Calculations of optical absorption in low-bandgap polymers and molecules using time-dependent quantum chemical methods

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LiTH-IFM-EX-04/1347-SE
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Linköping, 4 October, 2004
Tidsberoende kvantkemiska beräkningar av optisk absorption hos polymerer och molekyler med litet bandgap
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Sammanfattning
Abstract

The vertical electronic excitation energies for the narrow-bandgap polymers LBPF, EP37 and EP62 have been calculated using Density Functional Theory (DFT). Also the vertical excitation energies for the acceptor unit of LBPF have been calculated using the Hartree–Fock (HF), DFT and Coupled Cluster (CC) methods. The calculations cover the visible and infrared wave length region and two strong transitions are obtained, one corresponding to the \( \pi \) to \( \pi^* \) transition and one corresponding to the \( \pi \) to Acceptor transition. The excitation energies obtained from DFT are below the corresponding experimental results and attempts have therefore been made to perform bench-marking calculations using a hierarchy of CC methods.

Nyttelord
Plastic solar cells, low bandgap polymers, absorption spectra, Hartree-Fock method, Density functional theory, Coupled cluster methods
Abstract

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Acknowledgements

I would like to thank my supervisors Dr. Patrick Norman and Professor Olle Ingaläs for giving me the opportunity of working with this interesting and instructive project. Patrick has given me all the time that I needed to, in a pedagogical and patient way, explaining, helping and explaining again and I will thank him for that. I have learnt a lot and have developed my interest for physics. I would also like to thank the Ph.D students in the Theory and Modelling group for helpful and interesting discussions. Most of all I would like to thank Anders Hansson, who has helped me with small and big problems, has proofread all that I have written and always has been interested in discussing small and big questions. Also Johan Henriksson deserves a special mentioning for helping me with everything from computational problems to deep physical questions. I will also thank Nils-Christer Persson in the Applied Physics group for interesting discussions and information.
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Chapter 1

Introduction

A polymer consists of atoms that are (more or less) arranged in a long chain. This chain is called the backbone of the polymer. The atoms in the chain come in regular order and that order repeats itself all along the length of the polymer chain. Every repeated part of the chain is called a monomer. Two monomers are called a dimer and three monomers are called a trimer. Semi-conducting polymers is a field that is of interest in the market of future electronic and devices. Because of their low cost, their ease of fabrication, their suitability for large area coating and the possibility to design the materials to get the required properties, organic materials are attractive alternatives to conventional inorganic semiconductors. One class of conjugated polymers that are attractive especially because of their high mobility and stability is polyfluorenes. Polyfluorenes have an absorption range in the UV and blue region of the spectra. That makes this class of polymers suitable for use in for example light emitting diodes and field effect transistors. This absorption region is less suited for solar cells, where a large coverage of the solar spectrum is desirable. To lower the band gap and thereby fit the visible and infrared regions of the spectra, alternating fluorene copolymers which contain blocks of electron accepting and electron donating moieties along the polymer backbone have been synthesised [19].

The development of polymer solar cells is still in an early stage. Power conversion efficiencies of about 2.5% is reached [19], but a higher efficiency is desirable. The most common problem for all the applications of conjugated polymers is stability. To reach desirable lifetimes of conjugated polymers, they must be protected from air and humidity [5].

In this diploma work three so-called low-bandgap polymers, LBPF, EP37 and EP62, have been studied. These consist of a polymer backbone in which an acceptor unit has been introduced to lower the band gap. The introduced acceptor unit have been studied separately. The purpose of this work was to perform calculations of the absorption spectra of LBPF, EP37 and EP62 and the acceptor units.
Chapter 2

Group theory

2.1 Symmetry operations and symmetry elements

In quantum chemical calculations the symmetries of the nuclear skeleton is of importance. By making use of the symmetry of the nuclear framework in a molecule, the computational efforts and time, can be reduced. This chapter gives an introduction to group theory. For further reading, see Ref. [4].

A symmetry operator is an operator that acts on the molecule in such a way that the atomic positions is physically indistinguishable from the original ones. All symmetry operations that can be applied on a molecule leave the physical properties of it unchanged. There are five different types of symmetry operations: the identity operation, the rotation operation, the reflection operation, the rotation-reflection operation and the inverse operation.

A symmetry element is a geometrical entity, for example a point, a line or a plane about which the action of an operator takes place.

Identity operator

The identity operator is denoted by $E$ (from the German word Einheit) and is an operator that does nothing to the system. When applying the identity operator to a molecule, the final position of the nuclei is identical to the original.

Rotation operator

The rotation operator is an operator that rotates the molecule about an axis. An operator that rotates a molecule $2\pi/n$ ($n$ is an integer) about an axis is denoted $C_n$. One says that the molecule have a $n$-fold axis of symmetry. The symmetry axis having the largest $n$ is said to be the principle axis. If $C_n$ is a symmetry operator, then also $C_k^n$ is a symmetry operator. $C_k^n$ means that $C_n$ is applied $k$ times. Note that $C_n^n = E$. This means that rotating the molecule $n$ times about an axis of $n$-fold symmetry gives back the original positions of the nuclei.
Reflection operator

The reflection operator is an operator that reflects the molecule in a plane and it is denoted \( \sigma \) (from the German word Spiegel). If the symmetry plane is perpendicular to the principal axis, it is denoted \( \sigma_h \) (\( h \) means horizontal), and, if it contains the principal axis, it is denoted \( \sigma_v \) (\( v \) means vertical). Note that \( \sigma^2 = E \), i.e. reflecting the molecule twice in the plane gives back the original positions.

Rotation-reflection operator

The rotation-reflection operator first rotates the molecule about an axis. After that the molecule is reflected in the plane perpendicular to that axis. If the final positions of the atoms are indistinguishable from the original ones, the symmetry element is said to be an \( n \)-fold alternating rotation-reflection axis of symmetry. The reverse also applies, first a reflection and after that a rotation. The rotation-reflection operator is denoted \( S_n \). If \( S_n \) is a symmetry operator, then also \( S_n^k \) (where \( S \) is applied \( k \) times) is a symmetry operator. In general,

\[
S_n^k = \sigma_h C_n^k \quad \text{if } k \text{ is odd}
\]

\[
S_n^k = C_n^k \quad \text{if } k \text{ is even}
\]

where \( \sigma \) is the reflection operator and \( C_n \) is the rotation operator.

Inverse operator

The inverse operator inverts all points about the origin. For example, suppose one atom with the coordinates \((x, y, z)\). When applying the inverse operator to the atom the new coordinates become \((-x, -y, -z)\). The inversion operator is denoted \( I \). Note that \( S_2 = I \) and \( I^2 = E \).

2.2 Groups

A group \( G \) is defined as a set of elements which together with some combining operations obey a set of certain rules. When defining a group it is necessary to specify the combining operation. This combining operation have to follow some rules:

1. If \( X \) and \( Y \) are elements of \( G \), then \( XY \) is an element of \( G \). \( XY \) means “\( X \) combined with \( Y \)”, i.e. let \( X \) followed by \( Y \) operate.

2. The group must contain a unit element \( E \) such that \( ER = RE = R \), where \( R \) is any element belonging to the group.
2.2 Groups

3. The associative law is satisfied such that \(X(YZ) = (XY)Z\), where \(X, Y\) and \(Z\) are members of the group.

4. There exists an inverse element such that \(RR^{-1} = R^{-1}R = E\), where \(R\) is any element in the group and \(E\) is the unitary element.

A special kind of group is the point group. The symmetry axes and planes of the elements of a point group intersect at least one common point, i.e. at least one point is left unchanged for all symmetry operations. A molecular group is a point group. A crystal (of infinite size) does not belong to a point group since it contains translational symmetry, which is a symmetry that leaves no point unchanged in space.

A group table is a table that summarises the combined operations of a group. Table 2.1 shows a general group table where \(A, B, C,\ldots\) are the operations of the group. The operation that is first applied is given in the first row and the operation that is next applied is given in the first column.

\[
\begin{array}{ccc}
A & B & C \\
A & AA & AB & AC \\
B & AB & BB & CB \\
C & AC & BC & CC \\
\vdots & \vdots & \vdots & \vdots \\
\end{array}
\]

The \(C_{2v}\) and \(C_s\) point groups

The \(C_{2v}\) group has four symmetry elements, the unitary element, the rotation element and two reflection elements. The rotation element is a \(C_2\)-axis. The reflection elements are \(\sigma^{xy}_v\) (reflection in the \(xy\)-plane) and \(\sigma^{yz}_v\) (reflection in the \(yz\)-plane). Table 2.2 is a group table that shows the results of the combining operations for the \(C_{2v}\) group.

\[
\begin{array}{cccc}
E & C_2 & \sigma^{xy}_v & \sigma^{yz}_v \\
E & E & C_2 & \sigma^{xy}_v & \sigma^{yz}_v \\
C_2 & C_2 & E & \sigma^{xy}_v & \sigma^{yz}_v \\
\sigma^{xy}_v & \sigma^{xy}_v & \sigma^{xy}_v & E & C_2 \\
\sigma^{yz}_v & \sigma^{yz}_v & \sigma^{yz}_v & C_2 & E \\
\end{array}
\]
The $C_s$ group has two symmetry elements, the identity element (see Sec. 2.1) and the reflection element (see Sec. 2.1). The reflection element is a $\sigma_h$-plane. The results of the combinations of the elements are shown in Table 2.3, the $C_s$ group table.

Table 2.3. The $C_s$ group table.

<table>
<thead>
<tr>
<th></th>
<th>$E$</th>
<th>$\sigma_h^{yz}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$</td>
<td>$E$</td>
<td>$\sigma_h^{yz}$</td>
</tr>
<tr>
<td>$\sigma_h^{yz}$</td>
<td>$E$</td>
<td>$E$</td>
</tr>
</tbody>
</table>

2.3 Reducible and irreducible representations

By studying a set of matrices, which behave in the same way as the symmetry operations, the properties of the molecule are easier to understand. Given a set of orbitals $\{\phi_i\}_{i=1}^k$ this set of matrices is constructed by finding the actions of the symmetry operations on the orbitals,

$$P\phi_i = \sum_j \phi_j D_{ij}(P)$$

(2.1)

where $P$ is the symmetry operator and $D(P)$ is a matrix. This set of matrices is said to form a representation $\Gamma$ of the point group.

