MODELS OF EXTENDED ELECTRON STATES IN PROTEINS

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ABSTRACT. A new approach to the problem of electron states in the protein molecule is described. A 'dielectric cavity' model is used for the protein globule as a basis for the consideration of the extended states which are mostly formed by the polarization field of the protein macromolecule. In a protein solution the size of such a state can be compared with the size of the macromolecule. The share of the extended states in the biomolecular processes of charge transfer is discussed. Electron energies of the ground and the first excited self-consistent states are calculated. Typical values of the predicted energies of absorption bands and luminescence are found to be $\sim$ 1000 nm for the ground state's absorption band and $\sim$ 2000 nm for the excited state's luminescence. Various methods for the experimental observation of such states are discussed.

1. Introduction

Research into the theory of the polaron in condensed systems may significantly broaden our knowledge of the electron states and transfer in biological systems. The most general representation of the polaron may be given by the picture of an electron which, if placed in a polar medium, enters into a self-localised state where it does not form chemical bonds with the atoms of the medium. The polaron may be imagined as an electron being trapped by a potential well formed by electron-induced polarization of the surrounding molecules of the medium [1]. Using this representation, it was discovered that there are multiple, rather than a single, discrete polaron states which have their own potential wells consistent with the electrons trapped [2, 3]. One of the principal consequences is that the first excited self-consistent polaron state has a large excitation region, and may include about 10^3–10^4 and more molecules of the medium for water, ammonia and other polar liquids. These findings in their turn point to the necessity of critically analyzing the problem of long-distance electron transfers [4, 5], namely their biological role and impacts. This paper is concerned with a study of precisely these states in protein macromolecules. We shall show that the allowance for the large-radius electron states may lead to many new results. The very fact that they exist suggests new types of absorption and luminescence in solutions of globular

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proteins. For a spherically symmetric protein with an electron acceptor in the centre of the globule the presence of an excited polaron state of large radius implies isotropy of binary chemical reactions under excitation.

In this paper we present the physical representation of the polaron in a condensed medium in agreement with the representation of the polaron properties of the protein molecule. We shall formulate simple mathematical models of the polaron states in the protein and discuss some of the effects to which they lead.

2. A Continuous Model

In order to introduce into what is meant by large-radius electron states in globular protein macromolecules it is necessary to examine continuous representations of these objects. It is also desirable to discuss the hierarchy of continual models we will use. The representation of a protein macromolecule that takes the form of a sphere in solution as its microphase was introduced by Bresler and Talmud [6] who proceeded from the hydrophobic properties of the protein. Progress in the modeling of protein globules led, in its turn, to a whole set of electrostatic models [7, 8]. The simplest of them, which is the model of a dielectric cavity, is shown in Figure 1a. The model assumes that $\varepsilon_1 < \varepsilon_0$, which corresponds to a low static dielectric permittivity of the protein medium compared to the strongly polarized solvent. We stress that, this model, although very simple, can give a qualitative explanation of a good many experimental findings on protein transport and electrophoresis [9]. A more realistic model of a three-layer globule is shown in Figure 1b. This model allows for the

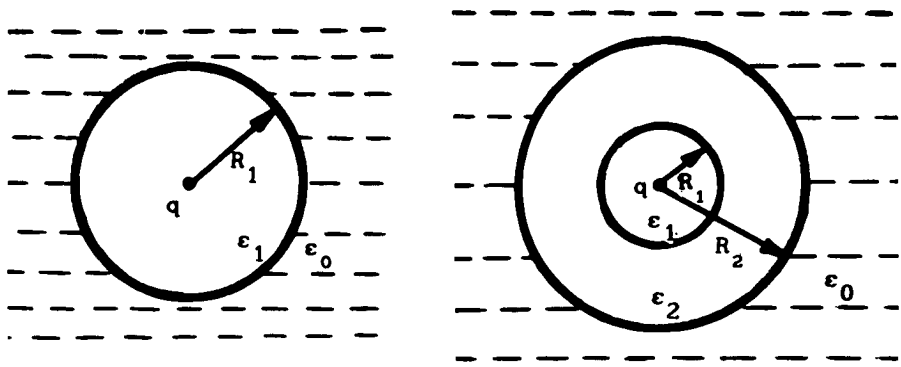

Figure 1. Two layer (a) and three layer (b) models of the protein globule.

