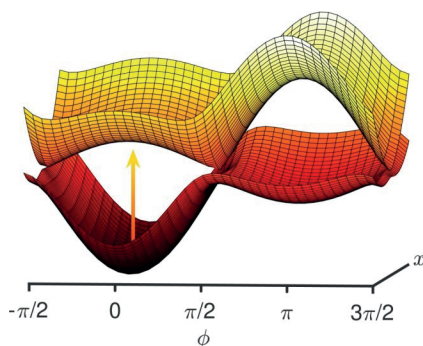


Reaction rates and quantum coherence effects in natural processes: photosynthetic energy transfer and photoisomerization

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The observation of wavelike energy transport in photosynthesis has triggered a debate about the extent to which quantum mechanics is necessary to understand biological processes. The relevance of quantum effects has been considered in the context of both photosynthesis and photoisomerization. Intimately related to the question of quantum coherence in biological processes is the time-scale of such reactions. The weak effect of environment-induced decoherence on photoisomerization, for example, has been justified by the supposed ultra-fast time-scale of the reaction. However, conclusions regarding reaction rates and coherent effects in such processes have been drawn on the basis of experiments using pulsed laser excitation. As is well known, the dynamics induced by incoherent, continuous wave natural sunlight differ substantially from the dynamics induced by ultra-fast excitation. In this work we present three results related to photoisomerization. First, we show that under natural incoherent excitation, the rate of product formation bears no connection to the rates observed under pulsed laser excitation. Second, oscillatory coherences, if generated, decay on time-scales that are small compared to the overall reaction time-scale. Third, stationary coherences, which arise in the presence of an environment, can have a small effect on the rate of reaction by enhancing or diminishing the probability of energy transfer through certain pathways. Similar results are presented for photosynthetic energy transfer, and implications for FRET are discussed.



Potential energy surfaces associated with the retinal chromophore, where x represents the molecular stretching coordinate and ϕ the molecular rotation coordinate. The natural light-induced cis-trans isomerization of retinal ($\phi = 0 \rightarrow \phi = \pi$) is the primary event in vision, and is used as an example throughout.

References

- [1] Engel, Gregory S., Tessa R. Calhoun, Elizabeth L. Read, Tae-Kyu Ahn, Tomáš Mančal, Yuan-Chung Cheng, Robert E. Blankenship, and Graham R. Fleming. "Evidence for wavelike energy transfer through quantum coherence in photosynthetic systems." *Nature* 446, no. 7137 (2007): 782–786.
- [2] Panitchayangkoon, Gitt, Dugan Hayes, Kelly A. Fransted, Justin R. Caram, Elad Harel, Jianzhong Wen, Robert E. Blankenship, and Gregory S. Engel. "Long-lived quantum coherence in photosynthetic complexes at physiological temperature." *Proceedings of the National Academy of Sciences* 107, no. 29 (2010): 12766–12770.

- [3] Johnson, Philip J. M., Alexei Halpin, Takefumi Morizumi, Valentyn I. Prokhorenko, Oliver P. Ernst, and R. J. Dwayne Miller. “Local vibrational coherences drive the primary photochemistry of vision.” *Nature chemistry* 7, no. 12 (2015): 980–986.
- [4] Brumer, Paul, and Moshe Shapiro. “Molecular response in one-photon absorption via natural thermal light vs. pulsed laser excitation.” *Proceedings of the National Academy of Sciences* 109, no. 48 (2012): 19575–19578.
- [5] Hoki, Kunihito, and Paul Brumer. “Excitation of biomolecules by coherent vs. incoherent light: Model rhodopsin photoisomerization.” *Procedia Chemistry* 3, no. 1 (2011): 122–131.
- [6] Axelrod, Simon, and Paul Brumer. “Reaction rates and quantum coherence effects in natural processes: photoisomerization of model retinal under incoherent excitation” (to be published).
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