- 2P316 紅色光合成細菌および高等植物の反応中心の吸収ピークの温度変化の理論
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A model for temperature-dependent peak shift of the photosynthetic reaction-center absorption
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Temperature dependence of the reaction-center absorption of purple bacteria and higher plant was modeled in the light of quantum chemical calculation. The 860 nm absorption, assigned to the lower excited state of the special pair dimer of bacteriochlorophyll-*a* (Bchl_a), shows striking temperature dependence, decreasing markedly with lowering temperature. In higher plant, the peak shift is not apparent, but some observations have been reported in PSI. A model for this temperature-dependent peak shift is given, by constructing potential-energy surfaces for the electronic excited and the ground state of the special pair. The excited-state potential is sensitive to the intra-pair distance and the mutual angle of the dimer molecules, the potential surface becoming markedly anharmonic. The anharmonic excited-state potential surface was calculated by the quantum-chemical approach. The other protein vibration modes were assumed to be harmonic and were represented by a single reorganization energy λ . Employing these potential surfaces, the absorption band was calculated as a function of temperature. The large peak shift with temperature could successfully be reproduced. This mechanism does not rely on the thermal expansion which has been assumed so far to be effective in the peak shift without detailed calculation. The peak shift is due to density-of-vibrational-states difference between the excited and the ground state potential surfaces.

- 2P317 光合成反応中心スペシャルペアカチオンラジカルのスピン密度分布に関する理論的研究
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- Quantum chemical study of the spin density distribution of the special pair cation radical in the bacterial photosynthetic reaction center
- Hideki Yamasaki, Yu Takano, and Haruki Nakamura. (Institute for Protein Research, Osaka University)

Electronic asymmetry of the special pair (SP) in the photosynthetic reaction center is one of the important factors for the electron transfer (ET) in the primary charge separation process. Spectroscopic studies such as EPR and ENDOR showed that the fraction of the charge localized on L-side bacteriochlorophyll of the special pair (SP_L) is 68% in the wild type of *Rb. sphaeroides*. Spin density distribution (SDD) changed from 22 to 83% with a variety of site-directed mutagenesis, implying that the interactions between SP and the protein are critical for the electronic asymmetry of the special pair cation radical (SP^{•+}). We have studied the effect of the structural asymmetry of SP itself and the protein polarity on SDD with the quantum chemical calculation, suggesting that the electronic asymmetry of SP^{•+} is derived from the conformational difference of methyl ester groups of SP halves and that the protein polarity should enhance the effect of this structural asymmetry. In this presentation, we show that the conformational difference of the phytyl groups of SP halves is also effective to the L-side distribution of the spin density of SP^{•+}. In addition, the effect of the amino acids surrounding SP on the electronic asymmetry of SP^{•+} has been investigated. The calculated SDDs of the wild-type and mutant proteins reproduce the experimental value qualitatively. Direct effects of the protein on the electronic structure of SP^{•+} are discussed.

- 2P318 光合成反応中心における光誘起電子移動に関する理論的研究：複数の QM 領域を持つ QM/MM 構造最適化
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- ¹京大院・工、²量子化学研究協会
- Theoretical Study of Photoinduced Electron Transfer in a Bacterial Photosynthetic Reaction Center: Multi-core QM/MM geometry optimization
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Photosynthetic reaction center (PSRC) converts photon energy into chemical energy initiated by the charge separations. The X-ray structure of PSRC of Rhodobacter sphaeroides revealed that it contains seven chromophores arranged in pseudo C2 symmetry. They are special pair (P), two bacteriochlorophylls b (BA and BB), two bacteriopheophytins b (HA and HB), and two ubiquinones (UQ10). It is well-known that the photoinduced electron transfer (ET) in the PSRC is unidirectional: the excited electron in P is transferred unidirectionally only along the A-branch. Previously, we have studied kinetics of the ET by calculating transfer integral in the Marcus formula (J.Hasegawa and H.Nakatsuji, J.Phys.Chem.B, 102, 10420, 1998). On the other hand, energetic reason of the unidirectional ET is still not clearly explained. In the present study, we have developed multi-core QM/MM algorithm Gaussian03 as platform. Our program can optimize several QM regions in a self-consistent manner. Using the program, we optimized PSRC of Rhodobacter sphaeroides in various states in the photoinduced ET. On the basis of the results, we also discussed driving force of the ET.

- 2P319 紅色光合成細菌 *Sphaeroides* の光反応中心におけるプロトン移動反応の理論研究
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- Theoretical investigation of the proton transfer in the photosynthetic reaction center of *Rh. Sphaeroides*
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In the photosynthetic reaction center (RC) from *Rhodobacter sphaeroides*, the light induced long range electron and proton transfer reactions occur to reduce a bound secondary ubiquinone (Q_B) to a ubiquinol. With this reduction, the RC converts light energy to chemical energy. The detailed mechanism of electron transfer and proton transfer toward Q_B is unknown. We focused on the proton transfer reaction toward Q_B which is coupled with the second electron transfer. In our previous calculation, ASP and HIS residues are assumed to be protonated and formed hydrogen bond network with water molecules as a pathway of proton transfer from the bulk region. But, Quantum Mechanics (QM) and Molecular Mechanics (MM) calculation revealed that Q_B is protonated almost instantly after the first electron transfer in that state, and this result is conflicted with the experimental results which show Q_B^- state holds several seconds with a single flush of light. We investigated the thermal stability of the protonation pattern of ASP residues located near from Q_B in MM and calculated the sequential proton transfer's minimal energy potential in QM/MM to understand what determines the ready state of the proton transfer.