

The effect of image force on the efficiency of electron tunneling through macromolecular structures

Elmar G. Petrov

The Bogolubov Institute for Theoretical Physics, Ukrainian Academy of Sciences, 252143 Kiev, Ukraine

Received: 29 June 1992 / Accepted: 4 February 1993

Abstract. In electron tunneling (ET) along the boundary of two media with different high-frequency dielectric permittivities, the energy gap for the tunneling electron is affected by image forces. Macromolecules and macromolecular structures contain segments possessing different permittivities. Therefore, in any description of ET one must take image forces into account. Here, the spatial form of donor-acceptor ET through bridged molecular groups situated near macromolecular segments is investigated. It is shown that image forces can significantly reduce the energy levels of an electron on the bridge groups. As a result, the ET rate in the donor-bridge-acceptor system can increase by many orders of magnitude. The effect is more favorable for extended bridged chains. This fact may be used in explaining donor-acceptor conductivity of electron pathways in real macromolecular biological structures. Bridged groups in electron pathways may be provided by molecular groups whose affinity for the tunneling electron is higher than that of other groups. Furthermore, the electron overlap integral between the bridged groups should be large enough. That is, the role of bridge can be played by the polypeptide chain backbone, by side-chains of some amino acids (particularly those with aromatic rings), and by conjugated systems of the carotinoid type situated near macromolecular segments or near the surfaces of membranes or channels.

Key words: Macromolecule – Dielectric permittivity – Donor – Acceptor – Bridge chain – Electron tunneling – Image forces

1. Introduction

Macromolecular structures are common in both animate and inanimate objects. In recent years the problems

posed in bioenergetics, and in molecular and biomolecular electronics, have led to many studies of the electron-transport properties of individual macromolecules and macromolecular assemblies. This paper is concerned with the influence of polarization properties of heterogeneous media (either an individual macromolecule or a macromolecular assembly) on electron tunneling (ET) in the donor-bridge-acceptor (D-B-A) model. The discussion is primarily concerned with macromolecules of biological origin.

It is necessary to note here that, for biological systems, experimental data associated with a large conductivity have been reported by Smith et al. (1987); Hörber et al. (1988); Amrein et al. (1988); Alekperov et al. (1989) (see also the discussion in the paper by Garcia and Garcia (1990)). These authors used scanning tunneling microscopy (STM) methods (see, for example, Binning et al. 1982; Binning and Rohrer 1987; Tersoff and Hamman 1985; Garcia et al. 1983; Lang 1985; Hansma and Tersoff 1987; Golovchenko 1986; Hansma et al. 1988). Thus, it was noted by Smith et al. (1987) that the resistance of two chains in a layer of fatty acids is only $10^3 \Omega \cdot \text{cm}$, whereas the resistance for electron tunneling through monolayers of fatty acids placed on oxidized metal surfaces is equal to 10^9 – $10^{15} \Omega \cdot \text{cm}$ (Mann and Kuhn 1971). Alekperov et al. (1989) described results on specific conducting channels in a macromolecular assembly, the “photosynthetic reaction center” of purple bacteria. However, it is not possible to say that STM experiments provide definite evidence for a large conductivity of macromolecular structures. To answer this important question we need additional experimental data. Nevertheless, STM experiments did show that the physical mechanisms of ET in biological macromolecular structures do require further experimental and theoretical study.

At the present time there is no generally accepted physical approach for the description of the tunnel current through macromolecular structures. Various hypotheses have been put forward. Thus, it has been suggested by Alekperov et al. (1989) that the conducting channels in the reaction center are associated with the

Abbreviations: ET, Electron tunneling; HOMO, Highest occupied molecular orbital; LUMO, Lowest unoccupied molecular orbital

possibility of ET in the system of conjugated π -bonds (porphyrin ring, phytol carbon-hydrogen chains, aromatic aminoacids). This proposal is not inconsistent with the known structural properties of biological systems but it does not explain the physical nature of the ET processes. The hypothesis (Hörber et al. 1988) of electron injection from a tip into the system of molecular orbitals, which are distributed in energy, is more preferable from a physical point of view. An explanation for the large conductivity of thick organic materials was put forward by Garcia and Garcia (1990), and by Duke and Gibson (1982). In order to observe electron injection in organic macromolecules it is necessary to have the LUMO and (or) the HOMO of these macromolecules situated close in energy to the Fermi level. However, according to quantum mechanical calculations (Petrov 1984; Beratan et al. 1987; Da Gama 1990; Goldman 1991), such a situation does not exist for proteins.

The purpose of this work is to demonstrate the role of structural molecular inhomogeneity in the formation of ET channels. The well known long-range, electron-transfer donor-acceptor model is used to show that a special mutual disposition for bridged molecular groups and donor site near the boundary of the macromolecular segments can significantly enhance the ET properties of macromolecular structures compared with ET through homogeneous segments.

2. Physical model for long range D-A ET

In the theory of ET through organic molecules the bridge structures serve as an electron pathway for ET between donor (D) and acceptor (A). There are numerous papers on the theory of ET where the bridge is the focus of attention (see, e.g., McConnell 1961; De Vault 1980; Petrov 1984; Beratan et al. 1987; Da Gama 1990; Goldman 1991; Closs and Miller 1988; Dreyer 1984; Marcus and Sutin 1985; Larsson 1982, 1983; Larsson et al. 1988; Finckh et al. 1988; Lin 1989; Bertrand 1987; Sneddon and Brooks 1988; Joachim 1987; Heitele et al. 1989; Reimers and Hush 1990; Kharkyanen et al. 1978; Davydov and Gaididei 1985; Ostapenko and Petrov 1989). Without going into a detailed analysis one may note that if the electron-vibrational states of the quantum system with a finite number of degrees of freedom are in equilibrium with the thermal bath (the environment with an infinite number of degrees of freedom), then the ET rate from D to A is given by:

$$k \equiv k_{D \rightarrow A} = \frac{2\pi}{\hbar} \sum_{\mu\nu} |M_{\mu\nu}|^2 W(E_\mu) (1 - W(E_\nu)) \delta(E_\mu - E_\nu) \quad (1)$$

where $M_{\mu\nu}$ is the matrix element characterizing the quantum electron jump from the μ -th donor state to the ν -th acceptor state and $W(E_\mu)$ is the distribution function for the energy. The specific forms of $M_{\mu\nu}$ and $W(E)$ depend on the model used for the ET process. If the D and A molecules divided by the bridge (B) are at the distance which is large compared with molecular dimensions (Fig. 1), their interaction is negligible and when we consider ET between D and A the non-adiabatic terms for the

