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# *Ab initio* calculation of electronic coupling in the photosynthetic reaction center

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**ABSTRACT** **We have carried out an *ab initio* electronic structure calculations of electron transfer couplings between chromophores in the bacterial photosynthetic reaction center. The couplings agree remarkably well with parameters obtained from recent quantum dynamical modeling of experimental data assuming an explicit intermediate mechanism. We also have computed couplings on the M-side of the reaction center and have found that the interaction of the primary donor to the M-side intermediate bacteriochlorophyll is quite small because of destructive interference of the two localized coupling matrix elements. This may explain the slow rate of electron transfer down the M-side of the reaction center.**

The initial steps of photosynthesis take place in photosynthetic bacteria in a chlorophyll–protein complex known as the photosynthetic reaction center (RC). In the primary charge separation reaction that takes place in the RC on light excitation, an electron is transferred from the excited state of the special pair of bacteriochlorophylls (BChl), $P^*$, to the primary acceptor, a bacteriopheophytin on the L-side of the RC designated $H_L$, in ≈3 ps, at room temperature, over a distance of 20 Å (1–4). There are slight variations in rate for different organisms, and the rate is more or less independent of temperature, increasing slightly at liquid helium temperature (2, 5). Transfer down the M-side of the protein, which has chromophores in a nearly symmetrical position to the L-side, is estimated to be 30× slower than the L-side rate (6), for reasons that are not yet understood in detail.

The structure of the RC in the bacterium *Rhodopseudomonas viridis* was determined, via x-ray crystallography, by Deisenhofer *et al*. more than 10 years ago (7, 8). Since determination of this structure, there has been an intense experimental and theoretical effort to produce a detailed description of the mechanism of the primary charge separation event. The greatest outstanding controversy is the role of the BChl molecule $B_L$, which is positioned between $P$ and $H_L$. Because direct transfer over a 20-Å distance in 3 ps is implausible, there is a consensus that $B_L$ must participate in the primary electron transfer, either as an explicit intermediate or via a superexchange mechanism. However, distinguishing between these two mechanisms has proven to be remarkably difficult, via either theoretical or experimental efforts. Experiments aimed at directly observing an intermediate via subpicosecond or femtosecond pump-probe spectroscopy (9–11) have led to ambiguous results, with nonexponential kinetics in various spectral regions subject to a range of interpretations: for example, heterogeneity in the ensemble of reaction centers (12, 13) or complexity in the quantum dynamics (14–16). Zinth and coworkers have been the strongest proponents of the view that an explicit intermediate has been observed (10); their kinetic scheme entails a rate-determining initial step from $P$ to $B_L$ followed by a very rapid transfer of the electron from $B_L$ to $H_L$. Recent measurements by this group on a modified reaction center in which $H_L$ has been altered chemically to raise its redox potential have been claimed to provide the first direct observation of a $P^+B^-$ intermediate (13).

On the theoretical side, one set of efforts have centered around the calculation of the diagonal energy of the putative intermediate, $P^+BH^-$, as compared to the energy of $P^*$. Results ranging from ≈0 to 1 eV (1 eV = $1.602 \times 10^{-19}$ J) have been obtained for this energy gap, depending upon assumptions made concerning ionization of protein residues, treatment of solvent, method of estimating the gas phase energy difference of the chromophores, and computational details of the chromophore–protein interactions (17–20). The most recent work of Gunner and Honig (20), which includes a quantitative treatment of solvation via a Poisson–Boltzmann calculation, arrives at a best estimate of 0.3 eV for the energy gap, which mandates a superexchange mechanism; however, the authors point out that this value depends critically on assumptions concerning the protonation states of ionizable residues, as well as other uncontrolled approximations, such as estimation of the gas phase energetics of the chromophore diabatic states.

A second quantity that can be calculated theoretically is the off-diagonal electron transfer matrix elements $H_{ij}$ between the charge localized diabatic chromophore states $i$ and $j$, which up to now have been obtained from semiempirical electronic structure calculations (21–23). In what follows, we designate state 1 the donor state, state 2 the intermediate state, and state 3 the acceptor. If the explicit intermediate mechanism of Zinth and coworkers is correct, $H_{12}$ should be on the order of 10–30 $cm^{-1}$, and $H_{23}$ should be larger than this, with the precise value of the latter obtainable from the details of the kinetics. For superexchange, the effective coupling between states 1 and 3 is obtained from the formula:

$$J_{eff} = H_{12}H_{23}/(E_1 - E_2), \qquad [1]$$

where $E_i$ is the energy of state $i$, evaluated at the crossing point of the donor and acceptor potential surfaces. Unfortunately, here too the semiempirical calculations span a wide range of values (see Table 1), some of which are consistent with the explicit intermediate mechanism. However, even the largest results obtained are too small to yield a sufficiently large $J_{eff}$ by using the energy gap estimated above 0.3 eV, for a 3.5-ps transfer rate.