By a similarity transformation the set of matrices $D(P)$ are transformed into block diagonal matrices,

$$M^{-1}D(P)M = \begin{bmatrix} D^1(P) & [0] & [0] & \cdots \\ [0] & D^2(P) & [0] & \cdots \\ [0] & [0] & D^3(P) & \cdots \\ \vdots & \vdots & \vdots & \ddots \\ \vdots & \vdots & \vdots & \vdots & D^j(P) \end{bmatrix}$$

(2.2)

where $M$ is a matrix, independent of the group elements of $P$. Since $D(P)$ represents the group, every set of blocks will also represent the group. A block diagonal matrix is a matrix where the non-zero elements are placed around the diagonal.

With a similarity transformation means that there exists a matrix $Q$ such that two matrices $A$ and $B$ are connected by the relation

$$Q^{-1}AQ = B$$

(2.3)

For a similarity transformation according to Eq. (2.3), the determinants, the eigenvalues $\lambda$ and the traces of matrices $A$ and $B$ are equal,

$$\det(A) = \det(B)$$

(2.4)

$$\text{Trace}(A) = \text{Trace}(B)$$

(2.5)

$$\lambda_A = \lambda_B$$

(2.6)
2.3 Reducible and irreducible representations

That means that a similarity transformation preserves the physical properties of the molecule described by the matrix, i.e. the group table (see Sec. 2.2) is not affected. A similarity transformation can reduce the dimensions of the blocks in the block diagonal matrix such that a $i \times i$-matrix becomes a $j \times j$-matrix, $i > j$. If, after a similarity transformation, all the matrices in the representation $\Gamma$ can be written in identical block form, $\Gamma$ is said to be an reducible representation. Identical block form means that every block matrix in $D(P)$ has the same dimension as the corresponding block matrices in all the other $D(P)$’s belonging to the representation. When it is not possible to reduce the dimensions of the matrices any further, then the irreducible representation (irrep) of the group is found.

A character is the trace (sum of the diagonal elements) of a matrix in the irrep. A character table is a table where these characters are collected. Each row in the character table represents an irreducible representation of the point group and each column represents a symmetry operation. Irreps where the character of a $2\pi/n$ rotation is equal to +1 for the highest $n$ are denoted by $A$ and −1 are denoted by $B$. The four irreps of $C_{2v}$ are $A_1$, $A_2$, $B_1$ and $B_2$. The two irreps of $C_s$ are $A'$ and $A''$ (for description of the $C_{2v}$ and $C_s$ point groups, see Sec. 2.2).

Table 2.4 shows the character tables for the point groups $C_{2v}$ and $C_s$.

<table>
<thead>
<tr>
<th></th>
<th>$E$</th>
<th>$C_2$</th>
<th>$\sigma^{x'y'}_v$</th>
<th>$\sigma^{y'z'}_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$B_2$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_1$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>$E$</th>
<th>$\sigma^{y'z'}_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A'$</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A''$</td>
<td>1</td>
<td>-1</td>
</tr>
</tbody>
</table>
Chapter 3
Quantum chemistry

3.1 The Schrödinger equation

A central problem in quantum mechanical calculations is to solve the time-independent Schrödinger equation \[ (3.1) \]
\[
H |\Psi\rangle = E |\Psi\rangle
\]
where \( H \) is the Hamiltonian operator, \( |\Psi\rangle \) is the eigenfunction and \( E \) is the energy of the system. The Schrödinger equation can be solved exactly only for the simplest of systems. In quantum mechanical calculations one is often concerned with larger systems and the problem must thus be reduced to find approximate solutions to the equation. In this chapter some notations and theories connected with the problem of finding these solutions are introduced.

3.1.1 Hamiltonian

The total Hamiltonian for a system of \( N \) electrons and \( M \) nuclei is

\[
H = - \sum_{i=1}^{N} \frac{1}{2} \nabla_i^2 - \sum_{A=1}^{M} \frac{1}{2M_A} \nabla_A^2 - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}} + \sum_{A=1}^{M} \sum_{B>A}^{M} \frac{Z_A Z_B}{R_{AB}}
\]

where the first term in Eq. (3.2) is the operator for the kinetic energy of the electrons. The Laplacian operator \( \nabla_i^2 \) is an operator acting on the \( i \)th electron. The second term is the operator for the kinetic energy of the nuclei. The Laplacian operator \( \nabla_A^2 \) acts on the \( A \)th nuclei and \( M_A \) is the ratio of the mass of nucleus \( A \) to the mass of an electron. The third term describes the Coulomb attraction between nucleus \( A \), with atomic number \( Z_A \), and an electron \( i \) at a distance \( r_{iA} \) from that nucleus. The fourth term corresponds to the repulsion between electrons \( i \) and \( j \) at a distance \( r_{ij} \) from each other. The fifth term represents the repulsion

| (21) |
between nuclei $A$ and $B$ with atomic number $Z_A$ and $Z_B$ respectively. The distance between the nuclei is $R_{AB}$.

For further reading about the Hamiltonian the reader is referred to Ref. [18].

### 3.1.2 Born-Oppenheimer Approximation

The idea of the Born–Oppenheimer approximation is built on the fact that the nuclei are much heavier than the electrons. Because of this difference in weight, the motions of the nuclei are much slower than the motions of the electrons. To a good approximation the motions of the electrons and the motions of the nuclei in a molecule can be separated. In this work the electronic problems are of interest and then the Born-Oppenheimer approximation simplifies the Hamiltonian by neglecting the second term (the kinetic energy of the nuclei) and treat the fifth term (the repulsion between the nuclei) in Eq. (3.2) as a constant. The remaining terms constitute the electronic Hamiltonian,

\[
H = -\sum_{i=1}^{N} \frac{1}{2} \nabla_i^2 - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_A}{r_i A} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}} + v_{nn} \tag{3.3}
\]

where

\[
v(r_i) = -\sum_{A=1}^{M} \frac{Z_A}{r_i A} \tag{3.4}
\]

is the external potential. In quantum chemical calculations the electronic Schrödinger equation,

\[
H\Psi(\{R\}, \{r\}) = E\Psi(\{R\}, \{r\}) \tag{3.5}
\]

has to be solved. The electronic wave function $\Psi(\{R\}, \{r\})$ depends explicitly on the coordinates of the electrons, $\{r\} = (r_1, ..., r_N)$ and parametrically on the coordinates of the nuclei, $\{R\} = (R_1, ..., R_A)$. That means that for different positions of the nuclei, $\Psi$ is a different function of the coordinates of the electrons.

For more reading about the Born–Oppenheimer approximation the reader is referred to Ref. [20].
3.2 Orbitals

An *orbital* is a wave function describing a single particle, in this work an electron. When completely describing an electron, it is necessary to describe both the spatial and the spin degrees of freedom.

A *spatial orbital* is a function $\psi_i(r)$ of the position vector $r$ of the electron, that describes the spatial distribution of the electron in such a way that

$$P(r)dr = |\psi_i(r)|^2 dr$$

is the probability of finding the electron in the small volume element $dr$ located at position $r$. The spatial molecular orbitals form an orthonormal set $\{\psi_i\}$, i.e.

$$\int dr \psi_i^*(r)\psi_j(r) = \delta_{ij} \quad (3.7)$$

An electron can have either spin up or spin down. The two functions $\alpha(\omega)$ and $\beta(\omega)$ describes the spin of the electron where $\alpha(\omega)$ corresponds to spin up and $\beta(\omega)$ to spin down. These functions are normalised,

$$\int d\omega \alpha^*(\omega)\alpha(\omega) = \int d\omega \beta^*(\omega)\beta(\omega) = 1 \quad (3.8)$$

and orthogonal,

$$\int d\omega \alpha^*(\omega)\beta(\omega) = \int d\omega \beta^*(\omega)\alpha(\omega) = 0 \quad (3.9)$$

The *spin orbital* $\chi(r, \omega)$ is the wave function that describes both the spatial and the spin degrees of freedom of the electron. There are two possible spin orbitals for each spatial orbital $\Psi_i(r)$, one corresponding to spin up and one to spin down,

$$\chi(x) = \begin{cases} \psi_i(r)\alpha(\omega) \\ \psi_i(r)\beta(\omega) \end{cases} \quad (3.10)$$

where we have denoted the four coordinates $(r, \omega)$ of the electron by $x$.

The theory about orbitals can be read about in Ref. [20].

3.3 Hartree products and Slater determinants

In this work we are concerned with molecules and must thus consider many particle problems. As was mentioned in Sec. 3.1 the Schrödinger equation [see Eq. (3.1)] can be solved only for the simplest of cases. When studying many particle systems the problem is complicated by the interaction of the electrons and also by the fact that two electrons are indistinguishable from one another.

3.3.1 Hartree products

The Hamiltonian [see Eq. (3.2)] of a system of $N$ *noninteracting* electrons can be written as

$$H = \sum_{i=1}^{N} h(i) \quad (3.11)$$
where \( h(i) \) is the operator of electron \( i \) \((h(i) \) is further described in Sec. 3.3.1). If the operator \( h(i) \) has a set of eigenfunctions, for example a set of spin orbitals \( \{ \chi_j \} \) with corresponding eigenvalues \( \varepsilon_j \), i.e.,

\[
\begin{align*}
h(i)\chi_j(x) &= \varepsilon_j\chi_j(x) \\
(3.12)
\end{align*}
\]

then the eigenfunction of the total Hamiltonian can be written as a product of these eigenfunctions,

\[
\Psi^{HP}(x_1, x_2, ..., x_N) = \chi_i(x_1)\chi_j(x_2)\cdots\chi_k(x_N)
\]

which is called a Hartree product. The eigenvalue \( E \) is a sum of the energies corresponding to each spin orbital in the Hartree product,

\[
E = \varepsilon_i + \varepsilon_j + \cdots + \varepsilon_k
\]

The probability of simultaneously finding electron one in the small volume element \( d\mathbf{r}_1 \) at \( \mathbf{r}_1 \), electron two in \( d\mathbf{r}_2 \) at \( \mathbf{r}_2 \), etc. is given by

\[
|\Psi^{HP}(x_1, x_2, ..., x_N)|^2d\mathbf{x}_1d\mathbf{x}_2\cdots d\mathbf{x}_N
\]

\[
= |\chi_i(x_1)|^2d\mathbf{x}_1|\chi_j(x_2)|^2d\mathbf{x}_2\cdots |\chi_k(x_N)|d\mathbf{x}_N
\]

Equation (3.15) shows that the probability of finding a given electron in a small volume element \( d\mathbf{r} \) is independent of the positions of the other electrons.