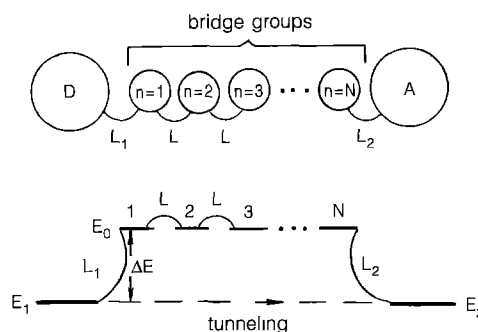


Fig. 1. Structural and energetic schemes for the D-B-A system

donor and acceptor states can be used. The electron and nuclear degrees of freedom are then separated (Frank-Condon approximation), and $M_{\mu\nu}$ can be written as

$$M_{\mu\nu} = V_{12} \langle \mu/\nu \rangle \quad (2)$$

where V_{12} is a purely electron part, and $\langle \mu/\nu \rangle$ is the overlap integral of the oscillation functions of the donor and acceptor states. If the acceptor state is freed from the electron faster than the electron gets to the acceptor from the donor, it can then be assumed in (1) that $W(E_\nu) \ll 1$ and, with allowance for (2), Eq. (1) then takes the form

$$k \equiv k_{D \rightarrow A} = \frac{2\pi}{\hbar} |V_{12}|^2 FC. \quad (3)$$

The Frank-Condon factor

$$FC = \sum_{\mu\nu} W(E_\mu) |\langle \mu/\nu \rangle|^2 \delta(E_\mu - E_\nu) \quad (4)$$

characterizes the nuclear oscillations of the D-B-A system and the environment. It can be calculated analytically in the harmonic approximation (for details see De Vault 1980).

If one knows the dependence of $M_{\mu\nu}$ on the physical characteristics of the bridge one can determine an optimal path for electron tunneling in a macromolecule. This optimal path is often called the electron pathway. It will be assumed below that the distance R between D and A is large enough for Eq. (2) to be valid. The dependence of the tunneling rate on R (Eq. (3)) will then be involved in the electron factor V_{12} . In accordance with the Marcus theory this dependence can also be involved in the FC factor, with allowance for the D-A interaction. However, at $R > 10 \text{ \AA}$ the above dependence can be neglected (Closs and Miller 1988; Marcus and Sutin 1985). Note that one Frank-Condon approximation is not enough to factorize the parameter $M_{\mu\nu}$ in the form of Eq. (2). It is necessary that the spectrum of oscillation levels of the donor and acceptor states should not get into the spectrum of the mediator states (i.e., the states where the electron is localized on the bridge) and, for spectral overlap, that the displacement from the equilibrium positions of nuclei of the bridge, when there is an extra electron on it, should be negligible. When the above conditions are satisfied the entire temperature dependence of the ET rate will be involved in the factor FC, and a purely electron jump parameter V_{12} will be calculated within the framework of the model by taking into account only the lowest energy level

in each electron term. The theoretical papers on ET mentioned in the Introduction are based on such a model, although the more general case is discussed (Petrov 1984; Lin 1989). We give the expression for V_{12} in the McConnell model, where D and A are divided by a bridge made up of N identical links (Fig. 1). Under tunneling conditions the donor energy level, $E_1 = E$, (and with the acceptor level isoenergetic with the donor level, $E_2 = E_1$) is situated below the band edge, $E_0 - 2|L| \cos[\pi/(N+1)]$, of the bridge states.

In order not to complicate the procedure for evaluation we set $N \geq 4$ and the band edge then corresponds to the energy $E_0 - 2|L|$. Ostapenko and Petrov (1989) have shown that the results for $N = 5-7$ are close to those for the case where $N \gg 1$. Therefore, (see e.g., Petrov 1984; Da Gama 1990; Kharkyanen et al. 1978)

$$V_{12} \approx \frac{L_1 L_2}{\sqrt{\Delta E^2 - 4L^2}} \exp[-\alpha(N-1)],$$

$$\alpha \equiv \ln \left| \frac{2L}{\Delta E - \sqrt{\Delta E^2 - 4L^2}} \right|. \quad (5)$$

In (5) $\Delta E \equiv E_0 - E_1$ and $L_1 (L_2)$ is the parameter describing electron jump between donor (acceptor) and the adjacent link of a bridge. It follows from (5) that the closer the donor energy to the band edge the slower (with increasing number of links N) the exponential fall of the donor-acceptor jump parameter. More detailed estimates of this effect are given in papers by Petrov (1984); Davydov and Gaididei (1985); Joachim (1987); Reimers and Hush (1990); and Ostapenko and Petrov (1989).

The aim of this paper is to clarify the effect of medium polarization properties on ET efficiency. Within the Frank-Condon approximation this means that one must examine the dependence of the main electron factor, the parameter describing the quantum electron jump V_{12} , on the dielectric permittivities of different parts of a macromolecule and medium. In turn, in order to use Eq. (5) to obtain the desired dependence it is necessary to know the effect of medium polarization on the position of electron energy levels when D, A and B occupy different positions relative to media interfaces with different dielectric permittivities.

3. The effect of image force on the energetic position of the electron

If the charge is in medium 1 with dielectric permittivity $\varepsilon = \varepsilon_1$ and is not very far from the boundary with medium 2 having $\varepsilon = \varepsilon_2$ then it is affected by an additional potential $\varphi^{(i)}$ caused by the image forces of medium 2. To evaluate $\varphi^{(i)}$ it is necessary to solve the system of equations

$$\varphi_1|_{\text{Bound}} = \varphi_2|_{\text{Bound}}, \quad \varepsilon_1 \frac{\partial \varphi_1}{\partial n} \Big|_{\text{Bound}} = \varepsilon_2 \frac{\partial \varphi_2}{\partial n} \Big|_{\text{Bound}} \quad (6)$$

(φ_1, φ_2 are the total potential generated by the charge e in media 1 and 2, $\partial/\partial n$ is the derivative over the normal to the interface of the media) which is a set of the boundary conditions. The methods used to obtain the expression $\varphi^{(i)}$, i.e. the solution of the system (6), for a

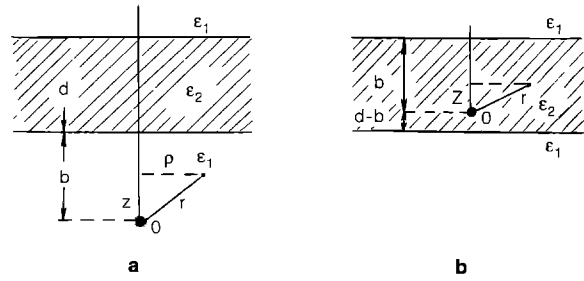


Fig. 2. Position of the charge e outside **a** and inside **b** a plate with $\varepsilon = \varepsilon_2$. Axis Z is perpendicular to the plate plane, 0 is the point of charge location, $r = (z^2 + \varrho^2)^{1/2}$ is the probe charge location

number of model situations are given by Landau and Lifshitz (1975) and by Smythe (1950).

