Roles of Proteins in the Electron Transfer in the Photosynthetic Reaction Center of *Rhodopseudomonas viridis*: Bacteriopheophytin to Ubiquinone

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Received 27 June 2000; accepted 15 August 2000

ABSTRACT: The electron transfer (ET) from bacteriopheophytin (H) to ubiquinone (UQ) in the photosynthetic reaction center (PSRC) of *Rhodopseudomonas (Rps.) viridis* was studied by *ab initio* quantum-chemical calculations. The ET from the H in L-region (H_L) to menaquinone (MQ) occurs through the super-exchange mechanism using Trp M250 as a bridge, while in the M-region Leu L189 works as a bridge in the ET from H_M to UQ. The transfer integral for the L-branch was 20 times larger than that for the M-branch, which was due to the difference in the amino acid residues placed between the chromophores. For the ET from MQ to UQ, the super-exchange mechanism using His M217 and His L190 as two subsequent bridges was by far the largest, showing the importance of these residues in the ET between MQ and UQ.
 J Comput Chem 22: 265–272, 2001

Keywords: electron transfer; roles of proteins; photosynthetic reaction center; *ab initio* MO method; transfer integral

Introduction

The photosynthetic reaction center (PSRC) converts photon energy into chemical energy through electron excitation and subsequent electron transfer (ET). The structure of chromophores and proteins of PSRC of *Rhodopseudomonas (Rps.) viridis* was determined by X-ray crystallography.[1] The chromophores involved are special pair (P, bacteriochlorophyll b dimer), two bacteriochlorophyll b (B_L, B_M), and two bacteriopheophytin b (H_L, H_M) in the L and M regions, menaquinone (MQ), and ubiquinone (UQ). They are arranged in a pseudo-C_2 symmetry (Fig. 1), and are supported by proteins consisting of 1200 amino acid residues. Despite the structural symmetry of the L and M branches, the

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Contract/grant sponsor: Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Culture, and Sports

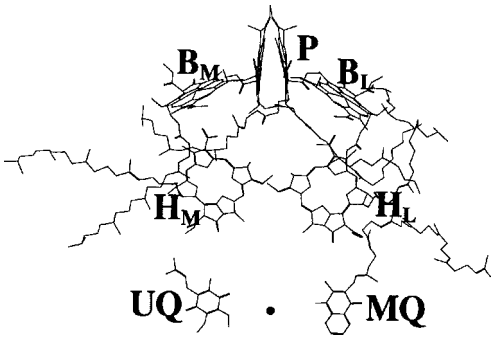

FIGURE 1. Structure of the chromophores in the photosynthetic reaction center of *Rps. virdis*. The nuclear coordinates are taken from ref. 1.

excited electron of a special pair (P^*) is transferred to UQ mostly through the L-branch.[2, 3] It takes 3 ps from P to H_L, 200 ps from H_L to MQ, and 100 μs from MQ to UQ.[4] After the oxidized special pair (P^+) is reduced through the ET from the cytochrome *c* unit,[5] another excitation-ET process takes place, and one more electron is transferred to UQ. The doubly reduced ubiquinone accepts two protons from the surrounding, and leaves from the PSRC.[4]

The rate of the ET reaction was expressed by Marcus[6] as,

$$k = \frac{2\pi}{\hbar}|H_{IF}|^2 \frac{1}{\sqrt{4\pi\lambda RT}} e^{-(\Delta G+\lambda)^2/4\lambda RT} \qquad (1)$$

which is composed of the so-called electronic part and nuclear part. The electronic part consists of the transfer integral H_{IF}, which describes electronic coupling between the initial and final states. The nuclear part is expressed by ΔG and λ, which are the change in free energy and the reorganization energy, respectively, accompanying the ET reaction.