See Ref. [20] for more reading about the Hartree product.

### 3.3.2 Antisymmetry principle and Pauli principle

An independent postulate of quantum mechanics is the antisymmetry principle, which says that a many-electron wave function must be antisymmetric with respect to the interchange of the spin and space coordinates of any two electrons (for further reading about the antisymmetry principle see Ref. [20]),

\[
\Phi(x_1, ..., x_i, ..., x_j, ..., x_N) = -\Phi(x_1, ..., x_j, ..., x_i, ..., x_N)
\]

(3.16)

The Hartree product (see Sec. 3.3.1) does not satisfy this requirement of antisymmetry, but by forming antisymmetric linear combinations of all different \( N \)-particle Hartree products it is possible to obtain a correctly antisymmetrised wave function. Consider first the simple two-electron case. There are two possible orbitals for each electron to occupy. Electron one can occupy either spin orbital \( \chi_i \) or \( \chi_j \). The same is true for electron two. Assume that electron one occupies \( \chi_i \) and electron two occupies \( \chi_j \). Then the Hartree product is

\[
\Psi_{12}^{HP}(x_1, x_2) = \chi_i(x_1)\chi_j(x_2)
\]

(3.17)

If electron two occupies spin orbital \( \chi_i \) and electron one occupies \( \chi_j \), the Hartree product is

\[
\Psi_{21}^{HP}(x_2, x_1) = \chi_i(x_2)\chi_j(x_1)
\]

(3.18)
The antisymmetric linear combination of Eqs. (3.17) and (3.18) is

\[ \Psi(x_1, x_2) = \frac{1}{\sqrt{2}} [\chi_i(x_1)\chi_j(x_2) - \chi_j(x_1)\chi_i(x_2)] \]  

where the factor \( \frac{1}{\sqrt{2}} \) is a normalisation factor. According to Eq. (3.19) the antisymmetric linear combination of the wave functions fulfills the requirement of antisymmetry with respect to the interchange of the coordinates of the electrons, i.e.

\[ \Psi(x_1, x_2) = -\Psi(x_2, x_1) \]  

The wave function vanishes if \( i = j \), i.e. if the two electrons occupy the same spin orbital. The statement that two electrons can not occupy the same orbital is called the Pauli principle (for further reading about the Pauli principle see Ref. [21]).

### 3.3.3 Slater determinants

Equation (3.19) can be written as a determinant,

\[ \Psi(x_1, x_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \chi_i(x_1) & \chi_j(x_1) \\ \chi_i(x_2) & \chi_j(x_2) \end{vmatrix} \]  

This determinant is called a Slater determinant. By generalising to an \( N \)-particle system, the Slater determinant can be written as

\[ \Psi(x_1, x_2, ..., x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_i(x_1) & \chi_j(x_1) & \cdots & \chi_k(x_1) \\ \chi_i(x_2) & \chi_j(x_2) & \cdots & \chi_k(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_i(x_N) & \chi_j(x_N) & \cdots & \chi_k(x_N) \end{vmatrix} \]  

where the factor \( \frac{1}{\sqrt{N!}} \) is a normalisation factor. When \( i = j \) two rows are the same and that means that two electrons occupy the same spin orbital. Two equal rows in a determinant makes it equal to zero, and so then the Slater determinant fulfill the Pauli principle (see Sec. 3.3.2). A useful short-hand notation of the Slater determinant is

\[ \Psi(x_1, x_2, ..., x_N) = A[\chi_i\chi_j \cdots \chi_k] = A\pi \]  

where only the diagonal elements of the determinant are shown. The antisymmetrisation operator \( A \) makes \( \pi \) fulfill the requirements of antisymmetry and contains the identity matrix \( I \) and permutation operators \( P_{i,j,...} \),

\[ A = \frac{1}{\sqrt{N!}} \left( I - \sum_{ab} P_{ab} + \sum_{abc} P_{abc} + \cdots \right) \]  

The theory about Slater determinants can be found in Ref. [20].
3.4 Variational principle

As was mentioned in the beginning of this chapter the main problem in quantum chemical calculations is to find the solutions of the time-independent Schrödinger equation [see Eq. (3.1)]. The variational principle (for more reading about the variational principle see Ref. [8], [18] and [20]) is a method of finding approximate solutions to the exact ground state,

\[ H|\Psi_0\rangle = E_0|\Psi_0\rangle \]  

(3.25)

For one Hamiltonian operator \( H \) there exists a number of exact solutions to the Schrödinger equation,

\[ H|\Psi_\alpha\rangle = E_\alpha|\Psi_\alpha\rangle \]  

(3.26)

where the eigenvalues can be ordered according to

\[ E_0 \leq E_1 \leq \ldots \leq E_\alpha \]  

(3.27)

The eigenvalues are real and the corresponding eigenfunctions can be chosen orthonormal,

\[ \langle \Psi_\alpha | \Psi_\beta \rangle = \delta_{\alpha\beta} \]  

(3.28)

To find an as good approximation as possible to the ground state, one starts with an initial guess of the wave function and minimises the expectation value of the Hamiltonian with respect to the orbitals. The lowest possible energy gives the best possible wave function. Assume that the initial guess of the wave function is \( \Phi \), then the expectation value of the Hamiltonian is

\[ \langle \Phi | H | \Phi \rangle = E \]  

(3.29)

The guessed wave function can be expanded and written as

\[ |\Phi\rangle = \sum_\alpha |\Psi_\alpha\rangle c_\alpha \]  

(3.30)

Inserting Eq. (3.30) in Eq. (3.29) and using Eq. (3.27) gives

\[ \langle \Phi | H | \Phi \rangle = \sum_\alpha |c_\alpha|^2 E_\alpha \geq E_0 \]  

(3.31)

which is the variational principle. The variational principle says that the expectation value of the Hamiltonian is an upper bound to the exact ground state energy.
3.5 Hartree–Fock equation

One way of finding the approximate solutions to the Schrödinger equation [see Eq. (3.1)] is to use the variational principle (see Sec. 3.4), i.e. to find the lowest possible energy

\[ E = \langle \Psi | H | \Psi \rangle \]  

(3.32)

where \( H \) is the full electronic Hamiltonian [see Eq. (3.3)] and \( | \Psi \rangle \) is a single Slater determinant (see Sec. 3.3), describing the ground state of an \( N \)-particle system. The Hartree–Fock equation

\[ f(i) \chi(x_i) = \varepsilon \chi(x_i) \]  

(3.33)

is the eigenvalue equation received after minimising the energy with respect to the choice of spin orbitals (orbitals are described in Sec. 3.2 and for the derivation of the Hartree–Fock equation the reader is referred to Ref. [20]). The operator \( f(i) \) in Eq. (3.33) is equal to

\[ f(i) = -\frac{1}{2} \nabla_i^2 - \sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + v^{HF}(i) \]  

(3.34)

and it is known as the Fock operator. The Hartree–Fock potential \( v^{HF}(i) \) is the average potential, felt by the \( i \)th electron due to the other electrons. The Hartree–Fock equation is non-linear because the Hartree–Fock potential in the Fock operator [Eq. (3.34)] depends on the spin orbitals of the other electrons (for further description the reader is referred to Ref. [20]).

The electronic Hamiltonian [see Eq. (3.3)] can be rewritten as

\[ H = \sum_{i=1}^{N} h(i) + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} g_{ij} + V_{nn} \]  

(3.35)

where \( V_{nn} \) is the potential energy between the nuclei, and

\[ h(i) = -\frac{1}{2} \nabla_i^2 - \sum_{A=1}^{M} \frac{Z_A}{r_{iA}} \]  

(3.36)

is a one-electron operator and

\[ g_{ij} = \frac{1}{r_{ij}} \]  

(3.37)

is a two-electron operator. By using Eq. (3.33) the expectation value of the Hamiltonian can be written as

\[ E = \langle \Psi | H | \Psi \rangle = \langle \Psi | \sum_{i=1}^{N} h(i) + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} g_{ij} + V_{nn} | \Psi \rangle \]  

(3.38)

\[ = \frac{1}{N!} (\langle \pi | \sum_{i=1}^{N} h(i) + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} g_{ij} + V_{nn} | \pi \rangle \]  

\[ + \langle \pi | \cdots | \mathcal{P}_{ab}\pi \rangle + \langle \mathcal{P}_{ab}\pi | \cdots | \pi \rangle + \langle \pi | \cdots | \mathcal{P}_{ac}\pi \rangle + \cdots ) \]
3.5.1 Coulomb term

The first term in Eq. (3.38) contains the expression

$$\langle \pi | \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} g_{ij} | \pi \rangle = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \langle \pi | g_{ij} | \pi \rangle$$

(3.39)

where

$$\langle \pi | g_{ij} | \pi \rangle = \int dr_i dr_j |\chi_a(r_i)|^2 r_{ij}^{-1} |\chi_b(r_j)|^2 = J_{ab}$$

(3.40)

called the Coulomb integral and is a two-electron integral that represents, together with the third term in Eq. (3.38), the electron-electron interaction (the third term is described below) in the Hartree–Fock approximation. The Coulomb integral contains $|\chi_a(r_i)|^2$ and $|\chi_b(r_j)|^2$ which can be interpreted as the electron density (see Sec. 3.1), or the probability density. The Coulomb integral represents the classical Coulomb repulsion between these “charge clouds”. It can be written

$$\langle \pi | g_{ij} | \pi \rangle = \langle \chi_a(x_i) \chi_b(x_j) | g_{ij} | \chi_a(x_i) \chi_b(x_j) \rangle$$

(3.41)

where the expression

$$\langle \chi_b(x_j) | g_{ij} | \chi_b(x_j) \rangle = \int dx_j |\chi_b(x_j)|^2 r_{ij}^{-1} = J_b(x_j)$$

(3.42)

is defined as the the Coulomb operator. The Coulomb operator represents the affect of the average local potential, arising from an electron in orbital $\chi_b$, on an electron at $x_i$. For more reading about the Coulomb integral and the Coulomb operator the reader is referred to Ref. [20].

