omega_n'(t)\; \omega_n'(t+\theta)>\, d\theta/\Delta^2, \tag{12}$$

where

$$\Delta = <\omega_n'^2(t)>^{1/2}, \tag{13}$$

For molecules of biological interest $\Delta\tau_c \gg 1$ (The correlation time τ_c associated to low frequency vibrational modes is about 10^{-11}–10^{-12} s, and Δ which is of the same order of magnitude than w is about 10^{14} s^{-1}). In this condition [3] one finds

$$<\exp -i\int_0^t \omega_n'(t')\,dt'> \sim \exp -\frac{\Delta^2 t^2}{2}. \tag{14}$$

The absorption band is a Gaussian line centred at the frequency $<\omega_n(t)>$ Its band width w is given by the following equation

$$w = 2\,35\,\Delta. \tag{15}$$

In a simpler way, it means that if τ_c is large we are in the static case and

$$<\exp -i\int_0^t \omega_n'(t')\,dt'> \sim \int e^{-\tau\omega_n' t}\, p(\omega_n')\,d\omega_n', \tag{16}$$

where $p(\omega_n')$ is the distribution law of ω_n', $p(\omega_n')$ may be expressed in terms of nuclear coordinates. R being one of these coordinates, the energy of the molecule in the ground state $E_0(R)$ and in the excited state $E_n(R)$ depend on R (fig 3) Introducing the quantity $x = \dfrac{R - R_0}{R_n}$ where R_0 and R_n are the quilibrium positions in the two states

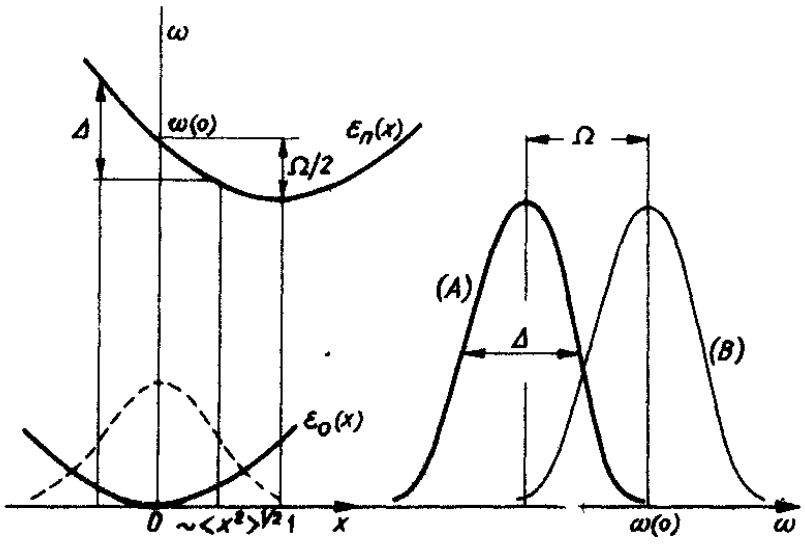

Fig. 3 Potential curves for the motion of nuclei in the ground state $Eo(x)$ and in the excited state $En(x)$
(B) and (A) are respectively the absorption and the fluorescence bands corresponding to the transitions between these two states

$$E_o(x) = \frac{1}{2}\hbar\Omega x^2, \tag{17a}$$

$$E_n(x) = \hbar(\omega_n(o) + \frac{1}{2}\Omega x^2 - \Omega x) \tag{17b}$$

Thus.

$$\omega_n(x) = \omega_n(o) - x\Omega, \tag{18}$$

$$p(\omega_n) \sim \exp - \beta E_o(x), (\beta = {}^1/kT), \tag{19}$$

and

$$Im\ \bar{\bar{\alpha}} \sim <\delta\ (\omega_n(o) \quad x\Omega - \omega)>_B, \tag{20}$$

where $<..>_B$ denotes a mean value obtained with help of the Boltzman law (19) As this law is a Gaussian function of x (equation 17), the absorption band is also a Gaussian line Its band width w is given by the relation

$$w = 2\,35\ <(\omega_n(x) - \omega_n(o))^2>_B^{1/2} = 2\,35\ (kT/\hbar\Omega)^{1/2} \tag{21}$$

As it may be seen on fig 3, Ω is equal to the Stokes shift of the maxima of the absorption and fluorescences bands

Let us consider, in the same formalism, the case of a dimer The equations of motion (7) may be written

$$\dot{q}_n = -\imath\omega_n(x_n)\, q_n - \imath\, M_{nm}\, q_m, \tag{22a}$$

$$\dot{q}_m = -\imath\omega_m(x_m)\, q_m - \imath\, M_{mn}\, q_n, \tag{22b}$$

x_n and x_m represent intramolecular vibrational modes. (The effect of intermolecular modes on Mnm is neglected).