Previously,[7–9] we have studied by the *ab initio* quantum-chemical method, called SAC(symmetry adapted cluster)/SAC-CI(configuration interaction) method,[10, 11] the excitation spectra of the PSRC of the *Rps. viridis* as a whole, and the mechanism and the unidirectionality of the ET from P to H. The assignment of the absorption spectrum and the linear dichroism spectrum were given. The unidirectionality of the ET was explained by the asymmetries of the transfer integrals between the L and M branches, which are caused mainly by small differences in the spatial arrangements of the L- and M-chromophores. The high efficiency in the charge separation and the low occurrence of the charge recombination were attributed to the difference in the spatial distribution of the HOMO and LUMO of P. On the other hand, the nuclear part was rather difficult to calculate by purely ab initio method,[7, 9] because it involves reorganizations of the chromophores and their environments in the course of the ET.

In this article we study the pathways and the mechanisms of the ETs from H_L to MQ, from H_M to UQ, and from MQ to UQ. The distances between the terminal atoms of the π-conjugated systems are 8.1, 8.8, and 12.8 Å for H_L–MQ, H_M–UQ, and MQ–UQ, respectively, which are larger than the previously studied cases, 6.9 and 5.0 Å for P–B_L and B_L–H_L. Furthermore, some π-containing residues of the proteins are present between the chromophores studied in this article. We examine here the direct and super-exchange mechanisms of ET, and in the latter case we investigate the role of these protein residues as bridges for the ETs. We calculate the transfer integrals for these ET processes by the *ab initio* molecular orbital method including the effect of proteins. We do not calculate the nuclear factor, because such calculation is regretably too difficult to do *ab initio* at the present stage of computational chemistry.

Some theoretical researches have been performed so far for the ET from MQ to UQ by the Monte Carlo simulations[12, 13] and by the semiempirical quantum-chemical calculations.[14] However, as far as we know, no *ab initio* theoretical calculations have been published for the ET processes studied in this article.

Calculation of Transfer Integral

When some intermediate bridge states exist between the initial and final states of the electron transfer, the transfer integral is expressed[15, 16] by the perturbation theory as,

$$H_{IF} = \langle I|H|F\rangle + \sum_V \frac{\langle I|H|V\rangle\langle V|H|F\rangle}{E_I - E_V} + \sum_{V_1,V_2} \frac{\langle I|H|V_1\rangle\langle V_1|H|V_2\rangle\langle V_2|H|F\rangle}{(E_I - E_{V_1})(E_I - E_{V_2})} + \cdots \qquad (2)$$

where H is the Hamiltonian of the total system, $|I\rangle$, $|V\rangle$, and $|F\rangle$ are the wave functions for the initial, virtual bridge, and final states, respectively, and E_I and E_V and are the energies of the initial and virtual bridge states, respectively. The first, second, and third terms correspond to the ETs occurring directly, through one bridge, and through two bridges, respectively, which are called direct, one-bridge, and two-bridge terms, respectively.

We calculate the transfer integral using the Hartree–Fock approximation. The neutral state $|\Psi_D\Psi_B\Psi_A\rangle$ is described by the product of the wave functions of the separate systems as,

$$|\Psi_D\Psi_B\Psi_A\rangle = \left|\phi_1^D\phi_2^D\ldots\phi_{N_D}^D\phi_1^B\phi_2^B\ldots\phi_{N_B}^B\phi_1^A\phi_2^A\ldots\phi_{N_A}^A\right\rangle \quad (3)$$

where ϕ_i^R denotes ith MO of the R state. Ψ_D, Ψ_B, and Ψ_A, are the Hartree–Fock wave functions of the donor, bridge, and acceptor, respectively. Because there is one additional electron in the present system, the initial and final states are described by adding one additional electron to the donor and acceptor, respectively,

$$|I\rangle = \left|\Psi_D^\Theta\Psi_B\Psi_A\right\rangle \quad (4)$$

$$|F\rangle = \left|\Psi_D\Psi_B\Psi_A^\Theta\right\rangle \quad (5)$$

where Ψ_D^Θ and Ψ_A^Θ are the anionized state of the donor and acceptor with one additional electron in their LUMOs.