Of special interest in the electron tunneling problem are the systems where the charge is near or inside a plate, ball or cylinder. These systems model the situation that exists when the electron is on a structural group positioned near or inside a bilayer lipid membrane, outside or inside a globular protein, on a α -helical part of the macromolecule and in ion channels. The problem of whether the use of macroscopic characteristics is justifiable in describing the purely quantum process (electron tunneling in molecular systems) will be discussed in the following section. We now give the necessary expressions for $\varphi^{(i)}$ based on the solution of the system of (6).

a) A charge in and off a plate

If the charge e is at a distance b from the plane of an infinite plate of thickness d and $\varepsilon = \varepsilon_2$ placed in a medium with $\varepsilon = \varepsilon_1$, then at any point of the medium in the region $-\infty < z \leq b$ (Fig. 2a) the potential generated by the charge e is given by:

$$\varphi(r) = \frac{e}{\varepsilon_1 r} + \varphi^{(i)}(r). \quad (7)$$

Then the potential

$$\varphi^{(i)}(r) = -\frac{e\zeta}{\varepsilon_1} \sum_{n=0}^{\infty} \zeta^{2n} \{ [2dn + 2b - z]^2 + \varrho^2 \}^{-1/2} - [(2dn + 2d + 2b - z)^2 + \varrho^2]^{-1/2} \},$$

$$\left(\zeta \equiv \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + \varepsilon_1} \right), \quad (8)$$

is entirely due to the presence of the plate. The additional electrostatic energy $q\varphi^{(i)}(r)$ that acts on the probe charge q is associated with the potential $\varphi^{(i)}(r)$. At the point $r = 0$ (when $z = 0, \varrho = 0$) the initial charge is affected by the potential $\varphi^{(i)} \equiv \varphi^{(i)}(0)$, called the image force potential, and the additional energy $E^{(i)} = e\varphi^{(i)}$ is determined by

$$E^{(i)} = -\frac{e^2\zeta}{2\varepsilon_1} \left[\frac{1}{b} + \frac{1}{d} \frac{\zeta^2 - 1}{\zeta^2} S(\zeta, d) \right] \quad (9)$$

where (Neumcke and Lauger 1969)

$$S(\zeta, d) = \sum_{n=1}^{\infty} \frac{\zeta^{2n}}{n + d}. \quad (10)$$

In (10) $\Delta \equiv b/d$ is an arbitrary quantity and thus the sum $S(\zeta, \Delta)$ is found numerically. However, in the important case of charge proximity to the plate one can put $\Delta \approx 0$ in $S(\zeta, \Delta)$ and obtain

$$S(\zeta, 0) = -\ln(1 - \zeta^2). \quad (11)$$

Correspondingly, according to (9)

$$E^{(i)} = -\frac{e^2 \zeta}{2\epsilon_1} \left[\frac{1}{b} + \frac{1}{d} \frac{1 - \zeta^2}{\zeta^2} \ln(1 - \zeta^2) \right]. \quad (12)$$

The magnitude of $(1 - \zeta^2) \ln(1 - \zeta^2)/\zeta^2$ is finite (of the order of 1) for all values of the parameter ζ in the range $-1 < \zeta < 1$. Thus, at $d \gg b$ Eq. (12) becomes:

$$E^{(i)} = -\frac{e^2 \zeta}{2\epsilon_1 b} \quad (13)$$

which corresponds to the situation where the charge is located near the half-space boundary.

If the charge is far from the boundary and assuming that $\Delta \gg 1$ in Eq. (10) one has:

$$S(\zeta, \Delta) \approx \frac{1}{\Delta} \sum_{n=1}^{\infty} \zeta^{2n} = \frac{1}{\Delta} \frac{\zeta^2}{1 - \zeta^2} \quad (14)$$

and, consequently, according to (9) the effect of the image force on the charge becomes zero ($E^{(i)} = 0$).

If one lets the charge e be located inside the plate at a distance b from its boundary (Fig. 2 b), then

$$\begin{aligned} \varphi^{(i)}(r) = \frac{e}{\epsilon_2} \sum_{n=0}^{\infty} \zeta^{2n} \{ & \zeta^2 [(2d(n+1) + z)^2 + q^2]^{-1/2} \\ & + [(2d(n+1) - z)^2 + q^2]^{-1/2} \\ & + \zeta [(2d(n+1) - 2b + z)^2 + q^2]^{-1/2} \\ & + [(2dn + 2b - z)^2 + q^2]^{-1/2} \} \end{aligned} \quad (15)$$

and the additional image-force induced energy acting on the charge e has the form:

$$\begin{aligned} E^{(i)} = \frac{e^2}{\epsilon_2} \left\{ \frac{\zeta}{2} \left(\frac{1}{b} + \frac{1}{d-b} \right) + \frac{1}{d} \sum_{n=1}^{\infty} \frac{\zeta^{2n}}{n} \right. \\ \left. + \frac{\zeta}{2} \sum_{n=1}^{\infty} \zeta^{2n} \left(\frac{1}{dn+b} + \frac{1}{d(n+1)-b} \right) \right\}. \end{aligned} \quad (16)$$

It follows from (16) that, independent of the location of the charge inside the plate, the energy generated by the polarization properties of the medium with $\epsilon_1 < \epsilon_2$ is always positive. When $b \leq d/2$, Eq. (16) may be written in a convenient and compact form:

$$E^{(i)} = \frac{e^2 \zeta}{2\epsilon_2} \left\{ \frac{1}{b} + \frac{1}{d} \left[\frac{2}{\zeta} S(\zeta, 0) + S(\zeta, \Delta) + \frac{1}{\zeta^2} S(\zeta, -\Delta) \right] \right\}. \quad (17)$$

Near the boundary and when $\Delta \ll 1$ one gets the following equation by substituting (11) in (17)

$$E^{(i)} = \frac{e^2 \zeta}{2\epsilon_2} \left[\frac{1}{b} - \frac{1}{d} \frac{(1 + \zeta)^2}{\zeta^2} \ln(1 - \zeta^2) \right]. \quad (18)$$

