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ELECTRON TUNNELING AS A BASIS FOR SEMICONDUCTION IN PROTEINS

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16. Abstract

Electron tunneling is investigated as a possible mechanism for the conduction of electrical current in solids composed of protein molecules. An intermolecular potential barrier is assumed which takes into account the applied electric field and the possibility of image charge effects. The WKB approximation is used to calculate the net tunneling current density and resulting conductivity. The results suggest that electron tunneling per se is not a suitable mechanism for explaining the observed conductivities in such materials.

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SUMMARY

Organic solids composed of biological macromolecules such as proteins are known to be semiconductors. Electron tunneling from molecule to molecule in the solid has been proposed by others as a possible mechanism for the electrical conduction which is observed. Apparent qualitative agreement between the form of the experimental and theoretical conductivities based on tunneling has been shown; but no attempt to obtain a quantitative estimate has, until now, been made. This report is a quantitative investigation of such a mechanism within the framework of the WKB approximation. The intermolecular potential barrier is represented by the sum of the image charge potential and an applied potential which produces a bias between neighboring molecules. An approximate form for the tunneling coefficient is developed which is valid for applied electric fields below about 10^5 volts per centimeter, a limit well above normal experimental conditions. The conductivity, calculated on the basis of the model and assumptions chosen, is several orders of magnitude smaller than that observed experimentally. The severe quantitative disagreement arises from the fact that the potential barrier symmetry is relatively unchanged in low electric fields. In addition to the quantitative failure, the tunneling model also fails to predict the well-known "compensation law" for the behavior of the conductivity with activation energy. These results suggest that electron tunneling per se is not the mechanism for the conduction of electrical current in proteins.

INTRODUCTION

Semiconduction in materials composed of organic macromolecules is an established empirical fact. There exists, however, no suitable theoretical explanation which can account for many of the experimental details that have been observed. For example, while the temperature dependence of the conductivity is given by

$$\sigma(T) = \sigma_o e^{-E_A/2kT} \tag{1}$$

where the activation energy E_A is in the range of 2 to 3 electron volts, the so-called "pre-exponential factor," σ_o actually has the form

$$\sigma_o = e^{\xi E_A + \eta} \tag{2}$$

where ξ and η are independent of both T and E_A. Equation (2) is known as the compensation law. Eley (ref. 1) suggested some possible mechanisms which might explain the behavior of the conductivity in this form, but did not investigate them extensively. Following one of the suggestions, Kemeny and Rosenberg (ref. 2) treated an organic molecular solid as a collection of molecules with potential barriers surrounding them, and calculated the conductivity by assuming that the electrons tunnel from one molecule to the next. They considered only the simplified cases of either rectangular or triangular intermolecular potential barriers, and obtained qualitative agreement with the combined form of equations (1) and (2).

This report presents a calculation of the tunneling current using an intermolecular potential barrier which we believe is more realistic. An expression for the current density is developed within the independent particle and WKB approximations, and a numerical estimate of the magnitude of the current density is made.

ELECTRON TUNNELING

The probability per unit time that an electron in state α on one side of a barrier will make a transition to state β on the other side is (ref. 3)

$$P_{\alpha\beta} = \left(\frac{2\pi}{\hbar}\right) |M_{\alpha\beta}|^2 \rho_\beta f_\alpha (1 - f_\beta) \tag{3}$$

where ρ_β is the density of states for one spin at β, and f_α and f_β are the probabilities of occupation of the states α and β, respectively. The quantity $M_{\alpha\beta}$ is the tunneling matrix element for a transition from state α to β. Bardeen (ref. 4) has shown that the matrix element may be written as

$$M_{\alpha\beta} = -i\hbar J_{\alpha\beta}(x) \tag{4}$$

where $J_{\alpha\beta}(x)$ is the matrix element of the x-component of the current density operator J_x evaluated in the barrier region:

$$J_{\alpha\beta}(x) = \langle \psi_\alpha | J_x | \psi_\beta \rangle \tag{5}$$

where ψ_α and ψ_β are the wave functions which describe the states α and β. The matrix element $M_{\alpha\beta}$ vanishes unless the transverse wave number k_t is conserved in the process. If state α is considered to be on the left of the barrier, the current from left to right is obtained by summing $P_{\alpha\beta}$ over all states α of fixed k_t, summing over k_t, multiplying by the electronic charge e, and finally multiplying by 2 to account for electron spin. Since the probability per unit time for a transition from state β to state α is

$$P_{\beta\alpha} = \left(\frac{2\pi}{\hbar}\right) |M_{\beta\alpha}|^2 \rho_\alpha f_\beta (1 - f_\alpha) \tag{6}$$

the net current density flowing from left to right through the barrier is

$$J = 2e \sum_{k_t} \int (P_{\alpha\beta}\rho_\alpha - P_{\beta\alpha}\rho_\beta)\, dE = \left(\frac{4\pi e}{\hbar}\right) \sum_{k_t} \int \left\{ |M_{\alpha\beta}|^2 \rho_\beta f_\alpha (1 - f_\beta)\rho_\alpha - |M_{\beta\alpha}|^2 \rho_\alpha f_\beta (1 - f_\alpha)\rho_\beta \right\} dE \tag{7}$$

where E is the total energy for a fixed k_t. The density-of-states factors allow the sum over the initial states to be replaced by an integral. Furthermore,

$$|M_{\alpha\beta}|^2 = |M_{\beta\alpha}|^2 \tag{8}$$

so equation (7) reduces to

$$J = \frac{4\pi e}{\hbar} \sum_{k_t} \int |M_{\alpha\beta}|^2 \rho_\alpha \rho_\beta (f_\alpha - f_\beta)\, dE \tag{9}$$

The matrix element has been evaluated by Harrison (ref. 3) in the WKB approximation and is given by

$$M_{\alpha\beta} = \left(\frac{1}{2\pi}\right) \rho_\alpha^{-1/2} \rho_\beta^{-1/2} \exp\left(-\int_{x_1}^{x_2} |k_x|\, dx\right) \tag{10}$$

where x_1 and x_2 are the classical turning points of the motion (see fig. 1),

$$k_x = \left\{\frac{2m}{\hbar^2}\left[V(x) - E_x\right]\right\}^{1/2} \tag{11}$$

V(x) is the barrier potential energy, and E_x is the "x-directed" part of the electronic energy of motion.

DESCRIPTION OF MODEL

A sketch of the potential barrier employed in this calculation is shown in figure 1.

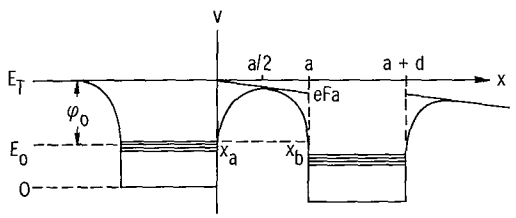

Figure 1. - Assumed electronic potential energy as a function of distance within the organic solid. Protein molecules are represented by a series of potential wells surrounded by finite potential barriers. The bottom of the well is the electronic ground state. A band of unfilled, higher lying energy states is shown for illustration. Scales of both ordinate and abscissa are arbitrary.

The organic solid is assumed to consist of a collection of molecules, each represented by a potential well surrounded by a potential barrier. Within an individual molecule the potential energy of an electron is assumed, as a first approximation, to be

$$V(x) = 0 \tag{12}$$

The nature of the potential energy within the molecules does not affect the tunneling coefficient in any way, so that this assumption is unimportant at this point. (The potential energy is important, however, in determining the flux of electrons impinging on the barrier.) The space between molecules is divided into two regions. In the first region $0 \leq x \leq (a/2)$, and in the second $(a/2) \leq x \leq a$, where a is the intermolecular separation. In the first region the potential barrier may be approximated by

$$V(x) = E_T - eFx - \frac{\gamma}{x} \tag{13}$$

and in the second

$$V(x) = E_T - eFx - \frac{\gamma}{a - x} \tag{14}$$

F is the externally applied electric field, E_T is the total depth of the potential well, and γ represents the strength of the interaction between an electron and the charge induced locally on the molecule when the electron emerges from it. In each region, what has been done is to ignore the attractive force exerted on an electron by any molecule which is more than one-half the intermolecular distance away. The forces cancel exactly when the electron is midway between the molecules (assuming that the molecular orientation is such that γ is the same for any two neighboring molecules). Otherwise the forces tend to lower the barrier a small amount at points away from the midpoint.