A conceptual picture of the virtual state for one bridge case is shown in Figure 2. As virtual states, the state where the hole of the acceptor is transferred to the bridge (left-hand side of Fig. 2) and the state where the electron of the donor is transferred to the bridge (right-hand side) are considered. We refer to the ET through the former as hole transfer (HT) and the latter as particle transfer (PT). The numbers of the virtual states in HT and PT are as many as the numbers of the occupied and virtual orbitals of the bridge, respectively.

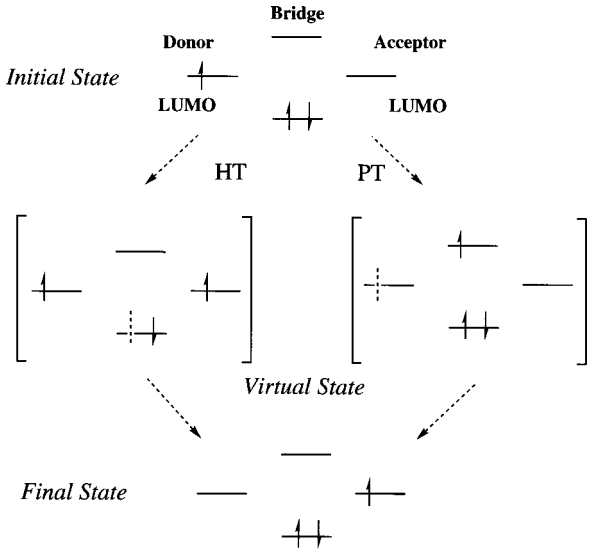

FIGURE 2. Conceptual picture of the initial, final, and virtual states in the one-bridge super-exchange mechanism.

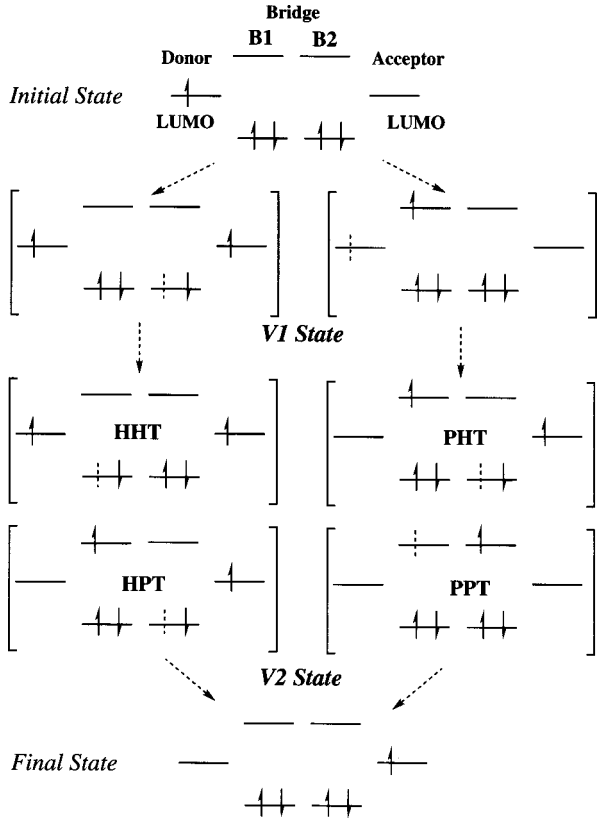

FIGURE 3. Conceptual picture of the initial, final, and virtual states in the two-bridge super-exchange mechanism.

A conceptual picture of the virtual state for the two-bridge case is shown in Figure 3. The virtual states are classified into four according to the orbital occupations of the bridges. They are hole–hole transfer (HHT), which uses the occupied orbitals of two bridges, hole–particle transfer (HPT), and particle–hole transfer (PHT), which use the occupied orbital of one bridge and the virtual orbital of the other bridge, and particle–particle transfer (PPT), which uses the virtual orbitals of two bridges.

