Orbital Factors Affected on Electron Transfer and Light Energy Conversion in Proteins and Model Systems: A Connection between Spin Exchange and Electron Transfer

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Abstract:-Donor-acceptor structures that retain the charge-photoseparated state long enough for secondary chemestry reactions of these charges to occur are of interest for use of light energy. The aspect of fundamental importance for natural and artificial photosynthesis is the role of orbital effects in the mechanism of conversion of light energy into chemical energy in the primary charge photoseparation. The suggested approach is based on an analogy between superexchange in electron transfer (ET) and such electron exchange processes as triplet-triplet energy transfer (TTET) and spin-exchange (SE). This approach allowes to estimate values of the exchange integral (I_{SE}) and rate constant of electron transfer (k_{ET}) using experimental data on long distance TTET and SE in bridged nitroxidebiradicals. Probing environment with dual fluorophore-nitroxidesupermolecules (FNS) in which fluorophore is tethered with nitroxide, a fluorescence quencher, opens unique opportunities to quantitative study orbital phenomena, molecular dynamics, micropolarity which affect intramolecular fluorescence quenching, electron transfer, photoreduction and light energy conversion. The estimated values of I_{SE} and$k_{ET}$for various systems were found to be in good agreement with corresponding experimental data. Suggested equations can be used for calculation of k_{ET} in unknown objects of interest.

Key-words: **-** Spin exchange, electron transfer, light energy conversion, donor acceptor pairs, albumin, fluorescent-nitroxide probe

1. Introduction

Electron transfer (ET) is a process that usually occurs via a quantum mechanical tunneling of an electron from one spatial location (at an atom or a chemical moiety) to another [1-4].

For a long time, researchers followed a paradigma that electron transfer between a donor and an acceptor centers can occur only at a short distance (< 6-7 Å). The similar idea was accepted for electron spin exchange. Nowadays Long-range Electron Transfer (LRET) up to 30 Å is a wide spread phenomenon of large number chemical in biological reaction, in particular. LRET between donor (D) and acceptor (A) centers can occur by three mechanisms: 1) superexchange via intermediate orbitals, this mechanism involves the direct electronic coupling between adjusting D and A groups (2) consecutive electron jumps via chemical intermediates and 3) mixing of the both mechanisms.

Biological electron transfer reactions play crucial role in the conversion of sunlight energy into the universal energy currency, adenosine triphosphate. Chemical energy is generated by a photoenzyme, the photosynthetic plant and bacterial reaction center (RC),through formation of charge separation in the donor-acceptor (D-A) pair. The obtained (D^+A^-) pair is formed by D^+ cation-radical, which is a strong oxidant, and A^- anion-radical, which is a strong reducing agent. The (D^+A^-) pair should be relatively long-lived in order to enable subsequent chemical reactions eventually producing stable chemical compounds.

The most important problems essential for understanding photosynthesis as well as developing biomimetics synthetic systems are the exact molecular structure and specific physical mechanisms that prevent immediate recombination of D^+ and A^-centers.For suggested cascade structures with optimal distance between the centers, the forward electron transfer between adjacent D-A_1 and A_i-A_{i+1} pairs was predicted to slow down with the optimum distance not exceeding 0.5 – 07 nm, when the direct electron transfer can be sufficiently fast[3, 5-7].Essential feature enabling the photosynthetic cascade to function is that recombination of the each D^+-A_i^- pair becomes progressively slower as A_i moves away from the donor. The aforementioned cascade mechanism is fulfilled in all the biological reaction centers (RCs) and, thus, should be taken into consideration when designing artificial system of light energy conversion. In this aspect, a quantitative information about quantum mechanical tunneling in electron transfer through intermediate bridges appear to be of primary importance.

This paper is organized as follows. The first Section provides a brief overview on the primary quantum mechanical grounds of different types of spin exchange processes, namely, static direct exchange and super exchange. Classic theories of electron transfer by Marcus, Levich, Jortner, and Anderson have been also considered. The close interrelations between spin exchange and electron transfer caused by a similarity of their orbitals overlap, have been emphasized.In the next two Sectionswe described semiempirical methods for calculation of values of the electron transfer rate constant on the base of experimental data on long distance TTET and SE in bridged nitroxidebiradicals and its application for the k_{ET} estimation in photosynthetic and mimetic donor-acceptor pairs.