To address this large uncertainty in the theoretical modeling, we have developed an algorithm to evaluate the off-diagonal tunneling matrix elements $H_{ij}$ by using *ab initio* quantum chemical methods. Specifically, charge-localized, restricted open-shell Hartree–Fock wavefunctions are used in the calculations; this level of theory has provided satisfactory comparisons with experiments, typically yielding matrix elements within 30% of experimental values (24), for example,

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Abbreviations: RC, reaction center; BChl, bacteriochlorophyll.

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Table 1. Semiempirical calculation of ET coupling matrix elements (values in $cm^{-1}$)

| Reactions | Warshel *et al.* (21) | Plato *et al.* (22) | Scherer and Fischer (23) |
|---|---|---|---|
| $P^*B \rightarrow P^+B^-$ | 5.9 | 5.4 | 10 |
| $P^+B^- \rightarrow P^+H^-$ | 15.0 | 44 | 27 |

when applied to intramolecular electron transfer through a molecular bridge. This is a much more satisfactory level of precision for the task at hand than could be obtained if Hartree–Fock calculations were used for diagonal energies because high level electron correlation method are required to obtain the better than 0.1-eV accuracy for the diagonal state energy that would be required to distinguish between electrotransfer mechanism. By using pseudospectral electronic structure methods as embodied in our Jaguar electronic structure code (25) and a standard formulation of the coupling matrix element between nonorthogonal determinants (29), a very efficient methodology can be derived, allowing computations of unprecedented size to be carried out. The results have been validated by comparison with calculations by other groups in the literature for smaller systems (29). For the present work, we used the 6-31G** basis set, which leads to 889 basis functions per model BChl (with the phytyl tail truncated as in ref. 26) or 1,778 functions for a two-porphyrin calculation. Computational of the ET matrix element requires only ≈14 hours on an IBM 390 workstation, which is at least one order of magnitude less computation time than would be required using an adiabatic state formalism and a conventional electronic structure code.

We have carried out a series of calculations for six pairs of molecules in the RC, with geometries taken from the *R. viridis* RC crystal structure: for the L-side acceptors, $P_LB_L$, $P_MB_L$, and $B_LH_L$ (we neglected the effect of $P_L$ on the $P_MB_L$ matrix elements, and visa versa), and, correspondingly, $P_LB_M$, $P_MB_M$, and $B_MH_M$ for the M-side acceptors. All results from the calculations are presented in Table 2. In addition to the chromophores, we have included in some calculations a small number of close-lying protein residues. These residues make only a small contribution to the matrix elements between $P_M$ and $B$ or between $B$ and $H$. Our preliminary conclusion is that the effects of the protein environment on the tunneling matrix elements are small, although we have not examined exhaustively all residues in the vicinity of the chromophores. Furthermore, we did a few calculations in which the Mg of one BChl of the special pair was removed; this resulted in very small deviations from the couplings of the native structure, suggesting as well that the effects of the protein ligands on the coupling are not significant. We also examined the effects of basis set on the matrix element by carrying out a few calculations with the 6-31G basis set, removing polarization functions; again, the effects were minimal, in agreement with the conclusions of other workers that the size of the basis set is not crucial to obtaining reliable values of the electron transfer matrix element (24), as long as a double zeta quality basis is used.

Table 2. *Ab initio* calculation of electrotransfer coupling matrix elements (values in $cm^{-1}$)

| Reactions | Protein residues | Coupling $H_{ij}$ |
|---|---|---|
| L-side of RC | | |
| $P_L^-B_L \rightarrow P_LB_L^-$ | none | 5.10 |
| $P_L^-B_L \rightarrow P_LB_L^-$ | L157-VAL | 6.46 |
| $P_L^-B_L \rightarrow P_LB_L^-$ | L157-VAL, M208-TYR | 10.31 |
| $P_L^*B_L \rightarrow P_L^+B_L^-$ | none | 7.24 |
| $P_L^*B_L \rightarrow P_L^+B_L^-$ | L157-VAL | 8.06 |
| $P_L^*B_L \rightarrow P_L^+B_L^-$ | L157-VAL, M208-TYR | 10.43 |
| $P_M^-B_L \rightarrow P_MB_L^-$ | none | 30.68 |
| $P_M^-B_L \rightarrow P_MB_L^-$ | L157-VAL | 31.51 |
| $P_M^-B_L \rightarrow P_MB_L^-$ | L157-VAL, M208-TYR | 33.53 |
| $P_M^*B_L \rightarrow P_M^+B_L^-$ | none | 32.27 |
| $P_M^*B_L \rightarrow P_M^+B_L^-$ | L157-VAL | 32.88 |
| $P_M^*B_L \rightarrow P_M^+B_L^-$ | L157-VAL, M208-TYR | 34.45 |
| $B_L^-H_L \rightarrow B_LH_L^-$ | none | 122.17 |
| $B_L^-H_L \rightarrow B_LH_L^-$ | M208-TYR | 121.28 |
| P without Mg on L-side | | |
| $P'^-_LB_L \rightarrow P'_LB_L^-$ | none | 9.14 |
| $P'^-_MB_L \rightarrow P'_MB_L^-$ | none | 35.02 |
| M-side of RC | | |
| $P_L^-B_M \rightarrow P_LB_M^-$ | none | 17.20 |
| $P_L^*B_M \rightarrow P_L^+B_M^-$ | none | 17.41 |
| $P_M^-B_M \rightarrow P_MB_M^-$ | none | 12.64 |
| $P_M^*B_M \rightarrow P_M^+B_M^-$ | none | 19.10 |
| $B_M^-H_M \rightarrow B_MH_M^-$ | none | 95.45 |