contribution of different factors to dielectric permittivity in the region $R_1 < r < R_2$. The factors are: the presence of amino acid residues, the penetration of water molecules into the superficial layer, the unsmoothness of the protein surface etc. We assume that, the solvent molecules cannot penetrate into the region $r < R_1$. In this model $\varepsilon_1 < \varepsilon_2 < \varepsilon_0$. Physical

values of dielectric permittivity can be found experimentally: $\varepsilon_1 \approx 4$ is the value for NN-dimethylacetamide, which is the monomeric analogue of a protein peptide framework (the solvent impervious region $r < R_1$); $\varepsilon_0 = 80$ is the value for water as a solvent; and the layer $R_1 < r < R_2$ is ascribed a mean value of $\varepsilon_2 \approx 40$, which in a more general sense is a parameter of the model. There are many models which assume that dielectric permittivity inside the globule depends on a coordinate (like $\varepsilon = |r|$) [10], including a good number of nonlocal continuous models of the dielectric cavity [11].

While substantiating a mathematical model of polaron-type electron states in the protein globule, the ratio $\langle r \rangle / \bar{a}$ is the most important parameter, where $\bar{a}$ is the mean distance between two neighboring atoms of the protein molecule, and $\langle r \rangle$ is the effective polaron radius. The estimate $\bar{a}$ draws a clear distinction between a protein macromolecule and an ionic crystal for which the criterion $\langle r \rangle / \bar{a} \gg 1$ shows that the model is continuous. In the ionic crystal polarization is caused by a small deviation of ions from their equilibrium states, so that $\bar{a} \sim a$ where a is the lattice constant. The protein molecule requires an additional averaging if the lifetime of the electron state is much larger than the characteristic time of oscillation for twisting degrees of freedom and for deviations of macromolecular polar groups, which normally is less than 10^{-12}s. This situation is illustrated in Figure 2 which is the result of a molecular-dynamic computer simulation. In this way, for the long-living states below, the model of a polar medium is 'more continuous' in the protein molecule than in the ionic crystal.

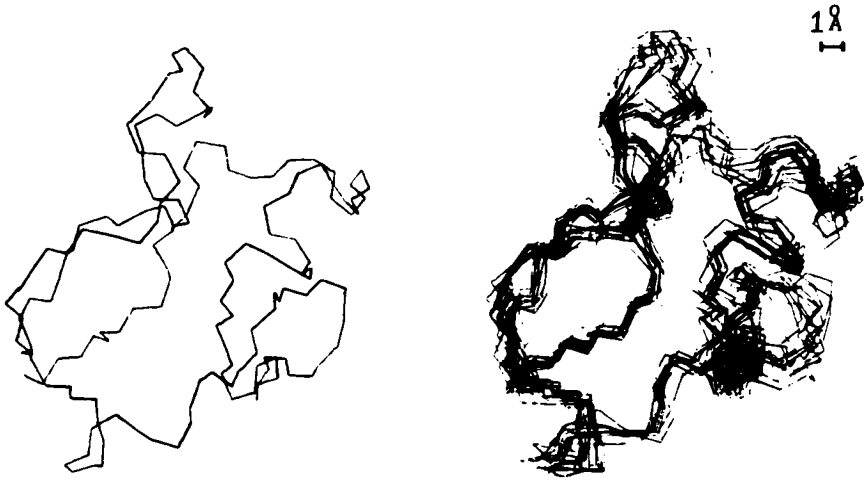

Figure 2. A plane projection of the instantaneous configuration of the main chain $(\text{-}N\text{-}C^{\alpha}\text{-}C\text{-})_{54}$ of a ferredoxin molecule (a), and superimposed projections of ten consecutive configurations of this molecule taken with a time Δt equal to 0,6 ps (b).

