ELECTRON TRANSFER:

Exploiting Thermal Motion

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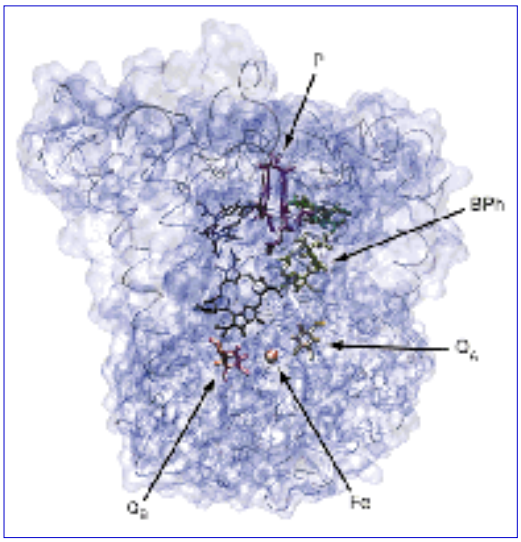
The molecular machines of living cells are made from soft materials--biopolymers like proteins and RNA. These machines work at physiological temperatures and thus experience thermal motion, yet their function, which requires correct alignment of parts and steering of reactions, is executed with precision. Proteins do not lose control even when electrons are the carriers of function and quantum dynamics, with its sensitivity to interference effects and minute positional changes, reigns.

What are the mechanisms that make protein function so robust against thermal motion? On page 114 of this issue, Balabin and Onuchic (1) provide a fascinating answer to this question. The authors combine molecular dynamics and quantum chemistry to study electron transfer processes in the photosynthetic reaction center (RC) of the bacterium *Rhodobacter sphaeroides* (2). They conclude that electron transfer may occur through a web of tunneling pathways, with constructive or destructive interference between pathways that is typical for the wavelike processes of quantum mechanics (3). The pattern of interference that arises is linked to the effect of thermal motion, which appears to be exploited by the RC to tune the reaction kinetics.

The RC acts as a solar battery that generates an electrical potential from sunlight. The first step in photosynthesis is the absorption of light by an antenna pigment. This absorbed energy is then transferred to the RC, which becomes electronically excited. The RC is responsible for using this electronic excitation to transfer electrons across the photosynthetic membrane these electrons are subsequently used to fix carbon. In the overall electron transfer process, two electrons combine with two protons, turning a quinone (Q_B) into a hydroquinone (Q_BH_2). The associated electron transfer proceeds in three steps. Balabin and Onuchic focus on the second and third steps, in which an electron is transferred from bacteriopheophytin (BPh) to quinone Q_A and from there to quinone Q_B. After the latter is turned into Q_B^-, it shifts inside the protein to a new location, speeding up the transfer of the second electron (4).

The RC functions not despite its thermal motion but by exploiting it. Electron transfer is strongly coupled through the Coulomb interaction to the surrounding medium and is thus controlled by thermal motion of the environment. The initial and final states of electron transfer--the states in which the electron is at the donor and at the acceptor, respectively--are only very weakly coupled to each other by an energy *D*. Quantum physics requires that the two states must be energetically well matched for the transfer to occur. This match is achieved sporadically through energy fluctuations induced by thermal motions of the surrounding protein matrix (see the figure), as described by the celebrated Marcus theory (5) and its generalizations (6).



Environment matters. Arrangement of prosthetic groups involved in the electron transfer reactions in the RC. The protein matrix is shown in transparent blue with its backbone presented by a thin black tube. Excitation energy is transferred from the light-harvesting proteins to a pair of bacteriochlorophylls (P) (purple); the energy drives the transfer of electrons through BPh to quinone Q_A and quinone Q_B. The thermal motion of the protein matrix is strongly coupled to the electron transfer process through Coulomb interaction and through alterations in the tunneling pathways of the electron, for example, between Q_A and Q_B. Figure produced with the program VMD (10).

The coupling energy *D* itself has long been considered immune to thermal motion, but researchers have recently started to question this assumption (7). Balabin and Onuchic now make a dramatic case for the dependence of *D* on thermal motion. The coupling arises through an effective conduction of electrons, which occurs easily within chemically bonded protein components but with difficulty when jumps between nonbonded elements, that is, between the edges of side groups, are necessary. The electrons often explore not a single path linking the donor to the acceptor, but rather a web of pathways. Because of the quantum nature of electron motion, interference effects arise between pathways. This effect is familiar from the diffraction experiment described in quantum mechanics textbooks: When electrons have to pass through a plate with two open slits, they experience destructive and constructive interference of their two possible routes, resulting in a diffraction pattern on the panel behind the plate. At any one point on the panel, the electrons experience a specific interference--destructive at points of low electron density, constructive at points of high electron density. Likewise, electrons transferred through the RC experience interference between donor and acceptor, arising from multiple paths as if

they were multiple slits in the RC.

Balabin and Onuchic show that when the interference effect is mainly constructive, as in the case of the BPh to Q_A transfer, the coupling and hence the electron transfer are almost independent of thermal motion. In contrast, in the case of destructive interference, such as the Q_A to Q_B transfer, thermal motion exerts a strong influence. In the latter case, thermal fluctuations provide the electron with an opportunity to take advantage of occurrences of minimum destructive interference, but the electron has to wait for these events to happen and, accordingly, the electron transfer rate depends on the degree of thermal motion.

