

Electron Transfer between Globular Proteins: Estimation of the Matrix Element

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Abstract - The dependence of the matrix element of probability of interpreting electron transfer on the mutual orientation of the donor and acceptor centers and on the distance between them was calculated. The calculation was performed under the assumption that the main channel for this process is the electron transfer via collective excitation of a polaron nature, similar to electron solvation. The results obtained agree with the experimental data and indicate a no exponential behavior of this dependence at transfer distances shorter than 20 Å .

Key words: globular proteins, electron transfer, super exchange, polaron model, heme, overlap integrals

INTRODUCTION

Electron transfer between globular proteins plays a fundamental part in the vital activity of biological organisms, including such processes as photosynthesis or oxidation-reduction reactions in mitochondria. One of the most intriguing problems of electron transport is how an electron can be moved over long distances about 10-30 Å [1]. Simple calculations show that the probability of direct electron transfer from donor to acceptor over such distances is negligible. A number of models have been put forward, and numerical computations have been carried out, being based on the "super exchange" hypothesis, according to which electron transfer over long distances occurs through intermediate electron states. In most of these approaches, either the electron levels of a single atom [2] or the transfer along chemical bonds of certain types [3, 4] have been considered as intermediate states. Meanwhile, it is known that the polypeptide chain and the surrounding water molecules influence, as a solvent, the electron states at the donor or the acceptor, thus modifying them substantially [5]. On the basis of this fact, we have proposed a mechanism of transfer via a collective electron excitation throughout the entire protein macromolecule [6]. We believe that this mechanism is most likely to be realized in electron transfer between globular proteins in solutions. In this case, the protein periphery contains a large number of polar groups, which can participate in formation of the excited state mentioned. On the other hand, there is a great body of experimental data on electron transfer between globular proteins (see [7, 8] and references therein), but no theoretical calculations of the matrix element for such transfer are available.

The purpose of this work was to compute the matrix element for electron transport between globular proteins on the hypothesis that this transport occurs via collective electron excitation.

MODEL AND CALCULATION METHOD

Basic provisions of the model. According to [9], the rate K of electron transfer between globular proteins in aqueous solution is

$$K = SK_a H_{et}^2 2\pi/\hbar (FC), \quad (1)$$

where S is the steric factor, K_a is the equilibrium constant, H_{et} is the matrix element of interaction, and FC is the Franck-Condon factor.

If electron transport proceeds via the super exchange mechanism, the matrix element is

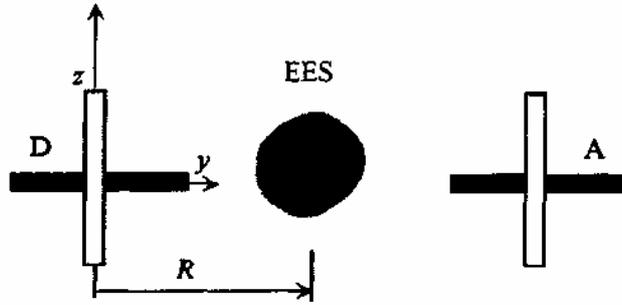


Fig. 1. (D) Donor, (A) acceptor, and (EES) excited electron state. Hems can be oriented along the y or the z axis.

$$H_{et}^2(d) = \frac{T_{md}^2}{(E_m - E_d)} \frac{T_{ma}^2}{(E_m - E_a)}, \quad (2)$$

where E_a , E_d , and E_m are the electron energies of the acceptor, the donor, and the intermediate electron state through which the transfer takes place, respectively; and T_{ma} and T_{md} give the relationship between this excited state and the electron states at the donor and the acceptor, respectively. For long-distance transfers, this relationship is written in terms of the integral $I(R)$ of overlap of the electron wave functions:

$$T_{md} \sim E_m I(R) = E_m \int \varphi_d(r) \varphi_m(r-R) dr, \quad (3)$$

where $\varphi_m(r-R)$ and $\varphi_d(r)$ are the electron wave functions of the excited intermediate and ground states of the donor, respectively; and R is the distance between their distribution centers. Our purpose was to calculate the dependence $I(R)$, since it is $I(R)$ that determines the dependence of transfer on the distance between the hems and their mutual orientation.

Below, we assumed that the excited state is located symmetrically with respect to the donor and acceptor centers (Fig. 1). The heme wave function was modeled by a normalized function distributed uniformly within an $11.35 \times 11.35 \times 5.35$ Å potential box. The overlap integral was studied versus both the distance and the heme orientation: the dependences $I_y(R)$ (the hems are parallel and lie in the same plane) and $I_z(R)$ (the hems are parallel and lie in different planes as in Fig. 1) were considered. The effect of the asymmetry of the excited electron state position with respect to the donor and the acceptor, and the internal distribution of the electron density over heme will be investigated elsewhere.

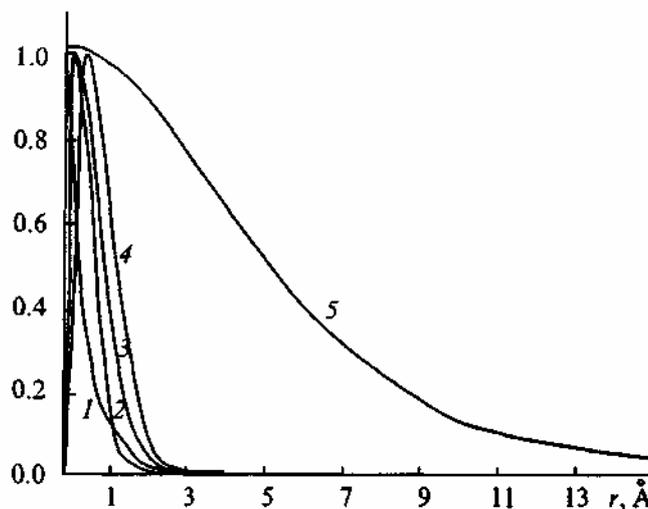


Fig. 2. Radial dependences of the atomic wave functions for s electrons at the heme: (1) H, (2) N, (3) C, and (4) the metal atom. (5) Radial dependence of the wave function of the excited state.

