*ON THE ENERGY TRANSFER IN BIOLOGICAL SYSTEMS**

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It seems likely that in various biological systems energy consuming chemical reactions are coupled to delocalized states of energy. Let us suppose that the circles in Figure 1 represent an aggregate of, say, 100 molecules to which we communicate an energy quant. We suppose one of the molecules, labeled m, to be close to another molecule or molecular aggregate S, which will eventually use the energy, and thus act as a sink. The question is how the energy quant can reach that sink. Two different mechanisms could be proposed, an individual and a collective one.

(*a*) *The individual picture:* At any given instant, the energy of excitation is considered to belong to one individual molecule of the system. Through a dipole-dipole interaction between two neighboring molecules in resonance, the energy "jumps" from one molecule to another. The energy in this picture "migrates" in a way similar to the Brownian motion of a particle, until it reaches S. This picture has been treated by J. and F. Perrin,[1] and T. Förster.[2]

(*b*) *The collective picture:* In this picture, which has been initiated by Frenkel[3] in solid-state physics and worked out by others,[4] the energy is delocalized, behaves more like a wave and can be directly transmitted to the sink. We feel that this mode of transmission, which, with certain modifications, holds also for an electron, has not been sufficiently appreciated in biology. Such delocalized states are represented in quantum mechanics as a superposition of localized states. Thus, for example, we might let the symbol Φ_k represent the absorbing molecules with the excitation localized on, say, the Kth molecule. Then the delocalized state would be represented by a superposition of the localized wave functions:

$$a_1\Phi_1 + a_2\Phi_2 + \ldots + a_N\Phi_N.$$

One describes the entire system (molecules plus sink) by the product of the wave function above and another wave function (call it ξ) which represents the sink. We can let ξ_0 represent the sink before it has trapped the energy, ξ_1, afterwards. The probability per unit time that the energy will be trapped is proportional to the square of the quantum mechanical matrix element of the coupling energy H' which connects the initial state

$$\Psi_i = (a_1\Phi_1 + a_2\Phi_2 + \ldots + a_N\Phi_N)\xi_0$$

to the final state

$$\Psi_f = \Phi_0\xi_1$$

where Φ_0 is the wave function of the aggregate of molecules in the ground state. Because of the short range of the forces which couple the sink to the collection of the molecules, the matrix element will be zero, unless $a_m \neq 0$. The matrix element for the transition of the energy to S will be equal to the coefficient a_m multiplied by the coupling energy:

$$\int \Psi_f^* H' \Psi_i d\tau = \int (\Phi_0 \xi_1)^* H^1 (a_1 \Phi_1 + a_2 \Phi_2 + \ldots + a_N \Phi_N) E_0 d\tau = a_m \int (\Phi_0 \xi_1)^* H^1 \Phi_m \xi_0 d\tau.$$

If the sink is strongly coupled to the adjacent molecule, that is, if

$$\int (\Phi_0 \xi_1)^* H^1 \Phi_m \xi_0 d\tau$$

is very large, then the probability per unit time for the energy to be trapped will be large, even though at the time of trapping a_m (i.e., the probability of the excitation being near to the sink) is small.

In the individual picture, S could absorb the energy only if it happened to migrate to m. A random migration of this kind would be slow if the number of the molecules in the collection were large, for example, 100 as in Figure 1. The excitation would have to make on the order of $(100)^2$ jumps before reaching S.

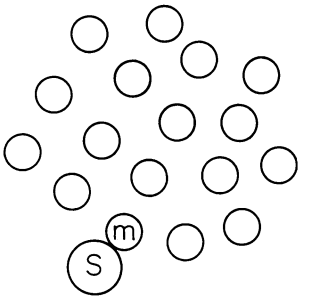

FIG. 1.

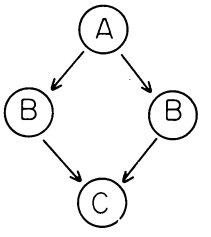

FIG. 2.

Speaking roughly, the individual picture is valid when the time needed for the thermal motions to destroy phase relationships is smaller than the time needed for the excitation to make a single jump. Let us try to make this criterion more precise. In the individual picture, one makes the perturbation expansion assuming that the coupling energy which causes excitation to migrate can be treated as a small quantity. Since the range of coupling is very short, a jump to the next nearest (from A to C in Fig. 2) neighbor is a second-order effect, involving excitation of the nearest neighbors (B) as intermediate states. The number of these intermediate neighbor molecules will be called n. In order for the picture of individual jumps to be valid, the perturbation series must converge—i.e., it must be easier for the excitation to make a short jump from A to B than a long one from A to C. If we assume that the effect of thermal motions is to broaden the excited level into a Lorentzian shape of width $\hbar\Gamma$, then the condition for convergence of the perturbation series turns out to be $\Gamma t_1/n^2 > 1$. Here t_1 is the time needed for a jump to an adjacent molecule.

We can try to apply these considerations to biological systems, say, to a granum of a chloroplast. If one accepts the idea of the photosynthetic unit of Emerson and Arnold,[5] then the situation is similar to that in Figure 1.

A photon is absorbed somewhere in a group of about 200 chlorophyll molecules and is transmitted to an enzyme system (S) where it is utilized. Franck and Livingston[6] have pointed out that since the fluorescence yield of chlorophyll *in vivo* is only 10^{-3}, the absorption must take place in a thousandth of the fluorescence decay time (10^{-8} sec), thus in 10^{-11} sec. If the transfer proceeded by individual random jumps, it would have to make 10^4 of these in 10^{-11} seconds, that is, t_1 would

have to be 10^{-15} seconds. A reasonable figure for the collision broadening of the excited level would be given by $\Gamma \sim 10^{13}$ sec^{-1}. Since the chlorophyl molecules are thought to be arranged in a monomolecular layer, we let $n = 2$, then

$$\frac{\Gamma t_1}{n^2} \sim 2 \times 10^{-3}.$$

Therefore the condition for convergence of the perturbation series is by no means fulfilled, and in order to get a valid approximation, one would have to solve the secular equation, which would lead to nonlocalized states. Further work in this direction is in progress.

The above considerations hold also for more extensive systems. It seems possible that they can be applied to biological processes other than photosynthesis. For example, excitation processes in the retina could be mentioned. The light wave focused on one visual rod is coherent within the area of this rod. It seems probable that this collective character of the excitation is important for the formation of the signal in the adjoining nervous system. It also seems possible that collective activities play a role in the function of the central nervous system and relations may be found, say, between conscience and nonlocalized electronic states, or S and storage of memory.

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[4] See the review of M. Kasha, *Revs. Mod. Phys.*, **31**, 162 (1959).

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*CALCIUM UPTAKE BY RAT KIDNEY MITOCHONDRIA**

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It has become increasingly apparent that an understanding of the biochemical events involved in the transport of calcium across biological membranes is essential to the ultimate elucidation of the mechanisms of action of vitamin D and parathyroid hormone. It is well established that the primary physiological action of vitamin D is to improve calcium absorption by the small intestine[1] and that parathyroid hormone is involved in blood calcium homeostatic mechanisms.[2] The hormone also has been shown to improve intestinal absorption of calcium.[3] *In vitro* experiments with everted intestinal loops or sacks have further demonstrated that vitamin D and parathyroid hormone increase the transport of calcium across the intestinal membrane.[4–7]

Slater and Cleland[8] found that heart muscle sarcosomes could take up large