Luminescence properties of flexible conjugated dyes

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Abstract

In this licentiate thesis the luminescence properties of two flexible conjugated dyes have been studied. The first, Pt1, is a platinum(II) acetylide chromophore used in optical power limiting materials. The second is a set of optical probes known as luminescent conjugated oligothiophenes (LCOs), which are used to detect and characterize the protein structures associated with amyloid diseases such as Alzheimer's disease.

MM3 and CHARMM force field parameters have been derived for the Pt1 chromophore and LCOs, respectively, based on potential energy surface references calculated at the density functional theory (DFT)/B3LYP level of theory. The parameters have been used to perform room temperature molecular dynamics simulations of the chromophores in solvent, where tetrahydrofuran was used for Pt1 and water for the LCOs. Conformationally averaged absorption spectra were obtained, based on response theory calculations at the time-dependent DFT (TDDFT)/CAM-B3LYP level of theory for a selection of structures from the simulations. For one of the LCOs, p-HTAA, force field parameters were also created describing the dominant first excited state, based on TDDFT/B3LYP reference potential energy surfaces. These were used for molecular dynamics simulations of the chromophore in the excited state, allowing the creation of an emission spectrum. A theoretically obtained Stokes shift of 112 nm could be computed based on the absorption and emission spectra, which is in good agreement with the experimental value of 124 nm.

In addition, a quantum mechanics/molecular mechanics study of the effects of solvation on the absorption properties of the p-HTAA chromophore in water has been conducted, resulting in two models for including these effects in the averaged spectra. The first includes explicit water molecules in the form of point charges and polarizable dipole moments, and results in an absorption wavelength that is blueshifted by 2 nm from a high quality reference calculation. The second model involves the complete removal of the solvent as well as the ionic groups of the chromophore. The resulting absorption wavelength is blueshifted by an additional 4 nm as compared to the first model, but requires only one fifth of the computational resources.
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# Contents

1 Introduction ................................................. 1

2 Electrostatics ............................................. 5

3 Density functional theory .................................. 9

4 Response theory ............................................ 13

5 Molecular mechanics ....................................... 19

6 Quantum mechanics/molecular mechanics ............... 27

7 Conformational averaging .................................. 31

8 Effects of solvation on p-HTAA ......................... 37

vii
<table>
<thead>
<tr>
<th>Contents</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.3 Other approximations</td>
<td>42</td>
</tr>
<tr>
<td>8.4 Absorption spectra</td>
<td>45</td>
</tr>
<tr>
<td>8.5 Conclusions</td>
<td>46</td>
</tr>
<tr>
<td>Bibliography</td>
<td>49</td>
</tr>
<tr>
<td>List of included Publications</td>
<td>51</td>
</tr>
<tr>
<td>Paper I</td>
<td>53</td>
</tr>
<tr>
<td>Paper II</td>
<td>63</td>
</tr>
</tbody>
</table>
At its most basic, a dye is a substance that attaches itself to another material and absorbs and emits light in a characteristic way. Their most common use, both in the past and today, has been aesthetic. For over 30,000 years [1], humans have been using dyes to color their clothes. Historically, these have mostly been natural dyes, harvested from plants or animals, but beginning with the creation of mauveine in 1856 [2], synthetic dyes have taken over. In more recent history it has become possible, with the aid of better understanding of chemistry and more advanced technology, to engineer dyes with highly complex behaviours for very specific uses. The molecules studied in the two articles included in this thesis represent examples of two such dyes.

The first, a platinum(II) acetylide chromophore [3], shown in figure 1.1, is used in optical sensor protection. The need for protection comes from the fact that the light that these sensors are supposed to register can also be used to disrupt them. Lasers that output light of very high intensities can be capable of not just blinding the sensors, but also destroying them. Since the lasers can be tuned to the same wavelengths that the sensors are supposed to detect, it is not just a simple matter of filtering out certain parts of the incoming light. Detecting the increased light intensity is possible, and it is also possible to use this in order to activate a shield to block the incoming light, but this process is relatively slow. By the time the light has been detected and the shield has been activated, enough light has already passed through to cause damage to the sensor. The purpose of the studied chromophores is to act as a passive shield, used in addition to the previously mentioned active shield. They have been designed to absorb light differently at different intensities. At low intensities the material is translucent, allowing all incoming light to pass through it, but for higher intensities the material becomes opaque, absorbing the light. This allows it to sit in front of the sensor during normal operation, letting light pass through it, but immediately responding by
Figure 1.1. A platinum(II) acetylide chromophore.

Figure 1.2. One of the LCOs in water together with an amyloid protein.
absorbing the light when the intensity reaches damaging levels. The material is only capable of doing this for a short time before it becomes saturated, but this is long enough that the active shield can be activated.

The second article studies a set of chromophores known as LCOs [4], luminescent conjugated oligothiophenes, which can be used in the study of amyloid diseases. Amyloid diseases, such as Alzheimer’s disease and type II diabetes, are characterized by aggregations of proteins. These aggregations appear due to a misfolding of naturally occurring proteins in the body and can form large fibril structures. Much is still unknown about the exact pathology of these diseases and how they connect to the protein aggregations. As such, there is a lot of interest in the study of the mechanisms behind the formation of the aggregations. To do this, staining of tissue samples with dyes such as Thioflavin T and Congo red is conventionally used. The fluorescence properties of these dyes change when they bind to the amyloid proteins, allowing the aggregations to be detected. The LCOs work in a similar way, attaching themselves to the protein aggregations. However, depending on the structure of the protein, the chromophores display different fluorescence properties. This allows not just for a simple detection of the aggregates, but it also provides information about their underlying structure. Figure 1.2 shows one of the LCOs together with an amyloid protein.

These two sets of molecules have very different functions, but what they have in common is that they are highly flexible conjugated systems. This means that at room temperature they will twist and turn, switching back and forth between many different conformations. At any point in time, it is possible to find them in and around any of a number of conformations. This behaviour will have an effect on the luminescence properties of the molecules, and it is this effect that has been studied in the included articles. A method of conformational averaging has been used, which combines classical mechanics, in the form of molecular dynamics simulations, with quantum mechanics, in the form of response theory calculations of ultraviolet-visible absorption and emission spectra. This method is detailed in Chapter 7, with the preceding chapters containing the theory that the method is built upon. In addition, Chapter 8 contains a study of the effects of solvation on one of the LCO chromophores.
2.1 The electric field and potential

The Coulomb force caused by one point charge, $q'$, acting on another point charge, $q$, is, in atomic units, given by

$$\mathbf{F} = \frac{qq'}{|\mathbf{r} - \mathbf{r}'|^3} (\mathbf{r} - \mathbf{r}'),$$

(2.1)

where $\mathbf{r}$ and $\mathbf{r}'$ give the positions of $q$ and $q'$, respectively. This can be generalized to the force experienced by the charge $q$ due to a charge distribution $\rho(\mathbf{r}')$:

$$\mathbf{F} = q \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} (\mathbf{r} - \mathbf{r}') d\tau$$

(2.2)

The electric field is defined as

$$\mathbf{E} = \frac{\mathbf{F}}{q}.$$  

(2.3)

That is, the force per unit charge that a stationary test charge would experience if placed in point $\mathbf{r}$. Thus, the force experienced by a charge $q$, placed at $\mathbf{r}$ is simply

$$\mathbf{F} = q \mathbf{E}(\mathbf{r}).$$

(2.4)

The electric potential is defined as

$$V(\mathbf{r}) = -\int_{\mathbf{r}_0}^{\mathbf{r}} \mathbf{E}(\mathbf{r}') d\mathbf{l},$$

(2.5)

where $\mathbf{r}_0$ is some reference point, usually chosen as infinity.
2.2 Electric dipoles and polarization

An electric dipole is a system of two charges of equal but opposite charge, \( q \) and \(-q\), separated by some distance, \( d \). The electric dipole moment is then defined as

\[
p = qd,
\]

(2.6)

where \( d \) is the vector from the site of the negative charge to that of the positive charge. There are many molecules that are natural dipoles, where the positive charge, in the form of the nuclei, and negative charge, in the form of the electrons, is not evenly distributed. The obvious example of this is the water molecule, where the electrons are more likely to be located near the nucleus of the oxygen atom than those of the hydrogen atoms. This causes the region around the oxygen to be more negative while the area around the hydrogens to be more positive, creating a dipole.

The potential from a dipole with its center located at the origin is just the sum of the potentials from the two charges:

\[
V(r) = \frac{q}{|r - r_+|} - \frac{q}{|r - r_-|},
\]

(2.7)

where \( r_+ \) and \( r_- \) are the vectors pointing to the positive and negative charge, respectively. This can be expressed using a Taylor expansion,

\[
V(r) = \frac{qd \cdot e_r}{r^2} + O\left(\frac{d^2}{r^2}\right),
\]

(2.8)

where all terms after the first can be neglected when the distance from the dipole, \( r \), is much larger than the distance between the two charges, \( d \). For an ideal dipole, where \( p \) is kept constant while \( q \) and \( d \) tend to infinity and zero, respectively, this expression becomes exact. Using the definition of the dipole, the potential can be written as

\[
V(r) = \frac{P \cdot e_r}{r^2}.
\]

(2.9)

For a material composed to a high degree of dipoles, the polarization density, \( P \), is defined as the amount of dipole moments per volume unit, \( d\tau \):

\[
P = \sum_i \frac{P_i}{d\tau}.
\]

(2.10)

When exposed to an electric field, atoms and molecules become polarized. As can be seen from Equation 2.4, the positive nuclei will have a force applied to them in the direction of the field while the negative electrons will have a force applied to them in the opposite direction. These forces cause a shift in the charges, changing the electronic structure of the molecule. As shown in Figure 2.1, this can induce a dipole in an atom or molecule. The strength of the induced dipole depends both on the strength of the applied field as well as the structure of the molecule. A stronger field will create a larger separation of the charges and a stronger dipole, but if the structure of the molecule
2.2 Electric dipoles and polarization

Figure 2.1. An atom, consisting of a positive nuclei and negative electrons, is polarized by a uniform electric field, creating a dipole.

is such that the positive and negative charges are tightly bound, an even stronger field is required to separate them.

