Geometrical and Electronic Structure Characterization of Conducting Hydroquinone Substituted Polypyrrole

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Abstract

The fundamental electronic and geometric structures of charged polypyrrole and a hydroquinone substituted polypyrrole, poly(pyrrol-3-ylhydroquinone), were investigated. A single electron was constrained over different sizes of the polymer chains, a polaron, with the purpose of finding the polaron size which minimizes the excitation energy. This was done using constrained density functional theory (CDFT) by the use of a relatively newly developed source code. The polaron size for polypyrrole was not found but could be estimated to exist for a periodic chain of about sixty monomers with the polaron stretching over the entire polymer chain. The polypyrrole with changed head groups, on the other hand, seems to possess a polaron size stretching over two monomers with a periodic structure of two monomers. This indicates that this particular material could have up to thirty times better storage capacity as compared to polypyrrole. The investigation was restricted to single electron constraints, so the possibility of an even better storage capacity exists. Investigation of the band structure indicates that the charged systems possess a similarity to a doped n-type material with an occupied impurity level inside the band gap. Geometrical structures seems to transition from an aromatic form to a quinoid form upon being charged.
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1 Introduction

Early success of inorganic compounds overshadowed the interest in organic compounds. Organic electrode materials has once again become of interest, although the concept of organic polymers as electrode materials are as old as the one of inorganic ones [28]. During the last couple of decades, the number of applications of organic electronics has increased and the chemical variety of the organic components has grown tremendously [7]. In rechargeable lithium ion batteries, organic compounds allows for new possibilities, some that are not easily accessible in inorganic materials. In addition to high theoretical capacities, organic electrodes potentially offer low cost manufacturing, recyclability [28] and the potential of being a light weight and flexible material. It has even been predicted in theory that conjugated polymers might be superconductive in some unidimensional structures [26].

A lithium ion battery is in principle an electrochemical cell consisting of two electrodes, an anode and a cathode, separated by an electrolyte. Generally, for electrochemical cells, the electrolyte may be either a liquid or a solid, and the electrodes may be solid, liquid or gaseous. Interfaces using solids are problematic unless the electrolyte is a polymer or the electrode materials are very thin. In addition to these components, there may be an electrolyte-permeable separator if the electrodes are solids with a liquid electrolyte. For lithium ion batteries, however, the electrodes are generally solids. The electrolyte is responsible for transporting the ionic component of the chemical reaction between the electrodes while restricting the electric components to an external circuit. Due to the low mobility of the ionic current moving through the electrolyte, as compared to that of the electrical current through the electrodes, a cell is usually built with large area electrodes separated by a thin layer of electrolyte. Today the need for lithium ion batteries are greater than ever. There exists cell phones, laptop computers, wireless sensor systems, smart phones and many more electronic devices. All of these require good batteries and they continue to push for more operating cycles, thinner interfaces and higher storage capacities [4]. When the batteries have been depleted, one would also like a simple way to recycle them. This is when organic batteries become attractive, since there is usually a simple chemical process to retrieve the lithium inside of them, and if the materials happen to be released into the environment the chemical components are usually not harmful to the environment [11].

Polypyrrole is a conducting polymer which shows promise as electrode material and research on it, in addition on many other conductive polymers, have been conducted thoroughly [26, 29, 12, 23, 22, 13]. It has already been successfully incorporated into bio sensors [29], lithium ion batteries [26] and more applications are sure to exist. In Table 1 the properties of some polymer based batteries are shown together with two reference points consisting of lead and nickel-cadmum batteries [26].

<table>
<thead>
<tr>
<th>Battery</th>
<th>U [V]</th>
<th>W [W kg⁻¹]</th>
<th>E [W h kg⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAc/PC</td>
<td>3.7</td>
<td>3.5</td>
<td>80</td>
</tr>
<tr>
<td>PPh/PC</td>
<td>4.4</td>
<td>7.0</td>
<td>80</td>
</tr>
<tr>
<td>PPy/PC</td>
<td>3.2</td>
<td>2.8</td>
<td>55</td>
</tr>
<tr>
<td>PTh/PC</td>
<td>3.4</td>
<td>2.5</td>
<td>50</td>
</tr>
<tr>
<td>PAni/PC</td>
<td>3.3</td>
<td>0.4</td>
<td>60</td>
</tr>
<tr>
<td>Lead</td>
<td>2.1</td>
<td>1.2</td>
<td>40</td>
</tr>
<tr>
<td>Ni-Cd</td>
<td>1.35</td>
<td>-</td>
<td>35</td>
</tr>
</tbody>
</table>

Table 1: Electronic properties of batteries with a given polymer as cathode/anode material. PAc is polyactetylene, PPh is polyphenylene, PPy is polypyrrole, PTh is polythiophene, PAni is polyaniline and PC is propylene carbonate. All the above batteries are used in conjunction with a LiClO₄/Li electrolyte material, with the exception of the last two which are there for reference as non-organic batteries [26].

Among other conducting polymers, polypyrrole and its derivatives are highly conducting, stable in oxidized states and possess interesting properties in their reduced states. The reduced state has been shown to be unstable in air, but can be made stable by the use of an inert atmosphere. This makes the reduced state hard to use in practice. Further, they have a simple synthetic process and the monomers initially used in the chemical process are highly available. The neu-
tral polypyrrole is a dielectric which has a bandgap of about 4\,eV which, upon oxidation, reduces to a gap of less than 2.5\,eV \cite{26}. Oxidised polypyrrole is also reactant with air which, upon reaction, reduces the conductivity of the material. This flaw can however be avoided by the use of bulky organic anions \cite{26}, which has shown to reduce this reactant tendency. Comparing different organic polymer based lithium ion batteries gives insight into the good properties of polypyrrole in these applications.

The quest for stable organic polymers with small, or vanishing, bandgaps are nothing new. One widely used method for achieving this, is by substitution of already well known polymers in the field of synthetic metals. Polypyrrole is one such candidate, and by adding handles to the material the electronic properties might shift for the better. Depending on how the electrons distribute themselves in the substituted material, one of two geometric configurations might occur. If the electrons tend towards a localization along the polypyrrole backbone, geometrical structure till transition towards a quinoid form. If the opposite holds, then the geometrical structure will tend towards a aromatic form. The definition of these structures are defined as in Figure 1 \cite{3}.

![Figure 1: Two valence bond isomers of the parent polymer, as well as the labeling of bonds used herein.](image)

In this report we intend to use the handle material as a possible electron storage unit. When polypyrrole is charged, it stores all of the charge in the pentagon rings. By introducing handles the possibility of storing some, and hopefully all, of the additional charge in the extensions exist. This would leave the electronic structure of the polypyrrole backbone unchanged, while potentially increase the storage capacity of the material, which would make the material more attractive for battery applications.

Herein a hydroquinone substituted polypyrrole, poly(pyrrol-3-ylhydroquinone), is investigated at uncharged and charged conditions using numerical methods. Previous experimental studies on the material has been done which shows the material to be a good conductor and to be stable at uncharged and charged conditions \cite{9}.