3.5.2 Exchange term

The second term in Eq. (3.38) contains

$$\langle \pi | g_{ij} | \mathcal{P}_{ab} \pi \rangle = \int dr_i dr_j \chi_a^*(r_i) \chi_b(r_i) r_{ij}^{-1} \chi_b^*(r_j) \chi_a(r_j) = K_{ab}$$

(3.43)

which is called the exchange integral. The exchange integral is, just like the Coulomb integral (see Sec. 3.5.1), a two-electron integral. Together with the Coulomb integral it represents the electron-electron interaction in the Hartree–Fock approximation. Unlike the Coulomb integral the exchange integral has no classical interpretation.

The so called exchange effects is not represented in the Hartree product (see Sec. 3.3.1), but arises when anti-symmetrising the Hartree product to yield a Slater determinant (see Sec. 3.3.3). The word exchange comes from the requirement of $|\Psi|^2$ being invariant according to the exchange of spin and space coordinates of electrons. The results of this requirement is further described in Sec. 3.5.3.
3.5 Hartree–Fock equation

The exchange integral [see Eq. (3.43)] can be written
\[
\langle \pi | g_{ij} | P_{ab} \rangle = (\chi_a(x_i) \chi_b(x_j) | g_{ij} | \chi_a(x_j) \chi_b(x_i))
\]
\[
= (\chi_a(x_i) | (\chi_b(x_j) | g_{ij} | \chi_a(x_j)) | \chi_b(x_i))
\]
\[
= (\chi_a(x_i) | K_b(x_j) | \chi_a(x_i))
\]
where \( K_b(x_j) \) is the exchange operator. The definition of the exchange operator is, when operating on orbital \( \chi_a(x_j) \), the exchange of orbitals \( \chi_a \) and \( \chi_b \),
\[
K_b(x_j) \chi_a(x_i) = \left[ \int dx_j \chi_a^*(x_j) r_{ij}^{-1} \chi_b(x_j) \right] \chi_a(x_i)
\]
(3.45)

For more reading about the exchange integral and the exchange operator see Ref. [20].

3.5.3 Exchange correlation and correlation energy

According to the Pauli principle (see Sec. 3.3.3), two electrons with the same spin cannot occupy the same spatial orbital. Then the motion of two electrons with parallel spins is said to be correlated. This exchange correlation gives the exchange term in Eq. (3.38). The theory about exchange correlation and correlation energy is obtained from Ref. [20].

Suppose two electrons with parallel spins occupying space orbital \( \psi_1 \) and \( \psi_2 \) respectively,
\[
\chi_1(x_1) = \psi_1(r_1) \alpha(\omega_1)
\]
\[
\chi_2(x_2) = \psi_2(r_2) \alpha(\omega_2)
\]
(3.46)
The corresponding Slater determinant is
\[
\Psi(x_1, x_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_1(r_1) \alpha(\omega_1) & \psi_2(r_1) \alpha(\omega_1) \\ \psi_1(r_2) \alpha(\omega_2) & \psi_2(r_2) \alpha(\omega_2) \end{vmatrix}
\]
(3.47)
and after expanding the determinant the probability of simultaneously finding electron one in \( dx_1 \) and electron two in \( dx_2 \) is
\[
|\Psi|^2 dx_1 dx_2 = \frac{1}{2} |\psi_1(r_1) \alpha(\omega_1)\psi_2(r_2) \alpha(\omega_2) - \psi_1(r_2) \alpha(\omega_2)\psi_2(r_1) \alpha(\omega_1)|^2 dx_1 dx_2
\]
(3.48)
The probability of finding electron one in \( dr_1 \) at \( r_1 \) and electron two in \( dr_2 \) at \( r_2 \) can be denoted by \( P(r_1, r_2) dr_1 dr_2 \) and is obtained by integrating over the spins,
\[
P(r_1, r_2) dr_1 dr_2 = \int d\omega_1 d\omega_2 |\Psi|^2 dr_1 dr_2
\]
(3.49)
\[
= \frac{1}{2} \left\{ |\psi_1(r_1)|^2 |\psi_2(r_2)|^2 + |\psi_1(r_2)|^2 |\psi_2(r_1)|^2 - [\psi_1^*(r_1)\psi_2(r_2)\psi_1(r_2) + \psi_1^*(r_1)\psi_2^*(r_2)\psi_2(r_2)\psi_1^*(r_2)] \right\} dr_1 dr_2
\]
where the orthonormality of the spins is used (see Sec. 3.2). Two electrons are indistinguishable, and the right-hand side of Eq. (3.49) shows the average probability of finding electron one in $d\mathbf{r}_1$ at $\mathbf{r}_1$ and electron two in $d\mathbf{r}_2$ at $\mathbf{r}_2$.

Suppose then two electrons with opposite spins occupying orbital $\chi_1$ and $\chi_2$ respectively,

$$
\chi_1(x_1) = \psi_1(r_1)\alpha(\omega_1) \\
\chi_2(x_2) = \psi_2(r_2)\beta(\omega_2)
$$

(3.50)

After the same procedure as above, the probability of finding electron one in $d\mathbf{r}_1$ at $\mathbf{r}_1$ and electron two in $d\mathbf{r}_2$ at $\mathbf{r}_2$ is

$$
P(\mathbf{r}_1, \mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2 = \int d\omega_1 d\omega_2 |\Psi|^2 d\mathbf{r}_1d\mathbf{r}_2
$$

$$
= \frac{1}{2} \left[ \psi_1(r_1) \psi_2(r_2) \right]^2 \left[ |\psi_1(r_1)|^2 |\psi_2(r_1)|^2 \right] d\mathbf{r}_1d\mathbf{r}_2
$$

(3.51)

Note that

$$
P(\mathbf{r}_1, \mathbf{r}_1) = 2|\psi_1(r_1)|^2|\psi_2(r_1)|^2
$$

(3.52)

and, if $\psi_1 = \psi_2$,

$$
P(\mathbf{r}_1, \mathbf{r}_1) = 2 \left[ |\psi_1(r_1)|^2 \right]^2
$$

(3.53)

The extra term, that appears for electrons with parallel spins [see Eq. (3.49)], disappears for electrons with opposite spins [see Eq. (3.51)]. This extra term represents the exchange correlation. It makes $P(\mathbf{r}_1, \mathbf{r}_1) = 0$ which means that the probability of finding two electrons at the same point in space is zero, i.e. the motion of two electrons with parallel spins is correlated.

According to Eqs. (3.52) and (3.53) $P \neq 0$ always applies, which means that there is always a probability of finding two electrons with opposite spins at the same point in space. This means that the motion of two electrons with opposite spins is uncorrelated. That is an approximation. In reality the motions of one electron depends on the other electrons. The Coulomb repulsion between electrons makes them avoid being at the same place. In the Hartree–Fock approximation the average, and not the exact, potential from the other electrons is taken into account. The difference between the exact energy and the Hartree–Fock energy, i.e.

$$
E_{\text{corr}} = E_{\text{exact}} - E_0
$$

(3.54)

is called the correlation energy.

### 3.5.4 Basis functions

The molecular orbitals (the eigenfunctions to the Fock operator [see Eq. (3.34)]) can be expanded in terms of a set of $K$ known basis functions $\{\phi_\mu(\mathbf{r})\}$, $\mu = 0, 1, 2, ..., K$

$$
\Psi_i = \sum_{\mu=1}^{K} C_\mu \phi_\mu
$$

(3.55)
This way of expanding the molecular orbitals as linear combinations of atom-type orbitals is called MO-LCAO (Molecular Orbitals as Linear Combinations of Atomic Orbitals). The molecular orbitals are orthogonal, but basis functions do not need to be. When the number of basis functions is increased, the Hartree–Fock energy is lowered and when the basis is large enough, the Hartree–Fock limit is reached. There are two different types of basis functions concerned with MO-LCAO, Gaussian orbitals, 

\[ \phi(r - R_A) \propto e^{-\xi |r - R_A|^2} \]  

and Slater orbitals, 

\[ \phi(r - R_A) \propto e^{-\xi |r - R_A|} \]  

where \( r \) is the position of the electron and \( R_A \) is the position of the nucleus. The Slater orbitals describe the features of the atomic orbitals more correctly compared to the Gaussian orbitals. In spite of that, the Gaussian orbitals are the orbitals that are most widely used. The reason is that the Gaussian orbitals, because of the squared exponent, lead to simpler integral evaluations. The Gaussian orbitals are not atom-like, but by using many so called primitive Gaussian orbitals, \( \phi^p \), an atomic-like contracted Gaussian orbital, \( \phi^c_\mu \) (centred at \( R_a \)), can be built up as a linear combination, 

\[ \phi^c_\mu (r - R_A) = \sum_{p=1}^{L} d^p_\mu \phi^p(r - R_A) \]  

where \( d^p_\mu \) is the contraction coefficients and \( L \) is the contraction length. By a good choice of the coefficients, the exponents and the length, the contracted Gaussian functions can be used as basis functions in molecular wave function calculations. For more reading about basis functions see Ref. [20].

In quantum mechanical calculations the basis set must be specified. In a minimal basis [20] there are as many basis functions as there are atomic orbitals in the shells that are occupied in the corresponding atom. For example, the minimal basis for water is 

\[ \{h_{1,1s}, h_{2,1s}, O_{1s}, O_{2s}, O_{2p_x}, O_{2p_y}, O_{2p_z}\} \]  

where \( h_{1,1s} \) is the 1s orbital of the first hydrogen atom, \( h_{2,1s} \) is the 1s orbital of the second hydrogen atom, \( O_{1s} \) is the 1s orbital of the oxygen atom, and so on.

In this thesis the basis sets 6-31G, 6-31G*, cc-pVDZ and aug-cc-pVDZ have been used. For more reading about these basis sets the reader is referred to Ref. [11].

In the 6-31G basis set six primitive Gaussian functions have been contracted to one contracted Gaussian function for the inner shells, in the case of water for the 1s orbital of the oxygen. There are also 3 + 1 primitive Gaussian functions for the valence shells, which means, in the case of water, the 1s orbitals for the hydrogen atom and the 2s2p_x2p_y2p_z orbitals for the oxygen atom. In the 6-31G* basis set, in the case of water, polarised \( d \)-functions have been added to the oxygen atom. That also applies for the cc-pVDZ basis set and in the case of aug-cc-pVDZ diffuse
functions have been added. Diffuse functions are functions with low exponents and will describe negative ions and negative regions of the molecules (regions that have more diffuse electron clouds). In a Double Zeta (DZ) basis the number of valence basis functions are doubled and there are different exponents in each of the two functions.