Comparing (18) and (12) shows that when the charge is inside the plate the contribution of the second term to (17)

is important if the dielectric permittivity of the plate ϵ_2 is much higher than that of the medium (i.e. when $\zeta \rightarrow 1$). In this case

$$E^{(i)} \simeq \frac{e^2}{2\epsilon_2} \left[\frac{1}{b} + \frac{4}{d} |\ln(1 - \zeta^2)| \right] \quad (19)$$

and the energy for the charge near the plate boundary changes logarithmically owing to $\ln(1 - \zeta^2)$. This result is, however, dependent on the assumption of a point charge. In fact, the electron charge is smeared over the atom or the molecule. In addition, the plate itself has a smeared boundary with the medium, the smearing having the atomic or molecular scale as a minimum. Thus, Eq. (19) indicates a tendency only. If the charge size is taken into account, as was done, for example, by Neumcke and Lauser (1969) in studying ion motion in a biomembrane, then instead of (17) one gets:

$$\begin{aligned} E^{(i)} = \frac{e^2 \zeta}{2\epsilon_2} \left\{ \frac{1}{b} + \frac{1}{d} \left[\frac{(1 + \zeta)^2}{\zeta^2} S(\zeta, 0) + S(\zeta, \Delta) \right. \right. \\ \left. \left. - S(\zeta, \gamma) + \frac{1}{\zeta^2} (S(\zeta, -\Delta) - S(\zeta, -\gamma)) \right] \right\}. \end{aligned} \quad (20)$$

In (20) the charge size is characterized by the radius r_0 , so that $\gamma \equiv r_0/d$. Correspondingly, the charge cannot approach the boundary at a distance b less than r_0 . When $r_0 \rightarrow 0$, Eq. (20) is transformed into Eq. (17).

b) A charge outside and inside a sphere

Let the charge e be at the point 0 at a distance $b > a$ from the center of a sphere of radius a (Fig. 3 a). The potential created by the sphere at any point P has the form ($a \leq r \leq b$)

$$\varphi^{(i)}(r, \theta) = \frac{e}{\epsilon_1 b} \sum_{n=0}^{\infty} \frac{n(1+K)}{1+n(1+K)} \frac{a}{r} \left(\frac{c}{r} \right)^n P_n(\cos \theta) \quad (21)$$

where $P_n(\cos \theta)$ is the Legendre polynomial, $K \equiv \epsilon_2/\epsilon_1$, and $c \equiv a^2/b$. Correspondingly, the polarization contribution to the charge energy is found from (21) for $r = b$, $\theta = 0$:

$$E^{(i)} = e \varphi^{(i)}(b, 0) = \frac{e^2 (1-K)}{\epsilon_1 b} \sum_{n=1}^{\infty} \frac{n}{1+n(1+K)} \left(\frac{a}{b} \right)^{2n+1} \quad (22)$$

It is obvious that for $\epsilon_2 > \epsilon_1$ and $\epsilon_2 < \epsilon_1$ the sphere polarization properties provide charge energy which decreases and increases, respectively. If the charge is distant from the sphere, at $b \gg a$, then in the sum of Eq. (22) it is possible to restrict consideration to the term with $n = 1$ and one obtains:

$$E^{(i)} \approx \frac{e^2 (\epsilon_1 - \epsilon_2)}{\epsilon_1 (2\epsilon_1 + \epsilon_2) b} \left(\frac{a}{b} \right)^3. \quad (23)$$

The absolute energy value $E^{(i)}$ is seen from Eq. (23) to decrease with increasing distance and is proportional to b^{-4} . The case of close proximity of the charge to the surface of the sphere is of particular interest. In the sum over n it is impossible to restrict consideration to one

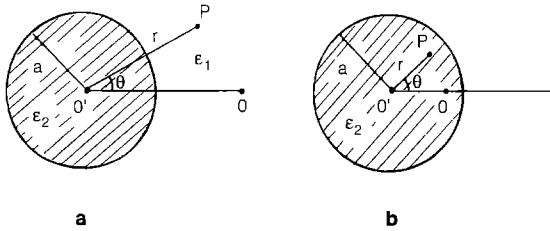


Fig. 3. A charge outside **a** and inside **b** a sphere. P is the probe charge location, $00' = b$ is the distance from the charge to the sphere center, a is the sphere radius

Table 1. The effect of image forces for static permittivities. Electron energies $E^{(i)}$ were estimated from Eq. (31)

$E^{(i)}$ (eV)	ϵ_1	ϵ_2	$2b$ (Å)
-0.32	4 (protein)	80 (water)	10
-0.68	2 (lipid)	80 (water)	10
-1.70	2 (lipid)	80 (water)	4
-1.36	2 (lipid)	80 (water)	5
0.24	4 (protein)	2 (lipid)	5
0.40	4 (protein)	2 (lipid)	3
-0.80	2 (lipid)	4 (protein)	3

term. The main contribution to the sum will then come from the terms with large values of n . Substituting $n(1+K) \gg 1$ in Eq. (22) one gets the approximation:

$$E^{(i)} \approx -\frac{e^2 \zeta a}{\epsilon_1 b^2} \frac{a^2}{b^2 - a^2}. \quad (24)$$

In Eq. (24) the quantity ζ has the same meaning as used previously in considering the problem of a charge outside and inside a plate. In close proximity to the surface

$$E^{(i)} \approx -\frac{e^2 \zeta}{2\epsilon_1 (b-a)}. \quad (25)$$

It follows from (24) that since $(b-a)$ is the distance to the surface, Eq. (25) is the same as Eq. (13) for the charge near the half space. If the charge is inside the sphere at distance b from the center, then at the point P (see Fig. 3b)

$$\varphi^{(i)}(r, \theta) = -\frac{e}{\epsilon_2 a} \sum_{n=0}^{\infty} \frac{(n+1)(1-K)}{1+n(1+K)} \left(\frac{r}{a}\right)^n P_n(\cos \theta). \quad (26)$$

It follows from (26) that the charge gains the energy

$$E^{(i)} = -\frac{e^2 (1-K)}{\epsilon_2 a} \sum_{n=0}^{\infty} \frac{n+1}{1+n(1+K)} \left(\frac{b}{a}\right)^{2n}. \quad (27)$$

For the charge near the sphere center

$$E^{(i)} \approx \frac{e^2 (\epsilon_2 - \epsilon_1)}{\epsilon_1 \epsilon_2 a}, \quad (b \ll a), \quad (28)$$

Therefore, for the charge not too far from the sphere boundary one can use the approximation used in deriving Eq. (24) to give:

$$E^{(i)} \approx -\frac{e^2 \zeta}{\epsilon_2 a} \left[K + \frac{a^2}{a^2 - b^2} \right]. \quad (29)$$

In the immediate vicinity of the boundary

$$E^{(i)} \approx \frac{e^2 \zeta}{2\epsilon_2 (a-b)}, \quad (b \lesssim a). \quad (30)$$