Density functional theory (DFT) has many strengths and different applications, but despite that it suffers from from numerous problems. Traditional exchange-correlation (XC) functionals suffer from different degrees of self-interaction errors (SIE), which causes problems when the electron density is derived from these. The shortcomings of traditional XC functionals imply that methods such as the time dependent DFT suffers from them as well. This report explores one method, namely constrained DFT (CDFT). CDFT has proven a valuable tool for determining electronic structures. At some level it offers a partial workaround to some of the problems with the SIE, but it also provides a route to diabatic electronic states \cite{8}. The electrical properties of polypyrrole is mostly known through experimental means. Using CDFT the electrical properties of the two polymers at charged conditions are calculated, which could give insight to the relative properties of the chosen materials.

2 Theory

2.1 The Hartree-Fock Approximation

The Schrödinger equation is the modern theory of describing quantum systems, but it’s generally difficult to solve for large systems using numerical methods. One of the first attempts of solving it for arbitrary systems was made long ago, and is called the Hartree-Fock (HF) approximation. This method still uses
wave functions for figuring out the electronic wave functions of a quantum system. First, note that the eigenenergy of a quantum system is given by

\[ E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle, \]  

(1)

where \( \hat{H} \) is the hamiltonian of the system and \( \Psi_0 \) is the ground state wave function. The wave function is a variable depending on the spatial coordinates of all the quantum objects in the system. For molecular systems one can, with good accuracy, treat the nuclei as classical particles and only focus on finding the quantum description of the electrons. Finding a function depending on, usually, a large number of electrons is a daunting task, one which one would like to simplify. The idea of the HF picture is to replace the wave function by something which can simplify the equations. The one used in the HF approximation is given by

\[ \Psi = \Phi_{SD} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\vec{r}_1) & \cdots & \chi_N(\vec{r}_1) \\ \vdots & \ddots & \vdots \\ \chi_1(\vec{r}_N) & \cdots & \chi_N(\vec{r}_N) \end{vmatrix}, \]  

(2)

which is called the Slater determinant. The functions inside the determinant are usually called single electronic wave functions and are defined by a real valued function \( \phi \) and a spin dependent object, usually a 2x1 matrix, \( \sigma \) through the relation \( \chi(\vec{x}) = \phi(\vec{r})\sigma(s) \). One can see that this determinant satisfies the asymmetrical condition \( \Psi(\cdots, \vec{r}_i, \cdots, \vec{r}_j, \cdots) = -\Psi(\cdots, \vec{r}_j, \cdots, \vec{r}_i, \cdots) \) as is required by fermions. Asserting the Slater determinant as the wave function to get an expression for an energy yields the HF energy

\[ E_{HF} = \sum_i^N \int \chi_i^*(\vec{r}_1) \left( -\frac{1}{2}\Delta_i - \sum_A \frac{Z_A}{r_{1A}} \right) \chi_i(\vec{r}_1) d\vec{r}_1 
+ \frac{1}{2} \sum_i^N \sum_j^N \int \int |\chi_i(\vec{r}_1)|^2 \frac{1}{r_{12}} |\chi_j(\vec{r}_2)|^2 d\vec{r}_1 d\vec{r}_2 
- \frac{1}{2} \sum_i^N \sum_j^N \int \chi_i(\vec{r}_1) \chi_j^*(\vec{r}_1) \frac{1}{r_{12}} \chi_j(\vec{r}_2) \chi_i^*(\vec{r}_2) d\vec{r}_1 d\vec{r}_2, \]  

(3)

where \( N \) refers to the number of electrons in the system, \( M \) is the number of atomic sites, \( Z_A \) is the number of protons at a given atomic site and \( r_{ij} \) denotes the distance \( |\vec{r}_i - \vec{r}_j| \). These energies correspond to a kinetic energy, coulomb energy from the nucleus-electron interactions, electron-electron interaction and a exchange energy which does not have a classical interpretation. This can be written in a very compact form that resembles the Schrödinger equation. Each single electronic wave function can be written in the form

\[ \hat{f}_i \chi_i = \varepsilon_i \chi_i, \]  

(4)

where \( \varepsilon_i \) is the energy associated with the single electronic wave function and the operator \( \hat{f} \) is defined by

\[ \hat{f}_i = -\frac{1}{2}\Delta_i - \sum_A \frac{Z_A}{r_{1A}} + \sum_j^N \int |\chi_j(\vec{r}_2)|^2 \frac{1}{r_{12}} d\vec{r}_2 
- \sum_j^N \hat{K}_j(\vec{r}_1). \]  

(5)

The exchange \( \hat{K}_j \) can only be defined through it acting on a spin orbital and is defined by

\[ \hat{K}_j(\vec{x}_1)\chi_i(\vec{x}_1) = \int \chi_j^*(\vec{x}_2) \frac{1}{r_{12}} \chi_i(\vec{x}_2) d\vec{x}_2 \chi_j(\vec{x}_1). \]  

(6)

All in all, the Schrödinger equation in the HF approach for the ground state energy falls down into the new form.
\[ \hat{H}_{HF} \Phi_{SD} = E_{HF}^{0} \Phi_{SD} = \sum_{i} N_{i} \Phi_{SD} = \sum_{i} \varepsilon_{i} \Phi_{SD}. \quad (7) \]

This approach seems very good, but when it comes to application it yields none exact results and energies larger than that of the ground state energy. This is because the Slater determinant is only an approximation of the true wave function. The missing energy is usually called the correlation energy, \( E_{C} \). Modern approaches for solving the Shrödinger equation builds on top of trying to describe quantum systems through means of electron densities [27]

### 2.2 The Hohenberg-Kohn Theorems

Using electron densities for describing quantum systems has to be approached with care. First of all it has to be proven that systems can be uniquely determined by the electron density. This was first done in 1964 by Hohenberg and Kohn [27, 14].

#### 2.2.1 The First Theorem

This theorem deals with the existence of a unique potential given an electron density, which in terms also fixes the Hamiltonian. The proof follows from an argument of contradiction. Assume now that two different external potentials yields the same electron distribution. Lets call the first external potential \( V_{ext} \) and the second one \( V'_{ext} \). These potentials characterize their own respective Hamiltonian and hence their own electronic wave functions called \( \hat{H} \), \( \hat{H}' \), \( \Psi \) and \( \Psi' \) respectively. Given one of these states, one can use the other state as trail wave function to the other one, which must then be different from the ground state energy of the respective Hamiltonian. This can be written as

\[ E_{0} < \langle \Psi' | \hat{H}' | \Psi' \rangle = \langle \Psi' | \hat{H} | \Psi' \rangle + \langle \Psi' | \hat{H}' - \hat{H} | \Psi' \rangle \quad (8) \]

and

\[ E_{0}' < \langle \Psi | \hat{H}' | \Psi \rangle = \langle \Psi | \hat{H} | \Psi \rangle + \langle \Psi | \hat{H}' - \hat{H} | \Psi \rangle, \quad (9) \]

where \( E_{0} \) and \( E_{0}' \) are the ground state energies of the two different systems. Now, given that the electron densities are the same for the two systems, the only difference in the Hamiltonian is the external potential which then yields

\[ E_{0} < E_{0}' + \int \rho(\vec{r}) \left[ V_{ext} - V'_{ext} \right] d\vec{r} \quad (10) \]

and

\[ E_{0}' < E_{0} - \int \rho(\vec{r}) \left[ V_{ext} - V'_{ext} \right] d\vec{r}, \quad (11) \]

where \( \rho \) is the electron density. By adding the two equations, one gets the following

\[ E_{0} + E_{0}' < E_{0} + E_{0}', \quad (12) \]

which is a contradiction. Therefore the external potential must uniquely determine the electron density [27, 14].