3.5.5 Roothaan equations

Now when we are familiar with basis functions it is time to introduce the Roothaan equations (the theory about Roothaan’s equations is obtained from Ref. [20]). It is possible to solve the Hartree–Fock equation numerically for simple atoms but difficult for molecular systems. With Roothaan’s equations the Hartree–Fock problem is converted to a problem that can be solved by using standard matrix techniques.

First introduce a set of $K$ known basis functions and expand the spatial molecular orbitals (for description of orbitals see Sec. 3.2),

$$
\psi_i = \sum_{\mu=1}^{K} C_{\mu i} \phi_{\mu}
$$

(3.60)

Inserting Eq. (3.60) in the Hartree–Fock equation [see Eq. (3.33)] and using the index $\nu$ gives a matrix equation

$$
f \sum_{\nu=1}^{K} C_{\nu i} \phi_{\nu} = \varepsilon_i \sum_{\nu=1}^{K} C_{\nu i} \phi_{\nu}
$$

(3.61)

Multiplying Eq. (3.61) with $\phi_{\mu}^*$ on the left and integrate gives

$$
\sum_{\nu=1}^{K} C_{\nu i} \int \phi_{\mu}^* f(\phi_{\nu}) d\mathbf{r}_i = \sum_{\nu=1}^{K} C_{\nu i} \varepsilon_i \int \phi_{\mu}^* \phi_{\nu} d\mathbf{r}_i
$$

(3.62)

where

$$
\int \phi_{\mu}^* f(\phi_{\nu}) d\mathbf{r}_i = F_{\mu \nu}
$$

(3.63)

is defined as the elements of the Fock matrix $F$ and

$$
\int \phi_{\mu}^* \phi_{\nu} d\mathbf{r}_i = S_{\mu \nu}
$$

(3.64)

is defined as the elements of the overlap matrix $S$. The overlap matrix $S$ and the Fock matrix $F$ are hermitian $K \times K$ matrices,

$$
F = \begin{pmatrix}
F_{11} & F_{12} & \cdots & F_{1K} \\
F_{21} & F_{22} & \cdots & F_{2K} \\
\vdots & \vdots & \ddots & \vdots \\
F_{K1} & F_{K2} & \cdots & F_{KK}
\end{pmatrix}
$$

(3.65)
3.5 Hartree–Fock equation

\[
S = \begin{pmatrix}
S_{11} & S_{12} & \cdots & S_{1K} \\
S_{21} & S_{22} & \cdots & S_{2K} \\
\vdots & \vdots & \ddots & \vdots \\
S_{K1} & S_{K2} & \cdots & S_{KK}
\end{pmatrix}
\]  

(3.66)

where \( K \) is the number of basis functions. Now, with these definitions, Eq. (3.61) can be written

\[
\sum_{\nu} F_{\mu\nu} C_{\nu} = \varepsilon_i \sum_{\nu} S_{\mu\nu} C_{\nu}
\]  

(3.67)

where \( i = 1, 2, \ldots, K \). This is the Roothaan equation. A more compact way of writing Eq. (3.67) is

\[
FC = SC\varepsilon
\]  

(3.68)

If the basis functions are chosen orthogonal \( S \) is a unitary matrix. Then Eq. (3.68) can be reduced to

\[
FC = C\varepsilon
\]  

(3.69)

and the molecular problem is a simple eigenvalue problem. Now the main task is to find the eigenvectors \( C \) and the eigenvalues \( \varepsilon \), i.e. to find a matrix \( C \) that diagonalises \( F \). Thus with the Roothaan’s equation the molecular problem is solved with respect to a set of coefficients instead of solving the Hartree–Fock equations in every point in space.

3.5.6 Self consistent field (SCF) solution

The Hartree–Fock equation is a nonlinear equation (see Sec. 3.5) and must be solved iteratively. The method used to solve the problem is the self consistent field (SCF) method. The idea of the SCF method is to begin with an initial guess of the spin orbitals, or actually at the expansion coefficient \( C_{\mu i} \) (see Sec. 3.5.5). With these guessed coefficients the elements \( F_{\mu\nu} \) of the Fock matrix \( F \) (see Sec. 3.5.5) are calculated. The Fock matrix is diagonalised to obtain new expansion coefficients and eigenvalues \( \varepsilon_i \). If the new expansion coefficients are equal to the old, the problem is solved and the best possible value of the energy is obtained. If the new coefficient differs from the old ones, the procedure starts over and \( F_{\mu\nu} \) is calculated with the new coefficients. This procedure is repeated until the new coefficients equal to the old ones.

For further reading about SCF the reader is referred to Ref. [20].
3.6 Beyond the Hartree–Fock approximation

So far the so called *ab initio* Hartree–Fock method has been described. Hartree–Fock describes a system of non-interacting particles, i.e. it is an *uncorrelated* method. To get closer to the exact energy of the system so called *correlated* methods are used. The correlated methods used in this thesis are Density Functional Theory (DFT) and Coupled Cluster (CC) methods. In DFT an exchange correlation functional is added while in CC the correlation appears in the wave function. The CC methods gives a systematic way of getting closer to the Full Configuration Interaction (FCI). The FCI method provides an exact solution of the many particle problem for a given basis set. In this chapter the basic ideas of DFT are presented. The CC methods used in this work is CC2, CCSD and CCR(3) (for further reading about FCI and CC the reader is referred to Ref. [20] and Ref. [6] respectively). The semi empirical method Zerners Intermediate Neglect of Differential Overlap (ZINDO) has also been used in this diploma work and for further reading the reader is referred to Ref. [15].

3.6.1 Density functional theory (DFT)

The theory of (DFT) is obtained from Ref. [15]. The idea of *Density Functional Theory* (DFT) is to replace the wave function $\Psi$ in the Schrödinger equation [Eq. (3.1)] with the $v$ and $N$ representable electron density $\rho$ (for further explanation the reader is referred to Ref. [16]). The wave function for an $N$-electron system depends on $3N$ (space) coordinates, three coordinates for each electron, while the density only depends on three (space) coordinates and is explicitly independent of the number of electrons. The electron density is defined as the number of electrons per unit volume in a given state, and it can be written as

$$\rho(r_1) = N \int \cdots \int |\Psi(x_1, x_2, ..., x_N)| d\mathbf{x}_1 d\mathbf{x}_2 \cdots d\mathbf{x}_N$$

(3.70)

The total number $N$ of electrons is obtained when integrating Eq. (3.70) over the three coordinates $x, y$ and $z$,

$$\int \rho(r) dr = N$$

(3.71)

The basis for DFT is two theorems stated by Hohenberg and Kohn. In the first theorem Hohenberg and Kohn show that the electron density $\rho(r)$ determines the external potential $v(r)$ [see Eq. (3.4)];

*The external potential $v(r)$ is determined, within a trivial additive constant, by the non-degenerated electron ground state density $\rho(r)$.*

Assume two different external potentials $v$ and $v'$ that differs with more than a trivial constant and that give the same electron density $\rho$ for the ground state. There would be two Hamiltonians $H$ and $H'$ with the same ground state densities
3.6 Beyond the Hartree–Fock approximation

although the normalised wave functions $\Psi$ and $\Psi'$ were different. Then we would have (with $\Psi'$ as a trial function)

$$E_0 < \langle \Psi'|H'|\Psi' \rangle = \langle \Psi'|H'\Psi' \rangle + \langle \Psi'|H - H'|\Psi' \rangle$$

$$= E_0' + \int \rho(r)[v(r) - v'(r)]dr$$  \hspace{1cm} (3.72)

where $E_0$ and $E_0'$ is the ground state energies for $H$ and $H'$ respectively. We also have (with $\Psi$ as a trial function)

$$E_0' < \langle \Psi|H'|\Psi \rangle = \langle \Psi|H\Psi \rangle + \langle \Psi|H' - H|\Psi \rangle$$

$$= E_0 - \int \rho(r)[v(r) - v'(r)]dr$$  \hspace{1cm} (3.73)

Adding Eqs. (3.72) and (3.73) gives

$$E_0 + E_0' < E_0' + E_0$$  \hspace{1cm} (3.74)

which of course is not true. This proof is a contradiction and the conclusion is that there cannot be two different potentials $v$ that determine the same ground state electron density. So, $\rho$ determines $N, v$ and all properties of the ground state.

The total energy functional of the ground state can be written (the notation $E_v$ is introduced to show the explicit dependence on $v$)

$$E_v[\rho] = T[\rho] + V_{ne}[\rho] + V_{ee}[\rho]$$

$$= \int \rho(r)v(r)dr + F[\rho]$$  \hspace{1cm} (3.75)

where $T[\rho]$ is the kinetic energy, $V_{ee}[\rho]$ is the repulsion energy between electrons, $V_{ne}[\rho]$ is the energy between electron and nuclei and by definition

$$F[\rho] = T[\rho] + V_{ee}[\rho]$$

$$V_{ee}[\rho] = J[\rho] + \text{non-classical term}$$  \hspace{1cm} (3.76)

where $J[\rho]$ is the classical Coulomb repulsion between electrons.

The second theorem of Hohenberg and Kohn is analogous to the variational principle (for a description of the variational principle see Sec. 5.4) and reads:

**For a trial density $\tilde{\rho}(r)$, such that $\tilde{\rho}(r) \geq 0$ and $\int \tilde{\rho}(r)dr = N$,**

$$E_0 \leq E_v[\tilde{\rho}]$$  \hspace{1cm} (3.77)

**where $E_0$ is the exact ground state energy and $E_v[\tilde{\rho}]$ is the minimised energy functional.**
function. Then, according to the variational principle for the wave functions, it states that

$$\langle \tilde{\Psi} | H | \tilde{\Psi} \rangle = \int \tilde{\rho}(r)v(r)dr + F[\tilde{\rho}] = E_v[\tilde{\rho}] \geq E_v[\rho] = E_0$$

(3.78)

where $\rho$ is the exact electron density of the ground state. The electron density $\tilde{\rho}$ must be $v$- and $N$-representable. The variational principle requires that the ground state satisfies the stationary principle

$$\delta \left\{ E_v(\rho) - \mu \left[ \int \rho(r)dr - N \right] \right\} = 0$$

(3.79)

from which the *Euler–Lagrange* equation is obtained as

$$\mu = \frac{\delta E_v[\rho]}{\delta \rho(r)} = v(r) + \frac{\delta F[\rho]}{\delta \rho(r)}$$

(3.80)

where $\mu$ is the chemical potential.