Using initial, virtual, and final states defined above, we can rewrite eq. (2) as,

$$H_{IF} = \langle\varphi_{D,L}|f|\varphi_{A,L}\rangle + \sum_V^{B,\text{occu}} \frac{\langle\varphi_{D,L}|f|\varphi_{B,V}\rangle\langle\varphi_{B,V}|f|\varphi_{A,L}\rangle}{\varepsilon_{B,V}-\varepsilon_{A,L}} + \sum_V^{B,\text{virt}} \frac{\langle\varphi_{D,L}|f|\varphi_{B,V}\rangle\langle\varphi_{B,V}|f|\varphi_{A,L}\rangle}{\varepsilon_{D,L}-\varepsilon_{B,V}}$$

$$+\sum_{V1}^{B2,\text{occu}}\sum_{V2}^{B1,\text{occu}}\frac{\langle\varphi_{D,L}|f|\varphi_{B1,V2}\rangle\langle\varphi_{B1,V2}|f|\varphi_{B2,V1}\rangle\langle\varphi_{B2,V1}|f|\varphi_{A,L}\rangle}{(\varepsilon_{B2,V1}-\varepsilon_{A,L})(\varepsilon_{B1,V2}-\varepsilon_{A,L})}$$

$$+\sum_{V1}^{B2,\text{occu}}\sum_{V2}^{B1,\text{virt}}\frac{\langle\varphi_{D,L}|f|\varphi_{B1,V2}\rangle\langle\varphi_{B1,V2}|f|\varphi_{B2,V1}\rangle\langle\varphi_{B2,V1}|f|\varphi_{A,L}\rangle}{(\varepsilon_{B2,V1}-\varepsilon_{A,L})\{(\varepsilon_{B2,V1}-\varepsilon_{A,L})+(\varepsilon_{D,L}-\varepsilon_{B1,V2})\}}$$

$$+\sum_{V1}^{B1,\text{virt}}\sum_{V2}^{B2,\text{occu}}\frac{\langle\varphi_{D,L}|f|\varphi_{B1,V1}\rangle\langle\varphi_{B1,V1}|f|\varphi_{B2,V2}\rangle\langle\varphi_{B2,V2}|f|\varphi_{A,L}\rangle}{(\varepsilon_{D,L}-\varepsilon_{B1,V1})\{(\varepsilon_{D,L}-\varepsilon_{B1,V1})+(\varepsilon_{B2,V2}-\varepsilon_{A,L})\}}$$

$$+\sum_{V1}^{B1,\text{virt}}\sum_{V2}^{B2,\text{virt}}\frac{\langle\varphi_{D,L}|f|\varphi_{B1,V1}\rangle\langle\varphi_{B1,V1}|f|\varphi_{B2,V2}\rangle\langle\varphi_{B2,V2}|f|\varphi_{A,L}\rangle}{(\varepsilon_{D,L}-\varepsilon_{B1,V1})(\varepsilon_{D,L}-\varepsilon_{B2,V2})}$$

$$+\cdots \tag{6}$$

The first term represents the direct ET, the second and third terms do one bridge HT and PT, respectively, and the fourth to seventh terms do two-bridge HHT, HPT, PHT, and PPT, respectively. f is the fock operator, $\varphi_{D,L}$ and $\varphi_{A,L}$ are the LUMOs of the donor and acceptor, respectively, and $\varepsilon_{D,L}$ and $\varepsilon_{A,L}$ are the LUMO energies of the donor and acceptor, respectively. Similarly, $\varphi_{B,V}$ and $\varepsilon_{B,V}$ and represent the MOs and the MO energies of the bridge appearing in the HT, PT, HHT, HPT, PHT, and PPT mechanisms shown in Figures 2 and 3. In formulating the above equations, orthogonality of the MOs of different molecules is assumed for simplicity. Further, in eq. (6), two approximations are adapted: one is to ignore two electron integral contributions in the energy denominators, and the other is that we included the fock matrix elements of only adjacent molecules in the respective ET route.

