Author: Eisenmayer, Thomas J.
Title: Coherent dynamics in solar energy transduction
Issue Date: 2014-12-15

Chapter 8

Conclusions and Outlook

8.1 Conclusions

The special pair in bacterial photosynthesis, where excitons evolve into charge transfer states at near unity efficiency, has been modeled using first-principles molecular dynamics to elucidate the relationship between nuclear motion and electronic structure. The frontier molecular orbitals are found to dynamically localize over the two halves of the special pair dimer induced by specific vibrational modes. One specific vibration is predicted to couple to the excitation involving a histidine coordinated to one half of the pair (P_M) closest to the primary acceptor. Full charge separation is most likely effectuated by proton displacements in the hydrogen bond network surrounding an interstitial water between primary donor and acceptor.

A coherent coupling between nuclear motion and charge transfer is also observed in a biomimetic system with the donor and acceptor moieties held together by hydrogen bonds. In this system the oscillatory photoinduced charge transfer starting from an excitonic state is simulated in real-time within a time-dependent Kohn-Sham formulation of Ehrenfest dynamics. High frequency N-H bond stretching is found to have the same oscillatory period as observed in the charge transfer from donor to acceptor. Furthermore, the energies of the excitonic and charge transfer states oscillate in quasi-resonance once the energy difference between the states matches the energy contained in the vibrational mode and it appears that only when this criterium is met the charge transfer is initiated.

Static density functional theory calculations on a large model of Photosystem II are found to provide an insightful picture of redox levels. The high oxidation potential observed for the reaction center is postulated to emanate from the low dielectric constant of the local protein environment around the special pair chlorophyll P_{D1}.

Finally, a promising system to bridge timescales between photoinduced charge separation and water oxidation catalysis that mimics photosynthetic redox mediation was considered. The proton-coupled electron transfer step that decouples spin and charge in this system upon oxidation was simulated in real-time illustrating a periodic collective motion of the molecule that facilitates the transfer of the proton.

8.2 Outlook

In much of chemistry the motion of the nuclei does not change the quantum mechanical state of the system. This is true for reactant and product states in chemical reactions that are characterized by two different probability densities pertaining to different regions of conformational space of a single quantum mechanical ground state. Then the adiabatic or Born-Oppenheimer approximation holds [1]. Nevertheless, nuclear motion is required to move between the different regions of conformational space. This motion, the so-called reaction coordinate, is often unknown and unspecified.

Starting in the metastable reactant state the nuclear motion to overcome the potential energy barrier and move into the product state is thought to be random or thermal, with temperature being the decisive parameter. However, a potential energy barrier is not a preordained quantity, it crucially depends on the nature of the nuclear motion or reaction coordinate that is chosen by the system to evolve the reactant into the product state.

In this respect, there are several interesting developments suggesting that specific nuclear vibrational modes may be used by enzymes to lower reaction barriers ([2]) or that nuclear motion plays a role in promoting catalytic product formation on surfaces [3]. In this thesis in Chapter 7 it was seen that proton transfer on a single adiabatic potential energy surface was effectuated after several periods of a collective nuclear motion of the molecule in vacuo. The collective nuclear motion in the explicitly solvated simulation was less pronounced and the transfer was almost an order of magnitude slower. It will be interesting to further examine how one can lower the potential energy barrier for chemical product formation through specific periodic motion of the nuclei.

The crucial point in this thesis and the most interesting research direction to pursue is beyond the adiabatic approximation, when multiple quantum mechanical states are non-negligibly coupled. This is the nonadiabatic realm that needs to be explored in order to meet with the societal demand for energy from non-depletable resources.

Consider a two-level system consisting of an excitonic and a charge transfer state coupled through periodic nuclear motion in Dirac's representation of Quantum Mechanics. Such two-level systems subject to an external time-dependent perturbation describe, for example, NMR and laser-induced Rabi oscillations. In Chapter 5 it was found that the energies of the exciton and charge transfer states oscillate in quasi-resonance during the photoinduced charge transfer, while in the frameworks of NMR and Rabi the energies of the states are constant. A smart strategy to deal with this is needed that may involve choosing a reference frame that rotates with the oscillatory perturbation. If the perturbation may be described by a sinusoidal function it can be decomposed into complex exponentials. Further simplification may be achieved if one of these terms cancels with a possible physical interpretation that the electronic system follows the nuclear motion only in a single direction in the complex plane.

An interesting computational development is the efficient implementation of time-dependent Kohn-Sham in the OCTOPUS quantum-chemical suite allowing real-time simulations of excited supramolecular complexes [4]. The Ehrenfest method for coupling the electronic quantum system and the classical nuclear motion seems to correctly predict the coherent nuclear motion that couples to photoinduced charge separation [5,6]. However, the method has limitations as the system will not fully collapse onto a pure eigenstate of the Hamiltonian and in the limit of long timescales no proper thermal equilibrium is reached [7,8]. Therefore, a firm theoretical foundation - possibly following Scully [9] - is needed to guide numerical simulations and experiments towards efficient systems for solar energy transduction.

8.3 References

[1] Max Born and J. Robert Oppenheimer, "Zur Quantentheorie der Molekeln", *Annalen der Physik*, **1927**, 389 (20), 457-484.

[2] S. Hay, N. S Scrutton, Good vibrations in enzyme-catalysed reactions, *Nature Chemistry*, **2012**, 4, 161.

[3] H. Hou, S. J. Gulding, C. T. Rettner, A. M. Wodtke, and D. J. Auerbach, The Stereodynamics of a Gas-Surface Reaction, *Science*, **1997**, 277 (5322), 80-82.

[4] X. Andrade, J. Alberdi-Rodriguez, D. A. Strubbe, M. J. T. Oliveira, F. Nogueira, A. Castro, J. Muguerza, A. Arruabarrena, S. G. Louie, A. Aspuru-Guzik, A. Rubio, and M. A. L. Marques, Time-dependent density-functional theory in massively parallel computer architectures: the octopus project, *J. Phys. Cond. Matt.*, **2012**, 24 233202.

[5] C. A. Rozzi, S. M. Falke, N. Spallanzani, A. Rubio, E. Molinari, D. Brida, M. Maiuri, G. Cerullo, H. Schramm, J. Christoffers and C. Lienau, Quantum coherence controls the charge separation in a prototypical artificial light-harvesting system, *Nature communications*, **2013**, 4, 1602.

[6] S. M. Falke, C. A. Rozzi, D. Brida, M. Maiuri, M. Amato, E. Sommer, A. De Sio, A. Rubio, G. Cerullo, E. Molinari, and C. Lienau ,Coherent ultrafast charge transfer in an organic photovoltaic blend, *Science*, **2014**, 344, 1001-1005.

[7] A. V. Akimov, A. J. Neukirch and O. V. Prezhdo, Theoretical Insights into Photoinduced Charge Transfer and Catalysis at Oxide Interfaces, *Chemical Reviews*, **2013**, 6, 4496.

[8] J. C. Tully, Perspective: Nonadiabatic Dynamics Theory, *J. Chem. Phys.*, **2012**, 137, 22301.

[9] Marlan O. Scully, Quantum Photocell: Using Quantum Coherence to Reduce Radiative Recombination and Increase Efficiency, *Physical Review Letters*, **2010**, 104, 207701.