**The Kohn–Sham equations**

By minimising the energy of a many electron system the ground state energy can be obtained and written as (a functional of $\rho$)

$$E_v[\rho] = \int \rho(r)v(r)dr + F[\rho]$$

(3.81)

which satisfies the *Euler equation*

$$\mu = v(r) + \frac{\delta F[\rho]}{\delta \rho(r)}$$

(3.82)

where the *Lagrange multiplier* $\mu$ is associated with the constraint

$$\int \rho(r)dr = N$$

(3.83)

The total electron density for any *interacting* system can be written as

$$\rho(r) = \sum_{i=1}^{\infty} n_i \sum_s |\Psi_i(r,s)|^2, \quad N = \sum_{i=1}^{\infty} n_i$$

(3.84)

and the exact ground state formula for the kinetic energy is

$$T = \sum_{i=n}^{\infty} n_i \langle \psi_i | -\frac{1}{2} \nabla^2 | \psi_i \rangle$$

(3.85)

where $n_i$ (that, according to the Pauli principle for explanation of the Pauli principle see Sec. 3.3.2) will be between 0 and 1) is the occupation numbers corresponding
3.6 Beyond the Hartree–Fock approximation

to the number of electrons in orbital $i$. The exact density matrix is normally not known since it requires an infinite number of orbitals. Kohn and Sham introduced the idea that the electron density approximately can be written as

$$\rho(r) = \sum_{i=1}^{N} |\psi_i(r)|^2$$  \hspace{1cm} (3.86)

in which case the kinetic energy is

$$T_s[\rho] = \sum_{i} \langle \psi_i | -\frac{1}{2} \nabla^2 | \psi_i \rangle$$  \hspace{1cm} (3.87)

where $n_i = 1$ for $N$ orbitals and $n_i = 0$ for the others. Equations 3.86 and 3.87 thus describes a system of $N$ noninteracting electrons. The kinetic energy [see Eq. 3.87] is an approximation since it only describes a noninteracting system. In order to make this kinetic energy exact, Kohn and Sham introduced the exchange-correlation energy. Rewrite Eq. 3.76 as

$$F[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho]$$  \hspace{1cm} (3.88)

where

$$E_{xc}[\rho] = T[\rho] - T_s[\rho] + V_{ee}[\rho] - J[\rho]$$  \hspace{1cm} (3.89)

is the exchange-correlation energy which contains the exact kinetic energy $T[\rho]$. Inserting Eq. 3.88 in Eq. 3.81 gives the chemical potential [see Eq. 3.80]

$$\mu = v(r) + \frac{\delta J[\rho]}{\delta \rho(r)} + \frac{\delta E_{xc}[\rho]}{\delta \rho(r)} + \frac{\delta T_s[\rho]}{\delta \rho(r)}$$  \hspace{1cm} (3.90)

The KS effective potential is defined as

$$v_{\text{eff}}(r) = v(r) + \frac{\delta J[\rho]}{\delta \rho(r)} + \frac{\delta E_{xc}[\rho]}{\delta \rho(r)}$$  \hspace{1cm} (3.91)

and

$$v_{xc}(r) = \frac{\delta E_{xc}[\rho]}{\delta \rho(r)}$$  \hspace{1cm} (3.92)

is the exchange-correlation potential.

The Hamiltonian that was introduced by Kohn and Sham

$$H = \sum_{i} \left( -\frac{1}{2} \nabla_i^2 \right) + \sum_{i} v_{\text{eff}}(r_i)$$  \hspace{1cm} (3.93)

describes a system of noninteracting electrons. Equation 3.93 is without electron-electron repulsion terms and the corresponding ground state electron density is $\rho$. 

The ground state wave function can be written (for description of the wave function see Sec. 3.3.3)

\[ \Psi = A[\chi_i \chi_j \cdots \chi_k] \]  
(3.94)

The one electron equations can be written as

\[ \hbar \chi_i = \left[ -\frac{1}{2} \nabla^2 + v_{\text{eff}}(r) \right] \chi_i = \varepsilon_i \chi_i \]  
(3.95)

Equations (3.95) are the Kohn–Sham equations.

The exact exchange correlation energy [see Eq. (3.89)] is difficult to know. It contains the difference between the exact and approximate kinetic energies \( T[\rho] \) and \( T_s[\rho] \) and the non classical term in Eq. (3.76). It can, by a good guess, be obtained. There are some methods of calculating the exchange correlation energy. If this exchange correlation energy is just exchange energy in Eq. (3.33) the theory is equivalent with the Hartree–Fock theory (see Sec. 3.5). The method used in this thesis is Becke’s 1988 gradient corrected exchange functional combined with Lee, Yang and Parr’s gradient corrected correlation functional (B3LYP). The number 3 means that there are 20% Hartree–Fock exchange correlation energy. For more reading about B3LYP the reader is referred to [16] and [24].
3.7 Absorption spectra of a molecule

The theory in this section is obtained from Refs. [3] and [11]. The spectral lines in a molecular absorption spectra originates from the absorption of a photon. That absorption occurs when the energy of the molecule changes. After the absorption, the molecule is said to be in an excited state.

Assume an electro-magnetic wave whose electric field component can be written as

\[ F_i = F_i^e \cos(kr - \omega t) \]  

(3.96)

where \( k \) is the propagation vector, \( \omega \) is the frequency (the relation between \( k \) and \( \omega \) is \( |k| = \omega/c = 2\pi/\lambda \), where \( c \) is the speed of light and \( \lambda \) is the wavelength), \( r \) is the position vector and \( t \) is the time coordinate. When the wavelength of the electro-magnetic wave is large compared to the length of a bond in the molecule Eq. (3.96) can be written as

\[ F = F_i^e \cos(\omega t) \]  

(3.97)

The size of a bond in a molecule is in the order of 0.1 nm and the wavelength of light in the visible region (that is of interest for solar cells) is in the order of 100 nm. The assumption according to Eq. (3.97) is thus reasonable. The charged particles in the molecule are affected by this electric field component and have at any moment in time a dipole moment. The dipole moment for the molecule is the sum of the dipole moments of all particles,

\[ \mu = \sum_{i=1}^{N} q_i r_i \]  

(3.98)

where \( q_i \) is the charge and \( r_i \) is the position vector of particle \( i \). According to the Born–Oppenheimer approximation (see Sec. 3.1.2) the total wave function of the molecule can be written as

\[ \Psi_{en}(\{r_i\}, \{R_A\}) = \Psi_e(\{r_i\}, \{R_A\}) \cdot \Psi_n(\{R_A\}) \]  

(3.99)

The dipole moment operator of the molecule is

\[ \mu = -e \sum_{i=1}^{N} r_i + e \sum_{A=1}^{M} Z_A R_A \]  

(3.100)

where \( Z_A \) is the atomic number of nucleus \( A \).

3.7.1 Transition moment and oscillator strength

Assume that the molecule is in the state \( \Psi' \). Add an external electric field. The probability of finding the molecule in another state \( \Psi'' \) is given by the squared transition moment

\[ M = \langle \Psi' | \mu_{\alpha} | \Psi'' \rangle \]  

(3.101)
where $\mu_\alpha$ is the electric dipole moment along the molecular axis $\alpha$. Inserting Eq. (3.100) in Eq. (3.101) gives the transition moment between the states $\Psi'$ and $\Psi''$

$$
\langle \Psi_{cm}'|\mu|\Psi_{cm}'' \rangle = \langle \Psi_{e}'|\Psi_{n}' \rangle - e \sum_{i=1}^{N} r_i |\Psi_{e}'|\Psi_{n}' \rangle + \langle \Psi_{e}'|\Psi_{n}' \rangle e \sum_{A=1}^{M} Z_A R_A |\Psi_{e}'|\Psi_{n}' \rangle
$$

(3.102)

where the second integral vanishes because of orthogonality. Then Eq. (3.102) can be written

$$
\langle \Psi_{e}'|\Psi_{n}' \rangle - e \sum_{i=1}^{N} r_i |\Psi_{e}'|\Psi_{n}' \rangle = \langle \Psi_{e}' \rangle - e \sum_{i=1}^{N} r_i |\Psi_{e}' \rangle \langle \Psi_{n}' \rangle
$$

(3.103)

where

$$
\langle \Psi_{e}' \rangle - e \sum_{i=1}^{N} r_i |\Psi_{e}' \rangle
$$

(3.104)

is the electronic transition moment and

$$
\langle \Psi_{n}' \rangle |\Psi_{n}' \rangle
$$

(3.105)

is the overlap integral between the nuclear states $\Psi_{n}'$ and $\Psi_{n}''$. The overlap integral [see Eq. (3.105)] gives the intensity of the transition. A transition that occurs without change of nuclear geometry is called a vertical transition. There are always transitions to other vibrational states of the same excited electronic states, but with lower intensity. The overlap between the vibrational state of the ground state and the vibrational state of the excited state is higher for the vertical transition compared to the transition with a change in the nuclear geometry.

The electronic transition moment [see Eq. (3.104)] is non-zero only if it spans the totally symmetric irreducible representation $A_1$ (for explanation of irreducible representations see Sec. 2.3). This means that the direct product of $\Psi_{e}'$, $\Psi_{e}'$ and $\sum_i r_i$ must span $A_1$ (see Table 2.1). Singlet and triplet states are orthogonal. So if for example $\Psi_{e}'$ is a singlet state and $\Psi_{e}'$ is a triplet state, the electronic transition moment is equal to zero at the non-relativistic level of theory.

The oscillator strength $f$ is related to the transition moment [see Eq. (3.101)] as

$$
f = \frac{2}{3} E \sum_{\alpha=x,y,z} |M_\alpha|^2
$$

(3.106)

where $E$ is the transition energy.