CALCULATION OF MATRIX ELEMENT

The matrix element describing the transition of an electron from one molecule to the next has the form, in this case,

$$M_{\alpha\beta} = \left(\frac{1}{2\pi}\right) \rho_\alpha^{-1/2} \rho_\beta^{-1/2} \exp - \left[\int_{x_1}^{a/2} \sqrt{\frac{2m}{\hbar^2} \left(E_T - eFx - \frac{\gamma}{x} - E_x \right)}\, dx \right.$$

$$\left. + \int_{a/2}^{x_2} \sqrt{\frac{2m}{\hbar^2} \left(E_T - eFx - \frac{\gamma}{a - x} - E_x \right)}\, dx \right] \tag{15}$$

The classical turning points are found by setting the integrands equal to zero. Thus for the region $0 \leq x \leq (a/2)$

$$E_T - E_x - eFx - \frac{\gamma}{x} = 0 \tag{16}$$

for which the smaller root is

$$x_1 = \frac{E_T - E_x - \sqrt{(E_T - E_x)^2 - 4\gamma eF}}{2eF} \tag{17}$$

Similarly, for $(a/2) \leq x \leq a$

$$(E_T - E_x)(a - x) - eFx(a - x) - \gamma = 0 \tag{18}$$

from which

$$x_2 = \frac{E_T - E_x + eFa - \sqrt{(E_T - E_x + eFa) + 4\gamma eF}}{2eF} \tag{19}$$

It will be convenient to make the following substitutions and change of variable

$$E_T - E_x = b \tag{20a}$$

$$eF = c \tag{20b}$$

$$x = t^2, \qquad 0 \leq x \leq (a/2) \tag{20c}$$

$$a - x = u^2, \qquad (a/2) \leq x \leq a \tag{20d}$$

The first integral thus becomes

$$I_1 = 2\sqrt{c} \int_{t_1}^{\sqrt{a/2}} \sqrt{- t^4 + \frac{b}{c} t^2 - \frac{\gamma}{c}}\, dt \tag{21}$$

while the second is

$$I_2 = - 2\sqrt{c} \int_{\sqrt{a/2}}^{u_2} \sqrt{u^4 + \frac{(b - ca)}{c} u^2 - \frac{\gamma}{c}}\, du \tag{22}$$

where

$$t_1 = \sqrt{x_1} \tag{23a}$$

$$u_2 = \sqrt{a - x_2} \tag{23b}$$

The integral in equation (21) may be cast into standard elliptic form by making the

substitutions

$$p^2 = \frac{1}{2}\left(\frac{b}{c} - \sqrt{\frac{b^2}{c^2} - 4\frac{\gamma}{c}}\right) \tag{24a}$$

$$q^2 = \frac{1}{2}\left(\frac{b}{c} + \sqrt{\frac{b^2}{c^2} - 4\frac{\gamma}{c}}\right) \tag{24b}$$

Comparing equation (24a) with equation (17) reveals that

$$x_1 \equiv p^2 \tag{25}$$

so that equation (21) becomes

$$I_1 = 2\sqrt{c}\int_p^{\sqrt{a/2}} \sqrt{(t^2 - p^2)(q^2 - t^2)}\, dt \tag{26}$$

This integral can be found in a table of elliptic integrals (ref. 5) and may be written as

$$I_1 = \frac{2\sqrt{c}}{3}\left\{q\left[(q^2 + p^2)E(\varphi, k) - 2p^2F(\varphi, k)\right] + \frac{\frac{a}{2} - q^2 - p^2}{\sqrt{\frac{a}{2}}}\sqrt{\left(q^2 - \frac{a}{2}\right)\left(\frac{a}{2} - p^2\right)}\right\} \tag{27}$$

provided that $q^2 \geq (a/2) \geq p^2$. $E(\varphi, k)$ and $F(\varphi, k)$ are the incomplete elliptic integrals of the first and second kinds, respectively, and

$$k^2 = \frac{q^2 - p^2}{q^2} \tag{28a}$$

$$\sin\varphi = \frac{q}{\sqrt{\frac{a}{2}}}\sqrt{\frac{\frac{a}{2} - p^2}{q^2 - p^2}} \tag{28b}$$