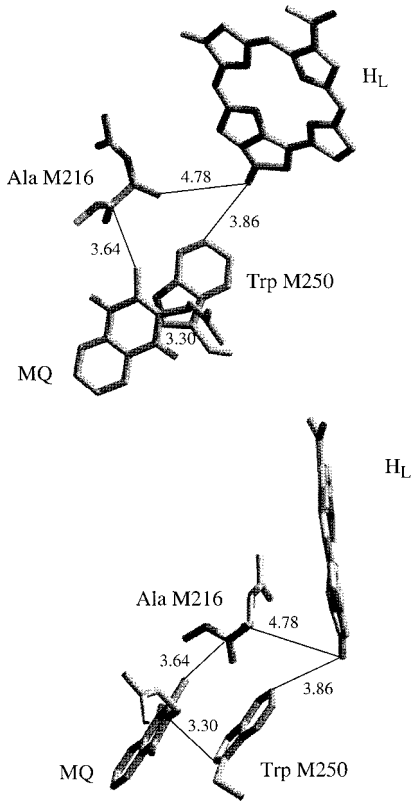

FIGURE 4. Top view and side view of the structures of H_L and MQ and the protein residues between H_L and MQ. Distances between closest heavy atoms are given in Å.

Computational Details

The wave functions of the initial, final, and bridge states are described by the products of the wave functions of the separated systems, which are calculated here by the Hartree–Fock method. The geometries of the chromophores are taken from the X-ray crystallographic data[1] (1PRC in Brookhaven Data Bank). The resolution of this X-ray structure is 2.3 Å. Because transfer integral is quite sensitive to the distances between molecules, the geometrical change within this resolution may affect the result. However, the distances we used in this study is the experimentally most probable ones and no other reasonable choice exists. Probably, as discussed below, the vibrational and relaxation effects would be important in the actual ET processes, which we do not take into account in this articler. For chromophores, the side chains that seem not to participate in the π-conjugation are cut off, and the terminals are substituted by hydrogen atoms. The residues of the proteins like tryptophan, phenylalanine, etc., which are expected to participate in the ET process, are taken from the main protein chain as they are in the X-ray geometry as shown in Figures 4 to 6, and dealt with as the bridges of the ET process. As the transfer integral decays very rapidly as a function of the distance, only the residues that are close to both chromophores can participate in the ET process. The protein main chains not included in the electronic structure calculations are represented by the point charge model, that is, the atoms of proteins and waters are substituted by the point charges recommended previously for proteins[17] and waters.[18] The effects of the other chromophores are also represented by the point charge model using the Mulliken charges calculated by the HF model. Asp, Lys, Arg, Glu are assumed to be in their ionic states.

We used Huzinaga's (63/5)/[2s2p] set for carbon, nitrogen and oxygen[19] and Huzinaga's (4)/[1s] set

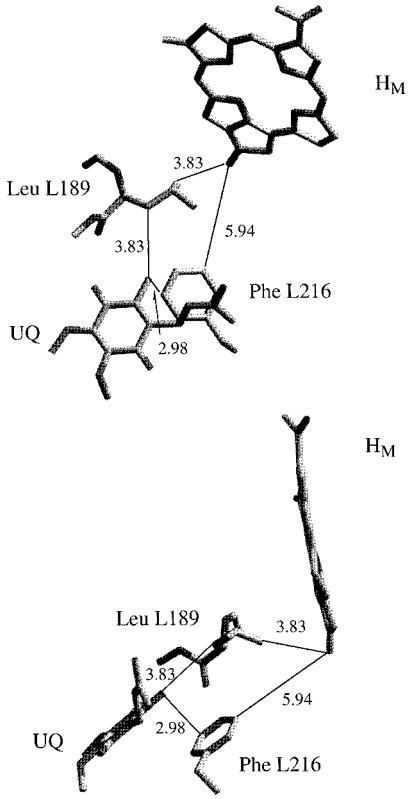

FIGURE 5. Top and side views of the structures of H_M and UQ and the protein residues between H_M and UQ. Distances between closest heavy atoms are given in Å.