#### 2.2.2 The Second Theorem

From the first theorem it follows that one can describe a quantum system using electron densities, but it says nothing of what can be said about the ground state. The second theorem deals with this, and states that the ground state energy is obtained only when the ground state density \( \rho_{0}(\vec{r}) \) is asserted. This is proven by the the use of the variational principle and the fact that each electron density \( \tilde{\rho}(\vec{r}) \) defines its own Hamiltonian and hence its own wave function \( \tilde{\Psi} \). Then by properties of the ground state

\[ \langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle \geq \langle \Psi_{0} | \hat{H} | \Psi_{0} \rangle, \quad (13) \]

which in terms of densities then yields

\[ E \left[ \tilde{\rho} (\vec{r}) \right] \geq E \left[ \rho_{0} (\vec{r}) \right]. \quad (14) \]

Therefore only the ground state density yields the ground state energy [27, 14].
2.3 Density Functional Theory

Changing from the approach of using wave functions to using densities instead seems very appealing, but has proven problematic to implement in practice. The issues of using pure density methods for determining the electronic structure is that the kinetic energy as a functional of the electron density is unknown and that the electron-electron interaction is unknown. Kinetic energy as a functional of electron density is problematic to derive, but is also a physically vague quantity. As for the electron-electron interaction the problem is that the classical quantity contains a nonphysical self-interaction, but also neglects to take into account phenomena such as antisymmetry of wave functions. Instead the modern way of doing DFT is by using the Kohn-Sham approach [27, 14].

2.3.1 The Kohn-Sham Approach

Considering that the pure density approach is difficult to implement, the next best step would be to use a hybrid method. The exact electronic energy functional is defined by

\[ E[\rho] = T[\rho] + E_{\text{elec}}[\rho] + E_{ncl}[\rho], \]

where \( T \) is the kinetic energy functional, \( E_{\text{elec}} \) is the energy from electron-electron interaction and \( E_{ncl} \) is the energy of the electron-nucleus interaction. The idea of Kohn and Sham (KS) was to rewrite the expression in terms of known classical terms and gather everything, which is unknown, in to a separate term as

\[ E[\rho] = T_S[\rho] + J[\rho] + E_{\text{elec}}[\rho] + E_{ncl}[\rho], \]

where \( T_S \) is the kinetic energy as in the HF approximation, \( J \) is the classical electron-electron interaction energy and \( E_{\text{exc}} \) is the so called exchange-correlation interaction energy as defined by

\[ E_{\text{exc}}[\rho] = (T[\rho] - T_S[\rho]) + (E_{\text{elec}}[\rho] - J[\rho]). \]

The problem has hence fallen on finding a functional for the exchange-correlation energy. As for the rest of the terms, they are written as they where in the HF approximation. Inserting the terms as they have been defined yields the energy of the KS approach, which can be written

\[ E[\rho] = T_S[\rho] + J[\rho] + E_{\text{exc}}[\rho] + E_{ncl}[\rho] \]

\[ \begin{align*}
&= \frac{1}{2} \sum_i \langle \varphi_i | \Delta | \varphi_i \rangle \\
&\quad + \frac{1}{2} \sum_i \sum_j \int \int \frac{1}{r_{12}} |\varphi_i(r_1)|^2 |\varphi_j(r_2)|^2 d\mathbf{r}_1 d\mathbf{r}_2 \\
&\quad + E_{\text{exc}}[\rho] - \sum_i \int \sum_A \frac{Z_A}{r_{1A}} |\varphi_i(r_1)|^2 d\mathbf{r}_1,
\end{align*} \]

(18)

where \( \varphi_i \) denotes different single electron orbitals, \( N \) is once again the number of electrons in the system, \( M \) is the number of different atomic sites and \( Z_A \) is the number of protons associated with an atomic site. As was done in the HF approximation, this can once again be written in a compact form. In alignment with the Schödinger equation, the KS orbitals in equation (18) can be rewritten as

\[ \left( -\frac{1}{2} \nabla^2 + \frac{\rho(\mathbf{r}_2)}{r_{12}} - \sum_{A=1}^{M} \frac{Z_A}{r_{1A}} + V_{xc}[\rho(\mathbf{r}_1)] \right) \varphi_i(\mathbf{r}_1) = \varepsilon_i \varphi_i(\mathbf{r}_1), \]

(19)

where \( \varepsilon_i \) is the eigenenergy associated with the electronic wave function \( \varphi_i \) [27, 14].

2.3.2 Exchange and Correlation

The classical electron-electron potential contains some neglecting facts. For example, consider a system containing only a single electron. That leads to a non-zero electron density which, by means of the classical potential, interacts with itself. This error is called the self interaction error (SIE). Consider further what happens when two electrons occupy the same space. Electrons with different spin should be able to occupy the same quantum state, while electrons with the same spin should not. The classical
coulomb potential does not take this into consideration, which poses a problem. These are two effects that should be taken into account in the exchange-correlation potential. The exchange potential is what needs to be described to take into account the Pauli principle, and the correlation potential is what needs to be taken into account for correcting the SIE [27].

2.3.3 The Generalized Gradient Approximation

Search for an expression of the exchange-correlation energy has been a topic of great research for years, but has yet to yield an exact expression. So far there exists a vast number of different approximations for this potential and they all come with different trade-offs. The Generalized Gradient Approximation (GGA) is an attempt on an XC potential, which builds on top of the Local Density Approximation (LDA) and empirical data. The two components of the GGA is the exchange and correlation energies and can generally be written like

\[ E_{\text{GGA}}^{\text{XC}}[\rho_\alpha, \rho_\beta] = E_{\text{GGA}}^\text{X}[\rho_\alpha, \rho_\beta] + E_{\text{GGA}}^\text{C}[\rho_\alpha, \rho_\beta], \]  

(20)

where \( \alpha \) and \( \beta \) denotes the different spin components of the electron densities. The exact form of the GGA is in fact only a well informed guess with appropriate boundary conditions which has shown to work well in applications. The exchange part of the GGA is written like

\[ E_{\text{GGA}}^\text{X} = E_{\text{LDA}}^\text{X} - \sum_\sigma \int F(s_\sigma) \rho^{4/3}(r) d\vec{r}, \]  

(21)

where \( s_\sigma = \frac{\nabla \rho_\sigma(\vec{r})}{\rho_\sigma^{4/3}(\vec{r})} \).