4. Efficiency of the tunneling pathways

The expressions given in the previous sections are sufficient to enable one to try to understand which of the ET pathways will be preferred in heterogeneous media. In fact, it is sufficient to make use of the following conclusion: when the charge approaches the boundary of the two media the charge energy increases if the dielectric permittivity is smaller on the other side of the boundary, and decreases if the permittivity is larger. The necessary qualitative estimates are obtained from the simplest equation, (13), which coincides with the limiting expressions (25) and (30). If one measures the charge energy in units of the Bohr energy, $E_B \equiv e^2/r_B \approx 27$ eV, where $r_B = 0.53$ Å is the Bohr radius, Eq. (13) can be rewritten in the form

$$E^{(i)} = -\left(\frac{r_B}{2b}\right) \frac{1}{\epsilon_1} \frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + \epsilon_1} E_B. \quad (31)$$

The static dielectric permittivities ϵ_{10} and ϵ_{20} may be substituted for ϵ_1 and ϵ_2 if the time, τ_l , for which the charge is found in its localization place proves to be much larger than the time, τ_p , required to establish stationary polarization around the charge (e.g. in a solvation process). In the other limiting case, when $\tau_l \ll \tau_p$, one must substitute the high-frequency dielectric permittivities $\epsilon_{1\infty}$ and $\epsilon_{2\infty}$ for ϵ_1 and ϵ_2 . In the D-B-A system for the electron on the donor and the acceptor $\epsilon_j = \epsilon_{j0}$; whereas for the electron on the bridge $\epsilon_j = \epsilon_{j\infty}$ if the electron passes from D to A in the tunneling regime. Let $\epsilon_1 = \epsilon_{10}$ and $\epsilon_2 = \epsilon_{20}$. Table 1 shows the effect of image forces on the position of electron levels. For the estimates of $E^{(i)}$ a weak polar protein has been used. In the case of proteins diluted in water ϵ can be of the order of several tens of units. For instance, for lysozyme $\epsilon \approx 11$ at high frequencies and $\epsilon \approx 44$ at low frequencies (Pethig 1979).

It follows from the Table 1 that the image forces for real parameter values can give a contribution to the charge energy from a tenth to more than one electron-volt. To what extent is it justifiable to use phenomenologic characteristics such as the dielectric permittivity media interface in the description of the quantum processes in macromolecular systems? Strictly speaking, to make use of these characteristics it is necessary to carry out averaging over small physical volumes (Landau and Lifshitz 1975) where the medium homogeneity is clear. Globular protein molecules (with effective radius ~ 50 Å), the bilayer lipid membrane (with thickness ~ 50 Å), fibrous proteins (with radius $\sim 10-30$ Å), and the α -helix (radius ~ 2 Å) have high heterogeneity. Therefore, one should be careful in characterizing these macromolecular structures by means of a definite dielectric permittivity for the description of quantum transport processes. Nevertheless, the dielectric properties of lipids, proteins, and water are different (Pethig 1979) and these differences are exploited for qualitative characterisation of electron-transport pro-

cesses in proteins. As examples, we cite the work of Balabaev et al. (1990) on clarifying the role of globular proteins in the formation of a polaron state and that of Kharkats and Ulstrup (1990) on electron transfer between a metallo-protein and a small redox co-factor. In earlier work, the microviscosity concept was employed to analyse data on molecular dynamics (Debrunner and Frauenfelder 1982; Goldanskii et al. 1986; Knapp et al. 1983). Thus, if we restrict ourselves to the consideration of the minimum number of parameters that characterize the properties of macromolecular structures, it is possible to use phenomenological quantities for the qualitative description of many charge-transport processes.

a) D-B-A system at the boundary of two media

If the D-B-A system in the near-membrane or intramembrane region close to the boundary of the channel is involved in an α -helix then the presence of media with different dielectric permittivities ϵ should affect the electron process. Apart from the energy $E^{(i)}$ associated with image forces, and taking into account the presence of different media, the charge solvation energy should also contribute to the electron energy. In the simplest case the solvation energy is given by the Born energy $E^{(B)}$. Generally, the Born energy is calculated as the resolution energy of a spherical charge of radius r_0 when it moves from a vacuum (a medium with $\epsilon = \epsilon_v = 1$) to a medium with $\epsilon \neq \epsilon_v$ and is written as (Neumcke and Lauger 1969)

$$E^{(B)} = \frac{e^2}{r_0} \left(\frac{1}{\epsilon} - \frac{1}{\epsilon_v} \right). \quad (32)$$

In what follows, qualitative estimates of Eq. (32) will be made by assuming that r_0 is the effective radius of the group on which the transferred electron is localized.

Since one is dealing with tunnel electron transfer from donor to acceptor the electron energy E_0 on the bridged group involves the Born energy $E_0^{(B)}$ and the image force energy $E_0^{(i)}$, where $\epsilon = \epsilon_\infty$. The energy E_1 is composed of $E_1^{(B)}$ and $E_1^{(i)}$ with $\epsilon = \epsilon_0$. In order not to introduce too many parameters we shall set the value of r_0 to be the same for all groups, with all bridged groups positioned at the same distance b_0 from the boundary of the media. The difference $\Delta E = E_0 - E_1$ in electron energies on the bridge and on the donor that enters into the quantum jump parameter (5) can then be represented as the sum of three terms,

$$\Delta E = \Delta E^{(0)} + \Delta E^{(B)} + \Delta E^{(i)}, \quad (33)$$

where $\Delta E^{(0)}$, which is the difference in energies, is independent of the polarization properties of the medium,

$$\Delta E^{(B)} = E_0^{(B)} - E_1^{(B)} = \frac{e^2}{r_0} \left(\frac{1}{\epsilon_{1\infty}} - \frac{1}{\epsilon_{20}} \right), \quad (34)$$

$$\begin{aligned} \Delta E^{(i)} = E_0^{(i)} - E_1^{(i)} = & \frac{e^2}{2b_0} \frac{\epsilon_{1\infty} - \epsilon_{2\infty}}{(\epsilon_{1\infty} + \epsilon_{2\infty}) \epsilon_{1\infty}} \\ & + \frac{e^2}{2b_1} \frac{\epsilon_{10} - \epsilon_{20}}{(\epsilon_{10} + \epsilon_{20}) \epsilon_{10}}. \end{aligned} \quad (35)$$

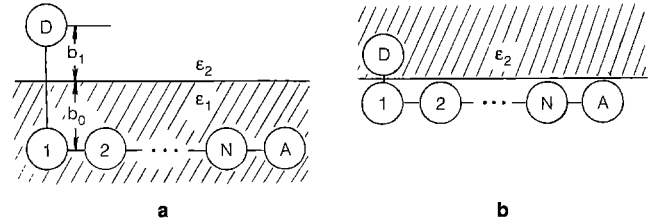


Fig. 4 a, b. Scheme for location of an N -link bridge and a donor in a medium with $\epsilon = \epsilon_2$: **a** $\epsilon_2 < \epsilon_1$; $b_0, b_1 > r_0$; **b** $\epsilon_2 > \epsilon_1$; $b_0, b_1 \approx r_0$ (according to Eq. (35))

