

**MODELING SOLVENT EFFECTS ON
EXCITATION ENERGIES FOR POLYENES**

A THESIS

**SUBMITTED TO THE DEPARTMENT OF CHEMISTRY
AND THE INSTITUTE OF ENGINEERING AND SCIENCES
OF
BILKENT UNIVERSITY**

**IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE**

By

YAN LI

August, 2006

I certify that I have read this thesis and in my opinion it is fully adequate, in scope and in quality, as a thesis of degree of Master of Science.

Assoc. Prof. Dr. Ulrike Salzner (Supervisor)

I certify that I have read this thesis and in my opinion it is fully adequate, in scope and in quality, as a thesis of degree of Master of Science.

Assoc. Prof. Dr. Ömer Dağ

I certify that I have read this thesis and in my opinion it is fully adequate, in scope and in quality, as a thesis of degree of Master of Science.

Dr. Gülay Ertay

I certify that I have read this thesis and in my opinion it is fully adequate, in scope and in quality, as a thesis of degree of Master of Science.

Assoc. Prof. Dr. Oğuz Gülseren

I certify that I have read this thesis and in my opinion it is fully adequate, in scope and in quality, as a thesis of degree of Master of Science.

Prof. Dr. Semra Bilgiç

Approved for the Institute of Engineering and Sciences

Prof. Dr. Mehmet Baray

Director of Institute of Engineering and Sciences

ABSTRACT

MODELING SOLVENT EFFECTS ON EXCITATION ENERGIES FOR POLYENES

YAN LI

M.S. in Chemistry

Supervisor: Assoc. Prof. Dr. Ulrike Salzner

August 2006

Excitation energies of polyenes in solution are about 0.3-0.4 eV lower than in the gas phase. Understanding the solvent effect is important to the design of low band gap conducting polymers.

This thesis is to evaluate this solvent effect theoretically by comparing the first allowed vertical excitation energies of polyenes, oligothiophenes and

oligopyrroles.

Influences of theoretical levels and basis sets on the optimised geometries, the HOMO- LUMO gap, and the TDHF excitation energies are reviewed and compared with experimental data in the gas phase. To calculate excitation energies, six levels with Stevens-Basch-Krauss pseudopotentials in connection with polarized split valence basis set (CEP-31g* basis in Gaussian 03 package) are employed in this thesis, including the HOMO-LUMO gap, CIS, TDHF, TDDFT, CASSCF and CASPT2.

Three methods to take solvent effects into account were tested: implicitly by using the polarized continuum model (PCM) method, explicitly by treating a solute-solvent cluster and the combination of both methods. In PCM, heptane is considered as the solvent. PCM can be applied at different theoretical levels. In the cluster model, four corresponding alkane molecules surrounding a solute molecule in a parallel orientation form the first solvation shell. Solvent effects are determined by whether a theoretical level can form an effectively bound cluster. The combination of both can yield a closest result to experimental data.

Further, solvent effects of water are evaluated with PCM and clusters. TDHF and PCM are applied for larger systems like oligothiophenes and oligopyrroles.

Keywords:

Solvent effects, excitation energies, polyenes, polarized continuum model, solute-solvent cluster model

ÖZET

POLİENLERİN UYARILMA ENERJİLERİ ÜZERİNDE ÇÖZÜCÜ ETKİLERİNİN MODELLENMESİ

YAN LI

Yüksek Lisans, Kimya Bölümü

Tez Yöneticisi: Doç. Dr. Ulrike Salzner

Ağustos, 2006

Polienlerin çözelti içerisinde uyarılma enerjileri, gaz fazındaki polienlerden yaklaşık 0.3-0.4eV daha düşüktür. Çözücü etkilerini anlamak düşük band aralıklı iletken polimerlerin tasarımında önemlidir.

Bu tezde; polienlerin, oligotiyofenlerin, oligopirollerin ilk izinli dikey uyarılma enerjileri karşılaştırılarak teorik olarak çözücü etkileri hesaplamaktadır.

Optimize geometrilere dayanan temel kümeler ve kuramsal basamakların etkileri, HOMO-LUMO aralığı ve TDHF uyarılma enerjileri tekrar gözden geçirildi ve gaz fazındaki deneysel sonuçlarla kıyaslandı. Bu tezde, HOMO-LUMO aralığı, CIS, TDHF, TDDFT, CASSCF ve CASPT2 içeren 6 basamağın Stevens-Basch-Krauss psüdotensiyelli düzeyinde polarize olmuş bağ değeri temel seti (Gaussian 03 temelinde CEP-31g*) uyarılma enerjilerini hesaplamada kullanılmıştır.

Çözücü etkisini hesaba katmak için 3 tane model var; polarize olmuş devamlı modelin (PCM) dolaylı kullanıldığı metod, çözünen-çözücü kümeleri şeklinde direkt olarak ele alındığı metod ve iki modelin birleştirilmesi ile ele edilen metod. Heptane, polarize olmuş devamlı modelinde (PCM) çözücü olarak göz önünde tutulmuştur. PCM başka teorik basamaklarda da kullanılmaya uygundur. Çözünen-çözücü kümeleri modelinde; çözünen molekül paralel pozisyonda yerleşmiş dört tane alkan molekülleri tarafından çevrilmektedir. Küme modelinde, çözücü etkisi teorik düzeyde etkili şekilde bağlanmış kümelerin oluşup oluşmaması ile belirlenebilir. İki modelin birleşimi, deneysel verilere en yakın sonuçları elde etmemizi sağlayabilir.

Ayrıca, suyun çözücü etkisi, PCM ve küme modelleriyle hesaplanmıştır. TDHF ve PCM, oligotayofenler ve oligopayrollar gibi büyük sistemler için uygulanmıştır.

Anahtar Kelimeler:

Çözücü etkisi, uyarılma enerjileri, polienler, polarize olmuş devamlı modeli (PCM), çözünen-çözücü kümeleri modeli

Acknowledgement

First of all, I like to appreciate a lot to Department of Chemistry and all the faculty members for offering me an opportunity to study Master in Bilkent University, which is well known for its first-rate education.

I am obliged very much to my supervisor, Dr. Ulrike Salzner for her great help, instructive guidance and kind patience.

I would like to acknowledge my thesis committee, Assoc. Prof. Dr. Ulrike Salzner, Assoc. Prof. Dr. Ömer Dağ, Dr. Gülay Ertaş, Assoc. Prof. Dr. Oğuz Gülseren and Prof. Dr. Semra Bilgiç for their careful reading of this thesis and their helpful comments.

I want to thank my parents and the rest of my family for their encouragement, support, guidance and love.

I specially thank three friends: Şerife Okur and Adnan Hazar, who are group members and provide useful discussions on the thesis, İlknur Çayırtepe, who interpreted the abstract into Turkish. I also appreciate the support of my dear friends: Oğuzhen Çelebi, Yaşar Akdoğan, İlknur Tunç, Olga Samarskaya, Anıl Ağırallı, A. Faik Demirörs, Nesibe Çıldır, Mehtap Küyükoğlu, Ünsal Koldemir, and Yurdanur Türker.

I am pleased to reserve my deepest gratitude for Xuanqian Xie, my husband. I feel happy and fortunate to share my success and all my life with him.

Table of Contents

Chapter 1. Introduction.....	1
1.1 Motivation.....	1
1.2 Theoretical Methods for the Ground State.....	2
1.2.1 HF Approximation.....	3
1.2.2 Dynamical and non-Dynamical Correlation Energy.....	3
1.2.3 Wave-Function-Based Electron Correlation Methods.....	3
1.2.3.1 Variational Correlation Methods.....	3
1.2.3.2 Perturbation Correlation Methods.....	4
1.2.4 Electron-Density-Based Correlation Method.....	5
1.3 Theoretical Methods to Calculate Excitation Energies.....	7
1.3.1 HOMO-LUMO Gap	8
1.3.2 CIS.....	8
1.3.3 TDHF.....	9
1.3.4 TDDFT.....	9
1.3.5 CASSCF and CASPT2.....	9
1.4 Basis Sets.....	10
1.4.1 What is a Basis Set?.....	11
1.4.2 Types of Improvements over a Minimal Basis Set.....	11
1.4.2.1 Split Valence Basis Sets.....	11
1.4.2.2 Polarization Functions.....	11
1.4.2.3 Diffuse Functions.....	11
1.4.3 Basis Sets used in This Thesis.....	12
1.4.3.1 “Split Valence” Basis Sets.....	12

1.4.3.2 Correlation Consistent Basis Sets.....	12
1.4.3.3 Effective Core Potentials (ECP) Split Valence Basis Sets	12
1.4.4 What Kind of Basis Set can be used?.....	13
1.4.5 How to Determine the Basis Set?.....	13
1.5 The First Two Singlet Excited States of Polyenes.....	13
1.6 Vertical and Adiabatic Excitations.....	14
1.7 Solvent Effects.....	14
1.7.1 Solute-Solvent Interactions.....	15
1.7.2 Factors that Affect the Magnitude of Dispersion Forces.....	15
1.7.3 How to Model the Solvent.....	15
1.7.4 Polarized Continuum Model (PCM).....	16
1.7.5 Response of the Solvent in Continuum Models.....	16
1.7.6 Applicable PCMs in Gaussian 03 Package.....	17
1.7.6.1 Onsager Model.....	17
1.7.6.2 Polarized Continuum Model (PCM).....	17
1.7.6.3 Integral Equation Formalism PCM (IEFPCM).....	18
1.7.6.4 Isodensity and Self-Consistent Isodensity PCM (IPCM and SCIPCM).....	18
1.7.6.5 Conductor-like PCM (CPCM).....	19
1.7.7 Explicit Cluster Models.....	19
Chapter 2. Method.....	21
2.1 Overview.....	21
2.2 Experimental Method---Spectra.....	21
2.3 Geometry Optimization	23
2.3.1 Effects of Theoretical Levels.....	23

2.3.2 Effects of Basis Sets.....	24
2.4 Excitation Energies.....	25
2.5 Computational Method.....	25
Chapter 3. Results and Discussion.....	26
3.1 Geometries	26
3.1.1 Bond Length and BLA.....	26
3.1.2 Effect of PCM on the Geometry.....	28
3.1.3 Effect of the Explicit Cluster on the Geometry.....	29
3.1.4 Binding Energy of the Cluster.....	30
3.1.5 Geometries of Clusters with Water Molecules.....	31
3.2 Orbital Energies.....	35
3.2.1 Effect of Theoretical Levels.....	35
3.2.2 Effect of Basis Sets.....	36
3.2.3 Effect of PCM.....	36
3.2.4 A Comparison of HOMO-LUMO Gaps with Experimental Excitation Energies.....	37
3.3 Excitation Energies.....	38
3.3.1 Experimental Data.....	38
3.3.2 BLA and TDHF Excitation Energies.....	39
3.3.3 The Preferred Basis Set to Calculate the Excitation Energy.....	40
3.3.4 The Accuracy of Theoretical Levels.....	41
3.3.4.1 CIS.....	41
3.3.4.2 TDHF and TDDFT.....	42

3.3.4.3 CASSCF, CASPT2 and MRMP.....	43
3.4 Solvent Effects.....	46
3.4.1 Solvent Effect in PCM.....	46
3.4.1.1 Effect of Dielectric Constant.....	46
3.4.1.2 Effect of PCMs.....	48
3.4.1.3 Effect of PCM at various theoretical levels.....	49
3.4.2 Solvent Effect of Cluster Models.....	49
3.4.2.1 How Many Solvent Molecules?.....	49
3.4.2.2 Other Methods to Optimize the Cluster Geometries.....	50
3.4.2.3 The Cluster Effects for Longer Polyenes.....	51
3.4.3 Solvent Effect of the Cluster Model in PCM.....	51
3.4.4 Solvent Effect of Water for Polyenes.....	53
3.4.4.1 Solvent Effect of Water for Polyenes in PCM.....	53
3.4.4.2 Determine a Favorable Cluster Model.....	55
3.4.4.3 Solvent Effect of Water for the Cluster of Hexatriene at PBE.....	55
3.4.4.4.Solvent Effect of Water for the Cluster of Butadiene at MP2.....	56
3.4.5 Solvent Effect for Oligothiophenes and Oligopyrroles.....	57
Chapter 4. Conclusions.....	60
Chapter 5. References.....	62

List of Tables

Chapter 3

Table 3.1.1 Bond length (Å) and BLA(Å) of hexatriene optimised at different theoretical levels with the basis set of Cep-31g* and experimental data.....	26
Table 3.1.2 Bond length (Å) and BLA (Å) of C ₆ H ₈ optimized at DFT (B3P86-30%) with various basis sets.....	27
Table 3.1.3 Bond length (Å) and BLA (Å) of C ₆ H ₈ in vacuum and PCMs at DFT (B3P86-30%)/Cep-31g*.....	29
Table 3.1.4 Solute-solvent distances (Å) of the C ₄ H ₆ *4C ₄ H ₁₀ cluster with geometries optimized at various theoretical levels.....	30
Table 3.1.5 Total energies (a.u.) of butadiene and butane and binding energies of the cluster with geometries optimized at various theoretical levels....	30
Table 3.2.1 Orbital energies (eV) and HOMO-LUMO gaps (eV) of C ₆ H ₈ at theoretical levels (the basis set is Cep-31g*).....	35
Table 3.2.2 Orbital energies (eV) and HOMO-LUMO gaps (eV) of C ₆ H ₈ at DFT (B3P86-30%).....	36
Table 3.2.3 Orbital energies (eV) and HOMO-LUMO gaps (eV) at DFT (B3P86-30%) of C ₄ H ₆ , C ₆ H ₈ and C ₈ H ₁₀ in the gas phase and in PCM (heptane).....	37
Table.3.2.4 HOMO-LUMO gaps (eV) at B3P86-30%/Cep-31g* and experimental excitation energies (eV).....	37
Table 3.3.1 Experimental data of excitation energies of polyenes (eV).....	38
Table 3.3.2 TDHF/Cep-31g* excitation energies and BLA of C ₆ H ₈ (the geometry is optimized with the basis set of Cep-31g*).....	39