for hydrogen.[20] This is the same basis set as that used in our previous study of the PSRC.[9] As the role of the 2s AOs of C, N, and O were expected to be small, only 2p orbitals of these atoms were treated in double. The Hartree–Fock calculations were performed by using The HONDO version 8 program.[21]

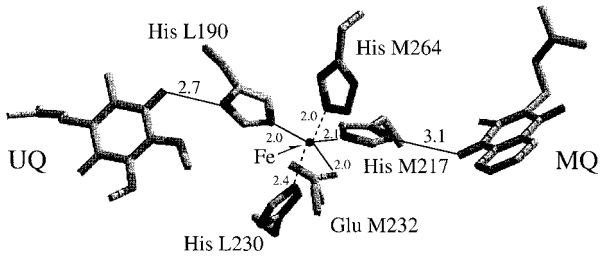

FIGURE 6. The structure of MQ, UQ, and the protein residues between MQ and UQ. Distances between closest heavy atoms are given in Å.

Results and Discussion

ET FROM H_L TO MQ AND FROM H_M TO UQ

Table I shows the transfer integrals for the ETs from H_L to MQ and from H_M to UQ. Figure 4 shows the geometries of H_L to MQ system. The protein residues, Ala M216 and Trp M250, exist in the region between H_L and MQ, while no water molecule exists in this region. We, therefore, included these two fragments as bridges in the present calculation. The direct term was 0.789, one-bridge terms for Ala M216 and Trp M250 fragments were 0.027 and 1.812, respectively, and two-bridge term through these two residues was 0.093. These results show that the one-bridge term for Trp M250 gives the largest contribution to the transfer integral and the ratio between the direct term and the one-bridge term with Trp M250 was about 1:2.

Figure 5 shows the structures of H_M, UQ, and the relevant protein residues, which are Leu L189, and Phe L216. Again, no water molecule exists around here. The calculated transfer integrals are shown in Table I. The direct term was 0.012, one-bridge term for Leu L189 and Phe L216 were -0.744 and -0.061, respectively, and two-bridge term through these two fragments was 0.214. Thus, the one-bridge route through Leu L189 is the largest, and the next is the two-bridge route. The direct term is very small, so that the ET in this system proceeds exclusively by super-exchange mechanism. The transfer integral is a summation of all terms, and therefore, the difference in sign of each term means a cancellation of each contribution. This implies that the existence of the two-bridge route weakens the total electronic coupling.

The square of the transfer integral is 7.409×10^{-12} for H_L–MQ and 0.336×10^{-12} for H_M–UQ. Therefore, the ET rate through L-branch is 20 times faster than the one through M-branch. This result agrees with the experimental result,[2] which shows that the ET from P to UQ occurs mostly through L-branch. In the L-branch ET, the one-bridge route through TrpM250 is the most important.

Now, we consider the origin of the asymmetry of the transfer integrals of the L- and M-branches for the ET from bacteriopheophytin to quinone. Comparing Figures 4 and 5, we see that the proteins and chromophores in these regions are arranged in pseudo-C_2 symmetry. Trp M250 in the L-branch corresponds to Phe L216 in the M-branch, both having π-conjugated rings. Ala M216 in the L-branch also corresponds to Leu L189 in the M-branch, both

TABLE I.
Transfer Integrals for the ETs from H_L to MQ and from H_M to UQ.