A dielectric medium is a material that contains atoms or molecules which, when exposed to an electric field, become polarized, causing the material as a whole to become polarized. This can occur in two ways: electronic and dipolar polarization. Electronic polarization, shown in Figure 2.2, is simply the creation of induced dipoles on a larger scale.

Figure 2.2. A material consisting of non-polar atoms is polarized by a uniform electric field.
When the atoms or molecules of the material are exposed to the electric field, each one experiences a charge shift, creating a dipole. In the case shown in Figure 2.2, the evenly distributed atoms in the material are polarized by a uniform electric field. In this specific case all induced charges inside the material cancel due to the positive ends of the dipoles meeting the negative ends of other dipoles nearby. On the edges of the material, however, a net charge is found, positive at the top and negative at the bottom. These charges, known as bound charges, can also be found inside the material if the distribution of dipoles is not homogeneous. They cause an electric field inside the material, opposite to the field that caused the polarization.

Dipolar polarization occurs for materials consisting of molecules which already are dipoles. In this case, applying an electric field will cause the molecules to try to line up with the field, physically rotating to do so. An example of this can be found in Figure 2.3, showing water being polarized by a constant electric field. Before the field is applied the water molecules are randomly oriented, with no average net charge anywhere due to the random placement of the positive and negative ends of the dipoles. When the field is turned on the molecules rotate and line up with the field, creating a situation similar to the one for electric polarization, with bound charge at the top and bottom of the material. While electric polarization is practically instantaneous, dipolar polarization is comparatively slow due to the fact that the molecule has to be physically rotated.

Figure 2.3. The polar water molecules are disordered, but line up when an external electric field is applied.
CHAPTER 3

Density functional theory

The time-independent Schrödinger equation has the following form:

\[ \hat{H}\Psi = E\Psi, \]  

(3.1)

where \( \Psi \) is the wavefunction describing the system and \( E \) is the energy of the system. \( \hat{H} \) is the Hamiltonian, of the form:

\[ \hat{H} = \hat{T}_n + \hat{T}_e + \hat{V}_{nn} + \hat{V}_{ee} + \hat{V}_{ne}, \]  

(3.2)

where \( \hat{T}_n \) is the kinetic energy of the nuclei, \( \hat{T}_e \) is the kinetic energy of the electrons and \( \hat{V}_{nn}, \hat{V}_{ee} \) and \( \hat{V}_{ne} \) are Coulomb interactions among nuclei, electrons and between nuclei and electrons, respectively. Since the mass of a nucleus is far greater than that of an electron, the movement of the nuclei will be much slower than that of the electrons. This fact leads to the Born–Oppenheimer approximation, in which the nuclei are approximated as being completely stationary. This means that the kinetic energy of the nuclei, \( \hat{T}_n \), vanishes completely and the Coulomb interaction between the nuclei, \( \hat{V}_{nn} \), is constant, which, while contributing to the final energy of the system, does not need to be included when solving the Schrödinger equation. What remains is the electronic Hamiltonian:

\[ \hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V}_{ext} \]

\[ = -\frac{1}{2} \sum_i \nabla_i^2 + \sum_{i<j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,k} \frac{Z_k}{|\mathbf{r}_i - \mathbf{R}_k|}, \]  

(3.3)

where the index has been dropped from the kinetic energy of the electrons and \( V_{ne} \) has been renamed \( V_{ext} \) to indicate that the potential caused by the fixed nuclei can now be seen as an external potential. While this is certainly a great improvement
Density functional theory (DFT) provides one path towards solving the problem and it does this by replacing the $3N$ degrees of freedom of the $N$ electrons with the 3 degrees of freedom found in the electron density, $\rho(\mathbf{r})$, which relates to the wavefunctions as

$$\rho(\mathbf{r}_1) = N \int \cdots \int |\Psi(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N, \sigma_1, \cdots, \sigma_N)|^2 d\mathbf{r}_2 \cdots d\mathbf{r}_N d\sigma_1 \cdots d\sigma_N.$$  \hspace{1cm} (3.4)

The two Hohenberg–Kohn theorems [5] show that this is possible. The first theorem states that the external potential, $V_{\text{ext}}$, is, up to a constant, uniquely defined by the ground state electron density, $\rho_0$. This means that given $\rho_0$, the external potential $V_{\text{ext}}$ can be recreated. This, combined with the fact that

$$N = \int \rho(\mathbf{r}) d\mathbf{r},$$  \hspace{1cm} (3.5)

allows us to fully recreate the Hamiltonian, from which the wavefunction can be found. Thus, no information has been lost and the system is fully described by the electron density.

The second theorem states that for a given $V_{\text{ext}}$, there is an energy functional, $E[\rho]$, which has as its minimum the exact ground state energy, and the density for which this minimum is obtained is the ground state density, $\rho_0$. The variational principle can therefore be used and the ground state density can be found by minimizing $E[\rho]$ with respect to variations in $\rho$, under the constraint that the density can be derived from an $N$-electron antisymmetric wavefunction. The energy functional can be written as

$$E[\rho] = T[\rho] + V_{\text{ee}}[\rho] + \int \rho(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) d\mathbf{r} = F[\rho] + \int \rho(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) d\mathbf{r},$$  \hspace{1cm} (3.6)

where $F[\rho]$ is a universal function of $\rho$. That is, it is the same for all systems, regardless of $V_{\text{ext}}$. The major problem at this point is that this universal energy functional is not known.

This problem can be cleverly side-stepped by the Kohn–Sham ansatz [6]. Kohn and Sham proposed that the fully interacting, many-body system could be replaced by some easier to solve auxiliary system with non-interacting electrons and the same ground state density as the real system. They rewrote the universal functional as

$$F[\rho] = T_s[\rho] + J[\rho] + E_{\text{xc}}[\rho]$$  \hspace{1cm} (3.7)

where $T_s[\rho]$ is the kinetic energy of the non-interacting electrons, $J[\rho]$ is the Coulomb interaction of the electron density with itself and $E_{\text{xc}}[\rho]$ is the exchange-correlation energy, which becomes equal to

$$E_{\text{xc}}[\rho] = T[\rho] - T_s[\rho] + V_{\text{ee}}[\rho] - J[\rho].$$  \hspace{1cm} (3.8)
The exchange-correlation energy contains the difference between the real system and a non-interacting auxiliary system.

Minimizing $E[\rho]$, subject to the constraint that the electron density should integrate to $N$, gives

$$\frac{\delta E}{\delta \rho} = \frac{\delta}{\delta \rho} \left( T_s[\rho] + J[\rho] + E_{xc}[\rho] + \int \rho(r)V_{\text{ext}}(r)dr \right)$$

$$= \frac{\delta T_s[\rho]}{\delta \rho} + \frac{\delta J[\rho]}{\delta \rho} + \frac{\delta E_{xc}[\rho]}{\delta \rho} + V_{\text{ext}}(r)$$

$$= \frac{\delta T_s[\rho]}{\delta \rho} + V_{\text{eff}} = \mu,$$

where $\mu$ is the lagrange multiplier due to the constraint and an effective potential, $V_{\text{eff}}$, has been defined. What we have arrived at is the minimization of a system of non-interacting electrons, moving in an effective potential, $V_{\text{eff}}$. As long as that potential is defined as

$$V_{\text{eff}} = \frac{\delta J[\rho]}{\delta \rho} + \frac{\delta E_{xc}[\rho]}{\delta \rho} + V_{\text{ext}}(r)$$

the ground state electron density of the non-interacting system is exactly that of the interacting system. The Hamiltonian of the non-interacting system is given by

$$\hat{H} = -\frac{1}{2} \nabla^2 + \sum_i V_{\text{eff}}(r_i),$$

which is separable and the total wavefunction is just a determinant formed from the $N$ lowest solutions to

$$\left( -\frac{1}{2} \nabla^2 + V_{\text{eff}}(r) \right) \psi_i(r) = \epsilon_i \psi_i(r).$$

The electron density from this non-interacting system is given simply by

$$\rho(r) = \sum_i |\psi_i(r)|^2.$$
equations and if they do not match, a new trial density is constructed from the calculated density and the process is repeated. In the simplest case, the new trial density is just the unchanged computed density, but there are also more advanced ways of mixing the computed density with the densities of previous iterations. When the input and output densities match, the process has converged and self-consistency has been reached.

