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Sarah Elizabeth Morgan

Ultrafast Quantum Effects and Vibrational Dynamics in Organic and Biological Systems

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Ultrafast Quantum Effects and Vibrational Dynamics in Organic and Biological Systems

Doctoral Thesis accepted by
the University of Cambridge, UK

Springer

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ISSN 2190-5053 ISSN 2190-5061 (electronic)
Springer Theses
ISBN 978-3-319-63398-5 ISBN 978-3-319-63399-2 (eBook)
DOI 10.1007/978-3-319-63399-2

Library of Congress Control Number: 2017946654

Printed on acid-free paper

This Springer imprint is published by Springer Nature
The registered company is Springer International Publishing AG
The registered company address is: Gewerbestrasse 11, 6330 Cham, Switzerland

Supervisor's Foreword

The remarkable efficiency and reliability of photosynthetic light reactions has been studied for many decades, giving us important insight into how sustainable solar energy transduction is directed by the molecular optoelectronics of biological nanostructures [1]. However, the recent and unexpected observation of robust quantum dynamics in photosynthetic complexes has challenged our fundamental understanding of biological photophysics, raising profound debates, and much interdisciplinary research, on the possible roles of quantum mechanics in biological and organic systems [2]. Understanding how such ephemeral and non-classical processes can impact the efficiency of organic light harvesting materials not only sheds new light on the marvels and intricacy of functional biological nanostructures; it could also provide a route towards new quantum design principles for artificial energy technologies [3]. At the same time, these processes challenge us to develop the theoretical tools capable of describing the complexity of the novel, real-time, non-equilibrium dynamics whose exploitation may prove to be just as important as basic electronic structure for the next generation of efficient energy materials.

Dr. Morgan's thesis is an important contribution to this exciting new field and focuses on the theoretical prediction and analysis of the sophisticated ultrafast optical spectra that probe the crucial first few picoseconds of quantum light harvesting. By studying the novel photophysics of thin films of organic pentacene, Dr. Morgan's doctoral work provides new insight into the process of singlet fission, a quantum mechanical effect that allows a single photon to be "doubled" into two electron-hole pairs, potentially boosting the efficiency of organic photovoltaics. Simulating the ultrafast nonlinear spectra of pentacene films, Dr. Morgan identified the experimental signatures of an entangled intermediate state, normally "dark" to standard optical probes, that leads to fission on sub-picosecond timescales [4]. Proving that this novel detection arises from quantum vibrational effects, this thesis also reports a collaboratively developed wavelet method to identify similar vibronic dynamics in photosynthetic reaction centres. This was then applied to real spectroscopic data to test the robustness of recently proposed quantum transport mechanisms in which vibronic effects generate coherent wave-like dynamics, even

in the presence of the aggressive fluctuation "noise" in the surrounding protein environment [5].

Such "noisy" interactions are the fundamental origin of energy dissipation and the—normally—rapid degradation of quantum effects in nanostructured systems. Elucidating the microscopic physics of protein vibrations is therefore of vital importance in the quest to understand how quantum effects can be stabilised and harnessed in molecular devices. The final part of this thesis looks at the dynamics of vibrational energy in real protein structures, using molecular dynamics and coarse-grained models to understand the role of nonlinear vibrational modes that, *inter alia,* can transfer vibrational energy over extremely long distances and/or even harvest it from their surroundings when excited out of equilibrium [6]. The structure-function relations underlying these rich protein dynamics have many potential applications for light harvesting functions, as well as an impact on several medically relevant, but still not well understood, biological processes such as allostery.

It is an immense pleasure to write this foreword for Dr. Morgan's thesis, which is a body of work that testifies, on every page, to her outstanding creativity and intellectual bravery. I am sure that every one of Dr. Morgan's many experimental and theoretical collaborators will be as inspired, delighted and proud as I am that this work has been recognised for this prestigious Springer Thesis Prize, and I look forward with great anticipation to seeing how the many deeply mined gems of theoretical insight contained in this thesis will inspire further work through the publication of this monograph.

Cambridge, UK
May 2017

Dr. Alex W. Chin

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Abstract

Recently, evidence has emerged that quantum coherences can be sustained in photosynthetic complexes over much longer timescales than initially expected. This evidence comes predominantly from a new technique called 2D electronic spectroscopy (2DES), which provides unprecedented access to the ultrafast quantum and vibrational dynamics of organic and biological systems. Intriguing suggestions have been made that these quantum coherences might be sustained or even regenerated by molecular vibrations; however, a full understanding of their origins has proved elusive. This is due to the exceptional difficulty of interpreting 2DES experiments, combined with the complexity of the underlying biological systems.