2.Theoretical grounds

2.1 Spin exchange

The direct spin exchange process with spin Hamiltonian H_{ex} (Eq. 1.8) occurs via direct overlap of the orbitals of the interacting species [4,8]

A(↑)B(↧) → A(↧)(B(↑)

Scheme 1.1 Direct spin exchange

The singlet-triplet (S-T) splitting, $E_{S\text{-}T}$, is $2J$, where J is the exchange integral, the magnitude of the exchange interaction (Fig. 1.3) which contributes to the Heisenberg spin Hamiltonian:

$$H_{ex} = -2J_{EX}S_1S_2 (1)$$

where S_1 and S_2 are spin operators. When J_{EX} is positive, the triplet states have lower energy than the singlet states, that is the ferromagnetic (spin parallel state) is favored compared to the antiparallel, antiferromagnetic state

According to theory and available data [4,8]

$$J = J_0 \exp(-\beta r) \qquad (2)$$

whereJ_0 is the exchange integral at Van der Waals distance, r is the spin-spin distance and β is the distance decay factor

In many systems, spin exchange takes place by superexchange through a bridge or a through space interaction mediated by the molecules of the intervening medium:

A(↑)X(↑↓)B(↧) → A(↧)X(↧↑)B(↑)

Scheme 1.2 Spin exchange via a bridge

Anderson [9] in his pioneering work used a perturbational approach to relate thesinglet-triplet splitting of a two-spin system to the magnitude of the electron-transfer superexchange coupling between the radical ion pair (RP) state and surrounding states n and that state to which it is coupled at the nuclearcoordinate of the relaxed RP state. Then McConnel [6] has shown that the electronic coupling matrix element (H_{AB}) between two redox centers separated by a covalent bridge composed of n identical repeat units depends on the coupling strength between the redox sites and the bridge (h_{Ab}, h_{bB}), the coupling between adjacent bridge elements (h_{bb}), and the tunneling energy gap (Δε). The latter was defined as the virtual energy required to remove an electron from the donor, or a hole from the acceptor, and place it on the bridge.

According to theory presented in [10]

$$H_{DA} = \frac{h_{Db}}{\Delta\varepsilon}\left(\frac{h_{bb}}{\Delta\varepsilon}\right)^{n-1} h_{bA} \qquad (3)$$

2.2 Electron Transfer

Electron transfer (ET) is one of the most ubiquitous and fundamental phenomena in Nature. ET is found to be a key elementary step in many important processes in chemistry, biology and physics including systems of the light energy conversion.[1-7.]

Electron transfer (ET), as in any other chemical reaction, is accompanied by a change in the nuclear and electronic configurations and is described by the Fermi's golden ruleequation for a transition with rate constant k_{tr}[11]

$$k_{tr} = \frac{J_{ex}^2}{h} FC(4)$$

which includes the exchange integral (an electronic coupling term) J_{ex} depending on the overlap of electronic wave functions in the initial and final state of the process; FC is the Franck-Condon factor related to the probability of vibrational and translationaltransition states accounting for the effects of nuclear motion. FC factor related to the much slower changes in the nuclear configuration, whereas the exchange integral depends on the instantaneous electronic configuration in the Born-Oppenheimer approximation.

According to the fundamental Marcus two state model [11] the distortion of the reactants, products and solvent from their equilibrium configuration is described by identical parabolas in reaction coordinate space for the initial and final states. Within the adiabatic regime (strong electronic coupling, where the resonance integral Jex, $V > 200$ cm^{-1}), the value of the electron transfer rate constant is given by the Marcus-Eyring theory of the transition state:

$$k_{ET} = \frac{k_B T}{h} \exp - \left[\frac{(\lambda + \Delta G_0)^2}{4\lambda\, k_B T}\right] \qquad (5)$$

whereλ is the reorganization energy defined as the energy for electron excitation without distortion of the nuclear frame and _G_0 is the process thermodynamicdriving force