3. A Polaron Model for an Infinite Isotropic Medium

A polaron description of the electron state in a polar medium usually starts with the as-

sumption that the mean Coulomb field induced by the surplus electron locally polarizes the medium. The electrical field in its turn influences the electron [1]. It is essential that the electron interacts only with the inertial part of polarization it induces, so that

$$\boldsymbol{P}(\boldsymbol{r}) = \boldsymbol{P}_0(\boldsymbol{r}) - \boldsymbol{P}_\infty(\boldsymbol{r}) \tag{1}$$

where

$$\boldsymbol{P}_0 = \frac{\varepsilon_0 - 1}{4\pi\varepsilon_0}\boldsymbol{D}\,, \qquad \boldsymbol{P}_\infty = \frac{\varepsilon_\infty - 1}{4\pi\varepsilon_\infty}\boldsymbol{D}$$

are specific dipole moments of static and high-frequency polarizations; ε_0 and ε_∞ are static and high-frequency dielectric permittivities, respectively, and $\boldsymbol{D}$ is electron induction. Hence

$$\boldsymbol{P}(\boldsymbol{r}) = \frac{\boldsymbol{D}(\boldsymbol{r})}{4\pi\tilde{\varepsilon}}\,, \tag{2}$$

$\tilde{\varepsilon}^{-1} = \varepsilon_\infty^{-1} - \varepsilon_0^{-1}$ is the effective dielectric permittivity. The vector of electric induction caused by the distributed electron charge with density $e|\Psi(\boldsymbol{r})|^2$ is equal to

$$\boldsymbol{D}(\boldsymbol{r}) = e\int |\Psi(\boldsymbol{r}')|^2 \frac{\boldsymbol{r} - \boldsymbol{r}'}{|\boldsymbol{r} - \boldsymbol{r}'|^3}\, d\boldsymbol{r}'\,, \tag{3}$$

where $\Psi(\boldsymbol{r})$ is the wave function which can be given from the solution of the Schrödinger equation

$$\frac{\hbar^2}{2\mu}\Delta\Psi(\boldsymbol{r}) + e\Pi(\boldsymbol{r})\Psi(\boldsymbol{r}) + W\Psi(\boldsymbol{r}) = 0\,, \tag{4}$$

where W is the electron energy. The potential $\Pi(\boldsymbol{r})$, created by the electron-induced polarization $\nabla\Pi(\boldsymbol{r}) = 4\pi\boldsymbol{P}(\boldsymbol{r})$, can, by (2) and (3), be found from the Poisson equation

$$\Delta\Pi(\boldsymbol{r}) + 4\pi\tilde{\varepsilon}^{-1}e|\Psi(\boldsymbol{r})|^2 = 0 \tag{5}$$

The system of nonlinear differential equations (4) and (5) fully determines the state of an electron in an infinite polar medium. Peckar [1] used variational principle to find the ground state of Equations (4) and (5). Balabaev and Lakhno [2] integrated them numerically and obtained solutions corresponding to the excited polaron states different from the ground state. The approach we have given here will be used further to describe the polaron states in a protein globule.

4. The Polaron Equation for a Protein Globule

Our mathematical model of polaron states in the protein globule described by the model of a dielectric cavity is based on the following assumptions:

(1) The globule is neutral and has zero effective surface net charge on the layer boundaries;

(2) The electron states in the globule are thought of as the acceptor's potential-bound polaron states;

(3) Each layer is described by a separate isotropic model of continual polar medium, and the electron wave function and the potentials are assumed to be smooth both within and on the boundaries of each layer;

(4) All the other assumptions are identical with those adopted to describe the polaron states in polar media [1].