Table 3.3.3 TDHF excitation energies of C_6H_8 with a same geometry optimised at B3P86-30%/Cep-31g* employing different basis sets.....	40
Table 3.3.4 CIS excitation energies (eV) with Cep-31g* and Cep-31+g*.....	42
Table 3.3.5 TDHF and TDDFT excitation energies (eV).....	42
Table 3.3.6 CASSCF, CASPT2 and MRMP excitation energies(eV).....	44
Table 3.4.1 TDHF/Cep-31g*//DFT (B3P86-30%)/Cep-31g* excitation energies (eV) in PCM with different solvents.....	47
Table 3.4.2 TDHF/Cep-31g*//B3P86-30%/Cep-31g* excitation energies (eV) and solvent effects (eV) with different PCMs.....	48
Table 3.4.3 PCM effect (eV) at various theoretical levels.....	49
Table 3.4.4 TDHF excitation energies (eV) in some explicit cluster models.....	49
Table 3.4.5 TDHF excitation energies (eV) of C_4H_6 and $C_4H_6*4C_4H_{10}$ cluster and cluster effects (eV) with geometries optimized at MP2, DFT (PBE, PBE0).....	51
Table 3.4.6 TDDFT excitation energies (eV) of C_4H_6 and $C_4H_6*4C_4H_{10}$ cluster and cluster effects (eV) with geometries optimized at MP2, DFT (PBE, PBE0).....	51
Table 3.4.7 TDHF excitation energies (eV) in the gas phase and in the clusters including four corresponding alkane molecules, and cluster effects (eV) at MP2 and PBE.....	52
Table 3.4.8 Excitation energies (eV) of C_4H_6 in vacuum, PCM, cluster and the cluster in PCM with geometries optimized at the MP2 level.....	53
Table 3.4.9 Excitation energies (eV) of C_4H_6 in vacuum, PCM, cluster and the cluster in PCM with geometries optimized at the PBE level.....	53
Table 3.4.10 Excitation energies (eV) of C_4H_6 in vacuum, PCM, cluster and the cluster in PCM with geometries optimized at the PBE0 level.....	54
Table 3.4.11 TDHF energies in PCM with heptane and water as the solvent.....	55

Table 3.4.12 TDHF//MP2 excitation energies (eV) and cluster effects (eV) of $C_6H_8 \cdot 4H_2O$ clusters (TDHF//MP2 of C_6H_8 is 5.05 eV in the gas phase.....	56
Table 3.4.13 TDHF//B3P86-30% excitation energies (eV) of oligothiophenes in vacuum, PCM, and Exp. data in matrix and in solution.....	58
Table 3.4.14 TDHF//B3P86-30% excitation energies(eV) of oligopyrroles in vacuum, PCM, and Exp. in solution.....	59

List of Figures

Chapter 1

Figure 1.7.1: Applicable PCMs in Gaussian 03 Package.....	17
Figure 1.7.2 C ₄ H ₆ *4C ₄ H ₁₀ cluster.....	20
Figure 1.7.3 C ₄ H ₆ *4H ₂ O cluster.....	20

Chapter 2

Figure 2.1.1 Overview of method.....	22
---	----

Chapter 3

Figure 3.1.1 C ₄ H ₆ *4C ₄ H ₁₀ cluster optimized at MP2.....	29
Figure 3.1.2 Designed and optimized geometries of the C ₆ H ₈ *4H ₂ O clusters....	32
Figure 3.1.3 Designed and optimized geometries of the C ₄ H ₆ *4H ₂ O clusters....	34
Figure 3.3.1: TDHF/ Cep-31g* and BLA of C ₆ H ₈	39

Chapter 1. Introduction

1.1 Motivation

In recent years, simulating solvent effects is an active area in theoretical chemistry. Since theoretical data in general are obtained on individual molecules, they correspond to experimental results in the gas phase. In the gas phase, molecules are regarded as isolated particles without interactions among each other, so computational methods are relatively accurate. However, most experiments take place in an environment of solution, rather than in the gas phase, so the solvent effect should be taken into account to approximate the exact value. In some cases, experimental data are only available in solution, so the solvent effect should be removed when they are compared to data in the gas phase.

Conducting organic polymers are semiconductors and have a low band gap ranging from about 1 to 4 eV. The band gap between valence and conduction band of conducting polymer is related with the lowest allowed excited energy of its monomer units and the strength of interaction between the repeat units¹. To design low band gap organic conducting polymers, it is desirable to start with monomer units having small excitation energies. Only data of polyenes are available in the gas phase and in solution. For polythiophenes and polypyrroles, there is no data in the gas phase. Solvent effects can lower excitation energies. For instance, the excitation energy of polyenes in solution is 0.3-0.4eV lower than in the gas phase². So solvent effects play an important role to calculate band gaps and excitation energies accurately, which is helpful to develop theoretical models for polyacetylene (PA) and other conducting polymers.

The aim of this thesis is to evaluate solvent effects of non-polar and polar solvents theoretically on the first allowed vertical excitation energies of polyenes from C_4H_6 to $C_{14}H_{16}$. We used polarized continuum model (PCM), an explicit cluster model and the combination of both. Before that, we tested the accuracy of theoretical levels in the gas phase. Furthermore, the applications of these approaches for thiophene and pyrrole oligomers are discussed.

1.2 Theoretical Methods for the Ground State

When the Schrödinger equation (SE) was introduced to determine the energy and wave function of a molecule system, it could not be solved exactly for real molecule systems due to electron-electron interactions and the resulting high dimensionality.

1.2.1 Hatree-Fock Approximation

The most prominent approximation is Hartree-Fock (HF) approach³. The HF approach treats electron-electron interactions by considering each electron independently moving in an external average field of all other electrons. The HF approach transforms the many-body SE into many single-electron equations. The exchange contribution is due to Pauli's exclusion principle, which prohibits two electrons from occupying the same quantum state. The correlation contribution is due to electron-electron Coulomb repulsion, which prohibits two electrons from being near to each other. HF only includes the correlation contribution for same spin electrons, entirely neglecting that for opposite spin electrons. Traditionally, HF is considered including electron exchange energy, but neglecting electron correlation, that is, the explicit electron-electron interactions.

1.2.2 Dynamical and non-Dynamical Electron Correlation Energy

Electron correlation energy is divided into dynamical and non-dynamical contributions⁴. Dynamical correlation energy arises from many small contributions from all filled orbitals giving a relatively large amount of stabilization energy to the total system energy as compared with non-dynamical correlation energy. Non-dynamical correlation arises from degeneracy or near-degeneracy. Neglected correlation has an effect on the geometry and on the electronic structure.

1.2.3 Wave-Function-Based Electron Correlation Methods

The problem with HF is that electrons are not paired up in the way that HF method supposes. Any two electrons of opposite spin have the same probability of being in the same region of space as being in separate regions of space. There are two distinct classes of wave-function-based methods (post-Hartree-Fock method) to improve the HF approach.

- Variational methods
- Perturbation methods

1.2.3.1 Variational Correlation Methods

That the expectation value for an approximate wave function is above the exact solution of SE for the same operator is called as “variational principle”. If we have a wave function, which contains adjustable parameters, and we try to minimize the expectation value of the energy by adjusting the parameters, then we are approaching the exact value.

The principle post-Hartree-Fock method using this variational principle is configuration interaction (CI). A linear combination of components, each of which presents an excited configuration wave function, is mixed with the HF wave

function. If the excited configurations are restricted to those arising from exciting one electron from an occupied orbital of the HF wave function to a virtual orbital, configuration interaction with single excitations (CIS) results. Similarly, CISD is restricted to include only single and double excitations.

Other approaches aim at optimising not only the coefficients of the various configurations, but also the coefficients of the basis functions in the MOs, the latter ones are frozen at the HF values in CI methods. This approach is called as multi-configuration self-consistent field (MCSCF). CASSCF is an example of this approach.

1.2.3.2 Perturbation Correlation Methods

Adding the electron-electron interaction term as a perturbation to the HF Hamiltonian operator and removing the average HF potential, as proposed by Møller and Plesset in 1933, provides a way to include the electron correlation effect. This is known as MP_n method⁵, n defining the order of truncation.

The correlation problem is recognized as a perturbation because the difference between the exact Hamiltonian operator and the exact solution of the approximate Hamiltonian operator is treated as perturbation. The HF solution is obtained as the first order correction term starting from a non-interacting Hamiltonian. The zero-order energy is the sum of the orbital energies. The first order energy is the normal HF energy. The first important correction is the second order term and this leads to MP2.

MP2 gives a reasonable proportion of the correlation energy. Higher order terms become expensive. MP3 and MP4 are often used, and higher level more than 4 are rarely concerned.

1.2.4 Electron-Density-Based Correlation Method

Density functional theory (DFT) is a conceptually different approach. In the first stage of DFT, the energy was expressed as a functional of the density of a uniform electron gas⁶. Then DFT is modified to improve the electron density around molecules via a gradient correction. In contrast to HF, electron correlation is included from the start via the exchange-correlation (xc) functional.

DFT is not a post-HF method, since not the wave function is constructed but the electron density. Nonetheless the modern implementation uses orbitals referred to as Kohn-Sham orbitals. The same SCF procedure is used as in HF theory. DFT includes a significant fraction of the electron correlation.

In HF theory, the energy has the form⁷:

$$E = V + \langle hP \rangle + 1/2 \langle PJ(P) \rangle - 1/2 \langle PK(P) \rangle$$

V: nuclear repulsion energy,

P: the density matrix,

$\langle hP \rangle$ is the one-electron (kinetic and potential) energy,

$1/2 \langle PJ(P) \rangle$ is the classical coulomb repulsion of the electrons, and

$-1/2 \langle PK(P) \rangle$ is the exchange energy resulting from quantum (fermion) nature of electrons.

In DFT, the exact exchange for a single determinant is replaced by a more general expression, the exchange-correlation functional, which includes two terms accounting for both exchange energy and the electron correlation.

$$E = V + \langle hP \rangle + 1/2 \langle PJ(P) \rangle + E_x(P) + E_c(P)$$

Where $E_x(P)$ is the exchange functional, $E_c(P)$ the correlation functional.

The essential difference between HF and DFT is that DFT is an exact theory⁶, that

is, the exact xc functional were used, the exact results would be achieved. HF considers the interactions of every electron with the average electric field formed by all the other electrons. It is a theory of approximation, neglecting the correlation. HF is motivated mainly because of the ability to solve the relevant equations. DFT suggests that the Hamiltonian depends on the total number of electrons, and positions and atomic numbers of nuclei, the former one we can obtain by integrating over all space of a very useful observable value, the electron density ρ . Since the exchange functional is unknown, many approximations exist.

The xc functionals for DFT are divided into three levels⁶:

- Local spin density approximation (LSDA).
- Gradient-corrected functional, so-called general gradient approximation (GGA), which includes both the density and its first derivative.
- Hybrid functional, which mixes a portion of exact Hartree-Fock exchange within DFT exchange-correlation functional.

Hybrid functionals are very popular, since better results than pure functionals of both local and non local are obtained⁸.

Three functionals used in this thesis are PBE, PBE0, and B3P86-30%.

For PBE, $E_{xc} = E_x(\text{PBE}) + E_c(\text{PBE})$.

For PBE0, $E_{xc} = 0.25 * E_x(\text{HF}) + 0.75 * E_x(\text{PBE}) + E_c(\text{PBE})$.

For B3P86-30%,

$E_{xc} = 0.3 * E_x(\text{HF}) + 0.7 * E_x(\text{LSDA}) + 0.72 * E_x(\text{B88}) + 0.81 * E_c(\text{LYP}) + 0.19 * E_c(\text{VWN})$

B3P86-30% yielded a better energy gap than B3LYP and B3P86-20%, $\pm 0.25\text{eV}$

of experimental excitation energies for butadiene and octatetraene⁹. For isolated solute molecules, B3P86-30% was used to optimise the geometry and to calculate the excitation energy at the TDDFT level.

PBE and PBE0 are evaluated as DFT methods for optimising the geometry and transition energy for isolated molecules. More important, studies on H-bonded systems indicated that DFT GGA could provide fairly accurate descriptions of those systems¹⁰, so PBE and PBE0 are tested to get the cluster effect.

1.3 Theoretical Methods to Calculate Excitation Energies

In analogy to the ground-state methods, excited-state methods can also be divided into as wave-function-based methods and electron-density-based methods⁶.

- Typical wave-function-based methods are TDHF, CI (CIS, CISD, multi-reference CI (MRCI)), multi-reference MP approach (MRMP), and multi-configuration self-consistent field methods (MCSCF, such as CASSCF and CASPT2).
- Other prominent wave-function-based methods are the equation-of-motion and linear response coupled cluster theories EOM-CC and LR-CC. The shortcoming of these methods is its limitation to fairly small molecules due to their high computational costs. They cannot be applied for conducting polymers.

In this thesis, we will focus on the HOMO-LUMO energy difference, CIS, TDHF, TDDFT, CASSCF and CASPT2.