The theory developed by Levich, Dogonadze [13] was related to non-adiabatic electron transfer between donor (D) and acceptor (A) centers. The theory is based on Fermi's Golden Rule (Eq. 1), the Landau-Zener Eq. [14,15] and the Marcus formula (Eq. 5). Using these concepts, the authors proposed a formula for non-adiabatic ET

$$k_{ET} = \frac{2\pi V^2}{h\sqrt{4\pi\lambda k_B T}} \exp\left[-\frac{(\lambda + \Delta G_0)^2}{4\lambda k_B T}\right] \quad (6)$$

A principle connection between exchange integral and electron transfer coupling factor was established by Anderson [9]. In the Anderson equationfor a radical (ion-radical) pair (RP): the indicated matrixelements couple the singlet and triplet RP states to states n, E_{RP} and Enare energies of these states, respectively, and $\lambda$is the total nuclear reorganization energy of the charge-transfer reaction:

$$2J = \Delta E_S - \Delta E_T = \left[\sum_n \frac{|\langle \Psi_{RP}|V_{RP-n}|\Psi_n\rangle|^2}{E_{RP} - E_n - \lambda}\right]_S - \left[\sum_n \frac{|\langle \Psi_{RP}|V_{RP-n}|\Psi_n\rangle|^2}{E_{RP} - E_n - \lambda}\right]_T$$

(7)

were Ψ is the corresponding wave function. The Anderson approach was effectively exploited [16-18].

3. Semi-empirical methods of calculation of ET rate constants

A semi-empirical approach for the quantitative estimation of the effect bridging the group on the long-distance electron transfer LDET was developed by Likhtenshtein [3,4,7,19].

The approach is based on analogy between superexchange in electron transfer (ET) and such electron exchange processes as triplet-triplet energy transfer (TTET) and spin-exchange (SE). The spin exchange and TT phenomena may be considered an idealized model of ET without or with only a slight replacement of the nuclear frame.

As was shown in [19], experimental data on the dependence of the rate constant of triplet trplet energy transferk_{TT} and the exchange integralJ_{SE} on the distance between the centers (ΔR) lies on two curves, which are approximated by the following equation:

$$k_{TT}, J_{SE} \propto \exp(-\beta\Delta R)$$

(8)

It was found that for systems in which the centers are separated by a “non-conductive” medium (molecules or groups with saturated chemicals bond) β_{TT} = 2.6 Å^{-1}. For systems in which the radical centers are linked by “conducting” conjugated bonds, β_{SE} is 0.3 Å^{-1}. The data on exchange integrals for paramagnetic center separated by “non condacting” media were obscured.

Above mentioned analogy can allow to predict corresponding distance dependent for SE and therefore for ET. We suggest that in the first approximation

$$V_{ET}^2, J_{SE}, J_{TT} \propto exp(-n\beta R) \quad (9)$$

where ($|V_{CR}|^2$) is the square of the resonance integral, J_{SE}ishe exchange integral, J_{TT} is the triplet-triplet transfer integral, $R$is the distance between the interacting centers and$\boldsymbol{\beta}_i$ is a coefficient which characterizes the degree of the integral decay (decay factor). In the first approximation, n = 2 for the ET and SE processes with the overlap of two orbitals and n = 4 for the TT process in which four orbitals overlap, that is, ground and triplet states of the donor and ground and triplet states of the acceptor).

The ratios

$$\gamma = \frac{J_{SE}^0}{J_{SE}^x} \quad (10)$$

were$J_{SE}^0$and J_{SE}^x are the exchange integrals for two non-bridged radicals and radicals tethered by a media x, can be considered as attenuation factor of the exchange interaction of SE through the given bridge. Taking into account Eq. 8.3 with value n = 2 for SE and ET, , an expression for the dependence of the attenuation parameters for SE and ET on the distance between remote donor and acceptor centers $D_R D_A$ can be given as Eq. 8.2 with β_{ET} (nc) = 0.5β_{TT} = 1.3 Å^{-1} for a “non-conducting” medium and β_{ET} (c) = 0.3 Å^{-1} for a “conducting” bridge. The value of $\sqcup_{ET}$ =

1.3 $Å^{-1}$ is found to be close to that obtained by analysis of k_{ET}, which is proportional to $|V_{CR}|^2$, on the distance ΔR in model and biological systems (Fig.1).
Similar but not identical approach was developed in [16]**.** The authors also paid attention on similarity of long-range intramolecular electron transfer and positive ions (hole) transfer, and triplet energy transfer and showed that $\beta^{TT}/\beta^{ET} = 2$.