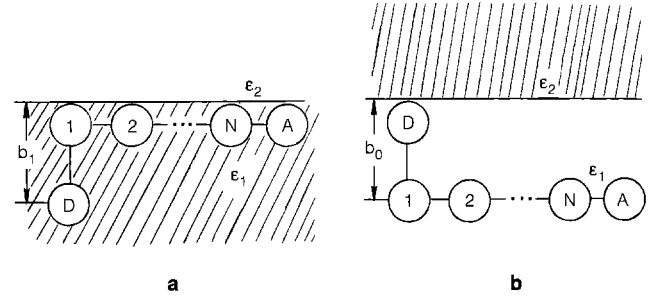


Fig. 5 a, b. Scheme for location of an N -link bridge and a donor in a medium with $\epsilon = \epsilon_1$: **a** $\epsilon_1 > \epsilon_2$; $b_0 \approx r_0, b_1 > r_0$; **b** $\epsilon_1 < \epsilon_2$; $b_0 > r_0, b_1 \approx r_0$ (according to Eq. (37))

The smaller the energy ΔE the more effective, according to (5), is the electron tunneling. It was assumed in Eqs. (34) and (35) that the donor is in a medium with $\epsilon = \epsilon_2$ at a distance b_1 from the boundary, and that the bridge is in a medium with $\epsilon = \epsilon_1$ (at a distance from the boundary of b_0). If the donor and the bridge are in the same medium with $\epsilon = \epsilon_1$, then

$$\Delta E^{(B)} = \frac{e^2}{r_0} \left(\frac{1}{\epsilon_{1\infty}} - \frac{1}{\epsilon_{10}} \right), \quad (36)$$

$$\Delta E^{(i)} = \frac{e^2}{2b_0} \frac{\epsilon_{1\infty} - \epsilon_{2\infty}}{(\epsilon_{1\infty} + \epsilon_{2\infty}) \epsilon_{1\infty}} - \frac{e^2}{2b_1} \frac{\epsilon_{10} - \epsilon_{20}}{(\epsilon_{10} + \epsilon_{20}) \epsilon_{10}}. \quad (37)$$

Before analysing Eqs. (34)–(37) we note that the inequality $\epsilon_0 > \epsilon_\infty$ always holds. Thus, if $\epsilon_{20} < \epsilon_{1\infty}$, then $\epsilon_{20} < \epsilon_{10}$. In addition, if $\epsilon_{10} > \epsilon_{20}$, then generally $\epsilon_{1\infty} > \epsilon_{2\infty}$. Thus, having the donor in the medium with the smaller dielectric permittivity (compared to the medium where the bridge is located) favours a decrease in the Born energy and improves the ET. The image force energy contributing to (35) acts in the opposite direction. At $\epsilon_2 < \epsilon_1$, the inequality $\Delta E^{(i)} > 0$ holds. To decrease the contribution coming from the image forces, the donor and the bridge should be removed from the boundary of the media. If $\epsilon_2 > \epsilon_1$ then in accord with (34) $\Delta E^{(B)} > 0$, and in accord with (35) $\Delta E^{(i)} < 0$. This means that image forces decrease the parameter ΔE and therefore provide more effective tunneling when the donor and the chain are closer to the interface of the two media. Both cases are schematically shown in Fig. 4.

Let the donor and the bridge be in the same medium with $\epsilon = \epsilon_1$. According to (36), in this case one always has $\Delta E^{(B)} > 0$. Therefore, according to (37) the image forces will promote ET if $\Delta E^{(i)} < 0$, with the effectiveness in-

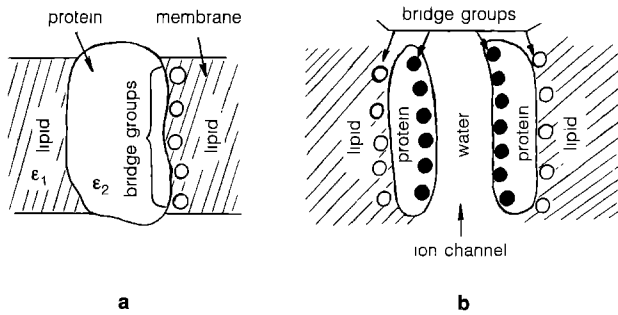


Fig. 6 a, b. Transmembrane position of molecular bridged groups. **a** on the lipid-protein boundary ($\epsilon_{1\infty} < \epsilon_{2\infty}$); **b** in the ion channel region on lipid-protein (from the lipid side) boundaries and on protein-water (from the protein side) boundaries

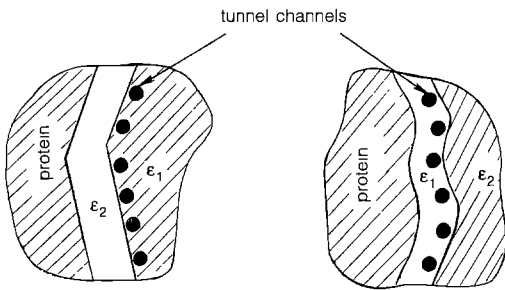


Fig. 7. Tunneling channels (electron pathways) in a protein along the boundary of media with different values of high-frequency dielectric permittivity $\epsilon_{1\infty} < \epsilon_{2\infty}$

creasing with $|\Delta E^{(i)}|$. Generally, the difference in the static values of the permittivities ϵ_{10} and ϵ_{20} is much greater than the difference in $\epsilon_{1\infty}$ and $\epsilon_{2\infty}$. Hence, if in (37) one has $\epsilon_{10} > \epsilon_{20}$, then at $\epsilon_{10} b_1 < \epsilon_{1\infty} b_0$ one has $\Delta E^{(i)} < 0$, and $|\Delta E^{(i)}|$ increases with decreasing b_1 and increasing b_0 . Thus, to make ET effective the bridge should be situated as far as possible from the boundary, and the donor as close as possible (Fig. 5a). In contrast, if the donor and the bridge are in the medium with the smaller dielectric permittivity ($\epsilon_1 < \epsilon_2$) then the donor must be further from the boundary and the bridge nearer (Fig. 5b). Equations (35) and (37) and the schemes in Figs. 5 and 6 allow one to make the general conclusion that the image forces will promote improved ET along a bridge situated in the medium with $\epsilon = \epsilon_1$ if the bridge is either far from (at $\epsilon_{1\infty} > \epsilon_{2\infty}$) or close to (at $\epsilon_{1\infty} < \epsilon_{2\infty}$) the interface of the media. Thus, for example, the transmembrane position of an individual polymer chain does not promote ET since the membrane consists of lipids and these have a lower ϵ than proteins or water. If the bridged groups are connected by a protein molecule piercing the membrane then they may be: a) hydrophobic and positioned deep in the lipid in a position near to the protein surface (Fig. 6a); b) polar and positioned deep inside the protein and far from its surface. If the protein molecule has segments with different values of ϵ_∞ then the electron tunneling pathway (bridged groups) fits to just these segments (Fig. 7). They can also be called the electron-conducting tunneling channels. For an individual α -helical, tunneling channel, there can be a pathway along the α -helix backbone; this is more advantageous than the pathway along the α -helix