The second problem is a bit trickier and concerns the exchange-correlation expression, $E_{\text{xc}}$, found in Equation 3.10. The general form of this functional is still unknown, so some sort of approximation has to be made. Many different forms of this functional have been proposed for many different uses, some incorporating empirical parameters to various degrees. One example is the local density approximation, proposed by Kohn and Sham [6], which approximates the exchange-correlation functional as the product of the electron density and the exchange-correlation of a uniform electron gas with the same density. One possible way to improve the quality of the exchange-correlation functional is the generalized gradient approximation. Functionals that belong to this category depend not just on the electron density, but also its gradient.
Response theory, introduced by Olsen and Jørgenson [7], uses the fact that a lot of information about the excited states of a system can be obtained from the way the properties of the ground state of the system respond to an external perturbation.

The time-dependent Schrödinger equation is

\[ i \hbar \frac{\partial}{\partial t} |\psi\rangle = \hat{H} |\psi\rangle, \]

where the Hamiltonian can be split into a time-independent and a time-dependent part as

\[ \hat{H} = \hat{H}_0 + \hat{V}(t). \]

In this case we will let the time-dependent part be due to an electric field, \( F(t) \), which in the dipole approximation causes the following interaction with the system:

\[ \hat{V}(t) = -\hat{\mu}_\alpha F_\alpha(t), \]

where \( \hat{\mu}_\alpha \) is the dipole moment operator and \( F_\alpha(t) \) is the amplitude of the electric field. Einstein summation is used to indicate summation over the three Cartesian axes. The electric field can be split into a sum of contributions from specific frequencies using Fourier decomposition,

\[ F_\alpha(t) = \sum_\omega \tilde{F}_\alpha e^{-i\omega t} e^{\epsilon t}, \]

where the term \( e^{\epsilon t} \), with an infinitesimal \( \epsilon \), has been included so that the field is slowly turned on at \( t = -\infty \).
Response theory

If the time-dependent part of the Hamiltonian, $\hat{V}(t)$, is small, it can be viewed as a perturbation of the time-independent Hamiltonian, $\hat{H}_0$, which means that the solution of the time-dependent Schrödinger equation can be expressed in terms of the eigenstates to the unperturbed system,

$$\hat{H}_0|n\rangle = E_n|n\rangle.$$  \hspace{1cm} (4.5)

Assuming these states are known, we can express the state of the system at time $t$ as

$$|\psi(t)\rangle = \sum_n c_n(t)|n\rangle.$$  \hspace{1cm} (4.6)

For the case where there is no external field perturbing the system, we find that

$$c_n(t) = c_n(0)e^{-iE_n t/\hbar}.$$  \hspace{1cm} (4.7)

Based on this we can introduce the coefficients $d_n(t)$ as

$$c_n(t) = d_n(t)e^{-iE_n t/\hbar},$$  \hspace{1cm} (4.8)

isolating the changes due to the small perturbation. Inserting the $d_n(t)$ coefficients into Equation 4.6 results in

$$|\psi(t)\rangle = \sum_n d_n(t)e^{-iE_n t/\hbar}|n\rangle,$$  \hspace{1cm} (4.9)

where we can see that requiring that $d(-\infty) = \delta_{0n}$ is the same as requiring that the system start in the ground state. This description can be inserted in the time-dependent Schrödinger equation,

$$i\hbar \frac{d}{dt} \sum_n d_n(t)e^{-iE_n t/\hbar}|n\rangle = \left( \hat{H}_0 + \hat{V}(t) \right) \sum_n d_n(t)e^{-iE_n t/\hbar}|n\rangle,$$  \hspace{1cm} (4.10)

which becomes

$$i\hbar \sum_n \frac{\partial}{\partial t} d_n(t)e^{-iE_n t/\hbar}|n\rangle + i\hbar \sum_n E_n d_n(t) (-iE_n / \hbar) e^{-iE_n t/\hbar}|n\rangle$$

$$= \sum_n d_n(t)e^{-iE_n t/\hbar}E_n|n\rangle + \sum_n \hat{V}(t)d_n(t)e^{-iE_n t/\hbar}|n\rangle,$$  \hspace{1cm} (4.11)

where the second term on the left obviously cancels the first on the right, leaving

$$i\hbar \sum_n \frac{\partial}{\partial t} d_n(t)e^{-iE_n t/\hbar}|n\rangle = \sum_n \hat{V}(t)d_n(t)e^{-iE_n t/\hbar}|n\rangle.$$  \hspace{1cm} (4.12)

Multiplying both sides from the left with $\langle m|e^{iE_n t/\hbar}$ and inserting $V(t) = -\mu_\alpha F_\alpha(t)$ produces
\[ i\hbar \frac{\partial}{\partial t} d_n(t) = -\sum_n F_\alpha(t) d_n(t) e^{i(E_m - E_n)t/\hbar} \langle m|\hat{\mu}_\alpha|n \rangle. \]  
(4.13)

If we expand the coefficients \( d_n(t) \) in a power series of the electric field,

\[ d_n(t) = d_n^{(0)} + d_n^{(1)}(t) + d_n^{(2)}(t) + \cdots, \]  
(4.14)

we can see that Equation 4.13 provides a relationship between \( d_n^{(N)}(t) \) and \( d_n^{(N+1)}(t) \) as

\[ d_n^{(N+1)}(t) = -\frac{1}{i\hbar} \int_{-\infty}^{t} F_\alpha(t') d_n^{(N)}(t') e^{i(E_m - E_n)t'/\hbar} \langle m|\hat{\mu}_\alpha|n \rangle dt'. \]  
(4.15)

Introducing the transition angular frequency, \( \omega_{mn} = (E_m - E_n)/\hbar \) and inserting the Fourier decomposition of the electric field from Equation 4.4 we arrive at

\[ d_n^{(N)}(t) = -\frac{1}{i\hbar} \int_{-\infty}^{t} \sum_{\omega_1} F_\alpha^{\omega_1}(t') d_n^{(N)}(t') e^{i(\omega_{mn} - \omega_1)t'/\hbar} e^{i\epsilon t} \langle m|\hat{\mu}_\alpha|n \rangle dt'. \]  
(4.16)

We know that if the system starts in the ground state, the zero order coefficients are just \( d_n^{(0)} = \delta_{n0} \), which allows us to carry out the integration for \( d_n^{(1)}(t) \), resulting in

\[ d_n^{(1)}(t) = \frac{1}{\hbar} \sum_{\omega_1} F_\alpha^{\omega_1}(m|\hat{\mu}_\alpha|0) e^{i(\omega_{m0} - \omega_1)t'} e^{i\epsilon t}. \]  
(4.17)

We could continue at this point, using Equation 4.16 to produce increasingly complicated expressions for the higher order coefficients, but we will stop here at the first order.

We can now expand the state of the system in orders of the perturbing field in the same way we expanded the coefficients,

\[ |\psi(t)\rangle = |\psi^{(0)}(t)\rangle + |\psi^{(1)}(t)\rangle + |\psi^{(2)}(t)\rangle + \cdots, \]  
(4.18)

where each component can be written as

\[ |\psi^{(N)}(t)\rangle = \sum_n d_n^{(N)}(t) e^{-iE_n t/\hbar} |n \rangle. \]  
(4.19)

Using this we can write the expectation value of the dipole moment operator,

\[ \langle \psi(t)|\hat{\mu}_\alpha|\psi(t)\rangle = \langle \psi^{(0)}(t)|\hat{\mu}_\alpha|\psi^{(0)}(t)\rangle \\
+ \langle \psi^{(1)}(t)|\hat{\mu}_\alpha|\psi^{(0)}(t)\rangle + \langle \psi^{(0)}(t)|\hat{\mu}_\alpha|\psi^{(1)}(t)\rangle \\
+ \cdots \\
= \langle \mu_\alpha^{(0)} \rangle + \langle \mu_\alpha^{(1)} \rangle + \cdots, \]  
(4.20)
where the first term contains the unperturbed expectation value, the second contains the first order correction and so on. With the first order coefficients that we have derived, we are able, after some simplification, to write the first and second terms:

\[
\langle \mu_\alpha \rangle^{(0)} = \langle \psi^{(0)} | \hat{\mu}_\alpha | \psi^{(0)} \rangle = \langle 0 | \hat{\mu}_\alpha | 0 \rangle, \tag{4.21}
\]

\[
\langle \mu_\alpha \rangle^{(1)} = \langle \psi^{(1)}(t) | \hat{\mu}_\alpha | \psi^{(0)}(t) \rangle + \langle \psi^{(0)}(t) | \hat{\mu}_\alpha | \psi^{(1)}(t) \rangle = \sum \frac{1}{\hbar} \sum_n \left[ \frac{\langle 0 | \hat{\mu}_\alpha | n \rangle \langle n | \hat{\mu}_\beta | 0 \rangle}{\omega_{n0} - \omega_1 - i\epsilon} + \frac{\langle 0 | \hat{\mu}_\beta | n \rangle \langle n | \hat{\mu}_\alpha | 0 \rangle}{\omega_{n0} + \omega_1 + i\epsilon} \right] F^{\omega_1 n 1}_{\beta} e^{-i\omega_1 t} e^{it}. \tag{4.22}
\]