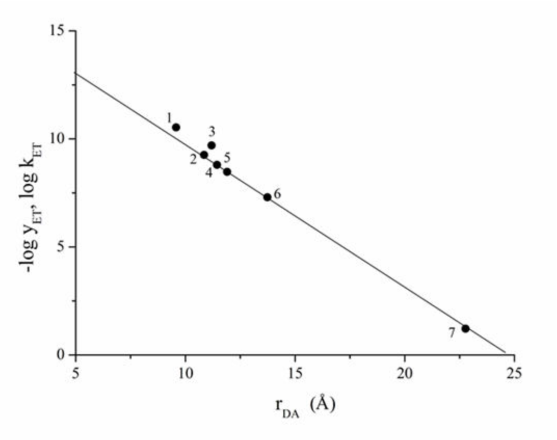


Figure 1 The observed linear dependence of the logarithm of the rate constant of the electron transfer in RCs of purple bacteria and plant photosystem I (log k_{ET}) on the edge-edge distance between the donor and acceptor centers (r_{DA}) (circles), solid line is the dependence predicted by Eqs. 9-10 for the exchange integral J_{SE}[19].

The empirical data on the exchange integral values (J_{ET}) for the spin-spin interactions in systems with known structure, that is, biradicals, transition metal complexes with paramagnetic ligands and monocrystals of nitroxide radicals have served as a basis for the estimation of the value of the attenuation parameter $\gamma_{\sqcap}$ for the exchange interaction through a given group X [19]. By our definition, the $\gamma_{\sqcap}$ is

$$\gamma_X = \frac{J_{RYZP}}{J_{RYXZP}} \qquad (11)$$

where R is a nitroxide or organic radical, P is a paramagnetic complex or radical and X, Y, and Z are chemical groups in the bridge between R and P.Table 1 shows the results of the calculation of parameter γ_X from empirical data on the spin exchange in the nitroxidebiradicals by Eq. 11

Table 1. Attenuation parameter γ_X calculated from empirical data on the spin exchange in nitroxidebiradicalsand complexes with paramagnetic ligands: γ_x for individual group, $\gamma_{hb}$for hydrogen bond and γ_v for Van der Waals contact.[19].

Group, X	γ_x	Group, X	γ_x
C_6H_4	6.00±0.03		
C=C	1.7	-NH-CO-	55
C=O C	8.4±0.4	γ_v	50
NH	6.5	γ_{hb}	10
O	5	H	12
S=O	2.1	SO_2	2.2
	3.5	RP=O	2.40±0.03

Thus, the experimental dependence of exchange parameters k_{TT} and J_{SE} on the distance between the exchangeable centers and the chemical nature of the bridge connecting the centers may be used for evaluating such dependences for the resonance integral in the ET equations (Eqs.9-10).

4. Estimation of spin exchange integral and ET rate constants in donor –acceptor pairs
Data presented in Table 1. and Eq. 9-10was used for the analysis of alternative.e electron transfer pathways in chemical and biological systems. The following equations for the spin exchange integral and rate constant of electron transfer in donor-acceptor pairs are suggested:

$$J_{SE} = J_0 \rho_{S1}\, \rho_{S2} \prod^i \ \gamma_i^{-1} \ldots\ldots\ldots \qquad (12)$$

and

$$k_{ET} = k_0 \rho_D\, \rho_A \prod^i \ \gamma_i^{-1} (13)$$

where $J_0 = 10^{14} s^{-1}$ exchange integral at Van der Waals contact , $\rho_{S1,2}$ - spin density at Van der Waals contact, γ_i - attenuation factors, $k_0 =$ 5x10^{10} s^{-1}

is therate constant of ET in a nonbridged DA pair Eqs. 12 and 13 predicteratio of values of exchange integral and ET rate constant J_X / k_X = J_0 / k_0 = 200.

Values of J_{SE} *and* k_{ET} calculated by Eqs. 12and 13 were compared with corresponding experimental data.For rate constant of recombination of charge separated primary and secondary quinons [17] (Fig. 2) in the photosynthetic reaction centers, employment Eq.13 led to following calculated value: calculated (this work) k_{ETqq}= $.5\times10^8$ s^{-1}as compare with k_{ETqq} = $.9\ \times10^8$ s^{-1}calculated byCalvo*et al.* and experimental k_{ETqq}= $.3\ \times10^8$ s^{-1} [17].