By making the substitutions

$$r^2 = \frac{1}{2}\left[\frac{b - ac}{c} + \sqrt{\left(\frac{b - ac}{c}\right)^2 + 4\frac{\gamma}{c}}\right] \tag{29a}$$

$$s^2 = \frac{1}{2}\left[\frac{b - ac}{c} - \sqrt{\left(\frac{b - ac}{c}\right)^2 + \frac{4\gamma}{c}}\right] \tag{29b}$$

in equation (22) and noting that

$$u_b = a - x_2 = s^2 \tag{30}$$

I_2 becomes

$$I_2 = -2\sqrt{c}\int_{\sqrt{a/2}}^{s} \sqrt{(u^2 + s^2)(u^2 + r^2)}\, du \tag{31}$$

This too is in a standard form and can be found in the tables (ref. 5). The result is

$$I_2 = \frac{2}{3}\sqrt{c}\left\{\sqrt{s^2 + r^2}\left[(s^2 - r^2)E(\varphi_1, k_1) - s^2 F(\varphi_1, k_1)\right] + \frac{\frac{a}{2} + r^2 - s^2}{\sqrt{\frac{a}{2}}}\sqrt{\left(r^2 + \frac{a}{2}\right)\left(\frac{a}{2} - s^2\right)}\right\} \tag{32}$$

provided that $r^2 \geq (a/2) \geq s^2$, and where

$$k_1^2 = \frac{r^2}{r^2 + s^2} \tag{33a}$$

$$\cos \varphi_1 = \frac{s}{\sqrt{\frac{a}{2}}} \tag{33b}$$

It should be noted that the two elliptic integrals are not quite the same. This arises because of the change in the origin of the dominant image charge as the electron traverses the barrier region.

Before inserting these results into the expression for $M_{\alpha\beta}$, it will be helpful to define two dimensionless variables, y and y_1. They are

$$y = \left(\frac{4\gamma c}{b^2}\right)^{1/2} \tag{34a}$$

$$y_1 = \left[\frac{4\gamma c}{(b - ac)^2}\right]^{1/2} \tag{34b}$$

The matrix element may now be written as

$$M_{\alpha\beta} = \frac{1}{2\pi} \rho_\alpha^{-1/2} \rho_\beta^{-1/2} \exp - \left\{\frac{\sqrt{2m}}{3\hbar eF} (E_T - E_x)^{3/2} \left[v(y) + \left(1 - \frac{ay}{2}\right)\sqrt{\frac{eF}{\gamma}}\, w(y_1)\right]\right\} \tag{35}$$

where

$$v(y) = \frac{\sqrt{1 + \sqrt{1 - y^2}}}{\sqrt{2}} \left[E(\varphi, k) - 2\left(1 - \sqrt{1 - y^2}\right)F(\varphi, k) + \left(\frac{\sqrt{\frac{\gamma}{eF}}}{y}\right)^{1/2} \left(\frac{\frac{ay}{2}\sqrt{\frac{eF}{\gamma}} - 2}{\sqrt{\frac{a}{2}}}\right)\right.$$

$$\left. \times \sqrt{\left(1 + \sqrt{1 - y^2} - \frac{ay}{2}\sqrt{\frac{eF}{\gamma}}\right)\left(\frac{ay}{2}\sqrt{\frac{eF}{\gamma}} - 1 + \sqrt{1 - y^2}\right)}\right] \tag{36}$$

and

$$w(y_1) = \frac{\left(\sqrt{1 + y_1^2}\right)^{1/2}}{\sqrt{2}} \left[\left(1 - \sqrt{1 + y_1^2}\right)F(\varphi_1, k_1) - 2E(\varphi_1, k_1) + \left(\frac{\sqrt{\frac{\gamma}{eF}}}{y_1}\right)^{1/2}\right.$$