It appears two resultant modes for the dimer, with the two proper frequencies $\omega_{\pm}(x_n, x_m)$

$$\omega\pm(x_n, x_m) = {}^1/2\left[\omega_n(x_n) + \omega_m(x_m) \pm ((\omega_n(x_n) - \omega_m(x_m))^2 + 4\, M_{nm}^2)^{1/2}\right]. \tag{23}$$

It must be notice that even if the two molecules are identical, the root mean square deviation σ_{nm} of the difference between their two proper frequencies is finite. If the two vibrational modes X_n and X_m are not coupled -which is generally the case in biological systems-.

$$\sigma_{nm} = <(\omega_n(x_n) - \omega_m(x_m))^2>_B^{1/2} \simeq 2\ <(\omega_n(x_n) - \omega_n(o))^2>^{1/2} \simeq 0\,6\, w. \tag{24}$$

Thus the vibrational modes remove the degeneracy which was existing between the two electronic oscillators

Three different cases may by distinguished·

a) $Mnm > \sigma\ nm$ strong coupling. The dimer absorption spectrum consists of two Gaussian band centred at the frequencies $\omega_n(o) \pm M_{nm}$ ($\omega_n(o)$ is supposed to be equal to $\omega_m(o)$) If the two vibrational modes x_n and x_m are not coupled the band width W' of these Gaussian lines is equal to $W/\sqrt{2}$ The circular dichroism has the classical form of the difference between two Gaussian bands,

b) $Mnm \ll \sigma\ nm$ That is the case of a very weak interaction between two different oscillators. There is a small perturbation of the proper frequencies $\omega_n(o)$ and $\omega_m(o)$ (Van der Waals interactions) and -generally- the appearance of a weak circular dichroism,

c) the most interesting case in biology is the following

$$Mnm < \sigma\ nm,$$

but $|\omega_n(o) - \omega_m(o)| < w$ (the widths of the absorption bands of the two monomers are supposed to be equal).

That is the case of weak coupling between two identical oscillators. The dimer absorption band is similar to the monomer spectrum but presents a freqnency shift equal to about $-2\ Mnm\ (\vec{s}_n \cdot \vec{s}_m)$ It appear also a S-shaped circular dichroism. It must be notice that in this case of weak coupling the circular dichroism is not the result of the difference between two Gaussian bands but (P a i l l o t i n [5]).

circular dichroism $\sim Im(\alpha)\ Re(\alpha)$

where α = Trace of $\bar{\bar{\alpha}}$.

3. TRANSPORT OF EXCITATIONS

The probability $p_n(t)$ to find, at the instant of time t, an excitation localized on the nth molecule of an aggregate is equal to the square modulus of $q_n(t)$ As an excitation is not necessarily localized it is useful to introduce the density matrix $\bar{\bar{G}}(t)$, such that

$$\bar{\bar{G}}(t), = \{G_{nm}(t)\},$$

where

$$G_{nm}(t) = q_n(t)\, q_m^*(t)\ \ (p_n(t) = G_{nn}(t)),$$

when $n \neq m$ Gnm is a measure of the extent of the delocalization of the excitation over the two molecules n and m.

To analyse the motion of excitations equations (22) must be written by taking into account the time fluctuations of the proper frequencies (equation 9) Introducing the matrix $\Gamma(t) = \{\Gamma_{nm}(t)\}$ defined as follows:

$$\Gamma_{nm}(t) = \exp\left(i \int_0^t (\omega_n(t') - \omega_m(t'))\, dt'\right) G_{nm}(t),$$

one obtains

$$\dot{\Gamma}(t) = -\imath M(t)\ \Gamma(t) + \imath\ \Gamma(t) M(t)$$

$$= -\imath [M(t),\ \Gamma(t)] = -\imath\ M^{\times}(t)\ \Gamma(t), \tag{25}$$

where

$$Mnm(t) = \exp\left(\imath \int_0^t (\omega_n(t') - \omega_m(t'))\ dt'\right) Mnm, \tag{26}$$