For a spherically symmetric case the assumptions (1–4) yield the following equations for the polaron in a protein globule

$$\frac{\hbar^2}{2\mu}\left(\frac{1}{r^2}\,\frac{d}{dr}\,r^2\,\frac{d}{dr}\right)\Psi(r)+e(\Pi(r)+\Phi(r))\Psi(r)+W\Psi(r)=0 \tag{6}$$

$$\frac{1}{r^2}\,\frac{d}{dr}\,r^2\,\frac{d}{dr}\,\Pi(r)+\frac{4\pi e}{\tilde{\varepsilon}_i}\,\Psi^2(r)=0 \tag{7}$$

$$R_{i-1}<r<R_i\,,\quad i=1,2,\ldots;\quad R_0\equiv 0\,,$$

where $\Phi(r)$ is the potential of acceptor

$$\Phi(r)=\begin{cases} q/\varepsilon_1 r+c_1\,, & r<R_1\\ q/\varepsilon_2 r\,, & r>R_1\end{cases} \tag{8}$$

for the two-layer model of the globule ($\varepsilon_2=\varepsilon_0$) and

$$\Phi(r)=\begin{cases} q/\varepsilon_1 r+c_1'\,, & r<R_1\\ q/\varepsilon_2 r+c_2'\,, & R_1<r<R_2\\ q/\varepsilon_3 r\,, & r>R_2\end{cases} \tag{9}$$

for the three-layer model of the globule ($\varepsilon_3=\varepsilon_0$). The constants c_1, c_1' and c_2' are defined from the continuity of potential $\Phi(r)$ at the boundaries of globular layers; $\Pi(r)$ is the potential of electron-induced polarization, μ is the electron effective mass, $\tilde{\varepsilon}_i^{-1}=\varepsilon_\infty^{-1}-\varepsilon_i^{-1}$ are the effective dielectric constants of the ith layer, and ε_∞ is the high-frequency dielectric constant which we assume identical for all the layers.

The natural boundary conditions for Equations (6) and (7) follow from the condition that the wave function is bounded and continual and that the potential is continual on the boundaries of globular layers, so that

$$\begin{aligned}&\Psi'(0)+\frac{\mu q e}{\varepsilon_1\hbar^2}\,\Psi(0)=\Pi'(0)=0\,,\quad \Psi(\infty)=\Pi(\infty)=0\\ &\Psi(R_i-0)=\Psi(R_i+0)\,,\quad \Psi'(R_i-0)=\Psi'(R_i+0)\\ &\Pi(R_i-0)=\Pi(R_i+0)\,,\quad \tilde{\varepsilon}_i\Pi'(R_i-0)=\tilde{\varepsilon}_{i-1}\Pi'(R_i+0)\end{aligned} \tag{10}$$

Equation (6) is the Schrödinger equation for the electron in the potential $-(\Pi+\Phi)$ which is given in a self-consistent way by (7). So, the nonlinear system of differential equations (6–7) with the boundary conditions (10) describes bound polaron states in the protein globule. Its solution determines the wave function of the electron state Ψ and the electron energy W, as well as the total energy of the state I_F, which is given by the functional

$$I_F[\Psi,\Pi]=\frac{\hbar^2}{2\mu}\int(\nabla\Psi)^2dr-e\int\Psi^2(\Pi+\Phi)dr+\sum_i\frac{\tilde{\varepsilon}_i}{8\pi}\int\limits_{\Omega_i}(\nabla\Pi)^2dr \tag{11}$$

The last term of (11) is integrated over regions Ω_i, which correspond to the layers of the dielectric cavity model. We should stress that Equations (6) and (7) may be given by an independent variation of the functional (11) with respect to the wave function $\Psi(r)$ and the potential $\Pi(r)$ with the wave function normalized by $\int \Psi^2(\boldsymbol{r})d\boldsymbol{r} = 1$.