One approach to tackling these challenges is to study simpler organic molecules first, which nonetheless exhibit fascinating ultrafast photophysics and have useful applications for photovoltaics. Therefore, here, I begin by presenting an extensive theoretical analysis of 2DES data for the organic material pentacene, which undergoes a novel process known as singlet fission. This work elucidates "dark" entangled states in pentacene and the importance of vibrations during fission.

Time-frequency analysis offers an opportunity to extract further information from oscillatory 2DES signals. I discuss the difficulties surrounding using time-frequency analysis to distinguish non-trivial regeneration of electronic coherences from interferences between vibrational modes. I use 2DES data from photosystem II as an example and propose that theoretical simulations are essential to unravel these complicated effects.

Ultimately, microscopic analysis of vibrations is required to fully understand the complex relationship between electronic and vibrational dynamics in organic and biological systems. This analysis may be particularly important for nonlinear collective protein modes. Therefore, in the final chapter, I use the nonlinear network model and molecular dynamics simulations to study vibrations in the Fenna–Matthews–Olson complex (FMO). This work suggests that localised, nonlinear discrete breather modes might be formed in biologically relevant parts of FMO and that the optical properties of FMO could be altered by protein vibrations. Overall, this approach represents a promising avenue for further research.

Acknowledgements

Firstly, I would like to thank my supervisor, Alex Chin, for his excellent advice, patience and unquenchable optimism, without which this dissertation would not have been possible. I have also been lucky to work with several fantastic experimentalists, including Artem Bakulin, Akshay Rao, Andrew Musser and Hannah Stern in Cambridge, as well as Eli Romero and Rienk van Grondelle from VU Amsterdam. On the theory side, Danny Cole made substantial contributions to the work on FMO and made many helpful suggestions. Dassia Egorova had significant input into the work on pentacene, in particular the simulations of the ultrafast dynamics, whilst the work on wavelet analysis of PSII builds on Javier Prior's work.

Sam Smith has always been happy to share ideas and both he and Tom Price have been great office-mates throughout. Several other friends have also been extremely supportive, not least Laura Brooks, Rosie Mantell, Helen Smalley and Catrin Treharne.

Eros Mariani first introduced me to condensed matter theory and encouraged me to begin my studies in Cambridge. Towards the end of my Ph.D., Petra Vértes has helped to inspire my interest in complex networks and has been incredibly generous with her time in doing so.

Above all, I would like to thank my family—Mum, Dad, Ba, Zoë, Ben, Sam and my wider family—for their constant support and encouragement. It means the world to me.

Contents

Nomenclature

Roman Symbols

E	Energy
$\vec{E}$	Electric field
$\hbar$	Reduced Planck constant
H	Hamiltonian
J	Electronic coupling
J_s	Spectral density function
$\vec{k}$	Wavevector
$\vec{P}$	Polarisation
q	Charge
$\vec{r}$	Displacement
R_c	Cut-off distance
$S_{R/NR}$	Rephasing/non-rephasing 2D signal
S_1	Singlet state
S	Huang-Rhys factor
t_d	Detection time
Tr	Trace
T	Waiting time
t	Time
TT_n	Higher lying multiexciton state
TT	Multiexciton state
U_0	Time evolution operator

Greek Symbols

β	$1/k_BT$, where k_B is the Boltzmann constant and T is the temperature
χ	Susceptibility
δ	Dirac delta function

ε	Permittivity
ε_0	Permittivity of free space
$\vec{\mu}$	Transition dipole moment
ω	Frequency
ϕ	Wavefunction
ρ	Density matrix
σ	Charge distribution
τ	Coherence time
ω_c	Cut-off frequency
ω_τ	Absorption frequency
ω_{t_d}	Emission frequency

Acronyms/Abbreviations

2D	Two dimensional
2DES	Two-dimensional electronic spectroscopy
Å	Angstrom
BChl	Bacteriochlorophyll
bRC	Bacterial reaction centre
C_α	Carbon alpha atom
CD	Circular dichroism
CT	Charge transfer
CWT	Continuous wavelet transform
DB	Discrete breather
DO	Displaced harmonic oscillator
DTP	6,13-di(2-thienyl) pentacene
ED	Electronic dimer
ENM	Elastic network model
ESA	Excited state absorption
eV	Electron volt
FMO	Fenna–Matthews–Olson complex
fs	Femtosecond
GSB	Ground-state bleach
h.c.	Hermitian conjugate
HOMO	Highest occupied molecular orbital
LA	Linear absorption
LD	Linear dichroism
LUMO	Lowest unoccupied molecular orbital
NADP	Nicotinamide adenine dinucleotide phosphate
NM	Normal mode
NMR	Nuclear magnetic resonance
NNM	Nonlinear network model
NR	Non-rephasing
PPC	Pigment–protein complex