$$\left. \times \left(\frac{\frac{ay_1}{2}\sqrt{\frac{eF}{\gamma}} + 2}{\sqrt{\frac{a}{2}}}\right) \sqrt{\left(1 + \sqrt{1 + y_1^2} + \frac{ay_1}{2}\sqrt{\frac{eF}{\gamma}}\right)\left(\frac{ay_1}{2}\sqrt{\frac{eF}{\gamma}} + 1 - \sqrt{1 + y_1^2}\right)}\right] \tag{37}$$

CALCULATION OF CURRENT DENSITY

The expression for the current density is, after inserting equation (35) into equations (9) and (15)

$$J = \frac{2e}{h} \sum_{k_t} \int_{E_1}^{\infty} \exp\left(\frac{-2\sqrt{2m}}{3\hbar eF} (E_T - E_x)^{3/2} \left\{ v(y) + \left[1 - \frac{ay}{2} \sqrt{\frac{eF}{\gamma}} \, w(y_1) \right] \right\}\right) dE \tag{38}$$

where E_1 is the energy associated with the motion of an electron parallel to the barrier surface (i.e., perpendicular to the net current direction) and is a function of k_t. The basic assumption proposed by Kemeny and Rosenberg (ref. 2) was that electrons are thermally excited from their molecular ground state to some intermediate state below E_T from which they then tunnel. Accordingly, the occupation probability of such a state on the left of the barrier can be assumed to be

$$f_d = \exp\left(\frac{-E}{kT}\right) \tag{39}$$

and on the right side it is

$$F_\beta = \exp\left(-\frac{E + eFa}{kT}\right) \tag{40}$$

Hence

$$J = \frac{2e}{h} \sum_{k_t} \int_{E_T}^{\infty} D(E_T - E_x) \left[\exp\left(\frac{-E}{kT}\right) - \exp\left(-\frac{E + eFa}{kT}\right) \right] dE \tag{41}$$

where $D(E_T - E_x)$ contains all the other factors in equation (38) and is known as the tunneling coefficient. Converting the sum over k_t to an integral and separating the "perpendicular" energy from the "x-directed" energy fields

$$J = \frac{2\bar{e}}{h^3} \int_0^\infty \int_0^\infty \int_0^\infty D(E_T - E_x) \exp\left(\frac{-p_y^2 - p_z^2}{2mkT}\right) \left[\exp\left(\frac{-E_x}{kT}\right) - \exp\left(-\frac{E_x + eFa}{kT}\right)\right] dE_x\, dp_y\, dp_z \qquad (42)$$

Carrying out the integration over p_y and p_z, the momentum components in the y and z directions, respectively,

$$J = \frac{4\pi mekT}{h^3} \int_0^\infty D(E_T - E_x) \exp\left(\frac{-E_x}{kT}\right) \left[1 - \exp\left(\frac{-eFa}{kT}\right)\right] dE_x \qquad (43)$$

The applied electric fields are typically less than 1000 volts per centimeter (~3 stat V/cm). If γ is assumed to be $e^2/4$ (its value for the image charge induced by an electron leaving a metallic surface) and if $E_T - E_x$ is of the order of 1 or 2 electron volts,

$$y^2 = \frac{e^3 F}{(E_T - E_x)^2} \simeq 5\times10^{-6}\, F \qquad (44)$$

(F in stat V/cm). A representative range for the intermolecular separation a is 10^{-8} to 10^{-7} centimeter so that

$$y_1 = \frac{e^3 F}{(E_T - E_x - eFa)^2} \simeq 5\times10^{-6}\, F \qquad (45)$$

as well. For values of y and y_1 this small.

$$v(y) \simeq w(y_1) \simeq 1 \qquad (46)$$

so that

$$D(E_T - E_x) \simeq \exp\left[\frac{-4\sqrt{2m}}{3\hbar eF} (E_T - E_x)^{3/2}\right] \qquad (47)$$