Table 2. The effect of image forces on ET as a function of D-A distance (in N units). Values derived from Eqs. (5), (38), and (39) using $b_0 = 2 \text{ \AA}$

E_0 (eV)	$E_0^{(i)}$ (eV)	ΔE (eV)	$\epsilon_{1\infty}$	$\epsilon_{2\infty}$
1.5	-0.36	1.14	2 (lipid)	3 (protein)
N	5	9	13	17
η	$1.8 \cdot 10$	$1.8 \cdot 10^2$	$1.8 \cdot 10^3$	$1.8 \cdot 10^4$
1.5	-0.49	1.01	2 (lipid)	3.5 (protein)
N	5	9	13	17
η	$5.6 \cdot 10$	$1.2 \cdot 10^3$	$2.5 \cdot 10^4$	$5.4 \cdot 10^5$
1.5	-0.64	0.86	3 (protein)	10 (water)
N	5	9	13	17
η	$2.9 \cdot 10^2$	$2.8 \cdot 10^4$	$2.8 \cdot 10^6$	$2.9 \cdot 10^8$

axis. If a macromolecular structure consists of parallel α -helices, then the tunneling pathway can be formed at the boundary of α -helical contacts.

We give a qualitative estimate of the efficiency of electron tunneling along the tunneling channel, taking into account the effect of the image forces on the state of the bridge. It is assumed that the donor is in a medium with certain ϵ values and thus that the Born donor and bridge energies, and also the image force energy for the donor, are fixed. Hence we write $\Delta E = E_0 - E_1$ in the form

$$\Delta E = \Delta E_0 + E_0^{(i)}, \quad E_0^{(i)} \equiv \frac{e^2}{2b_0} \frac{\epsilon_{1\infty} - \epsilon_{2\infty}}{(\epsilon_{1\infty} - \epsilon_{2\infty}) \epsilon_{1\infty}}. \quad (38)$$

In (38), $E_0^{(i)}$ is the image force energy of the bridged group at the interface of two media (the bridge is in the medium with $\epsilon = \epsilon_1$). At $\epsilon_{1\infty} < \epsilon_{2\infty}$ the contribution of $E_0^{(i)}$ to ΔE decreases the energy parameter ΔE . To make the image effect on the donor negligible (the corresponding energy enters into ΔE_0), we consider, in accord with (35) and (37) that the donor is distant from the interface of the media. For this it is sufficient in (35) and (37) to set $b_1 > 10r_B \approx 5 \text{ \AA}$. Previous studies (Pethig 1979; Bone and Pethig 1979) showed that for many proteins $\epsilon_\infty \approx 3-4$, although there do exist proteins with $\epsilon_\infty \sim 10$. For lipids $\epsilon_\infty \approx 2$. Thus, on the lipid-protein boundary ($\epsilon_{1\infty} \approx 2$, $\epsilon_{2\infty} \approx 3$) at $2b_0 = 4 \text{ \AA}$ one has from (38) that $E_0^{(i)} \approx -0.64 \text{ eV}$, and on the lipid-water boundary ($\epsilon_{1\infty} \approx 2$, $\epsilon_{2\infty} \approx 10$) $E_0^{(i)} \approx -1.19 \text{ eV}$.

We shall estimate the image force effect using the parameter $\eta = k_{D \rightarrow A} / k_{D \rightarrow A}^{(im)}$. When $k_{D \rightarrow A}$ and $k_{D \rightarrow A}^{(im)}$ rates are expressed by Eqs. (3) and (5) as $\Delta E = \Delta E_0$ and $\Delta E = \Delta E_0 + E_0^{(i)}$, respectively, then

$$\eta = \frac{\Delta E_0^2 - 4L^2}{\Delta E^2 - 4L^2} \left(\frac{\Delta E - \sqrt{\Delta E^2 - 4L^2}}{\Delta E_0 - \sqrt{\Delta E_0^2 - 4L^2}} \right)^{2(N-1)}. \quad (39)$$

If, for example, one lets a part of the α -helix be the bridge, then the protein chain backbone is in a less polar region than the aminoacid residues. If the electron tunnels along the backbone it is in a medium with $\epsilon = \epsilon_1$ close to the boundary with the medium having $\epsilon = \epsilon_2 > \epsilon_1$. According to (5) and (39) the change in ΔE for the given bridge structure causes variations in V_{12} and η . Numerical esti-

mates of the parameters for electron quantum jump between atoms of the protein chain backbone and directly between the peptide groups were found by Petrov (1984); Beratan et al. (1987); Da Gama (1990), and Goldman (1991). For the estimates we take $|L| = 0.25$ eV (the effective parameter for the electron jump between the closest peptide groups along the α -helix backbone (Petrov 1984), and $b_0 = 2$ Å (the average distance from backbone to residue center). Table 2 shows the $\eta - N$ dependence as a function of the high-frequency dielectric permittivities $\epsilon_{1\infty}$, $\epsilon_{2\infty}$. It is clear from Table 2 that image forces can increase the donor-acceptor ET rate by up to 8 orders of magnitude.

5. Discussion

The qualitative estimates obtained are not rigorous, but do allow one to formulate the principle that under identical conditions the most effective pathway for donor-acceptor ET is that which passes near the boundary of media with different values of ϵ . This pathway serves as the tunneling channel. For proteins, apart from the polypeptide chain backbone, the bridged groups can be provided by the aminoacid residues (for details see Petrov (1984); Larsson et al. (1988); Sneddon and Brooks (1988); Kharkyanen et al. (1978)). If these residues are on the boundary of media with different polarization properties then the formation of the tunneling channel becomes especially advantageous. A change in macromolecule conformation can shift the bridged groups to a region with a different ϵ -value and this can enhance or weaken ET along the tunneling channel. On the other hand, the variation in conformation depends on many factors (such as temperature, humidity, and acidity).

The considerations described here show that image forces produce a major effect on ET efficiency in systems where electron tunneling is performed by means of bridged groups. On the whole, the effect is generally associated with a lowering of the electron energy levels on the bridged groups.