Excited electron state. We assumed that transfer occurs via a collective electron excitation whose nature is similar to formation of a solvated electron in liquid or a polaron in crystal lattice [6]. Spherically

symmetrical states were examined. The wave function of such a state was approximated by the power series [10]

$$\varphi(r) = C_{norm} \exp[-0.4994r] \times (1.0248 + 0.4922r + 0.1168r^2), \quad (4)$$

where C_{norm} is the normalizing factor, and r is the distance expressed in angstroms. The error of this approximation does not exceed 0.3% for the function and 0.03% for the energy parameters. Note that the characteristic size of the state explored is on the order of 3-5 Å, which corresponds to the typical radius of a solvated electron. Figure 2 shows the atomic wave functions for s electrons at heme and the wave function of the excited state. It is seen that the size of the latter function is much larger than the sizes of the functions of the electron states localized at heme atoms; therefore, the potential-box approximation for the heme function is quite acceptable.

Integration method. The problem was reduced to calculating the space integral with respect to a single variable. This integral was found by the nested Gauss-Legendry quadrature formulas with ten nodes. The algorithm included sequential computation of single integrals. The duration of calculations by this algorithm with an IBM PC 486 (100 MHz) was several seconds.

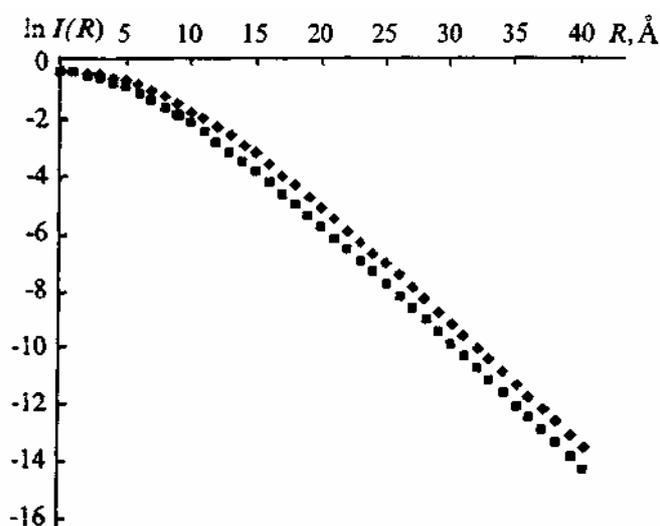


Fig. 3. Logarithms of the overlap integrals $\ln[I_y(R)]$ (rhombi) and $\ln[I_z(R)]$ (squares) versus distance R (Å). The notation is the same as in Fig. 1.

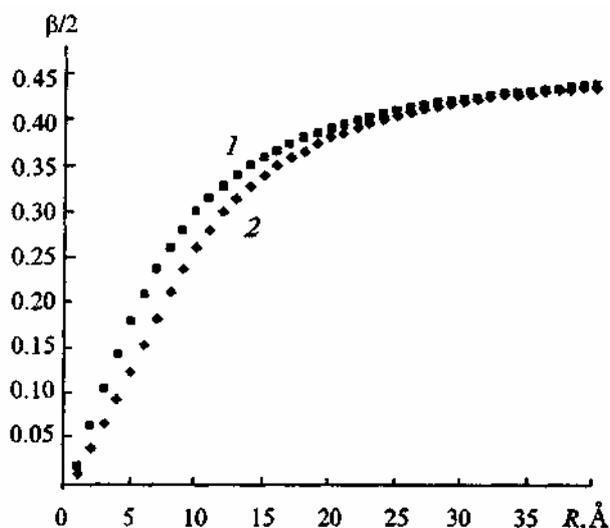


Fig. 4. Derivatives of the logarithms of the overlap integrals (1) $-d(\ln[I_y(R)])/dR = \beta_y/2$ and (2) $-d(\ln[I_z(R)])/dR = \beta_z/2$ versus distance R (Å). The notation is the same as in Fig. 1.

RESULTS

Figures 3 and 4 present the results of calculations of the overlap integrals $I_y(\mathbf{R})$ and $I_z(\mathbf{R})$, and also the parameter $\beta = -2d(\ln [I(R)]) / dR$ for two heme orientations shown in Fig. 1.

These calculations lead to the following conclusions:

- (1) the asymptotic behavior of the dependences $I(\mathbf{R})$ with increasing distance is exponential;
- (2) in the range $d = 2R = 10-20 \text{ \AA}$, these dependences differ substantially from exponential functions, with the parameter b varying from 0.3 to 0.8 \AA^{-1} ;
- (3) there is a weak dependence of the overlap integral on the heme orientation with respect to the excited state: this integral can change 2-3 times.

These results agree well with the experimental data [11] according to which the parameter $B \sim 0.7-1.4 \text{ \AA}^{-1}$. The scatter can be due to both the nonexponential behavior of $I(\mathbf{R})$ at transfer distances of $10-20 \text{ \AA}$, and the steric factors related to the mutual orientation of the donor and the acceptor.

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