1.3.1 HOMO-LUMO Gap

For polyenes, the first allowed singlet excitation is a single $\pi\text{-}\pi^*$ (HOMO-LUMO) transition. According to Koopman's Theorem, the negative of the HOMO energy corresponds to vertical excitation energy of an electron from the highest occupied orbital to the continuum. The negative of LUMO energy is the energy emitted when an electron is taken from the continuum to the lowest unoccupied orbital. Therefore, HOMO-LUMO gaps can approximate to the excitation energy of $\pi\text{-}\pi^*$ transitions. However, using HOMO-LUMO energy differences involves only the ground state and neglects relaxation of the electronic structure. Therefore, the HOMO-LUMO energy difference is only a crude approximation.

1.3.2 CIS

Configuration interaction calculation with single excitations (CIS) is the computationally and conceptually simplest wave-function-based method for calculating excited states⁶. CIS includes some electron correlation via having several different electron configurations mixed via the two-electron terms in Hamiltonian, which provide flexibility into the description of any electronic state. Due to the partial neglect of the dynamical electron correlation, CIS tends to overestimate excitation energies. According to Brillouin's Theorem, the singly excited configurations do not interact with the ground state; therefore CIS only introduces electron correlation into the description for the excited state. CIS is about as good for the excited state as HF for the ground state. In general, CIS method overestimates the excitation energy about 0.5-2eV compared with experimental data⁶.

1.3.3 TDHF

By its physical meaning, TDHF (time-dependent Hartree-Fock) level is synonymous for random phase approximation (RPA)⁶. The time-dependent Hartree-Fock equations, which were written for the first time by Dirac, constitute an approximation to time-dependent SE with the assumption that the system can be described by a single Slater determinant composed of time-dependent single-particle wave functions. Today time-dependent Hartree-Fock equations refer to those obtained in the first order time-dependent perturbation theory from Dirac's equation, that is, the linear response.

TDHF is a different approach from CIS. Analysis of the difference shows that TDHF includes cross terms, the so-called B-matrix⁶ that is missing in CIS. TDHF and CIS use Hartree-Fock ground state as reference state.

1.3.4 TDDFT

TDDFT (time-dependent DFT) approach is the most prominent method to calculate excitation energy for medium-sized and large molecules. TDDFT approach performs very well for many systems. TDDFT is an exact theory built on the analysis of the time-dependent linear response of the exact ground-state electron density to a time-dependent external perturbation, which yields exact excited-state energy and oscillator strength. However, the exact xc functional is unknown, which need to be employed in a practical calculation. TDDFT of approximate xc functionals shows failures with large π systems⁶.

1.3.5 CASSCF and CASPT2

Complete active space self-consistent field (CASSCF) involves complete active space. Each state is calculated as a linear combination of electronic configurations

obtained by all permutations of n electrons in m orbitals included in the active space. CASSCF includes non-dynamical correlation by optimising MO coefficients of each electron configuration, thus treating them on equal weight¹¹.

Since π orbitals lie between occupied and unoccupied σ levels, electronic excitations in conjugated system occur with π orbital space. Therefore, only π electrons are included in active space, with all valence σ electrons inactive. The correlation of σ electrons can be added by increasing the number of active electrons. For excited states of polyenes, which occur within the π system. Thus a reasonable choice for the active space is to include all π electrons and π orbitals, $n=m=4$ for butadiene, $n=m=6$ for hexatriene and so on.

CIS and TDHF use HF ground state molecular orbital coefficients for the excited states. CASSCF reoptimizes the orbital, for the excited states. Another advantage of CASSCF is that it includes multiply excited electron configurations. But CASSCF excitation energies are usually too high due to the lack of dynamic correlation.

Complete active space second order perturbation theory (CASPT2) is a combination of MP2 computation with a complete active space multi-reference wave function. CASPT2 includes dynamic correlation. Since correlation is usually more important in excited states, improving E_{corr} usually lowers excitation energies. CASPT2 is the most accurate method available.

1.4 Basis Sets

1.4.1 What is a Basis Set?

A basis set is a set of basis functions from which the wave function is constructed¹¹. The wave function under consideration, are all represented as vectors, the components of which correspond to coefficients in a linear combination of the basis functions.

1.4.2 Types of Improvements over a Minimal Basis Set

There are three types of improvement over a minimal basis set, which uses just one basis function per valence orbital, either Slater type or contracted gaussians.

1.4.2.1 Split Valence Basis Sets

Such as 6-31g, 6-311g, have 2 or 3 basis functions for each valence orbital. For example, with 6-31g, H is represented as H1s and H1s', C is represented as 1s, 2s, 2s', 2Px, 2Py, 2Pz, 2Px', 2Py' and 2Pz'. Core orbitals are composed of 6 gaussians, and valence orbitals are composed of 3 or 1 gaussians.

1.4.2.2 Polarization Functions

Polarization functions are higher angular momentum orbitals to enhance the flexibility within the basis set, effectively allowing molecular orbitals to be more asymmetric. d-type functions can be added to polarize valence p orbitals, and f-functions to polarize d-type orbitals, and so on. For example, 6-31g* adds d functions to each heavy atom, 6-311g** adds p-functions to hydrogen, add d functions to heavy atoms.

1.4.2.3 Diffuse Functions

Diffuse functions are large size version of s- and p- type functions. Basis set with diffuse functions are important for systems where electrons are far from the nucleus

such as systems in their excited states. 6-31+g* add diffuse function to heavy atoms. The longer polyenes are, the less electronic disturbance is caused by excitation. So diffuse functions are much more important for short polyenes than for long ones.

1.4.3 Basis Sets used in This Thesis

There are many kinds of basis sets. In this project, three basis sets are used and discussed:

1.4.3.1 “Split Valence” Basis Sets

“Split valence” basis sets by Pople and coworkers, like 6-31g, 6-311g.

1.4.3.2 Correlation Consistent Basis Sets

Correlation consistent basis sets by Dunning and coworkers, cc-pVNZ (N= D, T, Q and 5, for double, triple, quadruple and quintuple zeta quality respectively)

This type is specifically designed for high quality calculations using correlation methods. These basis sets yield convergence of the electronic energy for the complete correlation calculation. It is clear that these basis sets become very large very rapidly. The largest one can only be used for very small molecules, while the smallest is comparable in size to 6-31g. In addition, these basis sets can be augmented with diffuse functions. cc-pVNZ basis sets are the best choice if they are affordable. For longer polyenes, it is impossible. cc-pVTZ and cc-pVQZ are used for short polyenes like hexatriene as a reference.

1.4.3.3 Effective Core Potentials (ECP) Split Valence Basis Sets

To reduce the number of basis functions of heavy atoms, effective core potentials replace the chemically inert core electrons with an analytical function that represents the combined nuclear-electronic core to the remaining electrons.

Cep-31g* and Cep-31+g* seem good alternatives and will be tested in later part.

1.4.4 What Kind of Basis Set can be used?

In general, large basis sets give more accurate results by imposing fewer restrictions on the locations of the electrons in space. As a cost, larger basis sets require more time and more disk space. For routine calculations, a polarized basis set with double zeta is necessary at least⁸.

1.4.5 How to Determine the Basis Set?

The basis set has a significant influence on the geometry and the excitation energy. Comparing geometries and excitation energies employing basis sets of increasing quality, the best one can be determined when convergence is achieved.

1.5 The First Two Singlet Excited States of Polyenes

For polyenes, the first two singlet excited states of 1^1Bu and 2^1Ag symmetry are important.

1. 1^1Bu involving mainly a single excitation from HOMO to LUMO, is dipole-allowed. 2^1Ag is a double-excited state. 2^1Ag is dipole-forbidden and has a very low intensity.
2. The energy order of them was confirmed in 1970's¹².
 C_4H_6 : $1^1\text{Bu} < 2^1\text{Ag}$ 0.1eV
 C_6H_8 : 1^1Bu , 2^1Ag are virtually degenerate.
 For C_8H_{10} and longer polyenes, 2^1Ag is the lowest excited state.
 $\text{C}_{10}\text{H}_{12}$: $2^1\text{Ag} < 1^1\text{Bu}$ 0.4eV
3. 1^1Bu has an ionic character. 2^1Ag has a covalent character and is more

sensitive to the geometry variation²⁵.

4. Theoretically, 2^1Ag state is poorly described without extensive CI. So TDHF, TDDFT, and CIS give the first allowed singlet excitations as 1^1Bu state for all polyenes. 2^1Ag state can be treated with CASSCF, CASMP2.

1.6 Vertical and Adiabatic Excitations

When the electron absorbs energy and is excited, the charge distribution of molecule changes immediately, while the nuclei keep almost motionless due to their large mass. So the geometry of the excited molecule is the same as that of the ground state. The λ_{max} peak in the spectrum represents this vertical excitation or non-equilibrium excitation. After some time, the excited molecule relaxes its geometry. The energy difference between the ground state and the excited state, both in their equilibrium geometries is called adiabatic excitation energy (0-0 transition). In other words, vertical excitations require same geometries, namely the equilibrium ground state geometry, while adiabatic excitations require different geometries, the equilibrium ground state geometry and the equilibrium excited state geometry. The adiabatic transition energy is lower than the vertical one.

In the study of solvent effects for polyenes, we are concerned with vertical excitation, since the electronic excitation takes place instantaneously, resulting the solute's charge distribution changes synchronously, and the geometry of solute and solvent has to be adjusted after an interval.

1.7 Solvent Effects

1.7.1 Solute-Solvent Interactions

Solute-solvent interactions between non-polar solute and solvents are in a range of dispersion forces, the forces of attraction between an instantaneous dipole and induced dipole¹³. Solute-solvent interactions between polar solute and solvents are in a range of dipole-dipole or dipole-induced dipole forces. A special solute-solvent interaction is a hydrogen bond.

1.7.2 Factors that Affect the Magnitude of Dispersion Forces

The polarizability is a measure of the ease with which electron charge density is distorted by an external electric field and reflects the facility with which a dipole can be induced. Polarizability increases with increased atomic and molecular mass. In general, the greater the polarizability of molecules the stronger the intermolecular forces between them.¹³ Another factor is the molecular shape. Elongated molecules make contact with neighboring molecules over a greater surface than do more compact molecules. Therefore, the dispersion forces among elongated molecules are greater than among the more compact molecule¹³.

1.7.3 How to Model the Solvent?

The solute is surrounded by a great number of solvent molecules. A full quantum chemical treatment is impossible for a system of this size. Therefore, approximations are necessary to model the solvent. There are in principle three approaches.

Firstly, the solvent is regarded as a continuous electric field that represents a statistical average over all solvent degrees of freedom at thermal equilibrium¹¹.

The solvent is treated implicitly using the polarized continuum model.

Secondly, since solvent molecules in the first solvation shell have certainly the strongest effect on the solute, these solvent molecules may be treated explicitly

using a solute-solvent cluster model.

Lastly, solvent molecules of the first shell are treated explicitly, whereas those of other shells are treated implicitly. A combination of the first and second model is applied.

1.7.4 Polarized Continuum Model (PCM)

To treat solute-solvent interactions, imagine a cavity of vacuum is created in the solvent, in which the dielectric constant is 1 and the solute is inserted into this cavity as the second step. The charge of the solute is distributed on the surface of the cavity. Outside the cavity the medium is regarded a continuum characterized by its dielectric constant.

1.7.5 Response of the Solvent in Continuum Models

When a solute passes into solvent, the solute undergoes a sudden change in the charge distribution in an environment of polarizable solvent.

The introduction of the solute will induce change in the electric field of the solvent, the so-called the reaction field. When the reaction field is computed in a self-consistent fashion, we say self-consistent reaction field (SCRF).

Historically, large use in continuum models has been made of the approximation that it is sufficient to decompose the response function into two terms. Within this approximation, the polarization vector is composed of two parts¹⁴: the fast and the slow. The fast part is reduced to the terms related to the dynamic response of the solvent electrons whereas the slow part collects all of the other terms related to the nuclear degrees of freedom of the solvent. On the sudden time scale of electronic excitation by a photon, only the fast part is effective.

1.7.6 Applicable PCMs in Gaussian 03 Package¹⁵

SCRF approaches differ in how they define the cavity and the reaction field. In Gaussian 03 package, SCRF requests that a calculation be performed in the presence of a solvent using PCMs.

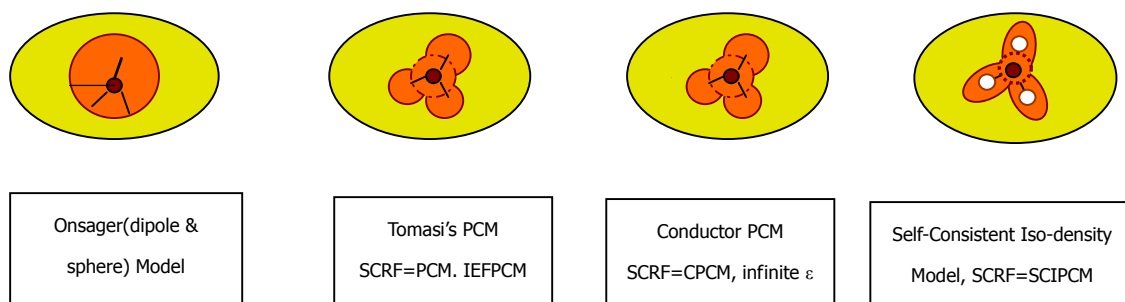


Figure 1.7.1: Applicable PCMs in Gaussian 03 package.