The current density thus becomes

$$J = \frac{4\pi mekT}{h^3} \int_0^{E_T} \exp\left(\frac{-4\sqrt{2m}}{3\hbar eF}\right)(E_T - E_x)^{3/2} \times \exp\left(\frac{-E_x}{kT}\right) \times \left[1 - \exp\left(\frac{-eFa}{kT}\right)\right] dE_x$$

$$+ \int_{E_T}^{\infty} \exp\left(\frac{-E_x}{kT}\right) \times \left[1 - \exp\left(\frac{-eFa}{kT}\right)\right] dE_x \qquad (48)$$

The integration breaks into two ranges because $D(E_T - E_x)$ becomes unity when $E_x \geq E_T$. The second integral is much smaller than the first and can be ignored. In addition, since $eFa/kT << 1$ for the range of field values chosen, equation (48) becomes

$$J = \frac{4\pi me^2Fa}{h^3} \int_0^{E_T} \exp\left(\frac{-4\sqrt{2m}}{3\hbar eF}\right)(E_T - E_x)^{3/2} \exp\left(\frac{-E_x}{kT}\right) dE_x \qquad (49)$$

Activation energies for semiconduction in many proteins have been found to be remarkably uniform, falling within a range of 2.6 to 3.1 electron volts (ref. 6). This is considerably less than the ionization potentials of such molecules ($E_T \simeq 10$ eV). Instead of restricting the electrons to a single excited level, however, as did Kemeny and Rosenberg (ref. 2), we assume here that a small band of energies exists, the lowest level of which lies in the observed range of activation energies. In such a case the logarithm of the tunneling coefficient may be expanded about the lowest level in a Taylor series. Denoting the lowest level by E_o

$$\ln D(E_T - E_x) = \frac{-4\sqrt{2m}}{3\hbar eF}\left\{(E_T - E_o)^{3/2} - \frac{3}{2}(E_T - E_o)^{1/2}(E_x - E_o)\right.$$

$$\left. + \frac{3}{8}(E_1 - E_o)^{-1/2}(E_x - E_o)^2 + \cdots\right\} \qquad (50)$$

Inserting this expression in equation (49),

$$J = \frac{4\pi m e^2 F a}{h^3} \exp\left(\frac{-E_o}{kT}\right) \int_{E_o}^{\infty} \exp - \left[\frac{4\sqrt{2m\varphi_o^3}}{3\hbar e F} + \left(\frac{-2\sqrt{2m\varphi_o}}{3\hbar e F} + \frac{1}{kT} \right) (E_x - E_o) + \frac{\sqrt{\frac{2m}{\varphi_o}}}{2\hbar e F} (E_x - E_o)^2 \right] dE_x \qquad (51)$$

where

$$\varphi_o = E_T - E_o \qquad (52)$$

The integration in equation (51) should, in principle, extend only over the allowed band of energy levels beginning at E_o. Because the integrand falls off so rapidly for higher energies, the error introduced by extending the range to infinity will not be too great. It will, if anything, produce an overestimate of the magnitude of the tunneling current. The integral in equation (51) may be readily evaluated (ref. 7). The result is

$$J = \frac{4\pi m e^2 F a}{h^3} \exp\left(\frac{-E_o}{kT}\right) \left\{ \left(\frac{\hbar e F \varphi_o^{1/2}}{\sqrt{2m}} \right) \exp \left[\frac{\left(\frac{-\sqrt{2m\varphi_o}}{\hbar e F} + \frac{1}{2kT} \right)^2 - \frac{8m\varphi_o}{3(\hbar e F)^2}}{\frac{\sqrt{\frac{2m}{\varphi_o}}}{2\hbar e F}} \right] \right\} \times \left\{ 1 - \operatorname{erf} \left[\frac{\frac{\sqrt{2m\varphi_o}}{\hbar e F} - \frac{1}{2kT}}{\left(\frac{\sqrt{\frac{2m}{\varphi_o}}}{2\hbar e F} \right)^{1/2}} \right] \right\} \qquad (53)$$

where erf is the error function.