As for the form of the functional \( F \) there exist two different classes of popular choices that are usually used. The first type of classes are based on the one first forwarded by Becke [27, 2], and then there is the second class for which one of the representative are the one put forward by Perdew [27, 17]. As for the correlation part of the XC energy there is no exact form to be used. There exists a vast ocean of these correlation energies, but two popular choices of these correlation energies are the ones by either Perdew [27, 15] or the one developed by Lee and Yang [27, 10].

2.3.4 Solving the Kohn-Sham Equations

Given the number of equations and the nature of the Kohn-Sham equations, solving the system of equations can be a daunting task. Instead the functional nature of the equations are usually transitioned into a parameter form by the use of basis functions. Basis functions can be chosen to be anything in practice, but they are usually chosen to be similar to different orbital types. Using basis functions, the electron orbitals can be written as

\[ \varphi_i = \sum_{\mu=1}^K c_{\mu i} \eta_\mu(\vec{x}), \]  

(24)

where \( K \) is the cardinality of the basis set, \( c_{\mu i} \) are real numbers and \( \eta_\mu \) are the basis functions of the basis set. Given the Kohn-Sham equations on the form (19), the equation can be written as

\[ \hat{f}_i \sum_\nu c_{\nu i} \eta_\nu = \varepsilon_i \sum_\nu c_{\nu i} \eta_\nu. \]  

(25)

Multiplying by a basis function \( \eta_\mu \) and performing integration yields the form

\[ \sum_\nu \mu \nu c_{\nu i} \varepsilon_\nu = \sum_\nu \mu \nu c_{\nu i} \eta_\mu. \]  

(26)

where the new terms are defined as

\[ F_{\mu \nu} = \int \eta_\mu \hat{f} \eta_\nu d\vec{r}, \]  

(27)

and

\[ S_{\mu \nu} = \int \eta_\mu \eta_\nu d\vec{r}. \]  

(28)
This can more compactly be written as a matrix equation which falls on the form

\[ FC = SC\varepsilon, \]  

(29)

where \( \varepsilon \) is a diagonal matrix of the orbital energies \( \varepsilon_i \). This very closely resembles a eigenvalue problem, with the exception of the matrix \( S \). This problem can be altered by transforming the basis into an orthogonal set, which would reduce the matrix \( S \) into an identity matrix. The remaining part is then a simple eigenvalue problem, with the exception of the dependence of the matrix \( C \) in \( F \). This is often tackled by an iterative method with the mentioned steps involve. This self dependence is why the procedure of solving the electron orbitals is usually called a self consistent field (SCF) method [24].

2.3.5 Constrained Density Functional Theory

The imposed constraint in CDFT can be one of many and is in general formalized with the notation

\[ E(N) = \min_{\rho} \max_{V} W[\rho, V; N], \]  

(30)

where

\[ W[\rho, V; N] = E[\rho] + V \left( \sum_{\sigma} \int w^\sigma(\vec{r})\rho^\sigma(\vec{r}) - N \right). \]  

(31)

Here the function \( w^\sigma(\vec{r}) \) is a weigh function that defines the property of interest, \( V \) is a Lagrangian multiplier and \( N \) is the number of electrons in the system. For example, to define a constraint for the spin components the choice \( w^\alpha = w^\beta \) would be appropriate and to define a constraint on the magnetization, the choice \( w^\alpha = -w^\beta \) would instead be made. In equation (30) and (31) there is a great deal of flexibility for constraining the ground state, which in practice becomes overwhelming. There exists atomic charge schemes to limit the number of constraints while being flexible enough to describe a variety of states. The goal of a variety of differently used prescriptions can be cast on the form

\[ N_A = \int w_A(\vec{r})\rho(\vec{r})d\vec{r}, \]  

(32)

where \( N_A \) is the charge constrained to an atomic site and \( w_A \) is a partition function. One such prescription which is simple to understand is the Becke population scheme. Here one partitions the space into Voronoi cells centered around the atomic sites and defines a set of functions that are nearly unity inside the cells, nearly zero outside and smoothly connects the two regions. Constrains can them be written on the form

\[ N_A = \int w_A^{\text{Becke}}(\vec{r})\rho(\vec{r})d\vec{r} \]  

(33)

where \( w_A^{\text{Becke}} \) is the so called Becke function. All of these prescriptions comes with different trade offs and some are more accurate for different systems. When a prescription has been chosen it is simple to come up with a weight function, \( w_F \), that constrains a number of charges to a fragment \( F \) as

\[ N_F = \sum_{I \in F} N_I = \int \sum_{I \in F} w_I(\vec{r})\rho(\vec{r})d\vec{r} = \int w_F(\vec{r})\rho(\vec{r})d\vec{r}, \]  

(34)

where

\[ w_F(\vec{r}) = \sum_{I \in F} w_I(\vec{r}). \]  

(35)

These prescriptions are simple to extent spin polarized constraints by adding more Lagrangians that depend on the spin polarization of the charges and in the end everything falls on the form

\[ W[\rho, V_F, V_{F'}; N_F, M_{F'}] = E[\rho] \]  

\[ + \sum_{F} V_F \left( \int w_F(\vec{r})\rho(\vec{r}) - N_F \right), \]  

\[ + \sum_{F'} V_{F'} \left( \int w_{F'}(\vec{r})\rho(\vec{r}) - M_{F'} \right), \]  

(36)

\[ E(N_F, M_{F'}) = \min_{\rho} \max_{V_F, V_{F'}} W[\rho, V_F, V_{F'}; N_F, M_{F'}]. \]  

(37)

A implementation of CDFT would need to find a
charge density which satisfies this condition and to illustrate how CDFT does this, consider equation (36) on the form

\[ E(N_k) = \min_{\rho} \max_{V_k} W[\rho, V_k, N_k] \]
\[ = \min_{\rho} \sum_k V_k \left( \int \sum_{\sigma} w_k^\sigma \rho^\sigma d\vec{r} - N_k \right) \] (38)

where \( \sigma \) is used to denote the spin of the electron. By requiring that (38) is stationary with respect to variations in the electron orbitals, subjected to their orthonormality yields the new expression

\[ \left( -\frac{1}{2} \nabla^2 + \int \frac{\rho(\vec{r}_2)}{r_{12}} d\vec{r}_2 - \sum_{A=1}^{M} \frac{Z_A}{r_{1A}} + V_{xc}[\rho(\vec{r}_1)] \right) + \sum_k V_k w_k^\sigma (\vec{r}_1) \phi_{i\sigma}(\vec{r}_1) = \varepsilon_{i\sigma} \phi_{i\sigma}(\vec{r}_1). \] (39)