Electron transfer from BPh to Q_A was found to be dominated by two constructively interfering paths, whereas the transfer from Q_A to Q_B appeared to proceed through a web of pathways with a high degree of destructive interference. The authors suggest that for the Q_A to Q_B transfer, the electron probes the different paths that arise in the course of thermal fluctuations and selects for the actual transfer event pathways that occur only for suitable conformations; the latter may deviate substantially from the crystal structure.

Electron transfer processes are ubiquitous in cellular bioenergetics and require high efficiency as well as robustness against thermal disorder. The scenario that emerged in the study of Balabin and Onuchic shows that natural systems can go beyond the ubiquitous thermal activation for barrier crossing in using thermal fluctuation to their advantage. This effect is likely to occur in instances other than the RC. An example has been found already in the light-harvesting system that fuels the RC with energy. This system contains aggregates of chlorophylls that, in the absence of thermal motion, share their excitation coherently in the form of so-called excitons but appear to revert to localized, less coherent excitations through thermal noise (8, 9).

References

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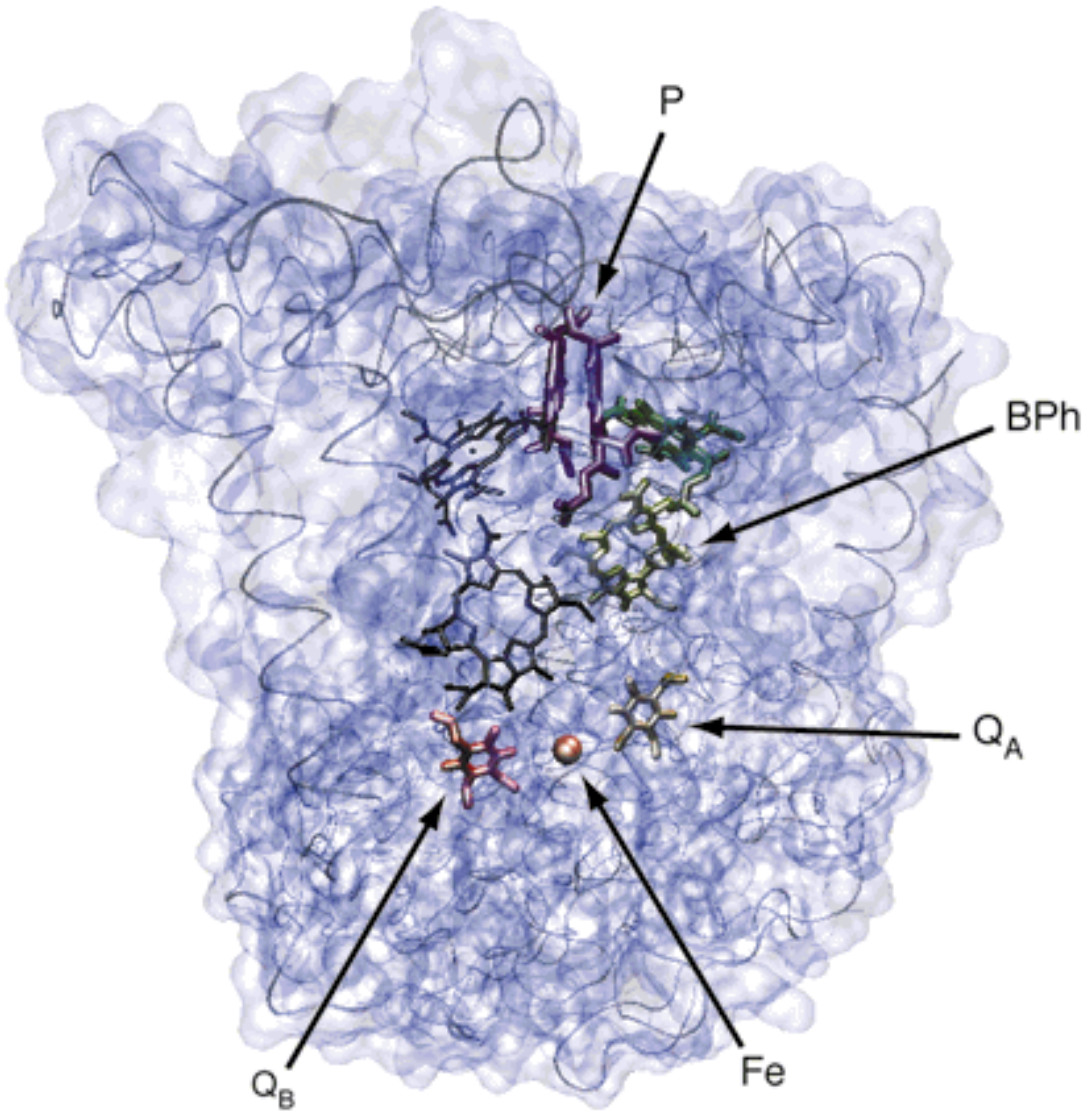

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