	H_L–MQ		H_M–UQ	
	Bridge	H_{DA} ($\times 10^{-6}$ au)	Bridge	H_{DA} ($\times 10^{-6}$ au)
Direct		0.789		0.012
1 bridge	Ala M216	0.027	Leu L189	−0.744
	Trp M250	1.812	Phe L216	−0.061
2 bridge	Ala M216, Trp M250	0.093	Leu L190, Phe L216	0.214
Total		2.722		−0.580
$\lvert H_{DA}\rvert^2$ ($\times 10^{-12}$ au)		7.409		0.336

being saturated hydrocarbons. Thus, the L- and M-branches are similar not only in geometry but also in the amino acid residue. The present theoretical analysis shown in Table I indicates that the inefficiency of Phe L216 in the M-branch as a bridge compared with Trp M250 in the L-branch makes the difference of the transfer integrals between the L- and M-branches. The present result further indicates that the mutation of these amino acid residues will largely change the rate of ET. For example, it is expected that the mutation of Phe L216 to Trp would increase the rate of the ET from H_M to UQ.

ET FROM MQ TO UQ

The structure of the ET system from MQ to UQ is shown in Figure 6. Between MQ and UQ, there are several protein residues, His L190, His L230, His M217, His M232, and His M264, and nonheme iron. No other molecule exists in the region between MQ and UQ. The nonheme iron was not included in the present calculations. Debus et al.[22] showed that when iron was depleted, the rate of the ET decreased only by half, implying that the existence of iron is not quite essential for the occurrence of the ET.

The results are shown in Table II. It shows the direct term, one-bridge terms for five fragments, and two-bridge terms for the different seven routes including His M217 and/or His L190, which are considered to be important from the calculated one-bridge terms. The present calculations show that the two-bridge term involving His M217 and His L190 dominants in this ET. The direct term was very

TABLE II.
Transfer Integrals for the ET from MQ to UQ.

	MQ–UQ		
	Bridge		H_{DA} ($\times 10^{-8}$ au)
Direct			-0.347×10^{-4}
1 bridge	His L190		2.155
	His L230		−0.282
	His M217		1.301
	Glu M232		0.047
	His M264		−0.001
2 bridge	His M217	His L190	46.626
	His M217	His L230	−0.643
	His M217	Glu M232	−0.148
	His M217	His M264	−0.153
	His M264	His L190	1.132
	Glu M232	His L190	−0.203
	His L230	His L190	−0.719
Total			49.112
$\lvert H_{DA}\rvert^2$ ($\times 10^{-12}$ au)			0.241

small, showing that the ET proceeds dominantly through the super-exchange mechanism. The lack of either His M217 or His L190 will drastically decrease the rate of the ET. As this ET is the rate-determining step in the ET from P to UQ, the rate modulation in this ET process affect the rate of the overall ET from P to UQ. His M217 and His L190 are so important so that we expect that the role of the nonheme iron is to fix these protein residues as the ligands at the places preferable for this ET. The experimental result[22] that the rate of the ET is not affected by the substitutions of iron into other divalent metals indicates that the electronic effect of iron itself is not large.

HOLE TRANSFER VS. PARTICLE TRANSFER

The contributions of the HT and PT for the one-bridge term and of the HHT, HPT, or PHT, and PPT for the two-bridge term are shown in Table III. From this table, it is generally difficult to say which is most important, HT or PT for the one-bridge case, and HHT, HPT, PHT, or PPT for the two-bridge case. For example, HT is more important than PT in the ET from H_L to MQ, but PT is more important than HT in the ET from H_M to UQ. Actually, this is a very interesting result, indicating the importance of the fock integral part in the numerator rather than the energy difference term in denominator. As the distance dependence of the fock integral is very sharp, this term often causes the main difference between the different terms. Though people usually discuss the ET route by considering the orbital energy difference alone, the present results indicate that such argument is dangerous. Examining the present calculated results we found that even the orbitals with very low or high orbital energy work as important MOs of the bridges.