$[M, \Gamma]$ or $M^{\times}\Gamma$ denotes a commutator

It appears clearly that the time fluctuations of $\omega_n(t)$ induce time fluctuations of the coupling matrix M Formally equation (25) is very similar to equation (9), $M^{\times}(t)$ playing the role of $\omega_n(t)$ Then firstly we have to look at the non fluctuating part of $Mnm(t)$ i e $<Mnm(t)>$ This mean value may be obtain with the help of equations (14) and (24)

$$<Mnm(t)> = Mnm\ \exp(\imath(<\omega_n> - <\omega_m>)t - t^2\ \sigma_{nm}^2) \tag{27}$$

If $Mnm > \sigma_{nm}$ (strong coupling), $<Mnm(t)>$ is not negligible and the motion of excitation is coherent

In the case of a dimer, and starting with localized excitations the time dependence of $\rho_1(t)$ is given by the following equation

$$\rho_1(t) = \frac{1}{2} + \frac{1}{2}(\rho_1(o) - \rho_2(o))\ \cos\ 2\ M_{12}\ t \tag{28}$$

The excitation is exchanged periodically between the two molecules

In the other hand if $Mnm < \sigma\ nm$ the motion is not coherent Only the fluctuating part of $Mnm(t)$ plays a role We must introduce a correlation time τ_c' and a characteristic frequency Δ' as those which were defined in equations (12) and (13)

$$\tau_c' = \frac{1}{\Delta'^2} \int_{-\infty}^{+\infty} <M_{nm}(t)\ M_{mn}(t+\theta)> d\theta, \tag{29a}$$

$$\Delta'^2 = M_{nm}^2 \tag{29b}$$

Then according to equations (14) and (21)

$$\tau_c' = \sqrt{\frac{\pi}{kT\Omega}}\ \exp[-(<\omega_n> - <\omega_m> - \Omega)^2/4\Omega kT], \tag{30}$$

if the two molecules are identical and if the Stokes shift $\Omega = 0$

$$\tau_c' \simeq 4/w$$

Then if $\tau_c'\Delta' = \frac{4Mnm}{w}$ is small, the motion of excitation is incoherent and is governed by a diffusion equation The rate of transfer L_{nm} of an excitation from the nth molecule to the mth is equal to

$$L_{nm} = \tau_c' M_{nm}^2 \tag{31}$$

This equation is similar to the Forster one (Forster [2]) For a symetrical dimer one obtains

$$\rho_1(t) = \frac{1}{2} + \frac{1}{2}(\rho_1(o) - \rho_2(o))\, e^{-2L_{12}t}, \tag{32}$$

$\rho_1(t)$ tends in an irreversible way towards an equilibrium value

If $\tau_c'\Delta'$ is not very small, the motion of excitations is coherent during a small time and a non-Markoffian motion must be expected (Lang of Firsov [4]) To sum up

a) if $Mnm > \sigma_{nm} \sim w$ (equation 24) the coupling is strong and the motion is coherent There is a reversible exchange of excitation between molecules and the frequency of exchange is proportional to Mnm r^{-3} mechanism (r is the distance between the considered molecules equations (8) and (4)),

b) if $Mnm < W$ and $\langle\omega_n\rangle \simeq \langle\omega_m\rangle$, the coupling is weak and the motion incoherent The rate of excitation transfer is proportional to M_{nm}^2 r^{-6} mechanism

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REFERENCES

[1] Agranovitch V M, *Teoria excitonov*, Nauka, Moscow (1968).
[2] Förster T, Am Phys., 2, 55 (1948).
[3] Kubo R., Lect. in Theor. Phys. Boulder, Intersc Publis., NY 1 120 (1958).
[4] Lang I. G., Firsov Y A., Sov Phys. JETP, 16, 1301–1312 (1963)
[5] Paillotin G, *Thesis*, Paris Sud (Orsay) (1974).

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PRZEKAZYWANIE ENERGII WZBUDZENIA W UKŁADACH BIOLOGICZNYCH

Streszczenie

Problem stanów wzbudzonych i przekazywania energii wzbudzenia ma duże znaczenie w wielu podstawowych procesach biologicznych Praca zawiera wyniki oryginalnych rozważań teoretycznych dotyczących przekazywania energii wzbudzenia przeprowadzonych na gruncie elektrodynamiki kwanto-

wej Rozwazania przeprowadzone są dla stosunkowo prostych modeli, lecz ich prostotă pozwala na przeprowadzenie podobnego typu rozumowania nawet dla bardzo złożonych układów biologicznych

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