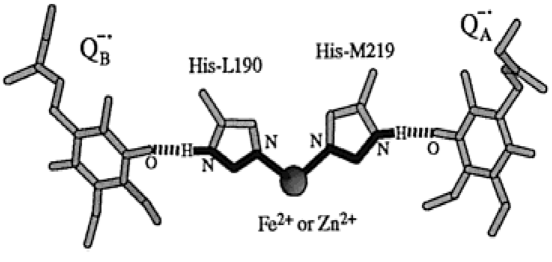
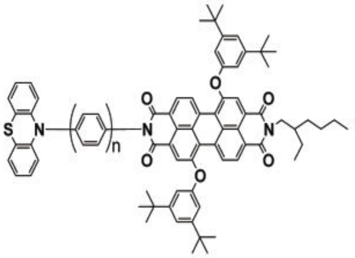


Figure 2 Segment of electron transfer chain of bacterial photosynthetic center [17]

Eq.12 with values $J_0\ \approx\ 10^{14}\ s^{-1}$, $\rho_{S1} = \rho_{S2} = 0.2$ and$\gamma_1\gamma_2 = 36$ for the donor-acceptor pair[18]:



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and two phenyl bridged groups gave calculated J_2 = 10^{10} s^{-1}as compared with experimental J_2 = $6x10^9$ s^{-1} [18] A good correlation between experimental J values (n = 2-5) and that predicted by Eq. 8.8 take place (Fig.3)

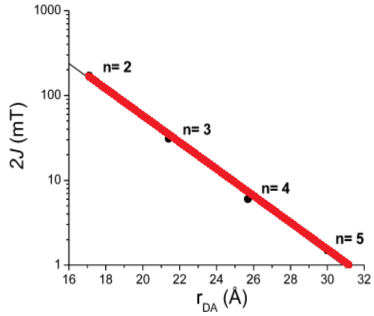


Figure 3 Logarithmic plot of the exchange integral 2J vs donor-acceptor distance, r_{DA}. Points experimental data [27],solid line predicted from Eq.12[18]

For the rate constant of charge separation in with n =1, Eq.8.9 predicted $k_{1CS} = 3\times\ 10^{10}\ s^{-1}$ versus experimental $k_{1CS} = 5\times\ 10^{10}\ s^{-1}$
As one can see from Fig. 4, for compound I with n = 1-3 experimental data of the charge recombination rate constant, k_{CS} vs donor-acceptor distance fit to the dependence predicted by Eq. 13, while the experimental dependence rate constant of charge separation is steeper that for predicted one. This discrepancy can be explained suggesting that the spin exchange and recombination involve the same triplet orbitals, while charge separation occurs from singlet orbital.

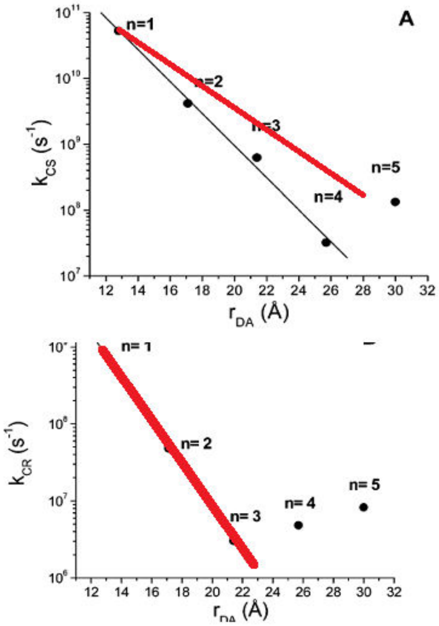
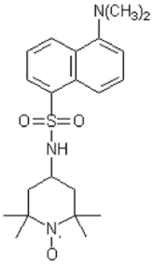


Figure 4 (A) Logarithmic plot of the charge separation rate constantk_{CS} vs donor-acceptor distance, $r_{DA.}$ (B) Logarithmic plot of the charge recombination rate constant, k_{CR} vs donoracceptor distance, r_{DA}, solid line predicted from Eq, 13. [18].