References

- Alekperov S, Vasiljev S, Kononenko A, Lukashev E, Panov V, Semenov A (1989) Scanning tunneling microscopy of photosynthetic reaction centers. *Chem Phys Lett* 164:151–154
- Amrein M, Stasiak A, Gross H, Stoll E, Travaglini G (1988) Scanning tunneling microscopy of rec A-DNA complexes coated with conducting film. *Science* 240:514–516
- Balabaev N, Lakhno V, Molchanov A, Atanasov B (1990) Extended electron states in proteins. *J Mol Electronics* 6:155–166
- Beratan DN, Onuchic J, Hopfield J (1987) Electron tunneling through covalent and noncovalent pathways in proteins. *Chem Phys* 86:4488–4498
- Bertrand P (1987) The contribution to the electron factor in bridge-assisted electron transfer processes. *Chem Phys Lett* 140:57–63
- Binnig G, Rohrer H, Gerber Ch, Weibel E (1982) Surface studies by scanning tunneling microscopy. *Phys Rev Lett* 49:57–61
- Binnig G, Rohrer H (1987) Scanning tunneling microscopy from birth to adolescence – Les Prix Nobel, EN 1986. The Nobel Foundation 1987:91–111
- Bone S, Pethig R (1979) Electronic and dielectric properties of protein-methylglyoxal complexes. In: *Submolecular biology and cancer*. Ciba Foundation. Ser. 67. London, pp 83–105
- Closs G, Miller J (1988) Intramolecular long-distance electron transfer in organic molecules. *Science* 240:440–447
- Davydov A, Gaididei Yu (1985) Facilitated electron tunneling through polymer molecules. *Phys Status Solidi (b)* 132:189–201
- Da Gama A (1990) Through-bond electron-transfer interaction in proteins. *J Theor Biol* 142:251–260
- Debrunner P, Frauenfelder H (1982) Dynamics of proteins. *Ann Rev Phys Chem* 33:283–299
- De Vault D (1980) Quantum mechanical tunneling in biological systems. *Q Rev Biophys* 13:387–564
- Dreyer J (1984) Electron transfer in biological systems: an overview. *Experientia* 40:653–675
- Duke CB, Gibbon HW (1982) *Encyclopedia of chemical technology*, vol 18, Wiley, New York
- Finckh P, Heitele H, Volk M, Michel-Beyerle M (1988) Electron donor/acceptor interaction and reorganization parameters from temperature-dependent intramolecular electron transfer rates. *J Phys Chem* 92:6584–6590
- Garcia R, Garcia N (1990) Electron conductance in organic chains: why are STM experiments possible on bare biological samples? *Chem Phys Lett* 173:44–50
- Garcia N, Ocal C, Flores F (1983) Model theory for scanning tunneling microscopy: application to AU (110) (1×2). *Phys Rev Lett* 50:2002–2005
- Goldanskii V, Krupyanskii Yu, Flerov V (1986) Rayleigh scattering of Moessbauer radiation data, hydration effects and glass-like dynamical model of biopolymers. *Phys Ser* 33:527–540
- Golovchenko J (1986) The tunneling microscope: a new look at the atomic world. *Science* 232:48–53
- Hansma P, Tersoff J (1987) Scanning tunneling microscopy. *J Appl Phys* 61:R1–R23
- Hansma P, Elings V, Marti O, Bracker C (1988) Scanning tunneling microscopy and atomic force microscopy: application to biology and technology. *Science* 242:209–216
- Heitele H, Finckh P, Weeren S, Pöllinger E, Michel-Beyerle M (1989) Solvent polarity effects on intramolecular electron transfer. I. Energetic aspects. *J Phys Chem* 93:5173–5179
- Hörber J, Lang C, Hänsch T, Hockl W, Möhwald H (1988) Scanning tunneling microscopy of lipid films and embedded biomolecules. *Chem Phys Lett* 145:151–158
- Joachim C (1987) Ligand-length dependence of the intramolecular electron transfer through-bond coupling parameter. *Chem Phys* 116:339–349
- Kharkats Yu, Ulstrup J (1990) Dielectric image effects in environmental reorganization free energies and inter-reactant work terms of metalloprotein electron transfer reactions. *Chem Phys* 141:117–129
- Kharkyanen V, Petrov E, Ukrainskii I (1978) Donor-acceptor model of electron transfer through proteins. *J Theor Biol* 73:29–50
- Knapp E, Firsher S, Parak F (1983) The influence of protein dynamics on Moessbauer spectra. *Chem Phys* 78:4701–4711
- Landau L, Lifshitz E (1975) *Electrodynamics of continuous media*. Pergamon Press, Oxford
- Lang N (1985) Vacuum tunneling current from an adsorbed atom. *Phys Rev Lett* 55:230–234
- Larsson S (1982) Electron transfer in biological systems. *Int J Quantum Chem* 9:385–397
- Larsson S (1973) Electron transfer in proteins. *Chem Soc Faraday Trans* 79:1375–1388
- Larsson S, Broo A, Källebring B, Volosov A (1988) Long distance electron transfer. *Int J Quantum Chem Quantum Biol Symp* 15:1–22
- Lin S (1989) Theory of photoinduced intramolecular electron transfer in condensed media. *J Chem Phys* 90:7103–7113
- Mann B, Kuhn H (1971) Tunneling through fatty acid salt monolayers. *J Appl Phys* 42:4398–4405
- Marcus R, Sutin N (1985) Electron transfers in chemistry and biology. *Biochim Biophys Acta* 811:265–322

- McConnell H (1961) Intramolecular charge transfer in aromatic free radicals. *J Chem Phys* 35:508–515
- Neumcke B, Läuger P (1969) Nonlinear electrical effect in lipid bilayer membranes. *Biophys J* 9:1160–1170
- Ostapenko M, Petrov E (1989) The donor-acceptor electron transfer with participation of short polymer chains. *Phys Status Solidi (b)* 152:239–247
- Pethig R (1979) Dielectric and electronic properties of biological materials. Wiley, Chichester
- Petrov E (1984) Physics of charge transfer in biological systems. Naukova dumka, Kiev (English ed.): World Scientific, Singapore
- Reimers J, Hush N (1990) Electron transfer and energy transfer through bridged systems. II. Tight binding linkages with zero asymptotic band gap. *Chem Phys* 146:89–103
- Smith D, Bryant A, Quate CC, Rabe J, Gerber Ch, Swalen J (1987) Images of a lipid bilayer at molecular resolution by scanning tunneling microscopy. *Proc Natl Acad Sci, USA* 84:969–972
- Smythe W (1950) Static and dynamic electricity. McGraw-Hill, New York, Toronto, London
- Sneddon S, Brooks III C (1988) The influence of geometrical fluctuations on electron tunneling barriers in proteins. *Int J Quantum Chem Quantum Biol Symp* 15:23–32
- Tersoff J, Hamman D (1985) Theory of the scanning tunneling microscope. *Phys Rev B* 31:805–813