Going at this from another direction, we can expand the dipole moment of the system, \( \mu(t) \), in terms of the perturbing field

\[
\mu(t) = \mu_0 + \alpha F(t) + \frac{1}{2} \beta F(t)^2 + \frac{1}{6} \gamma F(t)^3 + \cdots, \tag{4.23}
\]

where the polarizability, \( \alpha \), first-order hyperpolarizability, \( \beta \), and second order hyperpolarizability, \( \gamma \), have been identified, in addition to the permanent dipole moment, \( \mu_0 \). We can insert the Fourier decomposition of the field into this expression, obtaining

\[
\mu_\alpha(t) = \mu_0^{\alpha} + \sum_{\omega_1} \alpha_{\alpha\beta}(-\omega_1; \omega_1) F^{\omega_1}_{\beta} e^{-i\omega_1 t} e^{it} + \frac{1}{2} \sum_{\omega_1, \omega_2} \beta_{\alpha\beta\gamma}(-\omega_2; \omega_1, \omega_2) F^{\omega_1}_{\beta} F^{\omega_2}_{\gamma} e^{-i\omega_2 t} e^{2it} + \frac{1}{2} \sum_{\omega_1, \omega_2, \omega_3} \gamma_{\alpha\beta\gamma\delta}(-\omega_3; \omega_1, \omega_2, \omega_3) F^{\omega_1}_{\beta} F^{\omega_2}_{\gamma} F^{\omega_3}_{\delta} e^{-i\omega_3 t} e^{3it} + \cdots, \tag{4.24}
\]

where \( \omega_\sigma \) is the sum of the other frequencies, i.e. \( \omega_1 + \omega_2 \) for the \( \beta \) terms and \( \omega_1 + \omega_2 + \omega_3 \) for the \( \gamma \) terms. Comparing this expression with Equation 4.22, we can identify \( \alpha_{\alpha\beta}(-\omega_1; \omega_1) \) as

\[
\alpha_{\alpha\beta}(-\omega_1; \omega_1) = \frac{1}{\hbar} \sum_n \left[ \frac{\langle 0 | \hat{\mu}_\alpha | n \rangle \langle n | \hat{\mu}_\beta | 0 \rangle}{\omega_{n0} - \omega_1 - i\epsilon} + \frac{\langle 0 | \hat{\mu}_\beta | n \rangle \langle n | \hat{\mu}_\alpha | 0 \rangle}{\omega_{n0} + \omega_1 + i\epsilon} \right]. \tag{4.25}
\]

For field frequencies in the non-resonant region, the imaginary terms in the denominators can be neglected. In addition, we note that that for \( n = 0 \), the two terms in the sum become equal but with opposite sign, and we can thus exclude the ground state from the summation. We finally arrive at

\[
\alpha_{\alpha\beta}(-\omega_1; \omega_1) = \frac{1}{\hbar} \sum_{n \neq 0} \left[ \frac{\langle 0 | \hat{\mu}_\alpha | n \rangle \langle n | \hat{\mu}_\beta | 0 \rangle}{\omega_{n0} - \omega_1} + \frac{\langle 0 | \hat{\mu}_\beta | n \rangle \langle n | \hat{\mu}_\alpha | 0 \rangle}{\omega_{n0} + \omega_1} \right]. \tag{4.26}
\]
We see here that every single excitation energy can be found inside the expression for the polarizabilities, located at the poles. The residues of these poles also provide information about the transition dipole moments between the ground and excited states, $\langle 0 | \hat{\mu}_\alpha | n \rangle$, which can be used to construct the oscillator strengths as

$$ f_{n0} = \frac{2m_e}{3\hbar^2 e^2} E_{n0} \sum_{\alpha=x,y,z} |\langle 0 | \hat{\mu}_\alpha | n \rangle|^2, $$

(4.27)

where $E_{n0}$ is the excitation energy going from the ground state to excited state $n$. The dimensionless oscillator strength is proportional to the probability of absorption and thus we have everything we need to construct a linear absorption spectrum.

A proper derivation of these response functions should include the resonant region, since that is where the poles are located. For this, see e.g. the work of Norman [8].
Response theory
While one would wish that it was only a matter of feeding the system of choice into your favourite quantum chemistry method and waiting for the result, the sad truth is that in most cases you would be waiting for a very long time. Even with the clever methods, approximations and optimizations that have appeared over the last hundred years, first principles quantum chemical calculations are still very resource demanding, even for quite small systems. The upper limit for a geometry optimization is around a few hundred atoms and a dynamics simulation is only possible for systems of a few atoms, and even then only for very short time scales. This means that unless we introduce some new approximations, many of the systems we would like to study will be far beyond the capabilities of today’s computers. A small piece of a protein from the human body can consist of thousands of atoms, and even very small systems can contain hundreds of atoms when a solvent is added. A popular way of facing this problem when dealing with the movement of atoms comes in the form of molecular mechanics.

The basic idea behind molecular mechanics is that the potential energy of a system composed of atoms and molecules can be approximated as a simple analytical function of the positions of the atoms. An atom in this case includes both the nucleus as well as some amount of electrons, assumed to be in an ideal position around the nucleus. The potential energy function is split into contributions from different kinds of interactions of two or more atoms, such as bond stretching and angle bending. The specific form of the potential energy function and the parameters used in it are known as a force field. The included interactions and the form of these can differ depending on the purpose of the force field and the accuracy required. A typical energy function can look like this:

$$E = E_s + E_\theta + E_\omega + E_{vdw} + E_{el},$$  

(5.1)
where each term is a contribution from a certain kind of interaction, each of which
is a sum of all such interactions that occur in the system.

In addition to the positions, these functions also depend parametrically on
the bonds between the atoms and the type of the atoms. Type indicates the
chemical environment of the atom, and herein lies one of the main ideas behind
force fields. It says that structures that exist in similar environments behave in a
similar manner. For example, the carbon-carbon bond in ethane is quite similar
to the two found in propane. They have similar bond lengths and the change
in potential energy that occurs when the bonds are stretched or contracted is
almost the same. In the force field, the potential energy contributions that comes
from the stretching of these three bonds therefore have the same form. This
transferability is one of the main strengths of force fields, allowing parameters
that have been developed for one system to be reused to describe similar structures
in other systems. For example, in most force fields, knowing all the parameters
needed to describe isopentane is enough to describe all alkanes.

While the carbon-carbon bonds in ethane and propane are very similar, the
carbon-carbon bond in acetylene is quite different, both in terms of bond length
and bond strength. Using the same parameters to describe all of these bonds
would not lead to a good description of the system and indicates that the division
of atom types must be made at a finer level than to simply have one atom type for
each element. Where that line is drawn, however, depends on the force field. More
atom types allow for a more nuanced description of the interactions, but requires
the creation of more parameters. The parameters can be created by fitting the
force field energy to a reference energy, obtained either from experiments or higher
level quantum mechanical calculations.

5.1 Force field terms

The following section describes the most common interactions that occur in force
fields, using the CHARMM [9] force field as an example. Three of the terms are
bonded interactions, appearing based on the structure of the molecule provided by
the user, while the other two terms are non-bonded, appearing for each combina-
tion of two atoms that are not part of the same molecule. The non-bonded inter-
actions also appear within molecules, for atoms with more than a given number
of bonds separating them – usually two. For computational reasons, non-bonded
interactions are usually only computed when the two atoms are within a certain
cut-off radius.

5.1.1 Bond stretching

The stretching or contraction of a bond from its equilibrium length causes an
increase in the potential energy of the system. This change is approximated by
the bond stretch term, which is usually represented by a simple harmonic oscillator
of the form
5.1 Force field terms

\[ E_s = \frac{k_s}{2} (l - l_0)^2, \]  
\[(5.2)\]

where \( k_s \) is a force constant, which gives the strength of the bond, \( l \) is the distance between the atoms and \( l_0 \) is the equilibrium distance between the atoms. Both \( k_s \) and \( l_0 \) are constants specific to the combination of two atom types involved in the interaction. Generally, contracting a bond produces a steeper rise in energy than stretching it. Some force fields, such as MM3 [10], account for this anharmonicity by including higher order terms of \((l - l_0)\).

![Figure 5.1. Stretching of the bond between two atoms.](image)

5.1.2 Angle bending

\[ E_\theta = \frac{k_\theta}{2} (\theta - \theta_0)^2, \]  
\[(5.3)\]

where \( k_\theta \) is a force constant, \( \theta \) is the angle formed by the atoms and \( \theta_0 \) is the equilibrium angle. Each angle formed by a combination of three atom types requires its own \( k_\theta \) and \( \theta_0 \). Again, some force fields include higher order terms of \((\theta - \theta_0)\) to account for anharmonicity.

![Figure 5.2. Distortion of the the angle formed by two atoms bonded to a common third atom.](image)
5.1.3 Torsion

![Figure 5.3. Torsional interaction occurs when twisting around a central bond.](image)

In the case where four atoms are bonded, one after the other, twisting the structure around the central bond can produce changes in the potential energy. This torsional energy is a function of the dihedral angle, measured as the angle between the first and fourth atom while looking through the bond between the second and third atom. This term is usually represented as some form of Fourier series, such as

$$E_\omega = k_\omega (1 + \cos(n\omega - \delta)), \quad (5.4)$$

where $k_\omega$ is a force constant, $n$ is the periodicity and $\delta$ is a phase shift. Equation 5.4 comes from the CHARMM force field, which allows several such terms with different multiplicity to be assigned to the same set of four atoms. Other force fields have a fixed number of terms, such as MM3, which always includes terms of multiplicity 1, 2 and 3.