This is very similar to the Kohn-Sham equations, with the exception of the new introduced Lagrangian multipliers and the weight functions. From this it becomes apparent how CDFT controls the constrained charges and spins. The potential is altered in such a way that the new ground state satisfies the desired constraints. These constraint potentials are not yet fully specified. The parameters \( w_k \) are given as parameters to the system, but the Lagrangian multipliers \( V_k \) are only implicitly defined by the constrained fragments. Consider now what happens when the derivative of equation (38) with respect to the different Lagrangian multipliers is made. Then these constraints become clear and the results of this is

\[ \frac{dW}{dV_l} = \sum_{\sigma} \sum_i w_i^\sigma \frac{\delta W}{\delta \phi_{i\sigma}^*} + \frac{\partial W}{\partial V_l} = \sum_\sigma \int w_i^\sigma \rho^\sigma d\vec{r} - N_i \] (40)

where the condition \( \frac{\delta W}{\delta \phi_{i\sigma}^*} = 0 \) is used. Note that after differentiation the only remaining constraint is the one depending on the index \( l \). The separate conditions of equation (39) and (40) imply that \( V_l \) and \( \rho \) must be determined self-consistently to make \( W \) stationary. This is somewhat different than a minimizing or maximization problem, but one can show that in CDFT the solution of the problem can be found by alternating between minimizing with respect to the electron density \( \rho \) and maximizing with respect to the Lagrange multipliers. To investigate how this is done, note that equation (39) determine a unique set of orbitals \( \phi_i[V_l] \). These orbitals define an electron density \( \rho[V_k] \). This density can be used as input into \( W \) and in this manner one can consider \( W \) as a function of only \( V_l \). It is then possible to show that the second order derivatives of this function is given by

\[ \frac{\partial^2 W}{\partial V_k \partial V_l} = \sum_{\sigma} \sum_i \int w_i^\sigma(\vec{r}) \phi_{i\sigma}(\vec{r}) \frac{\delta \phi_{i\sigma}(\vec{r})}{\delta V_k} w_i^\sigma(\vec{r}) d\vec{r} d\vec{r} \]
\[ = \sum_{\sigma} \sum_i \int w_i^\sigma(\vec{r}) \phi_{i\sigma}(\vec{r}) \frac{\phi_{i\sigma}(\vec{r})}{\varepsilon_{i\sigma} - \varepsilon_{a\sigma}} \phi_{a\sigma}(\vec{r}) w_i^\sigma(\vec{r}) d\vec{r} d\vec{r} \]
\[ = 2 \sum_\sigma \sum_i \sum_{a>N_\sigma} \frac{\langle \phi_{i\sigma} | w_i^\sigma | \phi_{a\sigma} \rangle \langle \phi_{a\sigma} | w_i^\sigma | \phi_{i\sigma} \rangle}{\varepsilon_{i\sigma} - \varepsilon_{a\sigma}}, \] (41)

where the index \( i \) is summed over all the occupied orbitals and the index \( a \) is summed over the virtual orbitals. This means that the above expression is non-positive which means that the corresponding hessian matrix is non-positive definite as can be seen by

\[ \sum_{k,l} V_k \frac{\partial^2 W}{\partial V_k \partial V_l} V_l = \]
\[ 2 \sum_\sigma \sum_i \sum_{a>N_\sigma} \frac{\langle \phi_{i\sigma} | \sum_{k=1}^{m} V_k w_k^\sigma | \phi_{a\sigma} \rangle}{\varepsilon_{i\sigma} - \varepsilon_{a\sigma}} \leq 0. \] (42)
pression it can then be seen that the expression $W$ is globally concave, which means that this problem can be solved using a Newton method. A solution to the diabatic system can then be implemented using an outer SCF solver and an inner constraint loop. The outer loop is used to determine the minimizing electron density and the outer loop works to find the maximum with respect to the constraints [8].

3 Method

3.1 Software Specification

For the simulations different software was used. In the primary step of the Merck molecular force field simulation, Avogadro version 1.1.1 was used [6]. As for the Born-Oppenheimer relaxation of molecular structure simulations, Siesta version 3.2 patch level 4 was used [25]. CDFT simulations where made using SMEAGOL version 1.2 in conjunction with Siesta version 2.0.2 [21, 20, 18, 19] and some post graphics visualization was made using XCrysDen version 1.5.60 [1].

3.2 Initial Conditions

The considered polymers are shown in Figure 2 and Figure 3.

![Figure 2: Polypyrrole monomer.](image)

![Figure 3: Monomer of the polypyrrole with additional head group.](image)

The primary step in the investigation was to obtain a ground state geometrical and electronic band structure. First a Merck molecular force field [5] simulation was done to get an estimate of the initial structure. This was done for two monomers of each of the chosen substitutes. When a reasonable structure was achieved, basis vectors to span the crystal structures where chosen so that bonds seemed to be preserved between different crystal sites and atoms did not overlap. Polypyrrole was built quite compact initially, while the substituted polypyrrole was built such that the handles overlapped reasonably well. Then using Born-Oppenheimer molecular structure relaxation simulations the adiabatic structures where achieved. This was done using periodic boundary conditions (PBC) together with an XC potential as described by Perdew, Becke and Ernzerhof (PBE) [16] at an energy cut-off at $200\text{Ry}$, a convergence tolerance of $2 \cdot 10^{-4}$ and a function basis set of DZP. Later, due to the inability of the software to use the DZP basis set in the diabatic simulations, the parameters for the substituted polypyrrole were changed to a SZP basis set and a energy cut-off at $120\text{Ry}$ for the sake of comparison. The resulting structures for polypyrrole and the substituted polypyrrole were repeated with different number of monomers in groups of two and used as input to the CDFT simulations. The actual number of monomers to use was just a matter of guessing.

3.3 Constrained Molecular Structure Relaxation

Initially the number of monomers to do each individual simulation on were chosen to be in the range
of fourteen to eighteen monomers long with the DZP basis set. These monomer groups where then used together with a PBC so that every repeat unit contained a set of fixed number of monomer. The polarons where restricted to occupy all possible multiples of two monomer groups in these repeat units. This was initially done for systems where the atomic sites where not allowed to move. For polypyrrole this was no problem, but for the extended material structure the simulation times became unreasonably long. Hence this material was restricted to a length of two to ten monomers with the basis set SZP and an energy cut-off at 120\(\text{Ry}\). For the sake of consistency, polypyrrole was simulated for lengths in the range of six to ten monomer long periodic chains, in addition to the previous ones, with the DZP basis set and energy cut-off at 200\(\text{Ry}\). Once these simulations were done, data was collected and plotted. Following the spatially static simulations, new simulations where the atomic sites were allowed to change was made and charges were constrained in the same way as in the previous cases. Some of the simulations tended to flatten the systems, so the simulations were restricted to periodic cells which either stretched and compressed the system in the direction of the polymer chains. The chosen constrained variable consisted of a single spin up electron distributed over the entire polaron. Once the simulations were done, the data was collected and analyzed.