5. Solutions of Polaron Equations. The Ground State

The system (6–7) with the boundary conditions (10) can be integrated numerically. The case of polar media homogenity (all $\varepsilon_i = \varepsilon_0$) suggests an F-centre problem solved by Lakhno and Balabaev [3]. If one regards a many-layer model of a protein as being globular the solution of the problem (6–7) is analogous to the previous one. The system has a discrete set of solutions which are the self-consistent states of electron and polarization of the globule and its surroundings. Figure 3a shows a node-free solution (zero mode), and Figure 3b the solution with a node which corresponds to the excited self-consistent state (first mode). In this section we only dwell on the findings for the ground state.

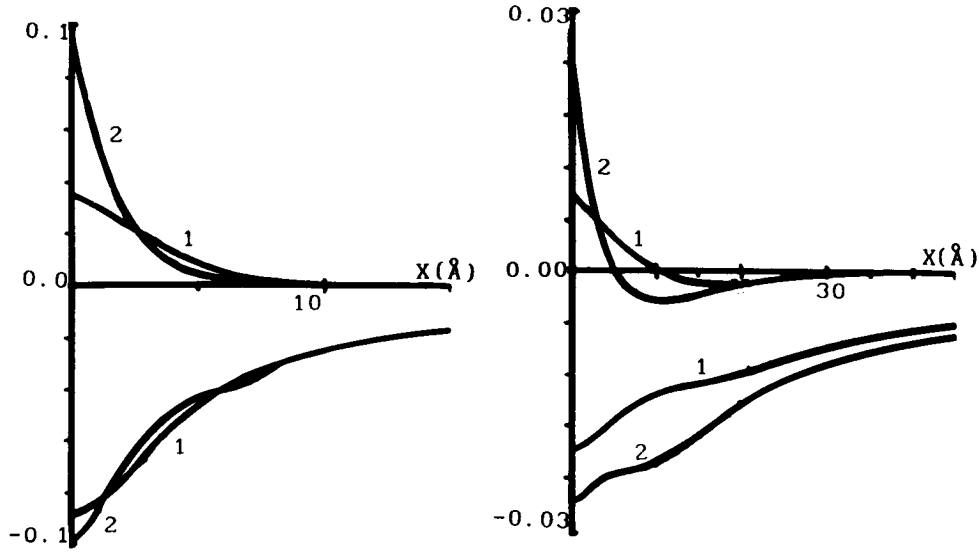

Figure 3. Solutions of the polaron equations for the two-layer (1) and the three-layer (2) models of the protein globule: a–zero mode, b–first mode. The upper part of the figure shows functions $\Psi(X)(\int 4\pi X^2\Psi^2 dX = 1)$ and the lower part shows functions $\Pi(X)\,\frac{\hbar^2}{\mu e^3}$ ($\approx$ 0.09 $\Pi(X)$).

For the two- and three-layer models of dielectric cavity Table 1 lists the following values which characterize the self-consistent ground state: electron (W_{1S}) and total (I_{1S}) energies; electron levels (non-self-consistent) in $2S$ (W_{2S}) and in $2P$ (W_{2P}) states and the corresponding total energies (I_{2S}, I_{2P}), as well as the states' radii ($\langle r\rangle_{1S}$, $\langle r\rangle_{2S}$, $\langle r\rangle_{2P}$) for both the

models.

Table 1. Polaron state characteristics in the protein globule.

Physical value[1)]	Two-layer model[2)]		Three-layer model[3)]	
	0-mode	1-mode	0-mode	1-mode
W_{1S}	−1.316	−0.401	−2.200	−1.035
W_{2S}	−0.529	−0.256	−0.697	−0.424
W_{2P}	−0.695	−0.283	−0.806	−0.413
I_{1S}	−0.508	−0.238	−1.243	−0.779
I_{2S}	0.280	−0.093	0.255	−0.169
I_{2P}	0.114	−0.120	0.146	−0.158
$\langle r\rangle_{1S}$	3.7	8.3	2.3	3.1
$\langle r\rangle_{2S}$	10.0	19.5	7.6	12.2
$\langle r\rangle_{2P}$	6.8	16.0	5.7	11.0