5.1.4 van der Waals interaction

The non-bonded van der Waals interaction is usually described by two terms: one that is strongly repulsive and one that is weakly attractive. It can be shown that the attractive part should be proportional to $r^{-6}$, where $r$ is the distance between the atoms. The repulsive part should tend to zero as $r$ tends to infinity, and it should do this faster than the $r^{-6}$ term. Different functions are used in different force fields, but the most common forms are exponential functions and $r^{-12}$ functions, such as the one used in the CHARMM force field, where the van der Waals interaction is given by the Lennard–Jones function:

$$E_{\text{vdw}} = \epsilon \left[ \left( \frac{r_{\text{min}}}{r} \right)^{12} - 2 \left( \frac{r_{\text{min}}}{r} \right)^{6} \right], \quad (5.5)$$
5.2 Molecular dynamics

where $\epsilon$ is a parameter usually created as a mean of two parameters specific to each of the two atom types involved in the interaction and $r_{\text{min}}$ is the distance for which the energy is at a minimum. The Lennard–Jones form is often used for computational reasons since $r^{-12}$ can efficiently be calculated as $r^{-6}$ squared.

5.1.5 Electrostatic interaction

The most common way of dealing with the electrostatic interaction is to simply assign each atom type a partial charge and then use the Coulomb interaction to calculate the interaction energy:

$$E_{\text{el}} = \frac{q_i q_j}{r},$$

(5.6)

where $q_i$ and $q_j$ are the charges of the atoms. Another method, which is employed by MM3, is to assign dipole moments to each bond, based on the two atom types involved, and then compute the interaction energy between these. The drawback of this approach is that it is not able to treat ions.

5.1.6 Other terms

Different force field can add other terms to incorporate more effects due to more complex distortions of the molecular structure. Examples of these can include combinations of the stretching, bending and torsion terms, such as the stretch-bend interaction. This deals with the fact that if there are three atoms forming an angle, compressing this angle will cause the repulsion between the two end atoms to increase, increasing the bond lengths between them and the central atom.

Another additional term that can be added is the out-of-plane term. When three or four atoms are bonded to one central atom, with the equilibrium position in a plane, distorting the structure by moving the central atom out of the plane will cause a change in energy that is hard to model just from the angle bending terms. This change can be modeled by the extra out-of-plane term, which is a function of the angle between the plane and the bonds connecting the central and outer atoms.

Some force fields include specific hydrogen bond interactions, which are calculated for hydrogen donors and acceptors within a certain distance of each other. In many force fields, however, hydrogen bonding is accounted for in the other interaction terms.

5.2 Molecular dynamics

The potential energy of a system, when described by molecular mechanics, is a simple analytical function of the $3N$ coordinates of the $N$ atoms. This is easily differentiated and the acceleration for atom $j$ can be found using Newton’s second law:

$$a_j = \frac{F_j}{m_j} = -\frac{1}{m_j} \nabla_j E,$$

(5.7)
where $m_j$ is the mass of atom $j$.

If the coordinates of the atoms at a given time, $t = t_i$, are $\mathbf{r}(t_i)$, the positions at $t = t_i + \Delta t$ can be expressed as a Taylor expansion around $t = t_i$:

$$
\mathbf{r}(t_i + \Delta t) = \mathbf{r}(t_i) + \frac{\partial \mathbf{r}}{\partial t} \Delta t + \frac{1}{2} \frac{\partial^2 \mathbf{r}}{\partial t^2} \Delta t^2 + \frac{1}{6} \frac{\partial^3 \mathbf{r}}{\partial t^3} \Delta t^3 + \cdots,
$$

(5.8)

where each partial derivative is evaluated at $t = t_i$. For a set time step, $\Delta t$, a series of positions are obtained:

$$
\mathbf{r}_{i+1} = \mathbf{r}_i + \frac{\partial \mathbf{r}}{\partial t} \Delta t + \frac{1}{2} \frac{\partial^2 \mathbf{r}}{\partial t^2} \Delta t^2 + \frac{1}{6} \frac{\partial^3 \mathbf{r}}{\partial t^3} \Delta t^3 + \cdots = \mathbf{r}_i + v_i \Delta t + \frac{1}{2} a_i \Delta t^2 + \frac{1}{6} b_i \Delta t^3 + O(\Delta t^4).
$$

(5.9)

The previous time step can be obtained by replacing $\Delta t$ with $-\Delta t$:

$$
\mathbf{r}_{i-1} = \mathbf{r}_i - v_i \Delta t + \frac{1}{2} a_i \Delta t^2 - \frac{1}{6} b_i \Delta t^3 + O(\Delta t^4).
$$

(5.10)

If Equations 5.9 and 5.10 are added, the velocity and hyperacceleration terms cancel and the expression for $\mathbf{r}_{i+1}$ can be written as

$$
\mathbf{r}_{i+1} = (2\mathbf{r}_i - \mathbf{r}_{i-1}) + a_i (\Delta t)^2 + O(\Delta t^4).
$$

(5.11)

Using Equation 5.7 to compute the acceleration and neglecting the higher order terms, this allows the time evolution of the system to be calculated, step by step. The method is known as the Verlet algorithm [11], which, due to the neglected terms, has an error in the order of $\Delta t^4$.

In many cases, such as when computing the temperature of the system, it is not just important to know the positions of the atoms, but also their velocities. One way of obtaining the velocity for time step $i$ is to subtract Equation 5.10 from Equation 5.9:

$$
v_i = \frac{\mathbf{r}_{i+1} - \mathbf{r}_{i-1}}{2\Delta t} + O(\Delta t^2).
$$

(5.12)

This has the disadvantage of having a relatively large error in the order $\Delta t^2$. An alternative is given by the velocity Verlet algorithm, for which both the position and the velocity terms have an error in the order of $\Delta t^3$. It also has the advantage of not requiring the coordinates from the previous step, $\mathbf{r}_{i-1}$. The position is given by the first three terms of the Taylor expansion in Equation 5.9:

$$
\mathbf{r}_{i+1} = \mathbf{r}_i + v_i \Delta t + \frac{1}{2} a_i \Delta t^2 + O(\Delta t^3).
$$

(5.13)

Differentiating this expression with regards to time gives the expression for the velocity of the next step:
5.2 Molecular dynamics

\[
\frac{\partial r_{i+1}}{\partial t} = \frac{\partial r_i}{\partial t} + \frac{\partial v_i}{\partial t} \Delta t + \frac{1}{2} \frac{\partial v_i}{\partial t} \Delta t^2 + O(\Delta t^3),
\]

\(v_{i+1} = v_i + a_i \Delta t + \frac{1}{2} b_i \Delta t^2 + O(\Delta t^3).\) \hfill (5.14)

An expression for \(b_i\) can be found by differentiating again:

\[
\frac{\partial v_{i+1}}{\partial t} = \frac{\partial v_i}{\partial t} + \frac{\partial a_i}{\partial t} \Delta t + \frac{1}{2} \frac{\partial b_i}{\partial t} \Delta t + O(\Delta t^3),
\]

\(a_{i+1} = a_i + b_i \Delta t + O(\Delta t^2).\) \hfill (5.15)

Rearranging this we find that

\(b_i \Delta t = a_{i+1} - a_i + O(\Delta t^2),\) \hfill (5.16)

which can be inserted in equation 5.14, resulting in

\(v_{i+1} = v_i + \frac{1}{2} (a_i + a_{i+1}) \Delta t + O(\Delta t^3).\) \hfill (5.17)

Equations 5.7, 5.13 and 5.17 make up the velocity Verlet algorithm. First, Equation 5.13 is used to calculate the coordinates of the next step. These are then used to calculate the acceleration of the next step using Equation 5.7. Finally, the velocity of the current step is calculated with Equation 5.17.
Molecular mechanics
Quantum mechanics/molecular mechanics

When only a small part of a large system is of detailed interest, it can be advantageous to split the description of the system into several parts, each treated at a different level of theory. The quantum mechanics/molecular mechanics (QM/MM) method takes this approach, splitting the system into some parts that are treated using quantum mechanics and some parts that are treated using classical molecular mechanics. Generally, the part of the system of most interest is treated at the highest level, with the quality of the description decreasing as the distance to this part grows. This allows the effect of the environment on the system of interest to be included without the increased computational cost that treating the full system at a higher level would bring or the loss in quality that treating the whole system at a lower level would cause.

In this work, only systems where the molecules are fully inside one region, described at only one level of theory, will be used. While it is certainly possible to use QM/MM methods to describe systems where an atom in one region is bonded to an atom in another region, the double counting of the energy makes this a somewhat tricky problem. The systems in question are single chromophores surrounded by a polarizable solvent, so the QM/MM treatment will deal with MM molecules consisting of point charges and dipole polarizabilities. A schematic view of such a system is shown in Figure 6.1, which also includes definitions of the vectors used in this chapter.