4 Results

4.1 Adiabatic Relaxation

For comparisons sake the initial geometrical and electronic band structures are included. Polypyrrole and the polypyrrole with hydroquinone head groups were simulated with a DZP basis set at a cut-off energy of 200\(\text{Ry}\). Later stages of the diabatic relaxation of the extended material required a SZP basis set and a cut-off energy at 120\(\text{Ry}\) to finish within a reasonable time frame, so the same was done for the adiabatic system. This is so that the same errors that occurs in diabatic systems, also occurs in the adiabatic system.
This, however, does not tell us any specifics about the systems. To get some more specifics, the lengths of different bonds where calculated. In Figure 7 and Figure 8 the bond lengths of the polypyrrole and the substituted polypyrrole systems in their respective ground states using the DZP basis are shown. As for the substituted material in its ground state using a SZP basis, the bond lengths are shown in Figure 9.

The associated density of states for polypyrrole are shown in Figure 10 and for the substituted material it
is shown in Figure 11 as obtained using a DZP basis set. The density of states for the substituted system using the SZP basis set is shown in Figure 12. Positive curves are the density of states for spin up electrons and negative curves are the same, but for spin down electrons. The actual bandgaps are measured from the eigenenergy points, so the actual bandgap might be perceived smaller from the figures.

Figure 10: Density of states for relaxed polypyrrole structure using a DZP basis set. The Fermi energy is estimated to be $-2.94 \text{eV}$ with a bandgap of approximately $2.01 \text{eV}$. The positive curve is the density of states for spin up electrons and the negative curve is the density of states for spin down electrons.

Figure 11: Density of states for the relaxed substituted polypyrrole structure using a DZP basis set. The Fermi energy is estimated to be $-4.15 \text{eV}$ with a bandgap of approximately $2.04 \text{eV}$. The positive curve is the density of states for spin up electrons and the negative curve is the density of states for spin down electrons.

Figure 12: Density of states for the relaxed substituted polypyrrole structure using a SZP basis set. The Fermi energy is estimated to be $-5.57 \text{eV}$ with a bandgap of approximately $2.03 \text{eV}$. The positive curve is the density of states for spin up electrons and the negative curve is the density of states for spin down electrons.

4.2 Spatially Static Diabatic Condition

Previous to any relaxation, the excitation of the free energies of the respective systems where evaluated. The excitation energies were calculated by the use the formula $E_{exc} = E_{F_{free}} - E_0 * n$, where $n$ is the total length of the periodic chain, in terms of groups of two monomers, and $E_0$ is the energy of the estimated ground state energy of a single uncharged monomer group. A second order degree polynomial was interpolated over the points for an estimate of the polaron size. For the substituted polypyrrole, the two shortest chains could not be interpolated between in this way due to the requirement of at least three points, so they have only been plotted in the graph. For the polypyrrole the results are shown in Figure 13 and for the substituted material the results are shown in Figure 14.
Figure 13: Excitation of free energy as a function of the number of constrained groups of two monomers for the polypyrrole system. Solid lines are interpolated second order polynomials and the points are calculated excitation of free energies. The range of the points and interpolated lines shows the number of monomers in groups of two for the periodic cell.

Figure 14: Excitation of free energy as a function of the number of constrained groups of two monomers for the substituted polypyrrole system. Solid lines are interpolated second order polynomials and the points are calculated excitation of free energies. The range of the points and interpolated lines shows the number of monomers in groups of two for the periodic cell.

The interpolated lines were extended to where they reached their turning point. Interpolation of these points gave some insight into the behavior of how the polaron sizes transitioned between different periodic polymer sizes. The resulting curves are represented in Figure 15 and 16 for the polypyrrole and the substituted polypyrrole respectively.

Figure 15: Polaron corresponding to free energy minimum and its dependence on the length of the periodic structure for polypyrrole.

Figure 16: Polaron corresponding to free energy minimum and its dependence on the length of the periodic structure for the substituted polypyrrole.

Having an estimate for the polaron sizes, the minimum excitation energies for different lengths of the periodic structure could be estimated. These values and the estimated minimum excitation energies are shown in Figure 17 and 18 for the respective polymers.

Figure 17: Estimated minimum free energies for a given length of the periodic structure for polypyrrole. The polaron size corresponding to the global free energy minimum is estimated to exist on a periodic structure consisting of about 60 Polypyrrole monomers.
4.3 Spatially Free Diabatic Relaxation

For this section it should be mentioned that all the results here are not converged to the same accuracy. However, most results yield a very noticeable pattern. As in the case with the spatially static atomic sites, the excitation of free energies are expressed for the relaxed diabatic cases. The schematics for calculating the values are done as in the previously mentioned case and the values are shown in Figure 19 and Figure 20 for polypyrrole and the substituted polypyrrole respectively.

It is quite obvious from these curves that polypyrrole has an expected polaron size outside the range of the calculations, and the substituted polypyrrole still seems to have a polaron size that is as small as possible. An estimate for the polaron size for polypyrrole can not be made in the same way as in the spatially static case due to the distributions of points. Instead, since the minimum excitation energy is always achieved with a polaron size stretching over the entire periodic polymer, the energies can be interpolated at those points. Also worth mentioning is that those systems were the quickest to converge, so the reliability of those values are better than the other ones. The resulting curve can be seen in Figure 21.

Figure 18: Estimated minimum free energies for a given length of the periodic structure for the substituted polypyrrole. The polaron size corresponding to the global free energy minimum is estimated to exist on a periodic structure consisting of two of the substituted polypyrrole monomers.

Figure 19: Excitation of free energy as a function of the number of constrained groups of two monomers for the polypyrrole system. Solid lines are interpolated second order polynomials and the points are calculated excitation of free energies. The range of the curves denotes the number of monomers in groups of two for the periodic cell.

Figure 20: Excitation of free energy as a function of the number of constrained groups of two monomers for the substituted polypyrrole system. Solid lines are interpolated second order polynomials and the points are calculated excitation of free energies. The range of the curves denotes the number of monomers in groups of two for the periodic cell.

Figure 21: Minimum excitation of free energy for a given length of the periodic structure for polypyrrole. The polaron size corresponding to the global free energy excitation minimum is estimated to exist on a periodic structure consisting of about 62 polypyrrole monomers.

Once again the estimated polaron size for polypyr-
role corresponding to the global energy minimum is outside the range of the calculations. The same estimations are meaningless for the substituted polypyrrole since it is possible to see where the minimum is. Another property of interest is the Fermi energy and the size of the bandgap. The Fermi energies as a function of the polaron size are shown in Figure 22 and 23 for the polypyrrole and the substituted polypyrrole respectively. The bandgaps are divided in terms of spin up and the spin down electronic states. The bandgaps for the spin up electrons are shown in Figure 24 and 25; and the bandgaps for the spin down electronic states are shown in Figure 26 and 27 for the respective polymers.