1.7.6.1 Onsager Model

The first model is Onsager model¹⁶, regarded as the basis of SCRF. This model defines the cavity as a spherical or ellipsoidal shape. Although it can give good results for many applications, it was proved as a consequence of the cancellation of errors, the neglect of higher order contributions to the electrostatic interaction balances out the unrealistic shape of the cavity. It does not perform well for polyenes, so it is not included in the thesis.

1.7.6.2 Polarized Continuum Model (PCM)

Other models are developed according to Onsager model, expanding the response to the electric field in a Taylor series and truncating at a certain level for including electrostatic interaction. Cavities are represented by overlapping spheres in analogy with space-filling models commonly used in chemistry or by isodensity

surfaces. The second and also the most widely used model is the polarized continuum model (PCM) proposed in 1981¹⁷.

1.7.6.3 Integral Equation Formalism PCM (IEFPCM)

An improved PCM, integral equation formalism PCM (IEFPCM), which defines the cavity as a series of overlapping atomic spheres 20% larger than the van der Waals radii¹¹, are used in Gaussian 03 package by default. The surface potential is calculated by numerical differentiation and its interaction can be computed self-consistently.

1.7.6.4 Isodensity and Self-Consistent Isodensity PCM (IPCM and SCIPCM)

Foresman et al. (1996)¹⁸ defined the cavity as that region of space surrounded by an arbitrary isodensity surface. The surface can be either located from the gas phase density, and held fixed (IPCM) or determined self-consistently (SCIPCM). With IPCM, one only needs to specify the isosurface level (typically in the range 0.0004-0.001) instead of a set of radii for the spheres. The surface is easier to integrate than that defined by overlapping of spherical atoms.

As the cavity and electron density must be coupled, SCIPCM (self-consistent isodensity Polarized Continuum Model) is designed to take the effect fully into account. The procedure includes solvation energy that depends on cavity, which depends on the electron density. It successfully solves for the electron density, which minimizes the energy. SCIPCM folds solvation effect into iterative SCF computation rather than comparing an extra step afterwards. SCIPCM demonstrates its strength in that it considers coupling between cavity and electron density, which is neglected in IPCM.

IPCM and SCIPCM tend to be considerably less stable than PCM, and can be subjected to erratic behavior in some system, like charged system, so their use is not

recommended¹¹.

1.7.6.5 Conductor-like PCM (CPCM)

Conductor-like PCM (CPCM)¹⁹ is quite different from the above, dielectric version. CPCM considers the media with infinite dielectric constant, like a conductor without potential. Such a situation can simplify the necessary electrostatic equations when calculating polarization free energy. In conductor-like screening model, the conductor polarization free energy is scaled by a factor of $2(\epsilon-1)/(2\epsilon+1)$ after computation¹¹. It was pointed out that CPCM is an approximation in polar environment¹⁸.

1.7.7 Explicit Cluster Models

SCRF theory does not include the correlation of instantaneous induced charge fluctuations in the solute and the solvent, which are short-range effects predominately associated in the first solvation shell²⁰. Its contribution is evaluated using an explicit cluster model.

Four butane molecules are added as the nonpolar solvent molecules parallel to the butadiene molecule (solute) shown in Figure 1.7.2. Four butane molecules are proved enough for considering the first solvation shell, and the theoretical level to optimise the geometry also limits the size of cluster.

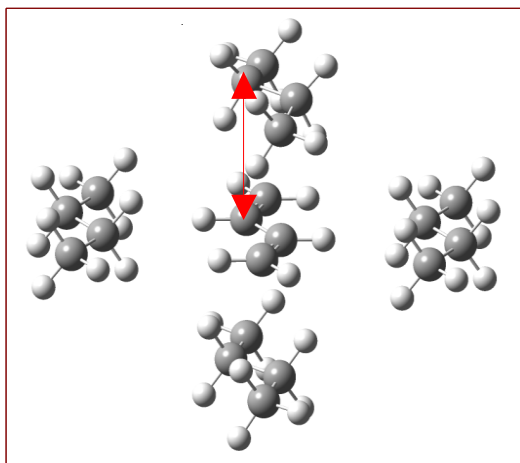


Figure 1.7.2 $\text{C}_4\text{H}_6 \cdot 4\text{C}_4\text{H}_{10}$ cluster (the distance of C1----C11, C1----C25, C1----C39, C1----C53, are 3.6Å.)

Four water molecules are added as the polar solvent shown in Figure 1.7.3. For $\text{C}_4\text{H}_6 \cdot 4\text{H}_2\text{O}$ cluster, O(water)----H(polyene) is 1.97 Å to take into account H-bonded interaction.

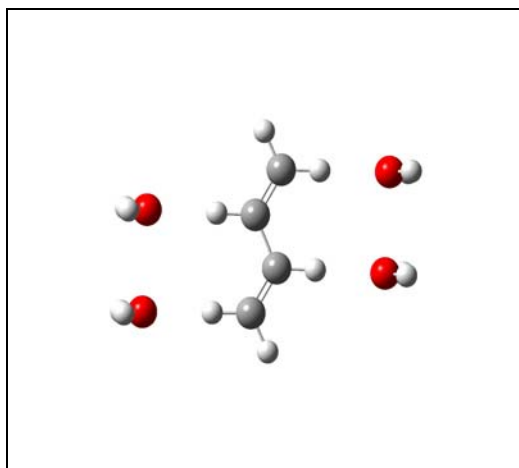


Figure 1.7.3 $\text{C}_4\text{H}_6 \cdot 4\text{H}_2\text{O}$ cluster

Chapter 2. Method

2.1 Overview, see Figure 2.1.1

2.2 Experimental Method---Spectra

The highest intensity ($\lambda_{\max}$) peak in UV absorption spectra corresponds to the first allowed vertical excitation energy, since electronic excitation is fast with respect to the nuclear relaxation. Only data for short polyenes are available experimentally in the gas phase, solutions, solid solutions and crystals²¹. The results show that excitation energies of unsubstituted polyenes are about 0.3-0.4 eV lower in dilute room temperature solutions and in solid solutions than in the gas phase².

Data in the gas phase

Butadiene in the gas phase²² is observed directly from the UV absorption spectra. Absorption spectra of hexatriene²³ and octatetraene²⁴, cooled to low rotational and vibrational temperature in supersonic molecules jets, are sharpened over those in room temperature static gas or in low-temperature crystals.

Absorption, emission and excitation spectra² of octatetraene, decapentaene and dodecahexatene are obtained in room temperature solutions and 77K glasses. Fluorescence and fluorescence excitation spectra were in agreement with absorption spectra, as shown by identical 0-0 transitions. Firstly, the solvent effect is taken into account by the formula:

$\nu(\text{solvent}) = \nu(\text{gas}) - k(n^2 - 1)/(n^2 + 1)$, n is the index of refraction. Secondly, $\lambda_{\max}$ is

```

graph TD
    Factors[Factors] --> CalcExc[Calculated excitation energy]
    CalcExc --> GAS[GAS]
    GAS --> Geom1[Geometries]
    Geom1 --> Basis1[Basis sets]
    Basis1 --> Methods1[6 methods: CIS, TDHF, TDDFT, CASSCF, CASPT2, ...]
    Methods1 --> ExpExc[Experimental excitation energy in gas]
    ExpExc --> SOLUTION[SOLUTION]
    SOLUTION --> Geom2[Geometries]
    Geom2 --> Basis2[Basis sets]
    Basis2 --> Methods2[6 methods: CIS, TDHF, TDDFT, CASSCF, CASPT2, ...]
    Methods2 --> CalcExcGas[Calculated excitation energy in gas]
    CalcExcGas --> AddPCM[Adding PCM at HOMO-LUMO, CIS, TDHF, TDDFT, CASSCF]
    AddPCM --> SolventEffect[Solvent Effect]
    SolventEffect --> Conclusions[Conclusions:]
    Conclusions --> ApplyPCM[Apply DHF/Cep-31g*/DFT/cep)31g* in PCM for oligothiophenes and oligopyrroles to get a solvent effect.]
  
```

The flowchart illustrates the computational workflow for studying the solvent effect on the photochemical reaction of oligothiophenes and oligopyrroles. The process starts with 'Factors' leading to 'Calculated excitation energy'. This leads to 'GAS' (Gas phase), which then leads to 'Geometries' and 'Basis sets'. 'Geometries' and 'Basis sets' lead to '6 methods: CIS, TDHF, TDDFT, CASSCF, CASPT2, ...'. This leads to 'Experimental excitation energy in gas'. 'Experimental excitation energy in gas' leads to 'SOLUTION' (Solution phase), which then leads to 'Geometries' and 'Basis sets'. 'Geometries' and 'Basis sets' lead to '6 methods: CIS, TDHF, TDDFT, CASSCF, CASPT2, ...'. This leads to 'Calculated excitation energy in gas'. 'Calculated excitation energy in gas' leads to 'Adding PCM at HOMO-LUMO, CIS, TDHF, TDDFT, CASSCF'. 'Adding PCM at HOMO-LUMO, CIS, TDHF, TDDFT, CASSCF' leads to 'Solvent Effect'. 'Solvent Effect' leads to 'Conclusions:'. 'Conclusions:' leads to 'Apply DHF/Cep-31g*/DFT/cep)31g* in PCM for oligothiophenes and oligopyrroles to get a solvent effect.'

obtained from 0-0 transitions due to an approximation²¹: λ_{max} occurs at about 0.2eV higher energy. The approximation was supported by the UV spectroscopy and electron impact spectroscopy of hexatriene. There are three peaks: the first is the 0-0 transition, and the second is λ_{max} . For octatetraene and all longer polyenes, the lowest energy peak has the highest intensity in the gas phase. The 0-0 transition of 4.41eV was regarded as the vertical transition²⁵. But theoretical results of octatetraene²⁶, showed 0.2eV energy lowering at optimized geometries. A second peak at 0.2eV higher energy with a substantial intensity exists for the longer polyenes as well. Thus theory and experiment seem to indicate that the 0-0 transition does not correspond to a vertical transition²¹. The correct vertical excitation energy is 0.2eV higher than the 0-0 transition energy, 4.61eV. So far, the longest polyene for which gas data and high level ab initio results are available is decapentaene²¹.

2.3 Geometry Optimization

Geometry is very crucial to the availability and accuracy of the result. The theoretical values of excitation energy depend on the geometry, the theoretical level and the basis set used. Geometry optimization also depends on the theoretical level and the basis set used. So effects of theoretical levels and basis sets on geometries are discussed.

2.3.1 Effects of Theoretical Levels:

The effects of theoretical levels will be discussed in the gas phase and in solution.

In this thesis, firstly, ground-state optimisations were performed in the gas phase at DFT (B3P86-30%, PBE, PBE0), Møller-Plesset perturbation in second order (MP2)

and HF levels.

It is well known that HF, due to its lack of correlation, exaggerates the bond lengths alternation (BLA) and overestimates the band gap²⁷. As a rule, the MP2 level is an excellent choice for geometry optimisation of minima that include correlation energy, and significant improvement can be obtained at fairly reasonable cost¹¹. But MP2 is limited to chain length of about 50 CH units due to its costly price. DFT over delocalizes structures¹¹. DFT tends to predict the formal single bond to be a bit too short and the formal double bonds to be somewhat too long in conjugated π system¹¹. GGA functionals tend to systematically overestimate bond lengths. The HF level tends to systematically underestimate bond lengths. Thus, it should be expected that hybrid functionals, which mix both of them, give a noticeable improvement in predicted bond lengths¹¹.

Theoretical evaluations of solvent effects start from geometry optimization implicitly in PCM and explicitly in cluster.

2.3.2 Effects of Basis Sets

Pople's basis sets, Dunning's correlation consistent basis sets, effective core potentials split valence basis sets are tested.

Three aspects to determine the effects of theoretical levels and basis sets are followed:

- Absolute values of the bond length of C=C and C-C;
- In conjugated system, like polyenes, C-C bond lengths tend to organize in an alternating pattern of longer and shorter bond length. In the discussion of the geometry, we need to take into account bond length alternation (BLA), which

probably influences the excitation energy. BLA is the difference of the bond length of the single and double bond. ($R_{\text{single}} - R_{\text{double}}$).

- HOMO-LUMO gap

2.4 Excitation Energies

Excitation energies depend on three factors in the input file: the geometry, the basis set and the theoretical level. Their effects on excitation energies are discussed. Based on the experimental data of polyenes in the gas phase, a reliable and feasible method is determined.

2.5 Computational Method

All calculations were performed using Gaussian 03 and Gaussian View package. Origin 6.0 Program is used to sketch the graphs.

Chapter 3. Results and Discussion

3.1 Geometries

3.1.1 Bond Length and BLA

The degree of bond alternation is very critical to study the conducting properties of polyenes, because it is one contribution to the band gap (E_g), which is one feature to distinguish the metal, semiconductor and insulator.

Firstly, the BLA of C_6H_8 is calculated as followed.

	1-2	2-4	BLA
(B3P86-30%)	1.368	1.463	0.095
PBE	1.387	1.465	0.078
PBE0	1.372	1.464	0.092
Mp2	1.381	1.472	0.091
Hf	1.352	1.478	0.126
Exp.	1.368 ²⁸	1.457 ²⁹	0.089

Table 3.1.1 Bond length (Å) and BLA (Å) of hexatriene optimised at different theoretical levels with the basis set of Cep-31g* and experimental data

Adding correlation can reduce BLA³⁰. The result shows that the largest BLA,

0.037Å larger than the experiment, is obtained at HF level, which has no correlation. As expected, DFT-hybrid functional (B3P86-30%) seems a good alternative for producing the closest bond lengths to experiment and a BLA a little bit larger than MP2. In addition, the exact exchange correlation decreases the double bond length significantly.