In QM/MM theory, the Hamiltonian is given by

\[ \hat{H} = \hat{H}_\text{QM} + \hat{H}_\text{QM/MM} + \hat{H}_\text{MM}, \] (6.1)

where \( \hat{H}_\text{QM} \) is the ordinary Hamiltonian that would be used for the QM system by itself, \( \hat{H}_\text{QM/MM} \) deals with the coupling of the QM part with the MM part and \( \hat{H}_\text{MM} \) describes the MM part. \( \hat{H}_\text{MM} \) is simply the potential energy function of the
Figure 6.1. A QM/MM system, where the vectors $R_n$ and $r_i$ indicate the positions of the nuclei and electrons of the QM region, respectively, and $R_k$ and $R_d$ indicate the positions of the point charges and induced dipole moments of the MM region, respectively.

force field. The tricky part is the QM/MM coupling, which can, when the MM part only contains point charges and polarizable dipoles, be further decomposed as

$$\hat{H}_{\text{QM/MM}} = \hat{H}_{\text{vdw}} + \hat{H}_{\text{el}} + \hat{H}_{\text{pol}}.$$  \hspace{1cm} (6.2)

The first term, $\hat{H}_{\text{vdw}}$, is computed entirely classically, with each atom in the QM region being assigned a van der Waals parameter, and the interaction energy between the atoms in the QM region and those in the MM region is calculated using a function like those described in Section 5.1.4, e.g. the Lennard–Jones potential. The positions of the atoms in the QM region are taken as the positions of the nuclei, which are fixed within the Born–Oppenheimer approximation. This means that the contribution of the van der Waals term to the QM/MM Hamiltonian is constant.

The second term, $\hat{H}_{\text{el}}$, is the electrostatic interaction between the nuclei and electrons found in the QM region and the point charges found in the MM region. This is just Coulomb interaction, so the operator becomes

$$\hat{H}_{\text{el}} = \sum_{k=1}^{M} \sum_{n=1}^{N} \frac{q_k Z_n}{|R_k - R_n|} - \sum_{k=1}^{M} \sum_{i=1}^{N} \frac{q_k}{|R_k - r_i|},$$  \hspace{1cm} (6.3)

where the index $k$ sums over the point charges in the MM part, $n$ over the nuclei of the QM part and $i$ over the electrons in the QM part. The first term gives the interaction energy of the MM point charges with the nuclei in the QM part, which is constant, and the second term gives the same interaction but with the electrons.

The third term of the coupling Hamiltonian, $\hat{H}_{\text{pol}}$, is the interaction of the nuclei and electrons of the QM region with the induced dipole moments of the MM region. This has the form
\[\hat{H}_{\text{pol}} = -\frac{1}{2} \sum_{d=1}^{D} \hat{\mu}_d^{\text{ind}} \cdot \left( \sum_{i=1}^{N} \frac{-(R_d - r_i)}{|R_d - r_i|^3} + \sum_{n=1}^{N} \frac{Z_n(R_d - R_n)}{|R_d - R_n|^3} \right) \]

\[-\frac{1}{2} \sum_{d=1}^{D} (\hat{\mu}_d^{\text{ind}} - \hat{\mu}_d^{\text{MMind}}) \cdot \sum_{k=1}^{M} \frac{q_k(R_d - R_k)}{|R_d - R_k|^3} ,\]

which requires a bit explanation. The first term is the interaction of the induced dipoles with the electric field of first the electrons of the QM region and then the nuclei of the QM region. The factor of one half before the term is due to the fact that some energy is used in the creation of the dipoles. The second term comes from the interaction of the induced dipoles with the electric field of the point charges in the MM region. Here, \(\hat{\mu}_d^{\text{MMind}}\) is introduced, which is the dipole moment induced by the MM point charges. Any interaction of these dipoles and the MM region does not involve the QM region at all and should thus be included in \(\hat{H}_{\text{MM}}\), not \(\hat{H}_{\text{QM/MM}}\). For that reason it is subtracted from \(\hat{\mu}_d^{\text{ind}}\), leaving the part of the dipole caused by the QM region.

In the linear approximation, the dipole moment induced by an electric field, \(E\), is given by

\[\mu = \alpha \cdot E,\]  

(6.5)

where \(\alpha\) is the polarizability tensor, which in the isotropic case is simply a constant. This relationship can be used to describe \(\hat{\mu}_d^{\text{ind}}\) and \(\hat{\mu}_d^{\text{MMind}}\). We find

\[\hat{\mu}_d^{\text{ind}} = \alpha_d \cdot \left( \sum_{i=1}^{N} \frac{-(R_d - r_i)}{|R_d - r_i|^3} + \sum_{n=1}^{N} \frac{Z_n(R_d - R_n)}{|R_d - R_n|^3} + \sum_{k=1}^{M} \frac{q_k(R_d - R_k)}{|R_d - R_k|^3} + \sum_{d' \neq d}^{D} \frac{3(R_d - R_{d'})^T(R_d - R_{d'})}{|R_d - R_{d'}|^5} \hat{\mu}_d^{\text{ind}} - \frac{\hat{\mu}_d^{\text{ind}}}{|R_d - R_{d'}|^3} \right) \]

(6.6)

where the final sum gives the electric fields from all the other dipole moments. We note that this dependence of the dipole moments on themselves means that they have to be obtained in some self-consistent manner. We also find that

\[\hat{\mu}_d^{\text{ind}} - \hat{\mu}_d^{\text{MMind}} = \alpha_d \cdot \left( \sum_{i=1}^{N} \frac{-(R_d - r_i)}{|R_d - r_i|^3} + \sum_{n=1}^{N} \frac{Z_n(R_d - R_n)}{|R_d - R_n|^3} \right). \]

(6.7)

Equations 6.6 and 6.7 can be inserted into Equation 6.4, which can itself be inserted into Equation 6.2, providing the full coupling Hamiltonian. For a more thorough derivation of the Hamiltonian and how it may be practically applied, see e.g. the work of Kongsted et al. [12].

If one wishes to further complicate matters, it is possible to add a third layer of theory outside the MM layer [13] in the form of the polarizable continuum
model, PCM. This encloses the system in a surface, representing the border to a linear dielectric medium on the outside. The system within induces charges on the surface, which in turn interact with the system.
7.1 Absorption

The ease with which the UV-visible absorption spectrum of a material composed of a certain kind of chromophore can be computed is very much connected to both how flexible the chromophore is and the conditions for which the spectrum is to be calculated. The easiest way of calculating the absorption spectrum is to simply use response theory to calculate the excitation energies and oscillator strengths for the zero temperature optimized structure of the molecule in a vacuum. The excitation energies give the positions of the peaks while the oscillator strengths give the relative heights.

Mostly, however, it is not the spectrum at zero temperature that is of interest, but the one at room temperature. This means that the chromophores will be in some vibrational state, twisting and vibrating. For a rigid molecule, this does not pose a problem, since this movement will just cause slight distortions around the equilibrium structure. The spectrum will be broadened due to the distortions, since the chromophores in the material will be found in many structures which are slight variations around the equilibrium, but the general shape will be the same. For a flexible molecule, however, things are more complicated. If it is flexible enough, the increased temperature might cause enough motion that it switches between conformations. The material will then be made up of a mixture of the chromophore in several different conformations. These may absorb light in wildly different ways, resulting in an absorption spectrum that cannot be recreated by a simple broadening of the zero temperature spectrum. If the conformations are well defined and the probabilities of finding the molecule in one of them at a certain temperature are known, then the problem can still be solved relatively easily. The spectra for the zero temperature optimized structures of each of the conformations
Conformational averaging can be calculated and then an averaged spectrum can be created, weighted by the probability of finding the molecule in each of the conformations. This is only really possible for smaller, semi-flexible molecules. For anything larger and more flexible, with a large number of less well defined conformations, this approach is just not feasible.

One way to get around the need for explicit knowledge of the conformations and their probabilities is to involve force fields. If a high quality description of the chromophore in question exists within the force field, this can be used to gain information about the behaviour of the movement and conformations of the chromophore at room temperature. If a long enough molecular dynamics simulation is run, allowing the chromophore to move and switch conformations as it would in reality, the trajectory can be sampled and a representative collection of uncorrelated structural snapshots can be obtained. A single absorption spectrum can then be computed for each of the snapshots and an average can be created from all of them. Since the MD simulation of the chromophore is representative of the movement of the chromophores in the material, the sampling of structures from the trajectory will be representative of a sampling of the structures found in the material, and therefore also their absorption properties.

What constitutes a long enough MD simulation depends entirely on the molecule of interest. A small molecule which switches easily between conformations does not require as long a simulation as one where the transitions between conformations are few and far between. As a minimum, a trajectory of a few hundred picoseconds is required, but the longer the trajectory the better, since that will make the likelihood higher that the entire conformational space will be sampled and that the samples are uncorrelated. Running several separate MD simulations is generally a good idea. The number of structures needed for the average also depends on the molecule of interest. The more conformations that are available and the more movement around these, the more snapshots are required to create a good average. Usually, at least a few hundred snapshots are required.

This method of conformational averaging has the added benefit of being able to include the effect of the environment on the conformational distribution of the chromophore. Generally, the system of interest is not in the gas phase, but in a solvent or some other environment where it interacts with other molecules. This steric interaction can affect the behaviour of the chromophore in such a way as to change both the probabilities of moving between different conformations as well as the movement when in one of the conformations. This effect is easily added to the method by simply including the appropriate environment in the MD simulation. This will, given a good description of the environment by the force field, alter the behaviour of the chromophore in the desired way, changing the conformational distribution. The electronic effects of the environment on the absorption spectrum of each snapshot can either be neglected by removing it entirely, or included by way of QM/MM methods, as described in Chapter 6. The method of conformational averaging is especially well suited for use with QM/MM techniques, since to capture the many ways a solvent can be distributed around a solute, an averaging of calculations for many different solvent positions is used. Since a large number of snapshots are already used to capture the many structures of the solute, the
sampling of solvent positions is already included.