Figure 22: Fermi energy as a function of the polaron size for polypyrrole. The range of the curves denote the number of monomers in groups of two for the periodic cell.

Figure 23: Fermi energy as a function of the polaron size for the substituted polypyrrole. The range of the curves denote the number of monomers in groups of two for the periodic cell.

Figure 24: Bandgap, with respect to the spin up electron states, as a function of the polaron size for polypyrrole. The range of the curves denote the number of monomers in groups of two for the periodic cell.

Figure 25: Bandgap, with respect to the spin up electron states, as a function of the polaron size for the substituted polypyrrole. The range of the curves denote the number of monomers in groups of two for the periodic cell.

Figure 26: Bandgap, with respect to the spin down electron states, as a function of the polaron size for polypyrrole. The range of the curves denote the number of monomers in groups of two for the periodic cell.

Figure 27: Bandgap, with respect to the spin down electron states, as a function of the polaron size for the substituted polypyrrole. The range of the curves denote the number of monomers in groups of two for the periodic cell.
Figure 27: Bandgap, with respect to the spin down electron states, as a function of the polaron size for the substituted polypyrrole. The range of the curves denote the number of monomers in groups of two for the periodic cell.

Note that these bandgaps are much smaller than those in the case of their corresponding uncharged cases, which could indicate that the charged polymers conduct current better than that of the uncharged systems (so-called self-doping mechanism). Given these electronic properties, it would be interesting to see how this implementation of CDFT distributes the electron densities along the polymer chains and that the calculations do what they actually are supposed to do. From the the structure relaxation simulations, these scalar fields are available and plotted by subtracting the spin up electron density by the spin down electron density and picking an appropriate isosurface value. The resulting density distributions for the periodic six monomer long polypyrrole chains are shown in Figure 28 and the corresponding systems for the substituted polypyrrole is shown in Figure 29.
In the case for both polymers the constrained charge is localized around the expected monomers. For the substituted polypyrrole the charge is distributed more or less evenly on both the backbone and the handle, but when the charge is constrained over all six monomers, the majority of the charge seems to be localized on the backbone. So far only the electronic structures and properties have been displayed, but also the geometric structure was looked into. The stretching of the individual polymers was investigated as a function of the polaron size. The stretching is defined by the relation $\frac{l_1}{l_0} - 1$, where $l_0$ is the length of the periodic cell previous to charging and $l_1$ is the length of the periodic cell after the system has been charged. In Figure 30 and 31 this quantity is presented for polypyrrole and the substituted polypyrrole respectively.

![Figure 30: Relative stretch of periodic cell for polypyrrole as a function of the number of constrained monomers in groups of two. The range of the curves denote the number of monomers in groups of two for the periodic cell.](image)

![Figure 31: Relative stretch of periodic cell for the substituted polypyrrole as a function of the number of constrained monomers in groups of two. The range of the curves denote the number of monomers in groups of two for the periodic cell.](image)

This does tell us something about how the material expands when it is subjected to a charge. It is strange that polypyrrole seems to expand the length of the periodic structure since the polymer is expected to be in a quinoid form, which should then contract the bonds connecting the pentagons. To investigate why this happens, the relative stretching of the bonds in the carbon chains for the shortest periodic polypyrrole chain are calculated. This is due to the fact that the stretching is at its most extreme there. Since the system is expected to fall into a quinone isomer state, the elongation is plotted with respect to how much the system moves into such a state. The results are shown in Figure 32.
Figure 32: Stretching of carbon bonds. The numbering of the x-axis goes from the first carbon in the chain and follows it along to the last one. The first three points belong to the first monomer and the fourth point is the carbon bond connecting two monomers, as is shown in Figure 1. The Blue curve is for the system with four constrained monomers and the red one is for the one with six constrained monomers. Positive values denotes that the bonds have moved in alignment to a quinoid form and negative value denotes that it has moved to a aromatic form.

Figure 33: Angles measured to explain the stretching of polypyrrole chain.

Figure 34: Change in angle between the carbon triplets as denoted in Figure 33. The numbering of the x-axis goes from the first carbon triplet in the chain and follows it along to the last one.

As it seems the charged systems makes the angles smaller relative to the uncharged system, which allows for the possibility of stretching of the periodic cell. Now given all the data that is at hand we can make an estimate of how the materials in their ground states behave.

4.4 Ground State Properties for Diabatic Systems

Given the scope of this investigation, some conclusions regarding the properties of these materials can be made. For polypyrrole the configuration which achieved the minimum excitation energy was for a periodic structure consisting of eighteen monomers with a single extra electron shared between them. The substituted polypyrrole, on the other hand, reached its minimum excitation energy for a periodic structure of two monomers with an additional electron shared between the two monomers. Estimated density of states for polypyrrole and the substituted material together with estimated Fermi energies and bandgaps are shown in Figure 35 and 36 respectively.
For these systems the induced charge in the respective cases, seem to act like a n-type dopant. Both of the systems have a single induced occupied electronic state in the spin up density curves, which seems to be what is left of the bandgap of the original electronic structure. Now it would be interesting to see how the additional charge changes the original geometry in each of the respective structures. Noticeably, the size of the achieved structure of polypyrrole is too large to be include in a report as this. Instead the bond lengths of the formed carbon chains are shown. Luckily, the same issue is not the case for the substituted polypyrrole and the change in different bond lengths are shown in Figure 39. For polypyrrole the measurement is restricted to the change in bond length in the carbon chain, as is shown in Figure 37. Polypyrrole in this case seems to be fairly periodic, so the difference in bond length for the first two monomers is shown in Figure 38.

Figure 35: Density of states for relaxed polypyrrole structure corresponding to the achieved system with lowest excitation energy. The Fermi energy is estimated to be $-1.37\,\text{eV}$ with a bandgap of approximately $0.13\,\text{eV}$ for the spin up electrons and a bandgap of approximately $1.73\,\text{eV}$. The positive curve is the density of states for spin up electrons and the negative curve is the density of states for spin down electrons.

Figure 36: Density of states for the relaxed substituted polypyrrole structure with a periodic structure of two monomers and a electron constrained over the two monomers. The Fermi energy is estimated to be $-3.93\,\text{eV}$ with a bandgap of approximately $0.72\,\text{eV}$ for the spin up electrons and a bandgap of approximately $1.91\,\text{eV}$ for the spin down electrons. The positive curve is the density of states for spin up electrons and the negative curve is the density of states for spin down electrons.

For these systems the induced charge in the respective cases, seem to act like a n-type dopant. Both of the systems have a single induced occupied electronic state in the spin up density curves, which seems to be what is left of the bandgap of the original electronic structure. Now it would be interesting to see how the additional charge changes the original geometry in each of the respective structures. Noticeably, the size of the achieved structure of polypyrrole is too large to be include in a report as this. Instead the bond lengths of the formed carbon chains are shown. Luckily, the same issue is not the case for the substituted polypyrrole and the change in different bond lengths are shown in Figure 39. For polypyrrole the measurement is restricted to the change in bond length in the carbon chain, as is shown in Figure 37. Polypyrrole in this case seems to be fairly periodic, so the difference in bond length for the first two monomers is shown in Figure 38.