Considerable simplification of the preceding expression developed for the current density can be achieved by noting the relative magnitudes of some of the terms. A reasonable assumption for φ_o is 5 electron volts, while barrier heights are of the order of 6 to 10 electron volts, and E_o is of the order of 2 to 3 electron volts. Using the free electron value for the mass of the electron yields

$$\frac{\sqrt{2m\varphi_o}}{\hbar eF} \simeq \frac{2.3\times10^7}{F} \tag{54}$$

At room temperature,

$$\frac{1}{2kT} \simeq 1.2\times10^{13} \tag{55}$$

Furthermore,

$$\frac{8m\varphi_o}{3(\hbar eF)^2} \simeq \frac{7.5\times10^{34}}{F^2} \tag{56}$$

so equation (53) becomes

$$J \simeq \frac{4\pi me^2Fa}{h^3}\left(\frac{\hbar eF\sqrt{\varphi_o}}{\sqrt{2m}}\right)^{1/2} \exp\left(\frac{-E_o}{kT}\right) \exp\left(\frac{-2\sqrt{2m\varphi_o^3}}{3\hbar eF}\right)\left\{1 - \operatorname{erf}\left(\frac{2\sqrt{2m\varphi_o^3}}{\hbar eF}\right)^{1/2}\right\} \tag{57}$$

Since the argument of the error function is very large ($\sim 10^5$) the following asymptotic expansion may be used (ref. 7).

$$(\operatorname{erf})(x) = 1 - (a_1 l + a_2 l^2 + a_3 l^3)\, e^{-x^2} + \cdots \tag{58}$$

where

$$l = \frac{1}{1 + nx} \tag{59a}$$

$$n = 0.4705 \tag{59b}$$

$$a_1 = 0.3480 \tag{59c}$$

$$a_2 = -0.0959 \tag{59d}$$

$$a_3 = 0.7479 \tag{59e}$$

For an electric field of 300 volts per centimeter (1 stat V/cm) and values of electron mass and barrier height used previously, $l \simeq 3\times10^{-6}$. This means that

$$\operatorname{erf}\left(\frac{2\sqrt{2m\varphi_o^3}}{\hbar eF}\right)^{1/2} \simeq 1 - 0.75\left(\frac{2\sqrt{2m}}{\hbar eF}\varphi_o^{3/2}\right)^{-1/2} \exp\left(\frac{-2\sqrt{2m}\ \varphi_o^{1/2}}{\hbar eF}\right) \tag{60}$$

Hence, the current density becomes

$$J = 3\left(\frac{\pi m}{2\varphi_o}\right)^{1/2} e^3F^2a \exp\left(\frac{-E_o}{kT}\right) \exp\left(\frac{-8\sqrt{2m\varphi_o^3}}{3\hbar eF}\right) \tag{61}$$

from which the electrical conductivity is

$$\sigma = \frac{J}{F} = 3\left(\frac{\pi m}{2\varphi_o}\right)^{1/2} e^3Fa \exp\left(\frac{-E_o}{kT}\right) \exp\left(\frac{-8\sqrt{2m\varphi_o^3}}{3\hbar eF}\right) \tag{62}$$

DISCUSSION

The conductivity given by equation (62) is not in the form required by the compensation law. If, though, the assumption is made that

$$\varphi_o^{3/2} = (E_T - E_o)^{3/2} \simeq E_T^{3/2}\left(1 - \frac{3E_o}{2E_T} + \cdots\right) \tag{63}$$

then equation (62) can be rewritten to have the proper form. This is the approach used by Kemeny and Rosenberg (ref. 2) in their calculation of the conductivity using both rectangular and triangular intermolecular potential barriers. Since E_o appears to be from 20 to 30 percent of E_T, however, stopping at the linear term is not obviously justified. Thus, there is a failure to agree even qualitatively with observed experi-

mental behavior. In addition, the model fails to produce any degree of quantitative agreement. Again, for the relatively high applied field of 300 volts per centimeter,

$$-\log_{10} \sigma \simeq 1.3 \times 10^{6} \tag{64}$$

Observed values of $-\log_{10} \sigma$ are in the range from 0 to 20. The large value for the negative of the logarithm means that σ is essentially zero.