7.2 Emission

When a photon is absorbed by a molecule, exciting it from the electronic ground state into some higher state, the potential energy surface that the nuclei move on is changed due to the change in electronic structure. The molecule then relaxes in this state until, after some time, a photon is emitted, returning the molecule to the ground state. Due to the potential surface differences, the structure for which the absorption occurs, \( R_i \), is not generally the same as the one for which emission occurs, \( R'_i \) and the energy of absorption, \( \Delta E \), is generally also not the same as the energy of emission, \( \Delta E' \). The difference in energy between the absorbed and the emitted energy, \( \Delta E - \Delta E' \), is know as the Stokes shift and is, in most cases, positive. The reason for this is that after the molecule has been excited to a higher state it relaxes to a lower vibrational state, losing some of its energy to the surrounding solvent through its vibrations. Then, when emission occurs and the molecule is returned to the ground state, it is often deposited in some higher vibrational state, which is again relaxed and the energy is lost to the neighbouring molecules. Thus, only a part of the energy of the absorbed photon is returned in the form of the emitted photon while the rest is dissipated to the environment in the form of heat. This process is illustrated in Figure 7.1

\[ \text{Energy} \]

\[ Q \]

\[ \Delta E \]

\[ \Delta E' \]

Excited state

Ground state

Figure 7.1. A photon is absorbed, exciting a system to a higher state, where it relaxes. The system eventually emits a photon, returning it to the ground state where it relaxes again.

The conformational averaging method can be used to compute emission spectra, but it requires some extra considerations over the absorption case. First, a description of the chromophore in the excited state is needed. Force fields are built
on the idea that parts of molecules with the same structure behave in basically the same way, meaning the force field parameters used to describe the structure can be reused for every occurrence of the structure in the molecule. This argument falls apart for the excited state. Due to the changes in electronic structure, possibly only in some parts of the molecule, there is no guarantee that any of the previous parameters apply. This means that new ones have to made specifically for the molecule in question. This can be a difficult and tedious process and puts conformational averaging for emission spectra calculations firmly outside the realm of black box techniques.

Second, depending on the shape of the excited state potential energy surface, some transitions from one conformation to another may become inaccessible at room temperature. For conjugated systems it is not uncommon that single bonds become double bonds and double bonds become single bonds in the excited state. This can turn bonds, around which groups could rotate around almost freely, very rigid and vice versa, causing some conformations to become inaccessible while others become accessible. If this is the case, just running a single dynamic in the excited state will not accurately sample the conformational space. The probability of ending up in a certain conformational region in the excited state is connected to the probability that absorption occurred in that region in the ground state. The easiest way to include this behaviour is the following. When the ground state snapshot from the MD trajectory are collected, not just the positions but also the velocities of each atom are saved. These can then be used to start a separate MD simulation, in which the excited state parameters are used to describe the chromophore. This dynamic is run for a time equivalent to the fluorescence lifetime, at the end of which the structure of the chromophore is collected. If an excited state dynamic is run for each ground state snapshot an equal number of excited state snapshots are obtained. This process is illustrated in Figure 7.2.

![Figure 7.2](image-url)

**Figure 7.2.** The nuclear vibrational coordinates, $Q$, of the ground state system when excitation occurs may determine the available conformations in the excited state.
The energy of emission from state $n$ to the ground state for a certain chromophore structure, $R_i$, is exactly the same as the energy of absorption from the ground state to state $n$ for the same structure. The emission energies for each of the excited state snapshots can therefore be obtained by just calculating the absorption energies of the structures. These can then be averaged to create the emission spectrum.
Effects of solvation on p-HTAA

The effect of the solvent on the absorption spectrum of a chromophore is twofold. First, the steric interaction with the solvent will influence the movement of the chromophore, affecting the conformational distribution, and second, the electric fields caused by the solvent will polarize the chromophore, changing its electronic structure. In the method of conformational averaging, detailed in Chapter 7, the first effect is included automatically as long as the solvent molecules are present in the molecular dynamics simulation. The second effect can be accounted for by explicitly including the solvent molecules in the response theory calculations of absorption energies and oscillator strengths. This can be done either at the same or lower level of theory as the solute. Use of the QM/MM method, detailed in Chapter 6, allows the solvent to be described by a force field.

In this chapter we will focus on the electronic solvent effect and how it affects the absorption spectrum of the p-HTAA molecule. The electronic structure of p-HTAA is investigated and what implications it has for the interaction with the solvent. The electric field produced by the solvent is then computed and how this affects the chromophore is analyzed. Finally, a study of how to efficiently include the solvent effects is conducted, resulting in two methods of varying quality and computational requirements.

8.1 The p-HTAA chromophore

The p-HTAA chromophore, shown in Figure 8.1, is composed of five thiophene rings, with methyl carboxylate ion substituents (CH$_2$COO$^-$) on rings 2 and 4. The ionic substituents, though vital for the function of the chromophore, are the cause of some interesting interactions, inside and outside the molecule.
Figure 8.1. The p-HTAA chromophore

Figure 8.2 shows an isodensity surface around the p-HTAA molecule with coloring based on the electric potential. Blue indicates a positively charged area, red indicates negative charge and grey indicates a neutral area. Unsurprisingly, the dominating charge in the system is extra negative charge located at the carboxylate ion groups. Other than that, some charge has been withdrawn from the hydrogens around the thiophene rings, leaving them slightly positive. Based on the discussion of dielectric materials in Section 2.2, one would expect that if a p-HTAA molecule were placed in a polar solvent such as water, the dipole moment of the solvent molecules would, on average, be oriented towards or away from these areas.

Figure 8.3 shows a snapshot taken from an MD simulation of a rigid p-HTAA molecule surrounded by water. As we would expect, the carboxylate ions are surrounded by water molecules with the positive hydrogen sides facing inward. The hydrogens of the thiophene rings, with their much lower charge, do not appear to have had much of a discernible effect on the orientations of the surrounding water molecules in this snapshot, but it might be possible to see some average effect over many snapshots. In the case of the carboxylate ions, however, it is obvious that the orientations of the water molecules are correlated to the positions of the charges in the solute and that, when averaged, the fields caused by the water molecules will not cancel. The question is how this will affect the absorption properties of p-HTAA. Determining an efficient way of doing this will be covered in the following sections.
Figure 8.2. An isodensity plot of the p-HTAA molecule with coloring based on the potential. Red indicates negative, blue positive and grey neutral.

Figure 8.3. A snapshot taken from a room temperature MD simulation, showing the p-HTAA molecule surrounded by water.
40 Effects of solvation on p-HTAA

8.2 QM/MM study

To study the effects of the solvent we first study the effect it has in a single snapshot, taken from an MD simulation of the p-HTAA chromophore in water. All such MD simulations were carried out using the CHARMM [9] force field as implemented in Tinker [14]. First, we remove the surrounding water and calculate the absorption spectrum of the isolated chromophore, removing all solvent effects. This was done at the time dependent DFT/CAM-B3LYP [15] level of theory with the aug-cc-pVDZ [16,17] basis set. This and all other QM and QM/MM calculations in this chapter were performed using the Dalton [18] program. The counterions were completely solvated at that point in the dynamic and too far away to be of any consequence, but were included in the form of point charges with charge $1.0$ a.u. This calculation resulted in one strong excitation found at a wavelength of $436$ nm.

Second, we wish to calculate the absorption spectrum of the snapshot while including the solvent. The best, or at least highest quality, way of doing this would be to simply include every water molecule from the snapshot in the calculation and describe it all using the same level of theory as before. Considering that this would mean including more than a thousand water molecules, this is far outside current computational capabilities. What we can do is go for something that is on the edge of those capabilities. The chromophore and counterions are described as before and any water molecules within $4\,\text{Å}$ of the chromophore are also included in the QM system, but using the 6-31G [19] basis set. For this snapshot, this means including 63 water molecules in the QM part. In addition, an additional $11\,\text{Å}$ of water around the chromophore is included, described using the polarizable MM potential of Ahlström et al. [20], which describes each water molecule by three point charges ($-0.669$ a.u. on the oxygen and $0.3345$ a.u. on the hydrogens) and an isotropic dipole polarizability (9.718 a.u. on the oxygen.) This area contains 1067 water molecules for this snapshot. The excitation found in this calculation is located at $401\,\text{nm}$. A difference of $35\,\text{nm}$, or $0.25\,\text{eV}$, is very large and it is now clear that just ignoring the effect of the water is not a realistic option. However, the solvent description above is also not a realistic option, for computational reasons, at least if it is to be used in conjunction with conformational averaging. This single calculation took 60 hours on 320 cores, which is not something one would like to repeat for hundreds of snapshots. What we can do is use it as a benchmark when trying to find another, less computationally intense, model of the solvent.

We start by investigating the simplest solvent model at our disposal, a non-polarizable water model. Turning off the polarizability of the water potential leaves a collection of point charges which can be easily and efficiently included in the calculation with next to no effect on the computational time required. Using this model, we perform a series of calculations with a progressively thicker shell of water molecules surrounding the chromophore. The included number of water molecules for each shell thickness is shown in Figure 8.4, ranging from 0 to $15\,\text{Å}$. The resulting excitation wavelengths are plotted as a function of the thickness of the included shell in Figure 8.5. For the full $15\,\text{Å}$ of non-polarizable water we find that the calculated excitation wavelength is $397\,\text{nm}$, and that it
Figure 8.4. The number of included water molecules as a function of the distance from the solute.