RATE OF THE ET IN H_L–MQ AND MQ–UQ SYSTEMS

The transfer integrals $|H_{DA}|^2$ for H_L–MQ and MQ–UQ systems are 7.409×10^{-12} and 0.241×10^{-12}, respectively. From the electronic factor alone, the ET rate for H_L–MQ is expected to be 30 times faster than the one for MQ–UQ. Experimentally the time for the ET was measured to be 200 ps for H_L–MQ and 100 μs for MQ–UQ,[4] which implies that the rate for H_L–MQ is 5×10^5 times larger than the one for MQ–UQ. Thus, the very slow ET from MQ to UQ cannot be explained by the electronic factor alone. For more detailed understanding of this ET, the inclusion of the nuclear factor, such as the vibronic effect, the free energy change and so on, is necessary.

Graige et al.[23] proposed a conformational gating mechanism for the ET from MQ to UQ. Namely, the rate-limiting step is a conformational change required before electron transfer. If this mechanism is the case, the rate of the ET from MQ to UQ estimated from the electronic factor should be larger than the experimental value, as the present result is.

Previously,[7, 9] the transfer integrals $|H_{DA}|^2$ for the ETs in the L-region from the special pair (P^*) to bacteriochlorophyll b (B_L) and from B_L to bacteriopheophytin b (H_L) were calculated to be 25×10^{-9} and 104×10^{-9} au, respectively, in comparison with the experimentally estimated values of 21×10^{-9} and 72×10^{-9} au, respectively. The time for the ET from P^* to H_L was measured experimentally to be 3 ps. From the electronic factor alone, the present result implies that the rate from H_L to MQ is about 3×10^{-4} times slower than that from P^* to H_L, while experimentally, it is 6×10^{-3} times. Therefore, the present transfer integral for the ET from H_L to MQ seems to be underestimated, if the nuclear facter is assumed

TABLE III.
Contributions of HT and PT for One-Bridge Term and HHT, HPT, PHT, and PPT for Two-Bridge Term.

	HT or HHT ($\times 10^{-6}$ au)	HPT or PHT ($\times 10^{-6}$ au)	PT or PPT ($\times 10^{-6}$ au)
(1) H_L–MQ			
Ala M216	1.129		−1.101
Trp M250	5.156		−3.344
Ala M216, Trp M250	0.089	0.140	−0.135
(2) H_M–UQ			
Leu L189	0.124		0.621
Phe L216	−0.011		−0.050
Leu L189, Phe L216	−0.113	0.340	−0.014
(3) MQ–UQ			
His M217, His L190	−0.174	0.078	0.563

to be the same for these two processes. These results mean that *ab initio* study of the nuclear factor is very important, and such study is now under progress.

Conclusion

The ET from H_L to UQ in the PSRC of *Rps. viridis* has been studied by *ab initio* molecular orbital calculations. Super-exchange mechanism utilizing the electronic states of the bridges, which are amino acid residues is shown to be dominant over the direct mechanism. For the ET from H_L to MQ, Trp M250 is shown to be important as a bridge, while Leu L189 works as a bridge in the ET from H_M to UQ, but from the calculated transfer integrals, the ET rate through the L-branch is 20 times larger than the one through the M-branch, supporting the L-branch selectivity of the ET. In this step, the main origin of the selectivity lies in the difference of the amino acid residues placed between the chromophores. In the ET between MQ and UQ, the contribution of the two-bridge super-exchange mechanism utilizing His M217 and His L190 as bridges was by far the largest. The mutation experiments of these amino acid residues would be a challenging issue for modifying and controlling the ET rates in the PSRC of *Rps. viridis*.

Further, the present calculations indicate that predicting the ET route by considering the energy difference of the pertinent MOs is rather dangerous because sometimes the Hamiltonian matrix element in the numerator of the perturbation theory is more sensitive than the denominator that is the energy difference.

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