Figure 37: Change in length of different carbon bonds for polypyrrole consisting of eighteen periodic monomers with a electron constrained over them all. The numbering goes from bond $a$ to $d$ as in Figure 1 and is repeated. A positive value indicates that the bond has moved to its quinoid form. Units are denoted in Ångström.

Figure 38: Change in length of different bonds for polypyrrole in the first two monomers of the periodic structure consisting of eighteen monomers with a electron constrained over the entire periodic chain. Units are denoted in Ångström.
Figure 39: Change in length of different bonds for the substituted polypyrrole consisting of two periodic monomers with an electron constrained over them both. Units are denoted in Ångström.

Both polypyrrole and the substituted polypyrrole moves towards its quinoid form, but polypyrrole has a stronger tendency to do so of the two. To get a better feeling of why this becomes the case, it would interesting to see where the extra electrons are located. Polypyrrole is too long to be plotted along all the eighteen monomers, but the systems is quite periodic so only the first two monomers are shown. Isosurfaces of electron abundance is shown in Figure 40 and Figure 41 for the respective excited ground state systems.

Figure 40: Electron spin density for the polypyrrole system with eighteen periodic monomers and a single electron constrained over them all. Only the first monomer pair is shown. Red isosurfaces denote an abundance of spin up electrons and blue isosurfaces denotes an abundance of spin down electrons.

Figure 41: Electron spin density for the substituted polypyrrole system with two periodic monomers and a single electron constrained to them both. Red isosurfaces denote an abundance of spin up electrons and blue isosurfaces denotes an abundance of spin down electrons.

This shows that the electrons in polypyrrole is mostly located at the bonds which are contracted, which is what is intuitively needed to explain the behavior of the bonds. For the substituted polypyrrole,
there is an abundance at the handles. Even there they do not seem to be restricted between the bond sites, but next to them. This is fairly similar to the \( p \)-orbital states.

5 Discussion

The results gives some insightful behavior to the respective polymers. Even though the results seem to indicate that the chosen polypyrrole substitute is the better choice of polymers for battery applications, there is room for doubt.

Given that the precision of the extended material structure relaxation simulations are done using both a smaller cut-off energy and a less accurate basis set, both the geometry and electronic property behavior could be nowhere close to the actual properties or the behavior of the properties. Higher accuracy simulations should be performed to see if this behavior is consistent with the currently apparent behavior. This would take considerable computational resources since the given results in them self required several days to come to the current results; and given the time spent in the queue for this given investigation, more accurate results could not be acquired in a reasonable time frame.

Also the results behavior in the far polaron length limit is not really known and one can imagine that when the periodic polymer chains become really long that the curves becomes less than ideal. The chances of being able to do numerical investigations of such systems that yield reasonable results are very unlikely. It might be possible to gain this length artificially by constraining a fraction of an electron on the chain. A polaron size of sixty monomers would be achieved by constraining 0.2 electrons on a periodic structure of twelve monomers.

Another note on structure, one can probably criticize the idea of long straight polymer chains. It is, for example, possible to imagine a structure of polymer chains which are twisting, like deoxyribonucleic acid (DNA), which could yield some very different results. Consideration of different structures is something which could be further looked into. If it turns out that the investigated polypyrrole substitute does not maintain its chemical structure upon charging, it still might be possible to use it in battery applications.

Playing around with the parameters and the constraints to allow for dynamic super cells is something that should be looked into as well, since that allows for further insight into how the material expands during certain distributions. It is also possible that this could change the entire electronic structure, since orbitals could be allowed to not overlap as much as they currently are. For polypyrrole this does not affect the situation as much since for those systems the chains are a little bit further apart from each other as compared to the substituted systems.

6 Conclusion

We have manage to use a relatively new source code in its early stages to calculate the molecular and electronic band structure for polypyrrole and polypyrrol-3-ylhydroquinone) in a charged diabatic state. Investigations such as these has been done previously, but most of them has been restricted to surface charges. The code utilized in this investigation has been applied to molecular structures with the intent of finding charged systems in their lowest energy states. This opens up for new possibilities to investigate properties and behaviors of materials in states which has previously been inaccessible.

Excitation energies for different sizes of charged segments with different lengths of periodic polymers were studied. The relations between the minimum excitation energy and its relationship to the length of the periodic structure was nearly quadratic which made an estimate for the global minima very simple to find. Polypyrrole was estimated to exist for periodic structure of about sixty monomers with an electron distributed over all the monomers. Poly(pyrrol-3-ylhydroquinone), on the other hand, yielded the minimum excitation energy at a periodic structure of two monomers and a single electron constrained to the two monomers. That means that the handles substituted in the material actually seem to uphold the intended function. It is quite surprising though
that the investigated substituted polypyrrole material can maintain its chemical structure, even in the highly charged state.

Bonds for the polypyrrole system behaved as was predicted by previous reports. Additional electrons transitioned from the pentagon chains to their respective quinoid isomer state. The localization of the additional charge in the hydroquinone rings made the substituted material backbone less affected by the excitation, which could possibly make the material more stable than its non-substituted counterpart.

Bandgaps of the two materials actually behaved the same. Both the materials acted like a usual n-type doped material with an impurity level introduced, into what seems to be the remains of the initial bandgaps in the respective initial uncharged states. This is interesting, considering how the conventional doping mechanism is described in modern material theory; usually the introduction of a second material is what allows for a valence electron to jump between different sites, causing the doping like behavior for the n-type doping process. Here instead the introduced charge in the system participates in a so-called self doping process.

Behavior of Fermi energy yields a pattern similar to parabolas in the different periodic structures. For polypyrrole the Fermi energy seems to be decreasing with the longer periodic structures and for the substituted polypyrrole the Fermi energy seems to be decreasing for shorter structures.

Poly(pyrrol-3-ylhydroquinone) seems to allow for higher storage capacity. This is given by the fact that the substituted polypyrrole material seems to be able to store a single electron on two monomers in the polymer chain, as compared to one electron on up to sixty monomers as is estimated for polypyrrole. This means that the investigated material could allow for up to thirty times higher storage capacities as compared to polypyrrole. The number could actually be higher, but the scope of this investigation only allowed for single electron constraints. Other possible issues related to the material still needs to be investigated.

One further comment on the results are the fact that the substituted polypyrrole materials was quite sensitive in simulations. On accident, one of the structures was built so that one of the hydrogen atoms bound to one of the oxygen atoms got caught up by one of the carbon atoms in the pentagon backbone. This completely changed the molecular structure and made the simulation never converging. Upon fixing, convergence was reached with a lower free energy minimum than that of the never converging one. There exists very similar chemical structures to that of poly(pyrrol-3-ylhydroquinone). Further investigation of possible chemical transitions should be made.
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