
Atomistic Modelling of Aggregate Chlorophyll Systems

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ABSTRACT

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DEDICATION AND ACKNOWLEDGEMENTS

Here goes the dedication.

AUTHOR'S DECLARATION

I declare that the work in this dissertation was carried out in accordance with the requirements of the University's Regulations and Code of Practice for Research Degree Programmes and that it has not been submitted for any other academic award. Except where indicated by specific reference in the text, the work is the candidate's own work. Work done in collaboration with, or with the assistance of, others, is indicated as such. Any views expressed in the dissertation are those of the author.

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TABLE OF CONTENTS

	Page
List of Tables	ix
List of Figures	xi
1 Introduction	1
1.1 Quantum Exploits in Light Harvesting Systems	1
1.1.1 Electronic Energy Transfer	1
1.1.2 Coherence	1
1.2 Light-Matter Response	1
1.3 Electronic Structure for Large Systems	1
1.4 The Aim	1
2 Mean-Field excited states	3
2.1 Theory	3
2.1.1 Δ -SCF and eigenvalue difference	3
2.1.2 Semi-empirical extensions	4
2.2 Benchmarking	5
2.2.1 Small Systems	5
2.2.2 LHII Chlorophyll	5
2.2.3 GFN methods	5
2.3 Extensibility	5
2.3.1 Non-orthogonality	5
2.3.2 Embedding	5
2.3.3 Scaling	5
3 Chlorophyll specific methods	7
3.1 Shortcuts in the Cassida equation	7
3.1.1 Approximations to Solutions	7
3.1.2 MNOK Integrals	7
3.2 Parameterization	7

TABLE OF CONTENTS

3.2.1	Reference Data	7
3.2.2	Objective Function	7
3.2.3	Minimization Algorithms	7
3.3	Benchmarking	7
3.3.1	Transition properties	7
3.3.2	Potential Energy Surfaces	7
3.3.3	Absorption Spectra	7
4	Exciton Method	9
4.1	Theory	9
4.1.1	Exciton States	9
4.1.2	Embedding	9
4.2	Truncated Chlorophylls	9
4.2.1	Rotation	9
4.2.2	Distance	9
4.3	LHII Pairs	9
4.3.1	Assignment of States	9
4.3.2	Comparison	9
5	Atomistic Modelling of Light Harvesting Complexes	11
5.1	LHII	11
5.1.1	Spectral Density	11
5.1.2	Molecular Dynamics Method	11
5.2	Approximating Spectral Densities	11
5.2.1	Hessians	11
5.2.2	Chlorophyll distances	11
5.3	Excitation Energies	11
6	Discussion	13
6.1	Transition Property Approximations	13
6.2	Further Investigations into LHII	13
6.3	Coherence	13
A	Appendix A	15
A.1	Electronic Structure Codes	15
A.2	Computational Hardware	15
	Bibliography	17

LIST OF TABLES

TABLE	Page
-------	------

LIST OF FIGURES

FIGURE	Page
--------	------

INTRODUCTION

Naturally occurring light harvesting systems present an interesting scientific challenge. With near perfect efficiency, the energy from a photon will be taken and transferred to a reaction centre, leading to charge transfer processes that culminate in powering biological systems. Making models that can predict and explain these effects are key to making similarly efficient photovoltaic systems.

1.1 Quantum Exploits in Light Harvesting Systems

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1.1.1 Electronic Energy Transfer

Begins a subsection.

1.1.2 Coherence

1.2 Light-Matter Response

1.3 Electronic Structure for Large Systems

1.4 The Aim

MEAN-FIELD EXCITED STATES

Preamble

2.1 Theory

2.1.1 Δ -SCF and eigenvalue difference

Δ -SCF predicts the excitation energy of a system by comparing the single point energy of the ground state and the excited state. Finding this excited state correctly can be an issue, but is usually assumed to be similar to the ground state. In its simplest form, the Δ -SCF method calculates the ground state, and then calculates the excited state by rerunning a self-consistent field (SCF) with the excited state occupation numbers. This then gives a full description of both the ground and excited state from the orbital coefficients output from the two SCF procedures.

Initially, the excited state could be calculated by relaxing the orbitals which contain the excited electron and hole in the ground state space, so that the excited state and ground state are orthogonal[?]. However, it was argued that this procedure would exacerbate errors from finding the ground state, and that the excited state was not a proper SCF solution[?]. Alternatively, it was proposed that an SCF like method, where instead of populating orbitals according to the aufbau principle, orbitals which most resemble the previous iteration's orbitals should be occupied. Each iteration in an SCF procedure produces new molecular orbital coefficients by solving the Roothaan-Hall equations[?], generally given as an eigenvalue problem:

$$(2.1) \quad \mathbf{FC}^{\text{new}} = \mathbf{SC}^{\text{new}} \epsilon$$

where \mathbf{C}^{new} are the next orbital coefficient solutions, \mathbf{S} is the overlap, and ϵ are the orbital energies. The Fock matrix \mathbf{F} is calculated from the previous set of orbital coefficients:

$$(2.2) \quad \mathbf{F} = f(\mathbf{C}^{\text{old}})$$

The amount of similarity of orbitals can be estimated from their overlap:

$$(2.3) \quad \mathbf{O} = (\mathbf{C}^{\text{old}})^\dagger \mathbf{S} \mathbf{C}^{\text{new}}$$

and for a single orbital can be evaluated as a projection:

$$(2.4) \quad p_j = \sum_i^n O_{ij} = \sum_v^N \left[\sum_\mu^N \left(\sum_i^n C_{i\mu}^{\text{old}} \right) S_{\mu v} \right] C_{vj}^{\text{new}}$$

where μ, v are orbital indices. The population can then be given by the set of orbitals with the highest projection p_j . This method can be used for any excited state, with the caveat that the orbital solution is in the same region as the ground state solution. For a few low lying states, this is generally true, and so Δ -SCF can be used to calculate a spectrum of excited states[?]. The method of using this orbital overlap is called the maximum overlap method (MOM).

Δ -SCF has been shown to be cheap alternative to TDDFT and other higher level methods, without considerable losses of accuracy in certain cases[?]. Additionally, as the excited state is given as solutions to SCF equations, the gradient of this solution can be given by normal mean-field theory. These gradients would be much cheaper than TDDFT or coupled cluster methods, and so would be advantageous for a dynamic simulation of LHII.

The final descent in response theory would be to eigenvalue difference methods. Here there is assumed to be no response of the orbital energies and shapes when interacting with light. As stated earlier, this would be recovered from the complete Cassida equation if the coupling elements in the \mathbf{A} and \mathbf{B} matrices are set to zero. This means that the difference between the excited state energy and the ground state energy is just the difference of the orbital energies between the orbital an electron has been excited to and the orbital has been excited from. Additionally, transition properties can be calculated by calculating transition density matrices from only the ground state. Hence, all the information needed can be given by a single SCF optimization. Generally, eigenvalue difference methods are not seen as accurate response methods, but can offer a quick and easy initial value[?].

2.1.2 Semi-empirical extensions

We tried to extend the range of DFT methods that could be used for Δ -SCF and eigenvalue difference methods by investigating whether a tight-binding method could predict transition

properties. We chose the recently published DFTB method parameterized by the Grimme group for this. This method has been parameterized for geometries, frequencies and non-covalent interactions, and uses an extended version of Hückel theory. The name they present is GFN-xTB, standing for "Geometries, Frequencies, Non-Covalent - eXtended Tight Binding". We chose this method for two reasons. The first being that it was already implemented

2.2 Benchmarking

2.2.1 Small Systems

2.2.2 LHII Chlorophyll

2.2.3 GFN methods

2.3 Extensibility

2.3.1 Non-orthogonality

2.3.2 Embedding

2.3.3 Scaling

CHLOROPHYLL SPECIFIC METHODS

Preamble

3.1 Shortcuts in the Cassida equation**3.1.1 Approximations to Solutions****3.1.2 MNOK Integrals****3.2 Parameterization****3.2.1 Reference Data****3.2.2 Objective Function****3.2.3 Minimization Algorithms****3.3 Benchmarking****3.3.1 Transition properties****3.3.2 Potential Energy Surfaces****3.3.3 Absorption Spectra**

EXCITON METHOD

P^{reamble}

4.1 Theory

4.1.1 Exciton States

4.1.2 Embedding

4.2 Truncated Chlorophylls

4.2.1 Rotation

4.2.2 Distance

4.3 LHII Pairs

4.3.1 Assignment of States

4.3.2 Comparison

ATOMISTIC MODELLING OF LIGHT HARVESTING COMPLEXES**P**^{reamble}
5.1 LHII**5.1.1 Spectral Density****5.1.2 Molecular Dynamics Method****5.2 Approximating Spectral Densities****5.2.1 Hessians****5.2.2 Chlorophyll distances****5.3 Excitation Energies**

P^{reamble}

6.1 Transition Property Approximations

6.2 Further Investigations into LHII

6.3 Coherence



APPENDIX A

This appendix covers the common computational details of this work. Included are the software packages, hardware used. These are not exhaustive list, and additional details are provided in the main chapters. However, wherever implementations or methodology details are missing, the information will be found here.

A.1 Electronic Structure Codes

This project has primarily used the `QCORE` software that is found as part of the `ENTOS` project. This is a software package for DFT and DFTB electronic structure calculations that has been written as a joint venture between the Miller group in California Institute of Technology and the Manby group in the University of Bristol. It is now being hosted by Entos Inc. It is a novel C++ implementation, with a focus on modularity, functional code and modern development practices to enable easier, cleaner and more reuseable code. All novel methods discussed in the chapters have been implemented in the `QCORE` package.

A.2 Computational Hardware

BIBLIOGRAPHY