Figure 8.5. The wavelength of the dominant transition as a function of the included layers of MM water.
converges to this value when including around 10 Å of water. We have overshot our target of 401 nm somewhat, but a reduction of error from 35 nm to 4 nm is a significant improvement. We have recovered a majority of the solvent effect using a calculation that only required around 3% of the computational time that our high quality reference calculation took.

We continue our investigation by performing the same calculations again, this time including the polarizabilities of the water molecules. The results are shown in Figure 8.5, where we can see that with a polarizable treatment of the water, the excitation wavelength converges at 403 nm and it does this slightly earlier than in the non-polarizable case, at 9 Å. We have reduced our error compared to the reference calculation by a further 2 nm, leaving just a 2 nm difference, though in the other direction. The absorption calculation for the system with the full 15 Å of polarizable water took 11% of the computational time needed for the reference calculation, which is a significant increase over the 3% needed for the system with non-polarizable water.

As a third test, we study the effect of combining polarizable and non-polarizable water molecules. Since the inclusion of the non-polarizable water molecules is basically free in terms of computational time, there is no reason not to include the full 15 Å of water surrounding the chromophore at the non-polarizable level. Starting from this, we can do calculations for an increasing shell of polarizable water molecules that replace the non-polarizable ones. The results of these calculations are shown in Figure 8.5. It should be noted that the data points for 0 Å and 15 Å are exactly the same as the 15 Å points for the studies of just non-polarizable and polarizable water, respectively. We find that the wavelength converges for around the same shell thickness, 9 Å, as the case of only polarizable water, but that it gets much closer to the converged wavelength much faster and it does so more smoothly.

Based on these studies, we can identify a cost-effective model which allows us to include the solvent effects to a high degree while not being prohibitively resource demanding. Including a 9 Å thick layer of polarizable water and a further 6 Å layer of non-polarizable water should provide reliably converged results at a relatively low computational cost. For this snapshot, this means including 352 water molecules in the polarizable region and 778 molecules in the non-polarizable region. This comes at a computational cost that is just 5% of the reference calculation, but only differs in excitation wavelength by 2 nm.

### 8.3 Other approximations

If we knew more about the reason why there is such a large difference in excitation wavelength when excluding the solvent, we might be able to find some other efficient way of dealing with it. The strong excitation that we have found is, to a large degree, localized to the conjugated backbone of the middle three thiophene rings. The carboxylate ion groups are not directly involved in the excitation, but based on their high negative charge and proximity to the part of the system that actually is, we can suspect that the polarizing effect of the ions might have an
8.3 Other approximations

effect on the results.

What we can do is to look at the electric field caused by the carboxylate ions inside the chromophore. For clarity, we do this for a highly symmetric system where all the rings of the p-HTAA chromophore are completely planar and in the trans position. The oxygens of the carboxylate ions, as well as the hydrogens of the substituent carbons, protrude symmetrically from the plane of the thiophene rings. We can approximate the electric field caused by just the carboxylate ions as that caused by point charges of charge $-0.5 \text{ a.u.}$, located at the oxygen sites. The resulting field intensities are plotted in Figure 8.6, where only the points within a certain radius of the atoms of the thiophene rings are shown. Unsurprisingly, the field is strongest closest to the ions, causing a field strength of 0.0255 a.u. at the site of the closest carbon-carbon bond in the conjugated backbone. At the equivalent bond in rings 1 and 3, the field strength is found to be 0.0065 a.u. and 0.0092 a.u., respectively.

\begin{figure}[h]
\centering
\includegraphics[width=0.6\textwidth]{figure8.6.png}
\caption{The electric field affecting the thiophene rings of the p-HTAA molecule. The upper panel shows the field caused by the carboxylate ion groups and the lower shows the field caused by both the carboxylate ion groups as well as the surrounding polarizable water. Field strengths are given in a.u.}
\end{figure}
We now wish to perform the same calculation again, but this time also include the electric field caused by the water surrounding the molecule. We do this by running a MD simulation of the rigid p-HTAA chromophore in water and collecting a number of snapshots. For each of these snapshots we perform a QM/MM calculation for the chromophore and a 15 Å thick layer of polarizable water, obtaining the induced dipole moments of each water molecule. These can then be used, together with the point charges of the water molecules, to calculate the electric field caused by the polarized water of each snapshot. These fields are then averaged in order to obtain the field caused, on average, by the surrounding water. This is then added to the field caused by the carboxylate ions, resulting in the plot shown in Figure 8.6. Just by looking at the intensity of the field we can see that it has decreased significantly in the area of the thiophene rings. The closest carbon-carbon bond now experiences an electric field of strength 0.0156 a.u., while the same bonds in rings 1 and 3 experience fields of strengths 0.0009 a.u. and 0.0010 a.u., respectively. It would appear that the primary effect of the solvent is that it negates the influence of the carboxylate ions.

This leads immediately to the possibility of approximating the solvent effects by simply removing the carboxylate groups entirely, replacing them with hydrogen atoms so that the substituents of thiophene rings 2 and 4 are simply methyl groups. This model system is shown in Figure 8.7. This is appealing for two reasons. First, it means that we would not have to include any explicit solvent in the absorption calculations at all. Second, it would remove a total of four oxygen atoms and two carbon atoms, replacing them by just two hydrogen atoms, reducing the size of the QM system. Thus, this model would be the least computationally costly by far. Performing the absorption calculation on the snapshot used in Section 8.2, we find that it requires just 1% of the computational time needed for the reference system. The dominant excitation wavelength is found at 395 nm, which is off by 6 nm from the reference value of 401 nm. Based on this single snapshot, it appears that this approximation works quite well.

![Figure 8.7. The cut down model system.](image)

Using this model we can directly study the polarizing effect that the carboxylate ions have on the rest of the molecule. Going back to the planar structure used for the study of the electric field, we can calculate the electron density both for the full molecule and the cut down model system. The density of the model system can be subtracted from that of the full system, allowing us to see the differences...
caused by the presence of the ions. The resulting density difference is shown in Figure 8.8. In this figure, the area around the carboxylate ion has been removed since there will obviously be a very high difference in density in that area. Blue indicates areas where the model system has more electrons than the full system and red indicates areas where the opposite is true. We can immediately see that these areas come in pairs, where the ion groups have polarized the system. These pairs seem mostly to be along the carbon-hydrogen bonds, with the degree of polarization depending both on the distance from the ions as well as the direction of the bond as compared to the direction of the electric field of the ions. As such, of the carbon-hydrogen bonds in thiophene ring 1 and 5, the one furthest away from the carboxylate ions is actually the ones that are the most polarized, due to the fact that the bond is almost parallel with the direction of the electric field, while the other carbon-hydrogen bonds are closer to perpendicular.

![Figure 8.8](image-url)

**Figure 8.8.** Difference in electron density obtained by subtracting the electron density of the cut down model system from that of the full p-HTAA molecule. Indicated differences in electron density are given in a.u.

### 8.4 Absorption spectra

Now that we have arrived at two models to include solvent effects for the p-HTAA chromophore, we can use these when computing absorption spectra using the method of conformational averaging. From a 400 ps dynamic of the p-HTAA molecule in water we extract 50 snapshots and calculate the absorption twice for each snapshot. Once including the full p-HTAA molecule, a 9 Å tick layer of polarizable water and a 6 Å thick layer of non-polarizable water, and once using just the cut down model system. In both cases, the QM region is described at the CAM-B3LYP level of theory using the aug-cc-pVDZ basis set. These calculations can then be used to create two averaged spectra: one from the full system with water and one from the model system. These are shown in Figure 8.9. While the
Effects of solvation on p-HTAA

spectrum obtained for the model system is blueshifted by 8 nm compared to the QM/MM spectrum, this appears to be a very systematic shift. The shapes of the spectra are almost identical and the width at half-maximum of the main peaks is also quite close. In addition, the strength of absorption, though normalized to one in the spectra, are almost identical as well. The peak absorption strength of the model system differs by just 1% compared to that of the QM/MM system.

Creating an averaged spectrum from just 50 snapshots is generally not a good idea since you cannot be sure that the conformational space has been properly sampled. Therefore, we take a look at a spectrum calculated using 300 snapshots taken from the same MD simulation as before, and with absorption calculated for the model system. The resulting averaged spectrum is shown in Figure 8.9. The main difference as compared to the 50 snapshot spectrum is that the main peak has been broadened. The shape and position, however, stay basically the same. Based on these results, one could assume that if more snapshots were added to the QM/MM spectrum, the same would happen there.

8.5 Conclusions

We have developed efficient methods for including solvent effect when calculating absorption spectra for the p-HTAA molecule. One was based simply on including the solvent explicitly in the absorption calculation using QM/MM methods. The other was based on an understanding of how the presence of the solvent affects the solute in this specific case, allowing certain parts of the p-HTAA molecule to be removed, creating a model system for which very efficient, though slightly less accurate, calculations could be performed. This first method is of course a much more general way of dealing with solvent effects, but the second shows that it is sometimes possible to find other ways of dealing with the problem by simply looking at what is going on in the system.
Figure 8.9. Theoretical absorption spectra for p-HTAA including the ten lowest excited states. Dashed lines indicate contributions from the first, second and remaining eight excited states.
Effects of solvation on p-HTAA
Bibliography


