# The spin density distribution of the special pair cation radical in the wild-type and mutated reaction center

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The spin density distribution (SDD) of the special pair cation radical ($SP^+$) in the photosynthetic reaction center (RC) was studied, using density functional calculations with a polarizable continuum model and a point charge model as the protein environment. The calculated SDD between the halves of SP from *Rhodobacter sphaeroides* agreed qualitatively well with the experimental value. The differences in the specific orientations of the ester carbonyl groups of the phytyl (Phyt) groups, as well as the methyl ester (Mes) groups, are one of the origins of the electronic asymmetry[1, 2].

The generality of the specific orientations was confirmed with 14 X-ray structures of a variety of type-II RCs. The interactions between the Mes and Phyt groups and the surrounding amino acids were investigated by structural and sequence alignments. The alignments revealed that specific van der Waals contacts and polar interactions are conserved among the type-II RCs, with a few exceptions, suggesting that the orientations of these groups are controlled by the specific interactions between them as the evolutionary consequence[2].

Since the significant changes of the SDD due to mutations are reported experimentally, the effects of the protein environment on the SDD were examined theoretically. The estimated SDDs of the mutated RCs qualitatively agree with the experimental values. The SDDs became closer to the experimental values by using a polarizable continuum model as the protein environment.

References: 1) Yamasaki et al. *Chem. Phys. Lett.* **2007,** *447*, 324-329. 2) Yamasaki et al. *J. Phys. Chem. B* **2008,** *112*, 13923-13933.