1) The values of energies W_{1S}, W_{2S}, W_{2P} and I_{1S}, I_{2S}, I_{2P} are in eV; the averaged radii $\langle r\rangle_{1S}$, $\langle r\rangle_{2S}$, $\langle r\rangle_{2P}$ in Å.
2) $\varepsilon_1 = 20$, $\varepsilon_2 = 80$, $\varepsilon_\infty = 2$, $R_1 = 15$ Å, $\mu = m_0$, $Z = 1$.
3) $\varepsilon_1 = 4$, $\varepsilon_2 = 40$, $\varepsilon_3 = 80$, $\varepsilon_\infty = 2$, $R_1 = 7$ Å, $R_2 = 15$ Å, $\mu = m_0$, $Z = 1$.

It can be seen that for the more realistic three-layer model the polaron radius in the ground state is $\langle r\rangle_{1S} = 2.3$ Å, that does not agree with the approximation of the continuous model. Accordingly, the quantity $\Delta W_{1S,2P} = |W_{2P} - W_{1S}| \cong 1.2$ eV ($\sim$ 1000 nm) falls just into the region of transitions with charge transfers of metal- containing proteins [12, 13].

6. The Excited Polaron States in the Protein Globule

Table 1 lists electron (W) and total (I) energies and radii $\langle r\rangle$ in the excited self-consistent state ($2S$) and the non-self-consistent states $1S$ and $2P$, which correspond to the potential polaron well $2S$ (Figure 3b). Note first of all that the radii of the excited self-consistent states of both two- and three-layer models, which are 19.5 Å and 12.2 Å, respectively, greatly exceed the mean distances between neighbouring atoms $\bar{a}$ of the medium, i.e. the continuous approximation is reasonably accurate in this case. Our calculation has shown close electron energies in the self-consistent, $2S$, and non-self-consistent, $2P$, states. In the three-layer case the $2P$ state has a higher energy level than the $2S$ state. Since the dipole transfer to the $1S$ state is only possible from the $2P$ state, the excited self-consistent $2S$ state can be expected to have larger lifetime in the three-layer model.

The table also yields the approximate estimate for the luminescence band for the three-layer model, which is $\Delta W_{2P,1S} = 0.61$ eV ($\sim$ 2000 nm) i.e. it lies in the far infrared range. It might be interesting to experiment with a band which, being the polaron one, could only be identified by a preliminary estimation of the qualitative effects which pH, ionic strength and temperature produce on the properties of the 'polaron bands'.

7. The Dielectric Cavity Model and the Theory of Electron Transfer

The above considerations show that the electrostatic model of the protein globule is suitable for a consistent description of various processes pertaining to photoexcitation and of electron transfer processes. For example, the probability ω with which the electron of the excited self-consistent $2S$ state of the protein molecule can tunnel from donor to acceptor, can be given by the following expression [14, 15]:

$$\omega = L^2 \exp\left(-\frac{E_r}{\omega}\right)(\pi/E_r T)^{1/2} \exp(-(E_r - J)^2/4E_r T)$$
$$E_r = 1/8\,\pi\tilde{\varepsilon} \int |\boldsymbol{D}_{2S} - \boldsymbol{D}_{\mathrm{acs}}|^2\, d\boldsymbol{r}\ , \tag{12}$$

where L is the matrix element of tunnelling; $\boldsymbol{D}$ can be determined from (3), J is the reaction heat, $\bar{\omega}$ is the averaged frequency of polarization oscillations in the molecule, and E_r is the total reorganization energy of the medium. Values L and $\boldsymbol{D}_{\mathrm{acs}}$ can only be determined if the acceptor model is defined.