Then we test the effect due to basis sets. In Table 3.1.2, BLA of C₆H₈ obtained with eight basis sets is summarized in Table 3.1.2.

	1-2	2-4	BLA
6-31g*	1.346	1.447	0.101
6-311g*	1.342	1.445	0.103
6-311g**	1.342	1.445	0.103
6-31+g*	1.347	1.448	0.101
Cep-31g*	1.368	1.463	0.095
Cep-31+g*	1.365	1.462	0.097
cc-pVTZ	1.339	1.442	0.103
cc-pVQZ	1.339	1.442	0.103
MP2/cc-pVTZ	1.350	1.446	0.096 (Exp.0.089)

Table 3.1.2 Bond length (Å) and BLA (Å) of C₆H₈ optimized at DFT (B3P86-30%) with various basis sets

That DFT (B3P86-30%)/Cep-31g* can produce accurate bond lengths, especially

the C=C bond length, is found due to an error cancellation. DFT (B3P86-30%) decreases the C=C bond length by adding HF exchange contribution; at the same time, Cep-31g* increases the bond length. MP2/cc-pVTZ is a combination of a well-known reliable method with the possible best basis set, so it can be a reference. DFT (B3P86-30%)/Cep-31g* obtains a BLA in perfect agreement with that obtained at MP2/cc-pVTZ and bond lengths, which are longer than those obtained with other basis sets and in agreement with experiment.

Although it is a kind compromise of the method and basis set, it is very practical to predict an excellent geometry for longer polymers. So DFT (B3P86-HF30%)/Cep-31g* is employed to optimise the geometry in the place of MP2.

C₆H₈ is a small molecule, where its π electrons do not conjugate very much. For infinite polyenes, BLA converged to 0.062 Å³¹, 0.058 Å³¹ and 0.100 Å³¹ at MP2, DFT (B3P86-30%) and HF for C₅₀H₅₂, respectively (basis set: Cep-31g*). MP2/6-31g*³², BLYP/6-31g*⁴ and B3LYP/6-31g*⁴ get BLA of 0.049 Å, 0.015 Å and 0.048 Å for infinite polyenes. Experimental values are 0.08 Å³³ and 0.09 Å³⁴. The values calculated at MP2 and B3P86-30% using the Cep-31g* basis set is smaller than experimental values about 22.5-27.5%, but uncertainty with respect to this value remains, because there is no reliable error estimate on the experimental data⁴.

3.1.2 Effect of PCM on the Geometry

PCM does not affect bond lengths and BLA of the ground state.

	C1-C2	C2-C4	BLA
Vacuum	1.368	1.463	0.095
PCM	1.368	1.464	0.096
SCIPCM	1.368	1.464	0.096
CPCM	1.369	1.464	0.095

Table 3.1.3 Bond length (Å) and BLA (Å) of C_6H_8 in vacuum and PCMs at DFT (B3P86-30%)/Cep-31g*

3.1.3 Effect of the Explicit Cluster on the Geometry

The explicit cluster is optimized at five theoretical levels. The optimized geometry at MP2 is shown in Figure 3.1.1. The positions of the butane molecules on the top and bottom rotate during the geometry optimization and cover the solvation shell better.

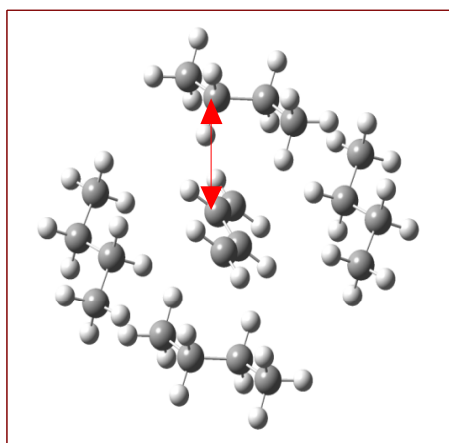


Figure 3.1.1 $C_4H_6 \cdot 4C_4H_{10}$ cluster optimized at MP2

	MP2	MP2 PCM	PBE	PBE0	B3P86-30%	HF
1-11	3.895	3.897	4.725	4.773	7.624	5.343
2-12	4.335	4.340	4.756	4.781	7.862	5.402
1-53	4.076	4.074	3.956	3.968	6.272	5.120
1-39	3.614	3.614	4.015	4.047	7.407	4.901
2-54	3.614	3.614	3.940	4.091	6.273	4.608
2-40	4.076	4.074	4.014	4.038	7.407	4.988
1-25	4.335	4.340	4.756	4.822	7.862	5.408
2-26	3.895	3.897	4.725	4.787	7.624	5.376

Table 3.1.4 Solute-solvent distances (Å) of the $C_4H_6 \cdot 4C_4H_{10}$ cluster with geometries optimized at various theoretical levels

The minimum solute-solvent distance is obtained at the MP2 level. It almost keeps constant when this cluster is added into PCM. DFT (PBE, PBE0) get medium results, and DFT (B3P86-30%) and HF produce a too long distance.

3.1.4 Binding Energy of the Cluster

	MP2	PBE	PBE0	B3P86-30%	HF
Butane	-28.26988	-28.58958	-28.61072	-29.27737	-27.77365
Butadiene	-25.85995	-26.14138	-26.14413	-26.70385	-25.38922
Molecules	-138.93947	-140.49968	-140.58701	-143.81332	-136.48383
Cluster	-138.96274	-140.50767	-140.59352	-143.81434	-136.48517
Binding E (hartree)	0.02326	0.00799	0.00651	0.00103	0.00135
Binding E (Kcal/mol)	14.60	5.01	4.09	0.64	0.85

Table 3.1.5 Total energies (a.u.) of butadiene and butane and binding energies of the cluster with geometries optimized at various theoretical levels

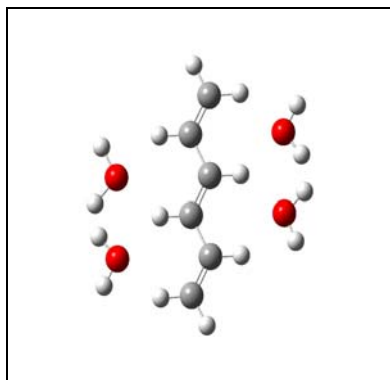
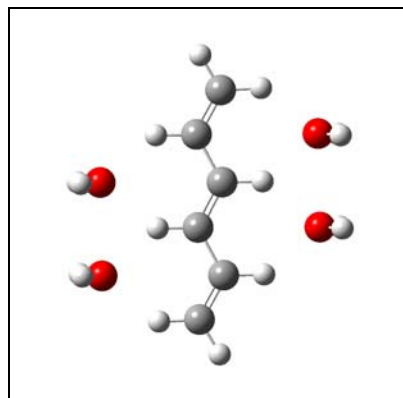
The MP2 approach predicts a significant binding energy. Compared with the MP2 level, the results of binding energy indicate that PBE and PBE0 include a part of solvent effect, while B3P86-30% and HF almost reflect nothing about solvent effect.

3.1.5 Geometries of Clusters with Water Molecules

In order to research the explicit effect produced by water, some cluster models of $C_6H_8 \cdot 4H_2O$ and $C_4H_6 \cdot 4H_2O$ (see Figures 3.1.2 and Figure 3.1.3) are used to evaluate the cluster effect roughly. The H-bonded interaction is included, since the distance of O (H_2O) and H (C_6H_8) is 1.97 Å. The optimized distance of O (H_2O) and H (C_6H_8) becomes longer, for instance, in a range of 2.87-3.88 Å for the 4th $C_6H_8 \cdot 4H_2O$ cluster, and the solute-solvent distance is around 3.21-3.99 Å.

Figures in the frame are the designed geometries. The other two as followed are optimized geometries observed from the horizontal and the top view.

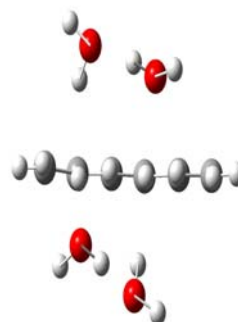
- The 4th cluster is the lowest in energy.
- The 1st cluster is 25.1 Kcal/mol higher than the 4th cluster in energy;
- The 2nd cluster is 10.04 Kcal/mol higher than the 4th cluster in energy;
- The 3rd cluster is 10.04 Kcal/mol lower than the 4th cluster in energy.

Figure 3.1.2 Designed and optimized geometries of the $C_6H_8*4H_2O$ clusters**Cluster 1****C6-1 (O-H=1.97 Å)****Cluster 2****C6-2 (O-H=1.97 Å)**

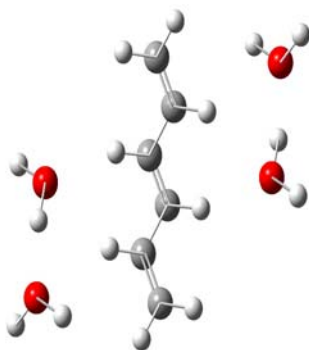
C6-1-1



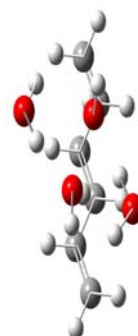
C6-2-1



C6-1-2



C6-2-2



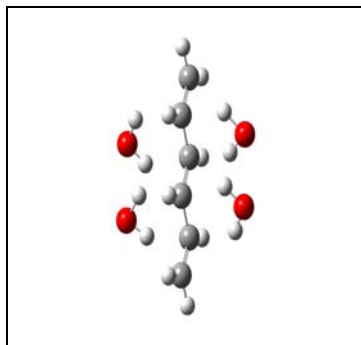
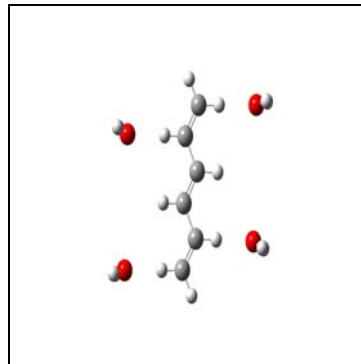
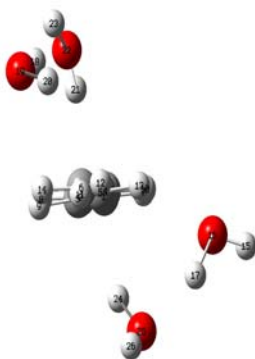
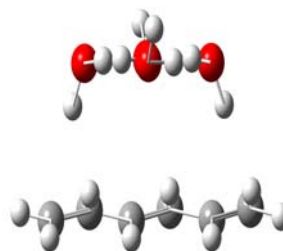
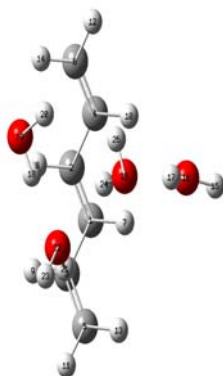
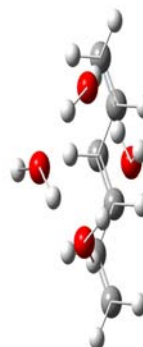
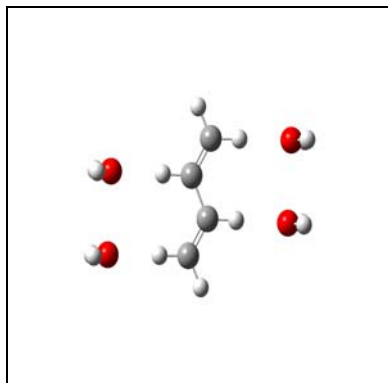
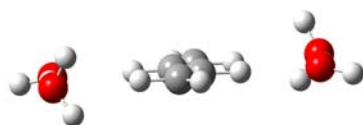
Cluster 3**C6-3 (C-H=1.97 Å)****Cluster 4****C6-4 (O-H=1.97 Å)****C6-3-1****C6-4-1****C6-3-2****C6-4-2**

Figure 3.1.3 Designed and optimized geometries of the $C_4H_6*4H_2O$ clusters

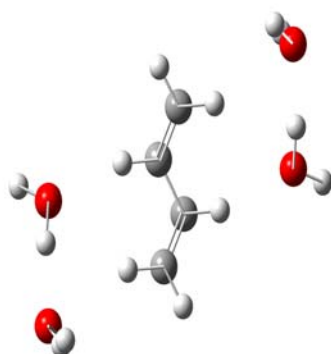
C4-1 (O-H=1.97 Å)



C4-1-1



C4-1-2



3.2 Orbital Energies

The straight HOMO-LUMO energy difference method can be used for approximating excitation energies. The HOMO-LUMO gap values of oligoenes obtained at the DFT-hybrid level are presented as an inverse function of size in quite good agreement with experiment³⁵. Here we will discuss effects of theoretical methods, basis sets and PCM on the HOMO-LUMO gap, and compare the HOMO-LUMO gap with the experimental excitation energies from C₄H₆ to C₁₄H₁₆.

3.2.1 Effect of Theoretical Levels

Geometry	HOMO	LUMO	HOMO-LUMO gap
B3P86-30%	-6.73	-1.70	5.03
PBE	-5.02	-2.19	2.83
PBE0	-5.95	-1.31	4.64
MP2	-7.68	2.18	-
HF	-7.87	2.43	10.30

Table 3.2.1 Orbital energies (eV) and HOMO-LUMO gaps (eV) of C₆H₈ at various theoretical levels (the basis set is Cep-31g*)

It is well known that within HF approximation the HOMO-LUMO gap (E_g) is overestimated and yields unphysical results. For instance, the LUMO is positive⁴.

MP2 uses HF ground-state wave function only using different geometries, so both of them give the HF HOMO-LUMO gap.