The failure of this model to predict the magnitude of the conductivity is not surprising. For low values of the applied electric field (i.e., $<10^5$ V/cm), the potential barrier will not be distorted much from its shape in zero applied field. Hence, the probabilities for tunneling from either side of the barrier to the other will be nearly equal, with the result that the net current will be extremely small. This fact does not appear to have been considered by Kemeny and Rosenberg in their discussion. The expressions they used are valid if tunneling is considered to proceed in one direction only. Such is the case, for example, in field emission from a metallic surface into vacuum, where there are filled electron states on only one side of the barrier. Tunneling through potential barriers between neighboring molecules does not have this natural asymmetry in the direction of current flow, since presumably there are filled electron states on both sides of the barrier. It is possible that the states are not identical on each side of the barrier, which could introduce the necessary asymmetry, but that is a question which is beyond the scope of the present discussion.

The restriction to low fields was made in this calculation only because they are normally encountered in practice, and because considerable simplification of the calculation is achieved by so doing. An investigation of the behavior of the tunneling current at higher electric fields presently can only be done with the aid of a computer and is under investigation. The implicit assumption has been made that the electric field existing between neighboring molecules is just the applied field. The presence of some kind of field-enhancing effect which might alter the local electric fields could drastically affect the barrier shape, and therefore the current density. This possibility will also be explored.

CONCLUSIONS

The conductivity obtained from the model used can be written in the form of the "compensation law," but the approximation required to do so (eq. (63)) is not a particularly good one. More serious, however, is the complete lack of quantitative agreement with observed conductivities. This failure is directly attributable to the fact that the barrier symmetry is not altered appreciably by low electric fields, such as are normally

encountered experimentally, so that the net current through the barrier is essentially zero. The present results suggest, therefore, that electron tunneling, unassisted by any enhancing effects, is not a suitable mechanism for the explanation of the electrical conductivities of proteins.

Lewis Research Center,
National Aeronautics and Space Administration,
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APPENDIX - SYMBOLS

a	intermolecular separation
b	difference between barrier height and x-directed energy, $E_T - E_x$
c	product of electronic charge and applied electric field, eF
$D(E_T - E_x)$	tunneling coefficient
E	total energy of an electron
E_A	activation energy
E_o	electronic energy level to which tunneling occurs
E_T	depth of molecular potential well
E_x	x-directed electronic energy of motion
$E_\perp$	electronic energy of motion parallel to barrier surface
$E(\varphi, k)$	incomplete elliptic integral of first kind
e	electronic charge
erf	error function
F	applied electric field
$F(\varphi, k)$	incomplete elliptic integral of second kind
f_α, f_β	occupation probabilities
h	Planck's constant
$\hbar$	Planck's constant divided by 2π
i	$\sqrt{-1}$
J	current density
J_x	x-component of current density operator
$J_{\alpha\beta}(x)$	matrix element of x-component of current density operator
k	Boltzmann constant
k, k_1	moduli of incomplete elliptic integrals
k_t	transverse component of wave number
k_x	x-component of wave number
$M_{\alpha\beta}$	tunneling matrix element
m	mass of an electron
$P_{\alpha\beta}$	probability per unit time for transition from one electronic state to another
p_y	y-component of momentum
p_z	z-component of momentum
T	temperature
t	integration variable, $\sqrt{x}$
u	integration variable, $\sqrt{a - x}$
$V(x)$	intermolecular barrier potential energy
$v(y)$, $w(y_1)$	dimensionless variables
x_1, x_2	classical turning points of electronic motion
y, y_1	dimensionless variables
α, β	electronic state indices
γ	constant in image charge potential energy expression

ξ, η constants

ρ_α, ρ_β density-of-states factors

$\sigma(T)$ electrical conductivity as a function of temperature

σ_o pre-exponential factor in electrical conductivity

φ_o difference between barrier height and energy level to which electrons tunnel, $E_T - E_o$

φ, φ_1 arguments of incomplete elliptic integrals

ψ_α, ψ_β wave functions for electrons in states α and β

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