Probing protein environment with dual fluorophore-nitroxide (FNO·) molecules in which fluorophore is tethered with nitroxide, a fluorescence quencher opens unique opportunities to study molecular dynamics and micropolarity of a protein medium, intramolecular fluorescence quenching (IFQ), electron transfer, photoreduction and light energy conversion [3,4,7,20-23].

The following scheme describes photophysical and photochemical processes in the dual molecule FN I:



(FN1)

incorporated into bovine serum albumin were investigated (Fig. 5)

$$\mathbf{FNO^{\bullet}} + h\upsilon \rightarrow \mathbf{F^{*}NO^{\bullet}}$$
$$\mathbf{F^{*}NO^{\bullet}} \rightarrow \mathbf{FNO^{\bullet}}$$
$$\mathbf{F^{*}NO^{\bullet}} \rightarrow \mathbf{F^{+}NO^{-}}$$
$$\mathbf{F^{+}NO^{-}} \rightarrow \mathbf{FNO^{\bullet}}$$
$$\mathbf{F^{+}NO^{-}} + \mathrm{RH} \rightarrow \mathrm{D}\text{-}\mathbf{FNOH} + \text{products}$$

Scheme 2 Light energy conversion in the dual fluorophore-nitroxide (FNO·) molecules

The fluorophore and nitroxide segments of the probes allow monitoring of molecular dynamics and also make it possible to measure micropolarity of the medium in the vicinity of the donor (by fluorescence technique) and acceptor (by ESR) moieties. Exchange, energetic and molecular dynamic factors affecting photoinduced electron transfer in a donor-acceptor pair (D-A)incorporated into bovine serum albumin were investigated (Fig. 5)[20-23] The kinetics of reversible and irreversible intramolecular electron transfer from the donor to the acceptor were monitored by picoseconds time resolved fluorescent and ESR techniques corresponding at temperature range from 70 K to 300 K.

For the fluorescent-nitroxide probe FNI, Eq.13 related to ET along the bridge chain, after taking ask_0 =5x10^{12} s^{-1},ρ_1 = ρ_2 = 0.4 and the corresponding attenuation factors γ_i picked up from Table 1, gave k_{ET} =1.1x10^8 s^{-1}, while the experimental value was found as k_{ET} (exp) =1.0±0.1x10^8 s^- [22]. s^-

For the fluorescent-nitroxide probe FN 1, Eq. for ET through the space, after taking k_0 =5x10^{12} s^{-1},ρ_1 = ρ_2 = 0.4 and β = 1.3 Å^{-1} ,gives the value of k_{ET} = 8.8x10^7 s^{-1}. For ET along the bridge chain, using Eq.13 with ρ_1 = ρ_2 = 0.4 and attenuation factors for phenyl segment γ_i = 0.4 (Table 1) led to k_{ET} =1.1x10^8 s^{-1}, while the experimental value was found as k_{ET} (exp) =1.0±0.1x10^8 s^{-1}.

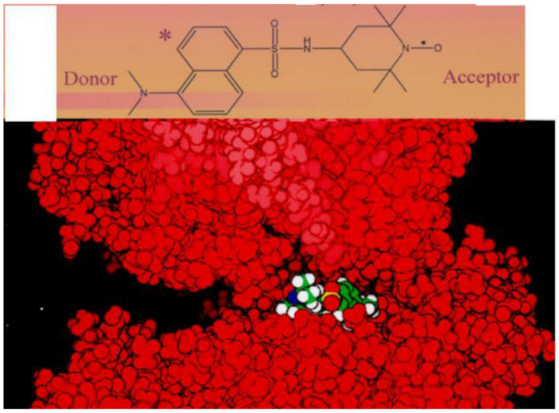


Figure5 Dual fluorophore-nitroxide (FNO·) molecule incorporated in the binding center of albumin.

Conclusion

Available theoretical considerations and experimental data have unambiguously proved a connections between electron transfer, spin exchange and triplet triplet energy transfer. When in these processes the same orbitals are involved, this connection is quantitative one. The suggested semiempirical approach allowed to estimate values of exchange integral and electron transfer rate constant are in fairly good agreement with corresponding experimental data and can be used for an estimation these values in unknown system of interest.

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