At DFT, the HOMO-LUMO gap mainly depends on the exchange functional⁴. From my result, the difference is very large.

The HOMO-LUMO gap of hexatriene at B3P86-30% is in good agreement with the experimental excitation energy (5.13eV).

3.2.2 Effect of Basis Sets

The size of basis set does not influence the HOMO-LUMO gap except Cep-31g* and Cep-31+g* basis sets.

	HOMO	LUMO	HOMO-LUMO gap
6-31g*	-6.75	-1.48	5.27
6-311g*	-6.96	-1.70	5.26
6-311g**	-6.98	-1.73	5.25
6-31+g*	-6.96	-1.80	5.16
Cep-31g*	-6.73	-1.70	5.03
Cep-31+g*	-6.84	-1.80	5.04
cc-pVTZ	-7.02	-1.77	5.25
cc-pVQZ	-7.04	-1.80	5.24

Table 3.2.2 Orbital energies (eV) and HOMO-LUMO gaps (eV) of C₆H₈ at DFT (B3P86-30%)

3.2.3 Effect of PCM

PCM has no effect on the HOMO-LUMO gap.

	HOMO	HOMO (PCM)	LUMO	LUMO (PCM)	HOMO-LUMO gap	HOMO-LUMO gap (PCM)
C ₄ H ₆	-7.29	-7.28	-1.13	-1.13	6.16	6.15
C ₆ H ₈	-6.73	-6.72	-1.70	-1.67	5.03	5.05
C ₈ H ₁₀	-6.38	-6.37	-2.06	-2.04	4.32	4.33

Table 3.2.3 Orbital energies (eV) and HOMO-LUMO gaps (eV) at DFT (B3P86-30%) of C₄H₆, C₆H₈ and C₈H₁₀ in the gas phase and in PCM (heptane)

3.2.4 A Comparison of HOMO-LUMO Gaps with Experimental Excitation Energies

As a result, HOMO-LUMO gaps are in good agreement with experimental excitation energies. The deviations are in a range of -0.36-0.23 eV.

	C ₄ H ₆	C ₆ H ₈	C ₈ H ₁₀	C ₁₀ H ₁₂	C ₁₂ H ₁₄	C ₁₄ H ₁₆
HOMO-LUMO gap	6.16	5.03	4.33	3.85	3.49	3.23
Exp	5.93	5.13	4.61	4.20	3.85	-

Table 3.2.4 HOMO-LUMO gaps (eV) at B3P86-30%/Cep-31g* and experimental excitation energies (eV)

3.3 Excitation Energies

3.3.1 Experimental Data

Polyenes	C ₄ H ₆	C ₆ H ₈	C ₈ H ₁₀	C ₁₀ H ₁₂	C ₁₂ H ₁₄
0-0 adiabatic	5.73 ^{a,1}	4.93 ^{a,1}	4.41 ^{a,1}	4.02 ²	
λ_{max} vertical	5.93 ^{a,1}	5.13 ^{a,1}	4.61 ^{a,1}	4.21 ^c	3.85 ^c
Gas (0-0)			4.38	3.98	3.65
Solution (0-0)			4.00 ^{b,2}	3.60 ^{b,2}	3.39 ^{b,2}

a. Direct absorption spectra of the $1^1\text{Ag} \rightarrow 1^1\text{Bu}$ transition of gas phase cooled to low rotational and vibrational temperatures in supersonic molecular jets

b. Fluorescence and Fluorescence excitation spectra at 77k glasses. $1^1\text{Ag} \rightarrow 1^1\text{Bu}$

C₈H₁₀ (3-methylpentane) C₁₀H₁₂ (3-methylpentane) C₁₂H₁₄ (hexane)

c. Corrected from 0-0 transition in the gas phase (approximate 0.2eV between 0-0 transition $\rightarrow \lambda_{\text{max}}$ vertical transition), which is corrected from 0-0 transition in solution:

$\nu(\text{solvent}) = \nu(\text{gas}) - k(n^2 - 1)/(n^2 + 1)$, n is the index of refraction.

1. See reference ²³.

2. See reference ².

Table 3.3.1 Experimental data of excitation energies of polyenes (eV)

3.3.2 BLA and TDHF Excitation Energies

Firstly, TDHF excitation energies are investigated to depend on BLA.

Geometry	TDHF (eV)	BLA (Å)
B3P86-30%	5.15	0.095
PBE	4.96	0.078
PBE0	5.11	0.092
MP2	5.05	0.091
HF	5.37	0.126
EXP	5.13	0.089
MP2 / cc-pVTZ	5.28	0.096

Table 3.3.2 TDHF/Cep-31g* excitation energies and BLA of C_6H_8 (the geometry is optimized with the basis set of Cep-31g*)

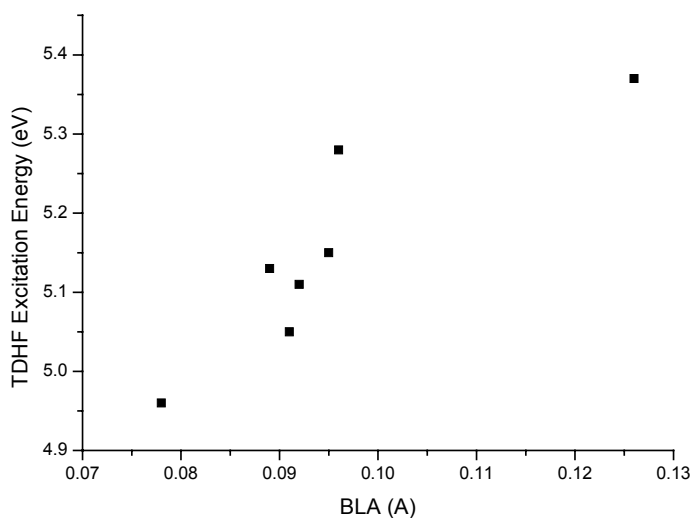


Figure 3.3.1 TDHF/ Cep-31g* and BLA of C_6H_8

TDHF excitation energies of C_6H_8 with various geometries show a roughly linear correlation to BLA. This finding is supported by reference. Peierls³⁶ et al. approximated the band gap, E_g , is proportional to BLA. More precisely, Ovchinnikov³⁷ et al. have established that the band gap has a Peierls and correlation component:

$$E_g = [(k \Delta R)^2 + \Delta_{\text{correl}}^2]^{1/2}$$

Choi et al. predicted that the ratio of $\Delta_{\text{correl}} / k \Delta R$ is about 1.5, a surprisingly large number⁴.

3.3.3 The Preferred Basis Set to Calculate the Excitation Energy

TDHF excitation energies of C_6H_8 calculated with eight basis sets and a same optimised geometry (B3P86-30%/Cep-31g*) are shown in Table 3.3.3.

Basis set	TDHF(eV)	Basis set	TDHF(eV)
6-31g*	5.23	Cep-31g*	5.15
6-311g*	5.13	Cep-31+g*	5.05
6-311g**	5.12	cc-pVTZ	5.05
6-31+g*	5.01	cc-pVQZ	-

Table 3.3.3 TDHF excitation energies of C_6H_8 with a same geometry optimised at B3P86-30%/Cep-31g* employing different basis sets

- TDHF/cc-pVTZ//DFT(B3P86-30%)/Cep-31g* is 5.05eV. TDHF/Cep-31g*//DFT(B3P86-30%)/Cep-31g* is 5.15eV, closer to experiment. It is due to an error cancellation that Cep-31g* reduces the excitation energy by optimising the geometry and TDHF level overestimates it.
- Diffuse function reduces the excitation energy substantially.
- cc-pVQZ is too large for the calculation.
- TDHF excitation energies converge to about 5.2eV, as shown by the small difference between the results with TDHF/cc-pVNZ//DFT(B3P86-30%)/cc-pVNZ level (N=T, 5.28eV; N=Q, 5.24 eV.)
- Pople's basis sets can be used in this research, however they are not available for heavy atoms in other conducting polymers. To keep consistent in the calculation, Cep-31g* is used as an acceptable and reliable basis set for all further transition energy calculations.

3.3.4 The Accuracy of Theoretical Levels

CIS, TDHF and TDDFT levels are employed to calculate the first allowed vertical transition energy from C_4H_6 to $C_{14}H_{16}$. These molecules are in a C_{2h} planar geometry, mainly due to the extensive experimental and theoretical evidence of planarity and conservation of the symmetry for 1^1Ag , 1^1Bu and 2^1Ag states³⁸. The geometry is optimized at B3P86-30%/Cep-31g* level.

CASSCF, CASPT2 and MRMP data from the literature were based on theoretically or experimentally determined ground-state geometries.

3.3.4.1 CIS

From the above result, the diffuse function reduces excitation energies substantially, so CIS results employing both Cep-31g* and Cep-31+g* basis sets

are listed in Table 3.3.4.

	C ₄ H ₆	C ₆ H ₈	C ₈ H ₁₀	C ₁₀ H ₁₂	C ₁₂ H ₁₄	C ₁₄ H ₁₆
CIS/Cep-31g*	6.45	5.46	4.81	4.34	4.00	3.74
CIS/Cep-31+g*	6.18	5.33	4.72	4.29	3.96	3.71
Exp (gas)	5.93	5.13	4.61	4.2	3.85	

Table 3.3.4 CIS excitation energies (eV) with Cep-31g* and Cep-31+g*

Cep-31+g* basis set indeed reduces CIS excitation energy of polyenes, but the influence of the diffuse function gets small when the chain length increases. For C₄H₆, the difference is 0.27 eV, which is a significant influence. For C₆H₈, the difference is 0.14 eV; for C₈H₁₀, it is 0.08 eV; for C₁₀H₁₂ it is 0.06 eV. It can be explained that the longer polyene is disturbed less by the excitation. A same effect is obtained for THDF. So for longer polyenes, the diffuse function is unnecessary. CIS/Cep-31g* overestimates the transition energy of polyenes around 0.15 eV-0.52 eV.

3.3.4.2 TDHF and TDDFT

	C ₄ H ₆	C ₆ H ₈	C ₈ H ₁₀	C ₁₀ H ₁₂	C ₁₂ H ₁₄	C ₁₄ H ₁₆
TDHF	6.08	5.15	4.54	4.10	3.78	3.54
TDDFT(B3P86-30%)	5.81	4.77	4.09	3.62	3.27	2.99
TDDFT(PBE)	5.60	4.50	3.81			

Table 3.3.5 TDHF and TDDFT excitation energies (eV)

- TDHF excitation energy is lower in a level of 0.20-0.37 eV than CIS, thus leading to better agreement with experiment. TDHF is still an overestimation in a range of 0.07-0.15 eV.
- The result shows that TDDFT underestimates 1^1Bu excitation energies very much for polyenes, even worse than the HOMO-LUMO gap. For C_4H_6 it is lower than experimental value in 0.12 eV, for C_6H_8 it is 0.36 eV, for C_8H_{10} it is 0.52 eV.
- TDDFT (B3P86-30%) is better than TDDFT (PBE).
- CIS, TDHF and TDDFT transition energies, which decrease with increasing chain length, are in agreement of BLA.

3.3.4.3 CASSCF, CASPT2 and MRMP

	C ₄ H ₆	C ₆ H ₈	C ₈ H ₁₀	C ₁₀ H ₁₂
CASSCF ¹	6.50Ag	5.45Ag	4.71Ag	4.20Ag
	8.19Bu	-	6.52Bu	6.19Bu
CASSCF ²	6.67Ag	5.64Ag	5.16Ag	4.32Ag
	7.73Bu	7.06Bu	6.62Bu	6.37Bu
CASSCF ³	6.64Ag	5.65Ag	5.23Ag	
	8.54Bu	7.36Bu	6.67Bu	
CASPT2 ³	6.23Bu	5.01Bu	4.38Ag	
	6.27Ag	5.19Ag	4.42Bu	
MRMP corrected ⁴	6.21Bu [*]	5.09Ag	4.47Ag	3.65Ag
	6.31Ag [*]	5.1Bu	4.66Bu	4.05Bu

1 Methods: using geometries optimized at DFT (B3P86-30%)/Cep-31g*, for C₄H₆, (4,4 nroot=2 and 3); for C₆H₈, (6,6 nroot=2), for ¹Bu state, converge failure; for C₈H₁₀, (8,8 nroot=2 and 4); for C₁₀H₁₂, (10,10, nroot=2 and 4).

2 Methods: using geometries obtained from experiment, except C₈H₁₀, which is optimized at the CASSCF level. For C₄H₆, QZ3p(4,8); for C₆H₈, DZp(6,12); for C₈H₁₀, DZp(8,12); for C₁₀H₁₂, DZp(10,10). See reference²⁵

3.Using the experimentally determined ground state geometry, see reference³⁹

4.MRMP results with (3s2p1d/2s) (6,12), (8,12), (10,10)

* MPMP without correction

Table 3.3.6 CASSCF, CASPT2 and MRMP excitation energies (eV)

CASSCF gives 2^1Ag state, which is confirmed from the electron density matrix or the dominating configurations in the eigenfunction. The 2^1Ag - 1^1Bu gap is overestimated in a range of 1.69-1.99 eV, 1.42-2.05 eV²⁵ and 1.44-1.90 eV³⁹. It indicates some inherent errors in CASSCF that CASSCF neglects dynamic correlation.

CASPT2 includes dynamical correlation. So it improves the result in three aspects:

- Lowering the 1^1Bu excitation energy, which is closer to the experimental data;
- Giving an accurate order of the first two singlet states of C_4H_6 and C_8H_{10} ;
- Giving a reliable gap of $1^1\text{Bu} \rightarrow 2^1\text{Ag}$.