It follows in particular from (3) that probability of the tunnelling in the electrostatic model considered is proportional to the rate of the chemical reaction and relates to the form of the electron states by the tunnelling matrix element L and inductions $\boldsymbol{D}_{2S}$ and $\boldsymbol{D}_{\mathrm{acs}}$. In this case of extended electron states we can expect that the constant of the reaction rate should relate to pH of the solution and spatial distribution of charged aminoacid groups, since the induction $\boldsymbol{D}_{2S}[\Psi]$ of (3) depends on the polaron wave function for the most polarisable parts

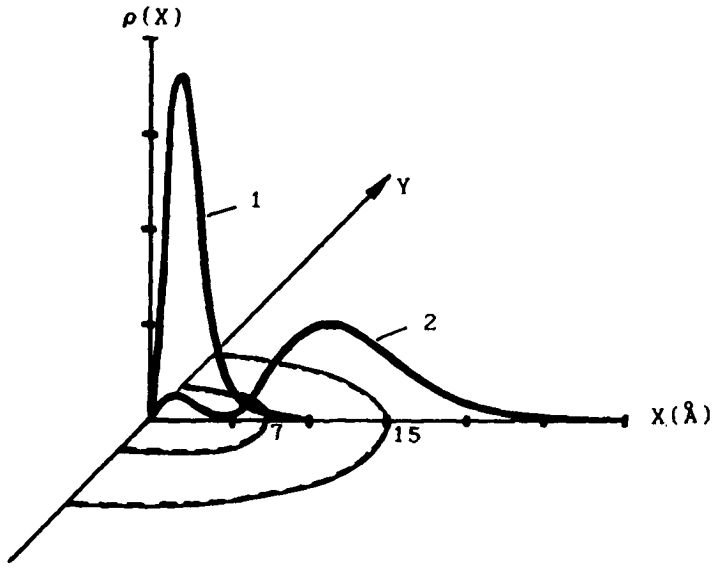

Figure 4. Distribution of electron density in the protein globule for the three-layer model; $\rho(X) = 4\pi X^2 \Psi^2(X)$; 1 is the zero mode and 2 is the first mode.

of the protein molecule in the layer $R_1 < r < R_2$ of our model (Figure 4).

8. Discussion

The representations of large-radius extended states introduced here give us a completely new approach to the problem of electron transfer to great distances. The above results for the model of a dielectric cavity show that the radius of the first excited state is comparable to the size of the globule, which suggests that the whole globule is involved in the process of forming such a state. If the acceptor is near the globule and the extended self-consistent state has much the same energy as one of the acceptor's electron states, then the representation of the electron as belonging either to the globule or the acceptor separately makes no sense. If the acceptor is far from the globule, then it is significant which is the value of the tunnelling matrix element L of the electron transfer (12). For a large-radius state it may be several orders more than for a small-radius state.

Every excited self-consistent state may be put in accordance configuration coordinates. For a consistent description of electron transfer it is necessary to take into account that the electron can jump into intermediate self-consistent acceptor states and then go to the ground state. Therefore a complex picture of electron transfer may be possible with branching the chemical reaction coordinate (see Figure 5). This example is a very simple case where the electron transfer from the state B to the state C may both be radiative and nonradiative, and in more general cases cascade radiative and nonradiative processes are possible.

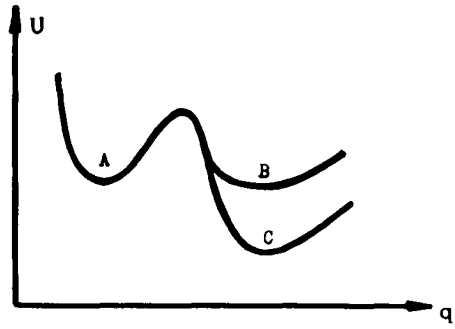

Figure 5. Simple branching of the configuration electron transfer coordinate q.

The existence of excited self-consistent states may lead to interesting effects on the lines of EPR and NMR, IR absorption etc., which can be used to identify these states. The discussion of these problems, however, is outside the scope of this paper.

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