### 3.7.2 Polarization propagator method

In this work we are concerned with the electronic wave function $\Psi_e$ and from now the notation $e$ is dropped. The polarization propagator method, or just the propagator method is a common method to describe a molecule in a time-dependent perturbing field. Consider the perturbation

$$
F_i(t) = \sum_{k=-N}^{N} F_k^i e^{-i\omega_k t}
$$

(3.107)
3.7 Absorption spectra of a molecule

where \( i = x, y, z \). Consider also the Taylor expansion of the time-dependent expectation value of the dipole operator

\[
\mu_i(t) = \mu_i^0 + \sum_k \alpha_{ij}(\omega_k) F_{jk}^{-i\omega_k t} + \text{higher order terms} \tag{3.108}
\]

where

\[
\mu_i(t) = \langle \Psi(t)|\mu_i|\Psi(t)\rangle \tag{3.109}
\]

and

\[
\mu_i^0 = \langle \Psi(0)|\mu_i|\Psi(0)\rangle = \langle \Psi_0|\mu_i|\Psi_0\rangle \tag{3.110}
\]

In the polarization propagator method we are only concerned with electrons and then the wave function \( \Psi \) is the electronic wave function. The coefficient \( \alpha \) in the second term of Eq. (3.108) is the polarization propagator. Other names of \( \alpha \) is linear response function or dynamic polarizability.

The time-dependent Schrödinger equation describes the time development of the wave function,

\[
i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = H |\Psi(t)\rangle \tag{3.111}
\]

where

\[
H = H_0 + V(t) = H_0 - \sum_k F_{ik}^\omega e^{-i\omega_k t} \tag{3.112}
\]

is the perturbed Hamiltonian. The wave function can be written as

\[
|\Psi(t)\rangle = e^{-P(t)}|\Psi_0\rangle \tag{3.113}
\]

where

\[
P(t) = \sum_{n>0} [p_n(t)|\Psi_n\rangle\langle\Psi_0| - p_n^*(t)|\Psi_0\rangle\langle\Psi_n|] \tag{3.114}
\]

\[
= \sum_{n>0} [p_n(t)\Omega_n - p_n^*(t)\Omega_n^\dagger] \tag{3.114}
\]

is an anti-Hermitian operator. If \( P(t) \) is anti-Hermitian then \( e^{-P(t)} \) is unitary and the wave function is always normalised. In the way of finding the coefficients, start with expanding \( p_n(t) \) in order of the perturbation

\[
p_n(t) = p_n^1 + p_n^2 + \cdots \rightarrow P = P^1 + P^2 + \cdots \tag{3.115}
\]

where the first order correction \( p_n^1 \) has a linear dependence of \( F_{ik}^\omega \), the second order correction contains a quadratic dependence of \( F_{ik}^\omega \) and so on.

Ehrenfest’s theorem and the Baker–Campbell–Hausdorff (BCH) expansion are useful in the procedure of finding \( p_n \).

Ehrenfest’s theorem

For any time-independent operator we have

\[
\frac{d}{dt} \langle M \rangle = \frac{1}{i\hbar} \langle \Psi(t)|[M, H]|\Psi(t)\rangle \tag{3.116}
\]
Baker–Campbell–Hausdorff

\[ e^A e^{-A} = \sum_{n=0}^{\infty} \frac{1}{n!} A^n B \]  
(3.117)

\[ AB = [A, B] \text{ defines super operator } A \]

Apply Ehrenfest’s theorem to \( \Omega_n^1 \). Then the first order equation is

\[ \frac{d}{dt} \langle \Psi_0| [P^1, \Omega_n^1] |\Psi_0 \rangle = \frac{1}{i\hbar} \left[ \langle \Psi_0|[P^1,[\Omega_n^1, H_0]]|\Psi_0 \rangle + \langle \Psi_0|[\Omega_n^1, V(t)]|\Psi_0 \rangle \right] \]  
(3.118)

(where also Baker–Campbell–Hausdorff has been used) which gives

\[ p_n^1 + i\omega_n p_n^1 = \frac{1}{\hbar} \langle \Psi_0| V(t) |\Psi_0 \rangle \]  
(3.119)

where \( \hbar \omega = E_n - E_0 \), and

\[ p_n^1(t) = \frac{1}{\hbar} \sum_{k=0}^{N} \frac{\langle \Psi_n|\mu_k|\Psi_0 \rangle}{\omega_k - \omega_n} F_{n,k} e^{-i\omega_k t} \]  
(3.120)

Now develop the expectation value of the dipole operator \( \mu_i(t) \) to the first order correction,

\[ \langle \Psi(t)|\mu_i(t)|\Psi \rangle = \langle \Psi_0| e^{P(t)} \mu_i(t) e^{-P(t)} |\Psi_0 \rangle = \langle \Psi_0| P(t) \mu_i(t) |\Psi_0 \rangle \]

\[ = \langle \Psi_0| \mu_i |\Psi_0 \rangle + \langle \Psi_0|[P^1, \mu_i]|\Psi_0 \rangle \]

\[ = \mu_i^0 - \frac{1}{\hbar} \sum_{n>0}^{N} \left[ \frac{\langle \Psi_0|\mu_j|\Psi_n \rangle}{\omega_k - \omega_n} F_{j,k} e^{i\omega_j t} \langle \Psi_n|\mu_i|\Psi_0 \rangle \right] \]

where it has been used that \( F_{n,k} \) is Hermitian and that \( \omega_{-k} = -\omega_k \), i.e \( F_{n,k} = F_{-n,-k} = F_{-n,k} \). After some rewriting Eq. (3.121) can be written as

\[ \langle \Psi(t)|\mu_i(t)|\Psi(t) \rangle = \mu_i^0 + \frac{1}{\hbar} \sum_{k=0}^{N} \left[ \frac{\langle \Psi_0|\mu_j|\Psi_n \rangle\langle \Psi_n|\mu_j|\Psi_0 \rangle}{\omega_n - \omega_k} + \frac{\langle \Psi_0|\mu_j|\Psi_n \rangle\langle \Psi_n|\mu_i|\Psi_0 \rangle}{\omega_n + \omega_k} \right] F_{n,k} e^{-i\omega_k t} \]

(3.123)

and we get

\[ \alpha_{ij}(\omega_k) = \frac{1}{\hbar} \sum_{n>0} \left[ \frac{\langle \Psi_0|\mu_j|\Psi_n \rangle\langle \Psi_n|\mu_j|\Psi_0 \rangle}{\omega_n - \omega_k} + \frac{\langle \Psi_0|\mu_j|\Psi_n \rangle\langle \Psi_n|\mu_i|\Psi_0 \rangle}{\omega_n + \omega_k} \right] \]  
(3.124)
3.7 Absorption spectra of a molecule

which is defined as the polarisability of the ground state. When \( \omega_k \to \omega_{n0} \) the polarisation propagator goes to infinity, i.e. the polarisation propagator has poles at the excitation energies. The corresponding residues are connected to transition moments as [see Eq. (3.101)]

\[
\lim_{\omega_k \to \omega_{n0}} (\omega_{n0} - \omega_k) \alpha_{ij}(\omega_k) = \langle \Psi_0 | \mu_i | \Psi_n \rangle \langle \Psi_n | \mu_j | \Psi_0 \rangle
\] (3.125)

and can thus describe the probability for transition from one state to another for a given perturbation.
Quantum chemistry
Chapter 4

Results and discussion

4.1 Computational details

Calculations have been made for three different molecules, LBPF, EP37 and EP62. In the case of LBPF, the electronic structures of the monomer and the dimer denoted LBPF I, and LBPF II, have been calculated. Their structures can be found in Fig. 4.1. In the case of EP37 the electronic structures of the monomer, denoted EP37 I, dimer, denoted EP37 II and trimer, denoted EP37 III have been calculated and their structures are shown in Fig. 4.2. For EP62 the electronic structure of the monomer has been calculated. The structure of EP62 is shown in Fig. 4.3. In the solar cells applications LBPF, EP37 and EP62 consist of more than three units, they are oligomers containing long chains of monomers. The notation LBPF IV, EP37 IV and EP62 IV represents these oligomers. LBPF, EP37 and EP62 contain groups that have been studied separately (see Figs. 4.4, 4.5 and 4.6). These groups are denoted X, Y and Z. The groups Y and Z have been studied for cases with three and four different kinds of side chains respectively and they are denoted Y_a, Y_b, Y_c, Z_a, Z_b, Z_c and Z_d.

The quantum chemical calculation programs that have been used in this thesis are Gaussian [1] and Dalton [2]. The results presented in Table 4.1 are calculated with Gaussian. The result that is obtained with ZINDO and is presented in Table 4.2 is calculated with Gaussian and the other results that are presented in the same table are calculated with Dalton. First geometry optimisations were made. The geometry optimisation gives the equilibrium structure of the molecule, i.e. the bonding lengths and angles that give the lowest possible energy. The equilibrium structures were calculated with B3LYP/cc-pVDZ for all cases. Using the coordinates of the equilibrium structure the time-dependent calculations were executed. Time-dependent calculations have been made with B3LYP/6-31G for all molecules and polymers. In addition ZINDO, HF/6-31G, HF/cc-pVDZ, HF/aug-cc-pVDZ, DFT/6-31G, DFT/cc-pVDZ, DFT/aug-cc-pVDZ, CC2/6-31G, CCSD/6-31G and CCR(3)/6-31G has been used for the molecule X_a. The electronic structure for some orbitals of special interest are visualised in GaussView.
Results and discussion

(a) LBPF I  
(b) LBPF II

Figure 4.1. The monomer and dimer of LBPF. LBPF I contains one benzothiadiazole (two nitrogen atoms and one phosphor atom) and two thiophene rings (one phosphor and four carbon atoms), one on each side of the benzothiadiazole.

(a) EP37 I  
(b) EP37 II  
(c) EP37 III

Figure 4.2. The monomer, dimer and trimer of EP37. EP37 contains four nitrogen atoms and one phosphor atom. EP37 also contains two thiophene rings, one on each side of the group in the middle.
4.1 Computational details

Figure 4.3. The monomer of EP62. EP62 contains one two nitrogen atoms. EP62 also contains three thiophene rings, one that is placed in the middle and one on each side of the group in the middle.

Figure 4.4. The molecule $X$, which has the same structure as LBPF but without the polyfluorene.

Figure 4.5. The molecule $Y$ with different side chains. The molecule $Y$ has the same structure as EP37 but without polyfluorene.
Results and discussion

4.2 DFT calculations

Table 4.1 shows the excitation energies $\Delta E$ with corresponding transition moments $M^{0\rightarrow n}$ and oscillator strengths $f^{0\rightarrow n}$ calculated with B3LYP/6-31G (the notation $0 \rightarrow n$ means transition from the electronic ground state to the electronic excited state $n$). A red-shift (lowering of the excitation energy) in the absorption spectra was expected when increasing the conjugation length of LBPF, EP37 and EP62. That red-shift occurs because of increasing of the band width as a result of interaction between atomic orbitals and thereby creating molecular orbitals. That shift in energy can be seen both for LBPF and EP37 (in the case of EP62 only the monomer is studied) in Table 4.1.