MRMP includes both dynamic correlation and σ electron correlation. MRMP produces a correct order of 1^1Bu and 2^1Ag state, the excitation energy of 1^1Bu state and the energy gap of 1^1Bu and 2^1Ag closest to experimental data.

CASSCF, CASPT2 and MRMP are very costly. Therefore they can be performed for short $\text{C}_{10}\text{H}_{12}$ at most.

Considering the accuracy and cost of all the theoretical levels, TDHF/Cep-31g*//DFT (B3P86-30%)/Cep-31g* is preferred to calculate the 1^1Bu transition energies. The good agreement to the experimental data seems to be a consequence of some error cancellation, but it is practical to reproduce the experimental data.

3.4 Solvent Effects

3.4.1 Solvent Effect in PCM

3.4.1.1 Effect of Dielectric Constant

The PCM does not show a distinguished influence using quite different solvents of heptane and water, whose dielectric constants are the highest and lowest of all the solvents under consideration here. So we test all the solvents in PCM to confirm this finding.

Solvent ID	Solvent	Dielectric constant	TDHF C ₄ H ₆	TDHF C ₆ H ₈
1	Water	78.39	5.85	4.91
2	Acetonitrile	36.64	5.84	
3	Methanol	32.63	5.85	
4	Ethanol	24.55	5.84	
5	Isoquinoline	10.43	6.08	5.15
6	Quinoline	9.03	6.08	5.15
7	Chloroform	4.90	5.80	
9	Dichloromethane	8.93	5.81	
10	Dichloroethane	10.36	5.80	
11	Carbontetrachloride	2.228	5.79	4.85
12	Benzene	2.244	5.77	
13	Toluene	2.379	5.78	

Solvent ID	Solvent	Dielectric constant	TDHF C ₄ H ₆	TDHF C ₆ H ₈
14	Chlorobenzene	5.621	5.76	
15	Nitromethane	38.2	5.83	
16	Heptane	1.92	5.82	4.88
17	Cyclohexane	2.023	5.81	
18	Aniline	6.89	5.74	4.80

Table 3.4.1 TDHF/Cep-31g*/DFT (B3P86-30%)/Cep-31g* excitation energies (eV) in PCM with different solvents

1. THDF excitation energies are calculated in PCM with seventeen solvents. Ten solvents give a similar result in a range of 5.80-5.85 eV. Isoquinoline and quinoline do not show a solvent effect. Results of five solvents are less than 5.80 eV. The results with carbontetrachloride, benzene, toluene, chlorobenzene and aniline are 5.79 eV, 5.77 eV, 5.78 eV, 5.76 eV and 5.74 eV. So similar effects in PCM with different solvents are obtained.
2. We found that very different dielectric constants yield the same effect like water and ethanol; similar dielectric constants can give very different results, like quinoline and dichloromethane. Dielectric constant is only one of the parameters of the solvent, so the change of only dielectric constant cannot change the solvent properly⁷. Alternatively, dielectric constant, radius and density of the solvent are specified appropriately to define a solvent explicitly⁷.

3.4.1.2 Effect of PCMs

	C ₄ H ₆	C ₆ H ₈	C ₈ H ₁₀	C ₁₀ H ₁₂	C ₁₂ H ₁₄	C ₁₄ H ₁₆	C ₁₆ H ₁₈	C ₁₈ H ₂₀	C ₂₀ H ₂₂
Vacuum	6.08	5.15	4.54	4.10	3.78	3.54	3.34	3.19	3.06
PCM	5.82	4.88	4.26	3.84	3.53	3.29	3.11	2.97	2.86
Δ PCM	0.26	0.27	0.28	0.26	0.25	0.25	0.23	0.22	0.20
SCIPCM	6.08	5.15	4.54						
Δ SCIPCM	0	0	0						
CPCM	5.78	4.85	4.24						
Δ CPCM	0.30	0.31	0.30						

Table 3.4.2 TDHF/Cep-31g*/B3P86-30%/Cep-31g* excitation energies (eV) and solvent effects (eV) in different PCMs (the solvent is heptane)

- The solvent effect for polyenes using PCM is 0.20-0.28 eV in the presence of heptane at the TDHF approach.
- IPCM cannot be used in a connection with the TDHF approach. In addition, CIS in IPCM is available, but 0.03 eV larger than that in the gas phase.
- SCIPCM can be used in a connection with the TDHF approach, but it shows no effect.
- CPCM gives a sufficiently similar solvent effect to that in PCM, although they differ in their underlying assumptions, which are included in the section 1.7.6.5.

3.4.1.3 Effect of PCM at various theoretical levels

	C ₄ H ₆	C ₆ H ₈	C ₈ H ₁₀	C ₁₀ H ₁₂	C ₁₂ H ₁₄	C ₁₄ H ₁₆
PCM(TDHF)	0.26	0.28	0.27	0.27	0.25	0.24
PCM(TDDFT)	0.22	0.24	0.24	0.24	0.23	0.22
PCM(CIS)	0.32	0.32	0.31	0.29	0.27	0.25
PCM(CASSCF)	0.02	-	0.01			

Table 3.4.3 PCM effect (eV) at various theoretical levels

- PCM effect: CIS>TDHF>TDDFT, no effect on the HOMO-LUMO gap.
- CASSCF does not show a solvent effect in PCM. It has to be noted that in PCM, CASSCF is by default an equilibrium excitation⁷, which includes a solvent relax process and is different from TDHF and TDDFT.
- In PCM method, at TDHF, TDDFT and CIS levels, the solvent effect decreases slightly with increasing chain length.

3.4.2 Solvent Effect of Cluster Models

3.4.2.1 How Many Solvent Molecules?

The TDHF excitation energy is calculated to determine how many solvent molecules are favorable in the cluster, where the geometry is optimized at MP2/Cep-31g* level.

TDHF	Vacuum	1 solvent ¹	2 solvent ²	4 solvent ³
C ₄ H ₆	6.08	5.93	5.83	5.75
C ₆ H ₈	5.15	5.02	4.90	-

1. One butadiene (hexatriene) is bound to one butane (hexane) molecule in a parallel orientation.

2. One butadiene (hexatriene) is bound to two butane (hexane) molecules posited at its top and bottom in a parallel orientation.

3. One butadiene (hexatriene) is bound to four butane (hexane) molecules posited at its top, bottom, left and right side in a parallel orientation (Figure 1.7.2).

Table 3.4.4 TDHF excitation energies (eV) in some explicit cluster models

The cluster of one butadiene surrounded by four butane molecules at the top, bottom, left and right side in a parallel orientation is employed as the ideal cluster structure in that it reduces the TDHF excitation energy substantially.

3.4.2.2 Other Methods to Optimize the Cluster Geometries

From solute-solvent distances and binding energies at various levels, only the MP2 level covers enough dispersion in the cluster model; lowering of excitation energies correlates with the solute-solvent distance. MP2 is a reliable method but also an expensive method. For instance, MP2 could not be applied for a larger cluster than C₄H₆*4C₄H₁₀ in my project. Thus we tested other levels to produce the solvent effect. DFT (PBE and PBE0) methods are reported to account for H-bonded interaction¹⁰, so they are employed to calculate the TDHF and TDDFT excitation energies.

	C ₄ H ₆	C ₄ H ₆ *4C ₄ H ₁₀	Cluster effect
MP2	5.96	5.75	0.21
PBE	5.92	5.78	0.15
PBE0	6.04	5.91	0.13

Table 3.4.5 TDHF excitation energies (eV) of C₄H₆ and the C₄H₆*4C₄H₁₀ cluster and cluster effects (eV) with geometries optimized at MP2, DFT (PBE, PBE0)

	C ₄ H ₆	C ₄ H ₆ *4C ₄ H ₁₀	Cluster effect
MP2	5.71	5.46	0.25
PBE	5.68	5.51	0.17
PBE0	5.78	5.63	0.15

Table 3.4.6 TDDFT excitation energies (eV) of C₄H₆ and the C₄H₆*4C₄H₁₀ cluster and cluster effects (eV) with geometries optimized at MP2, DFT (PBE, PBE0)

- The MP2 level gives a cluster effect of 0.21eV at TDHF approach, larger than PBE and PBE0 do (0.15 and 0.13eV).
- TDDFT approach shows a larger cluster effect than TDHF approach.

3.4.2.3 The Cluster Effects for Longer Polyenes

To research the cluster effects for longer polyenes, DFT (PBE) is used in the place of MP2.

	Gas	Cluster	Cluster effect	Gas	Cluster	Cluster effect
	TDHF//MP2	TDHF//MP2	at MP2	TDHF//PBE	TDHF//PBE	at PBE
C ₄ H ₆	5.96	5.75	0.21	5.92	5.77	0.15
C ₆ H ₈	5.05	-	-	4.96	4.84	0.12
C ₈ H ₁₀	4.45	-	-	4.32	4.22	0.10

Table 3.4.7 TDHF excitation energies (eV) in the gas phase and in the clusters including four corresponding alkane molecules, and cluster effects (eV) at MP2 and PBE

The cluster effects decrease with increasing chain length at the PBE level. It is deduced that the cluster effects will decrease with increasing chain length at the MP2 level.

3.4.3 Solvent Effect of the Cluster Model in PCM

MP2 produces a good cluster effect and DFT (PBE, PBE0) methods do some. We will see whether the effect will change at MP2 and DFT (PBE, PBE0) when the cluster is added into a continuum. Thus the solvent molecules in an inner shell are treated explicitly, while those in an outer shell are treated implicitly.

Butadiene	TDHF	Effect	TDDFT	Effect
Vacuum	5.96		5.71	
PCM	5.70	0.26	5.49	0.22
Cluster	5.75	0.21	5.46	0.25
Cluster in PCM	5.65	0.31	5.38	0.33

Table 3.4.8 Excitation energies (eV) of C₄H₆ in vacuum, PCM, cluster and the cluster in PCM with geometries optimized at the MP2 level

Butadiene	TDHF	Effect	TDDFT	Effect
Vacuum	5.92		5.68	
PCM	5.66	0.26	5.46	0.22
Cluster	5.77	0.15	5.51	0.17
Cluster in PCM	5.67	0.25	5.43	0.25

Table 3.4.9 Excitation energies (eV) of C₄H₆ in vacuum, PCM, cluster and the cluster in PCM with geometries optimized at the PBE level

Butadiene	TDHF	Effect	TDDFT	Effect
Vacuum	6.04		5.78	
PCM	5.78	0.26	5.57	0.21
Cluster	5.91	0.13	5.63	0.15
Cluster in PCM	5.8	0.24	5.54	0.24

Table 3.4.10 Excitation energies (eV) of C_4H_6 in vacuum, PCM, cluster and the cluster in PCM with geometries optimized at the PBE0 level

The method of the cluster in PCM reduces the excitation energies most at the MP2 level, compared with PCM and the cluster model. Solvent effect of the cluster in PCM is 0.31 eV at TDHF level and 0.33 eV at TDDFT level. Solvent effect of PCM is 0.26 eV at TDHF level and 0.22 eV at TDDFT level. Solvent effect of the cluster model is 0.21 eV at TDHF level and 0.25 eV at TDDFT level.

But at DFT (PBE, PBE0) levels, the method of the cluster in PCM shows a similar effect to PCM, which is larger than the cluster effect.

It can be explained that DFT (PBE, PBE0) methods can cover part solute-solvent interactions, but the cluster is not bound completely. So the cluster shows a similar effect in PCM to an isolated molecule.

3.4.4 Solvent Effect of Water for Polyenes

3.4.4.1 Solvent Effect of Water for Polyenes in PCM

In PCM, the solvent effect of water is less than that of heptane, and the difference is not dramatic. Water is a polar solvent with a large dipole moment and the maximum

dielectric constant of 78.39. PCM does not predict a different effect, so we add real water molecules explicitly.

TDHF	C ₄ H ₆	C ₆ H ₈	C ₈ H ₁₀	C ₁₀ H ₁₂	C ₁₂ H ₁₄	C ₁₄ H ₁₆
Gas	6.08	5.15	4.53	4.10	3.78	3.54
PCM(heptane)	5.82	4.88	4.26	3.84	3.53	3.29
PCM(water)	5.84	4.91	4.28	3.86	3.55	3.31

Table 3.4.11 TDHF energies in PCM with heptane and water as the solvent

3.4.4.2 Determine a Favorable Cluster Model

The C₆H₈*4H₂O clusters are illustrated above. The geometries are optimized at MP2/Cep-31g*. TDHF excitation energies of these C₆H₈*4H₂O clusters are calculated. With all geometries, similar results for the cluster effect are obtained. The largest solvent effect on the excitation energy is 0.05eV produced by the 4th cluster. To model the solvent effect, thousands of water molecules are necessary, however, the first solvation shell has certainly the strongest effect on the solute. Therefore, clusters with four water molecules are just simple models to test the cluster effect very roughly. The optimized solute-solvent distances show that water molecules have bonding interaction with the solute at the MP2 level. The magnitude of the cluster effect is small and does not depend on the geometry of the cluster, as similar excitation energies with different geometries indicate.