For all six pairs, we investigate the transfer of an electron from a negative ion state of the donor chromophore to the neutral state of the acceptor. This coupling is directly relevant to $B \rightarrow H$ electron transfer and is potentially relevant to $P \rightarrow B$ transfer as well, because $P^*$ has been shown to contain an admixture of internal charge transfer states $P_L^+P_M^-$ (27). To model the excited state, we take the ground state Hartree–Fock solution and move one electron from the highest occupied molecular orbital to the lowest unoccupied molecular orbital of the BChl molecule, producing a restricted open-shell Hartree–Fock wavefunction in which orbital relaxation has not been taken into account. This procedure is not capable of providing an accurate description of the excited state energetics; however, the electron transfer coupling matrix elements appear to be much less sensitive to the quality of the wavefunction than the diagonal energies, as noted above. The latter point is evidenced by the fact that the matrix elements of the excited state $P_L^*$ (or $P_M^*$) constructed in this fashion and the negative ion state $P_L^-$ (or $P_M^-$) yield nearly identical couplings with the charge separated state $P^+B^-$ in our calculations.

It is immediately obvious that our values for the $H_{ij}$ on the L-side are incompatible with a superexchange model with a large energy gap. Taking the gap as 0.3 eV, in accordance with the calculations discussed previously, and substitution of the largest conceivable values of $H_{12}$ and $H_{23}$ (34.45 $cm^{-1}$ and 122.17 $cm^{-1}$, respectively) into Eq. **1** leads to an effective electron transfer matrix element of only ≈2 $cm^{-1}$, which in turn yields an electron transfer rate two orders of magnitude slower than what is observed experimentally if standard nonadiabatic electron transfer theory is used to compute the rate and activationless transfer is assumed. It is difficult to imagine how this differential could be made up by any modification of the model assumptions.

Turning next to the explicit intermediate model, the value of 122 $cm^{-1}$ for $H_{23}$ is qualitatively consistent with the proposal of Zinth and coworkers (10, 11, 13) that the $B \rightarrow H$ transfer proceeds very rapidly. In fact, the value is remarkably close to the 135 $cm^{-1}$ coupling strength obtained by Makri *et al.* (16) from a phenomenological analysis of the kinetic data of refs. 13 and 28 (accepting the interpretation of the data proposed by the authors of those papers) by using path integral quantum dynamics to model the electron transfer. To obtain the $P \rightarrow B$ transfer rate, we use the exciton representation of the $P$ excited state, which is known from analysis of the optical spectrum (27) to have the form $(P_L^*P_M - P_LP_M^*)/\sqrt{2}$. Calculating the coupling matrix element between this wavefunction and $P^+B^-$, and using the localized coupling matrix elements in Table 2 with the maximal number of amino acids included, we obtain the result $J = 17$ $cm^{-1}$. This is again remarkably close to the value of 22 $cm^{-1}$ obtained by Makri *et al.* (16). The agreement of the *ab initio* data with that obtained by a rigorous quantum dynamical fitting of the experiment is encouraging with regard to the validity of both the calculations and the interpretation of the experimental results.

Turning to the M-side results, a similar analysis leads to a very small value for the coupling of $P$ to $P^+B_M^-$ because the prescription for calculating the exciton state matrix element involves subtracting the $P_L^*P_M$ and $P_LP_M^*$ coupling matrix elements, which, in this case, are quite close together, within a few wavenumbers based on the results in Table 2. The level of precision of the calculations is, in fact, not high enough to justify a quantitative evaluation of the magnitude of this coupling. However, the results qualitatively suggest that the slow rate of electron transfer down the M-side may be caused by greater equality in the coupling of $B_M$ to $P_M$ and $P_L$ as compared to the coupling of $B_L$ to $P_M$ and $P_L$, where there is an $\approx 20\ \mathrm{cm}^{-1}$ differential. This conclusion can only be tentative until a wider range of experimental data has been examined: for example, primary electron transfer in the heterodimer mutants and refinement of the assumptions in the computational model (it will be critical, for example, to examine the accuracy of the geometries obtained from the x-ray crystallographic structures).

In summary, we have carried out an *ab initio* computation of the electron transfer matrix elements between chromophores in the photosynthetic reaction center, including some protein residues in addition to the chromophores. These calculations are in sharp disagreement with models in which the energy gap between $P^*$ and $P^+B^-$ is $>0.1$ eV and are in excellent agreement with an explicit intermediate model obtained from a quantum dynamical modeling of experimental data. The values we have determined here for the coupling matrix elements now can be used in subsequent dynamical simulations, eliminating the need to treat the electronic couplings as adjustable parameters. Future work should involve *ab initio* computation of the diagonal matrix elements, which, although a considerably more difficult undertaking, is feasible with the correlation methods currently being developed in our electronic structure code.

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