There are two strongly allowed transitions for each molecule found in the calculations. The calculations gives a lower energy compared to the experimental value but there are some factors that affect the result and must be taken into account. The experimental values of $\lambda_{\text{max}}$ are obtained in film for LBPF, EP37 and EP62 and in CHCl$_3$ solution (chloroform) for the other molecules. Excitation energies of a polar molecule that are obtained in polar solvents are typically lower than excitation energies that are obtained in gas phase [10]. The calculations in this work are made in gas phase and therefore the experimental results obtained in CHCl$_3$ must be corrected before they can be compared with the calculated results. There are no estimated value of the energy shift for the molecule studied in solid state (film). The choice of basis set is another important point that affects the result. The results from the calculations presented in Table 4.1 should still not
4.2 DFT calculations

Table 4.1. Excitation energies $\Delta E$ (eV), electric dipole transition moments$^a$ $M_0^{0-n}$ (a.u.), and oscillator strengths $f_0^{0-n}$ for the strongly allowed low-lying states.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta E$</th>
<th>$M_0^{0-n}$</th>
<th>$f_0^{0-n}$</th>
<th>$\Delta E$</th>
<th>$M_0^{0-n}$</th>
<th>$f_0^{0-n}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LBPF</td>
<td>I  1.932</td>
<td>4.314</td>
<td>0.881</td>
<td>3.006</td>
<td>4.526</td>
<td>1.509</td>
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<tr>
<td></td>
<td>II 1.774</td>
<td>7.136</td>
<td>2.213</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>IV 2.27$^c$</td>
<td></td>
<td></td>
<td>3.22</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EP37</td>
<td>I  1.309</td>
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<td>0.745</td>
<td>2.997</td>
<td>4.238</td>
<td>1.319</td>
</tr>
<tr>
<td></td>
<td>II 1.153</td>
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<td></td>
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<td>2.335</td>
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<td></td>
<td>2.92</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EP62</td>
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<td>3.949</td>
<td>1.081</td>
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<tr>
<td></td>
<td>IV 2.00$^e$</td>
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<td>3.18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y</td>
<td>a  1.651</td>
<td>2.05$^f$</td>
<td>2.393</td>
<td>0.232</td>
<td>3.918</td>
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<tr>
<td></td>
<td>b  1.664</td>
<td>2.10$^f$</td>
<td>2.322</td>
<td>0.220</td>
<td>3.915</td>
<td>2.620</td>
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<tr>
<td></td>
<td>c  1.744</td>
<td>2.09$^f$</td>
<td>2.280</td>
<td>0.222</td>
<td>3.945</td>
<td>2.490</td>
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<tr>
<td>Z</td>
<td>a  2.035</td>
<td>2.35$^f$</td>
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<td>0.252</td>
<td>3.458</td>
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<td></td>
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<td>2.48$^f$</td>
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<td></td>
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<td>0.288</td>
<td>3.652</td>
<td>2.206</td>
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<tr>
<td></td>
<td>d  2.337</td>
<td>2.48$^f$</td>
<td>2.262</td>
<td>0.293</td>
<td>3.653</td>
<td>2.217</td>
</tr>
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</table>

$^a$The $y$-axis is the molecular long in-plane axis. $^b$The B3LYP/6-31$^*$ optimized structure is used in the calculations. $^c$Corresponding to the $\lambda_{max}$-value reported in Ref. [17]. $^d$Corresponding to the $\lambda_{max}$-value reported in Ref. [22]. $^e$Corresponding to the $\lambda_{max}$-value reported in Ref. [23]. $^f$Corresponding to the $\lambda_{max}$-value reported in Ref. [14] and obtained in CHCl$_3$ solution.

differ much if another basis set was used. In the next section (Sec. 4.3), the affect of calculations using different basis sets are discussed. Figure 4.7 shows the absorption spectra of the LBPF monomer. The features of the peaks in the spectra are characterised of a vertical electronic transition from one state to another. In Fig. 4.8 the electronic density for the orbitals of interest in the LBPF monomer are visualised. The orbitals are those which are involved in the electronic transition. The highest occupied orbital that is delocalised is called the $\pi$ orbital. The orbital with the electron density localised to the so-called acceptor group is in this thesis called the acceptor orbital and the lowest occupied orbital where the electron density is delocalised is called the $\pi^*$ orbital. The $\pi$ orbital is in this case of A$_2$ symmetry, the acceptor orbital is of B$_1$ symmetry and the $\pi^*$ orbital is also of B$_1$ symmetry. Then both the $\pi$ to acceptor and $\pi$ to $\pi^*$ transition is of B$_2$ symmetry (see Sec. 2.3). The notations $1^1B_2$ and $2^1B_2$ in Table 4.1 stand for the first and second excited singlet states of B$_2$ symmetry.
Results and discussion

Figure 4.7. The absorption spectra of LBPF I calculated with B3LYP/6-31G*.

(a) The $\pi$ orbital of LBPF I.  (b) The Acceptor orbital of LBPF I.

(c) The $\pi^*$ orbital of LBPF I.

Figure 4.8. The orbitals involved in the strongest allowed transitions of LBPF I.
4.3 Discussion about methods for time-dependent calculations

Table 4.2. Excitation energies $\Delta E$ (eV), electric dipole transition moments $M_0^{\mu-n}$ (a.u.), and oscillator strengths $f_0^{\mu-n}$ for the strongly allowed low-lying states in $X_b^\text{a}$.  

| Method  | Basis  | $\Delta E$ | $|M_0^{\mu-n}|$ | $f_0^{\mu-n}$ | $\Delta E$ | $|M_0^{\mu-n}|$ | $f_0^{\mu-n}$ |
|---------|--------|-------------|----------------|--------------|-------------|----------------|--------------|
| ZINDO   | -      | 2.378       | 3.243          | 0.613        | 3.723       | 2.937          | 0.788        |
| HF      | 6-31G  | 3.072       | 2.974          | 0.666        | 5.007       | 1.495          | 0.274        |
|         | cc-pVDZ| 3.027       | 2.993          | 0.664        | 4.967       | 1.412          | 0.243        |
|         | aug-cc-pVDZ | 2.814 | 2.848          | 0.559        | 4.660       | 1.614          | 0.297        |
| DFT     | 6-31G  | 2.324       | 2.216          | 0.280        | 3.900       | 2.745          | 0.720        |
|         | cc-pVDZ| 2.338       | 2.286          | 0.299        | 3.848       | 2.644          | 0.659        |
|         | aug-cc-pVDZ | 2.249 | 2.242          | 0.277        | 3.758       | 2.634          | 0.639        |
| CC2     | 6-31G  | 3.266       | 2.451          | 0.480        | 4.701       | 1.493          | 0.257        |
| CCSD    | 6-31G  | 3.548       | 2.278          | 0.451        | 4.889       | 0.712          | 0.061        |
| CCR(3)  | 6-31G  | 3.286       | -              | -            | -           | -              | -            |
| Exp     | -      | 2.66        |                |              |             |                |              |

$^a$The $y$-axis is the molecular long in-plane axis. $^b$The B3LYP/cc-pVDZ optimized structure in point group $C_s$ is used in the calculations. $^c$Corresponding to the $\lambda_{\text{max}}$-value reported in Ref. [14] and obtained in CHCl$_3$ solution.

Table 4.2 presents the results from time dependent calculations using HF, DFT (with the correlation functional B3LYP), CC2, CCSD and CCR(3). HF and DFT are calculated with the basis sets 6-31G, cc-pVDZ and aug-cc-pVDZ. The basis set aug-cc-pVDZ is very good for these calculations. In the case of the CC calculations the basis set 6-31G is used. In general this basis set is not sufficient at this level of theory. A basis set with polarising and diffuse functions should be used, but these calculations are currently not within reach due to the associated computational demands. The results from the CC calculations listed in Table 4.2 can thus differ from the optimal result that would be obtained with a better choice of basis set. But they still give an indication of the exact result, i.e. the exact solution to the Schrödinger equation. In this work the vertical transitions have been calculated. In the experimental results transitions to all vibrational states are included. The experimental $\lambda_{\text{max}}$ will thus not necessarily coincide with the calculated vertical excitation energy.

Table 4.2 shows that ZINDO and DFT give a lower excitation energy, compared to the experimental value. HF shows a quite good agreement with the experimental result and the CC methods gives a higher energy. It is well known that HF gives a highest occupied molecular orbital (HOMO) that is too low in energy. Despite that, HF gives a quite good agreement with experimental results. The reason is a cancellation of errors in the calculations (see Ref. [7]). DFT usually gives a higher energy for the HOMO state with respect to HF because of the correlation effects,
and thereby decreases the band gap (and gives lower excitation energies) providing there is a good guess of the exchange correlation energy functional (see Sec. 3.6.1). The CC calculations are those that are expected to give the best vertical excitation energies. The results presented in Table 4.2 also give an indication about that. The deviation between the result presented in Table 4.2 and the experimental excitation energy are believed to be due to the effects of the motions of the nuclei. After taking the energy shift from the solution, the choice of basis set and the motions of the nuclei into account, the vertical excitation energy calculated with the CC methods are expected to agree well with the experimental value of 2.66 eV.

In Ref. [7] calculations of the vertical excitation energy of butadiene using CC methods have been made. The basis sets used in the calculations are 6-31++G+2, cc-pVDZ+5 and cc-pVTZ'5 (for more information about these basis sets see Ref. [7]). The best CC vertical excitation energy from the calculations in Ref. [7] is estimated to be roughly 0.1 eV from the exact solution of the Schrödinger equation. As can be seen in Table 4.2, the results from the CC calculations converge with respect to the number of excited electrons that are incorporated, and that is an indication that CC also in this case is a good method of finding the exact vertical electronic transition energies.

The unexpected deviation between the vertical excitation energy calculated with DFT and the experimental result is an indication that DFT is not the best choice of method for time dependent calculations on these molecules. Many successful studies of time-dependent calculations using DFT have been reported and the only noticed case when this method is known to not be a good choice is for long range charge transfer excitations [9]. Examples of successful time-dependent DFT calculations can be found in Refs. [12], [13] and [10].
Bibliography