	1 st	2 nd	3 rd	4 th
TDHF//MP2	5.00	5.04	5.03	5.00
Cluster Effect	0.05	0.01	0.02	0.05

Table 3.4.12 TDHF//MP2 excitation energies (eV) and cluster effects (eV) of $C_6H_8*4H_2O$ clusters (TDHF//MP2 of C_6H_8 is 5.05 eV in the gas phase)

3.4.4.3 Solvent Effect of Water for the Cluster of Hexatriene at PBE

The geometry of the 4th cluster is optimized again at the PBE level, because TDHF excitation energy of $C_6H_8*4C_6H_{14}$ cluster is only available with the geometry optimized at the PBE level. The TDHF//PBE excitation energy of C_6H_8 is 4.96 eV in the gas phase. TDHF//PBE excitation energy of the $C_6H_8*4H_2O$ cluster is 4.92 eV, while that of $C_6H_8*4C_6H_{14}$ cluster is 4.84 eV. The $C_6H_8*4H_2O$ cluster shows a solvent effect (0.04 eV) less than the $C_6H_8*4C_6H_{14}$ cluster (0.12 eV).

3.4.4.4 Solvent Effect of Water for the Cluster of Butadiene at MP2

A $C_4H_6*4H_2O$ cluster similar to the 4th cluster is constructed. The geometry is optimized at the MP2 level. TDHF//MP2 excitation energy of the $C_4H_6*4H_2O$ cluster is 5.91 eV. The TDHF//MP2 excitation energy of the $C_4H_6*4C_4H_{10}$ cluster is 5.75 eV. The solvent effect of the $C_4H_6*4H_2O$ cluster is smaller (0.05 eV) than that of the $C_4H_6*4C_4H_{10}$ cluster (0.21 eV).

In explicit models of butadiene and hexatriene, water does not show a greater influence on the solute than a nonpolar solvent. It is in an agreement with PCM. Water has a permanent dipole moment, which is expected to reorient and produce a stronger reaction field. From the result, it is not so. Water as a polar solvent, has

a stronger affinity to polar molecules like other water molecules than to the solute molecule. It can explain why the optimized solute-water distance becomes large.

3.4.5 Solvent Effect for Oligothiophenes and Oligopyrroles.

For thiophene oligomers, experimental data exist for room temperature (RT) solutions, for matrix, for films and for single crystals⁴⁰. Pyrrole oligomers are even less investigated than thiophene oligomers. Only data in RT solution are available. Since excitation energies in the gas phase are not available, the solvent effect is unknown.

Polypyrrole and polythiophene can be considered to be derivatives of polyacetylene. We predict the solvent effect for polythiophenes and polypyrroles, based on the assumption that the theoretical error is similar to that for polyenes. TDHF transition energies in PCM for polyenes are about 0.28 eV lower than in the gas phase. Therefore, the theoretical solvent effect is smaller but comparable to the experimentally obtained values of 0.3-0.4 eV. The solvent effect for thiophene and pyrrole oligomers (dimer to hexamer) is obtained at the TDHF//B3P86-30% level in PCM.

	Calculated Vacuum	Calculated PCM(heptane)	Exp. in matrix ⁴¹	Exp. in solution dioxane ⁴² /benzene ⁴³
2-thiophene	4.25	4.13	3.67	4.05/4.13
3-thiophene	3.6	3.48	3.08	3.49/3.50
4-thiophene	3.26	3.15	2.75	3.16/3.18
5-thiophene	3.06	2.95		2.99/2.98
6-thiophene	2.93	--		2.85/2.86
2-thiophene (non-planar)	4.39	4.28		

Table 3.4.13 TDHF//B3P86-30% excitation energies (eV) of oligothiophenes in vacuum, PCM, and Exp. data in matrix and in solution

The excitation energy is calculated from the planar ground state to the planar excited state in the gas phase and in PCM. The solvent effect for oligothiophene at the TDHF level in PCM is about 0.11-0.12 eV at the presence of heptane.

In fact, oligothiophene has a non-planar geometry in the ground state in the gas phase and in solution^{44,45}, and it becomes planar in the excited state. The matrix forces the oligomer into the geometry closer to that of the excited states⁴⁵. From the results in matrix and in RT liquid solution, the effect due to the geometry change from non-planar to planar is known to have a lower excitation energy of about 0.4 eV.

2-thiophene is calculated with a nonplanar geometry in the gas phase and in PCM (heptane), the solvent effect is 0.11 eV, so the calculated solvent effect is not

influenced by the planar or nonplanar geometry. The calculated effect of the geometry change is 0.15 eV, smaller than the experimental data. This is caused by the problem of DFT with rotation barriers in conjugated systems.

The excitation energies in PCM (heptane) and in matrix have a deviation 0.40-0.46 eV.

For pyrrole oligomers, TDHF in PCM predicts a solvent effect of 0.10-0.15 eV, about half of that for polyenes, and very similar to that for thiophene oligomers. Since pyrrole oligomers are also non-planar in solution, theoretical excitation energies in the presence of solvent should be lower than experimental values. Therefore theoretical values seem to have a deviation of about 0.5 eV, slightly larger than thiophene oligomers.

	Calculated Vacuum	Calculated PCM (heptane)	Exp. in solution (acetonitrile) ⁴⁶
2-pyrrole	4.97	4.82	4.50
3-pyrrole	4.35	4.21	3.90
4-pyrrole	4.03	3.9	3.58
5-pyrrole	3.84	3.73	3.36
6-pyrrole	3.72	3.62	3.25

Table 3.4.14 TDHF//B3P86-30% excitation energies (eV) of oligopyrroles in vacuum, PCM, and Exp. in solution

Chapter 4. Conclusions

1. It is well known that correlation reduces BLA and band gap. TDHF/Cep-31g* excitation energies of C₆H₈, obtained with geometries optimized at various theoretical levels, have a roughly linear response to BLA.
2. There is little dependence of BLA on the basis set if only all electron basis sets are considered. BLA is about 0.008Å less with pseudopotential basis set.
3. PCM does not influence bond length, BLA or the HOMO-LUMO gap of the ground state.
4. Among all the methods, the highest level is MRMP, which includes the dynamic correlation, σ electron correlation and multi-reference configurations and gives an accurate description of the excited states and the first allowed vertical excitation energy. TDHF gives a similar result for the 1^1B_u state. Compared with MRMP, TDHF is an affordable method.
5. Solute-solvent interactions are dispersion force mainly discussed in this thesis. The results of excitation energies show that these solvent effects can be evaluated implicitly by PCM and explicitly by cluster models. These two effects are not additive, but a cluster in a continuum obtains the lowest excitation energies.
6. TDHF level in PCM can reproduce a red shift in the presence of a solvent well for polyenes, 0.20-0.28eV vs 0.30-0.4eV. Increasing the dielectric constant in PCM does not increase the solvent effect.
7. In the explicit method, MP2 can cover the solute-solvent effect by forming an efficiently bound cluster. DFT (PBE and PBE0) are reported to account for H-bonded interaction. In this project, they yield larger solute-solvent distances

and smaller binding energies than the MP2 approach. DFT (B3P86-30%) and HF do not give a solvent effect.

8. Water does not produce a stronger solvent effect than non-polar solvent in PCM or in explicit clusters. In cluster models, the optimized structures at MP2 and PBE show the solute-solvent distance is too large to be in a range of H-bonded interactions.
9. TDHF in PCM predicts a solvent effect for oligothiophenes of 0.11-0.12eV, and a solvent effect for oligopyrroles of 0.10-0.15eV, about half of that for polyenes.
10. TDHF excitation energies in PCM are compared with experimental results in a medium, where the solute molecule is planar in the ground state. The error for polyenes is 0.1-0.2eV. For thiophene oligomers, the accuracy is less with errors of about 0.4 eV. No matrix data exist for pyrrole oligomers. Comparison with RT solution data indicates the error increases further than thiophene oligomers.

Chapter 5. References

1. U. Salzner, J. B. Lagowski, P. G. Pickup, and A. Poirier, *J. Comp. Chem.* **18**, 1943-1953 (1997)
2. K. L. D'Amino, C. Manos, and R. L. Christensen, *J. Am. Chem. Soc.* **102**, 1777-1782 (1980)
3. Szabo, A.; Ostlund, N. S., *Modern Quantum Chemistry*; Mac Millan Publishing: New York 1982 and McWeeny, R.; Sutcliffe, B. T., *Methods of Molecular Quantum Mechanics*; Academic Press: London 1969
4. C. H. Choi, M. Kertesz, A. Karpfen, *J. Chem. Phys.* **107**, 6712-6721 (1997)
5. C. Møller, M. S. Plesset, *Phys. Rev.* **46**, 618-622 (1934)
6. A. Dreuw, M. H. Gordon, *Chem. Rev.* **105**, 4009-4037 (2005)
7. Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J.

- Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, (2004).
8. A. C. Scheiner, J. Baker, and J. W. Andzelm, *J. Comp. Chem.* **18**, 775-795 (1997)
9. U. Salzner, J. B. Lagowski, P. G. Pickup, and A. Poirier, *J. Phys. Chem. A* **102**, 2572-2578 (1998)
10. A. ST.-Amant, W. O. Cornell, P. A. Kollman, T. A. Halgren, *J. Comp. Chem.* **16**, 1483-1506 (1995)
11. C. J. Cramer, *Essential of Computational Chemistry*, John Wiley & Sons Ltd. (2002)
12. B. S. Hudson and B. E. Kohler, *J. Chem. Phys.* **59**, 4984-5002 (1974)
13. J. W. Hill, R. H. Petrucci, *General Chemistry An Integrated Approach*, Third Edition
14. J. Tomasi, B. Mennucci, R. Cammi, *Chem. Rev.* **105**, 2993-3093 (2005)

15. Foresman J. B., Frisch M. J., *Exploring Chemistry with Electronic Structure Methods*. 1st ed. Pittsburgh PA Gaussian Inc., 1994
16. L. Onsager, *J. Am. Chem. Soc.* **58**, 1486-1493 (1938)
17. S. Miertus and J. Tomasi, *Chem. Phys.* **65**, 239, (1982)
18. J. B. Foresman, T. A. Keith, K. B. Wiberg, J. Snoonian, and M. J. Frisch, *J. Phys. Chem.* **100**, 16098-16104 (1996)
19. Klamt, A. and Schüürmann, G., *J. Chem. Soc. Perkin Trans.* **2**, 799-805 (1993)
20. J. Li, C. J. Cramer, D. G. Truhlar, *International Journal of Quantum Chemistry*, Vol. **77**, 264-280 (2000)
21. U. Salzner, *Current Organic Chemistry*, **8**, 569-590 (2004)
22. D. G. Leopold, V. Vaida, and M. F. Granville, *J. Chem. Phys.* **81**, 4210-4217 (1984)
23. D. G. Leopold, R. D. Pendley, J. L. Roebber, R. J. Hemley, and V. Vaida, *J. Chem. Phys.* **81**, 4218-4229 (1984).
24. R. M. Gavin, Jr., C. Weisman, J. K. McVey, and S. A. Rice, *J. Chem. Phys.* **68**, 522-529 (1978)

25. Kenichi Nakayama, Haruyuki Nakano, Kimihiko Hirao, *International Journal of Quantum Chemistry*, Vol. **66**, 157-175 (1998)
26. Cave, R. J.; Davidson, E. R., *J. Phys. Chem.* **92**, 2173-2177 (1988)
27. sWilliam J. Hunt and William A. Goddard, III *Chem. Phys. Lett.* **3**, 414 (1969)
28. M. Trættemberg, *Acta Chem. Scand.* **22**, 628 (1968)
29. W. Haugen and M. Trættemberg, *Acta Chem. Scand.* **20**, 1726 (1966)
30. J. Q. Sun and R. J. Bartlett, *J. Chem. Phys.* **104**, 8553-8565(1996)
31. U. Salzner, *J. Chem. Theo. Comp.* submitted
32. S. Hirata, H. Torii, and M. Tasumi, *J. Chem. Phys.* **103**, 8964-8979 (1995)
33. C. S. Yonnoni and T. C. Clarke, *Phys. Rev. Lett.* **51**, 1191-1193 (1983)
34. H. Kahlert, O. Leitner, and G. Leising, *Syn. Met.* **17**, 467-478 (1987)
35. H. E. Schaffer, R. R. Chance, K. Knoll, R. R Schrock, R. Silbey, *J. Chem. Phys.* **94**, 4161-4170 (1991)
36. R. Peierls, *Quantum Theory of Solids* (Oxford University Press, Oxford 1954)

37. A. A. Ovchinnikov, II Ukrainskii, and GV. Kventsel, *Usp. Fiz. Nauk.* **108**, 81-111 (1972)
38. L. Serrano-Andrés, R. Lindh, B. O. Roos, and M Merchán, *J. Phys. Chem.* **97**, 9360-9368 (1993)
39. L. Serrano-Andrés, M. Merchán, I. Nebot-Gil, R. Lindh, and B. O. Roos, *J. Chem. Phys.* **98**, 3151-3162 (1993)
40. *Handbook of Theoretical and Computational Nanotechnology*, edited by Michael Rieth and Wolfram Schommers, Forschungszentrum Karlsruhe, Germany (2005)
41. D. Birnbaum, and B. E. Kohler, *J Chem. Phys.* **95**, 4783-4789 (1991)
42. R. Colditz, D. Grebner, M. Helbig, and S. Rentsch, *Chem. Phys.* **201**, 309–320 (1995)
43. F. Martinez, R. Voelkel, D. Naegele, and H. Naarmann, *Mol. Cryst. Liq. Cryst.* **167**, 227-232 (1989)
44. C. Aleman and L. Julia, *J. Phys. Chem.* **100**, 1524-1529 (1996)
45. H. A. Duarte, H. F. Dos Santos, W. R. Rocha, W. B. De Almeida, *J. Chem. Phys.* **113**, 4206-4215 (2000)

46. G. Zotti, S. Martina, G. Wegner, and A. D. Schlüter, *Adv. Mater.* **4**, 798-801 (1992)