Exploiting excited-state aromaticity for the design of efficient molecular motors: A quantum chemical study

Author: André Engberg

Supervisor: Prof. Bo Durbeej
Examiner: Dr. Marcus Ekholm
Abstract
In this work, a study of a recent approach in the design of light-driven molecular motors is presented. The approach involves enabling part of the motor to obtain aromatic-like properties through photoexcitation, and is found to significantly facilitate the rotary motion by reducing the barriers normally present in the excited-state potential energy surfaces of rotary motors.

1. Introduction
On October 25th, 1984, Nobel Laureate Richard Feynman gave a lecture where he presented his philosophy on thinking in unconventional ways. During his lecture, called “tiny machines”, Feynman asked, “How small can you make machinery?” and continued talking about the possibilities of constructing machines on the nanometer scale. He was convinced that this is possible since such machines already exist in nature, giving bacterial flagella as an example (corkscrew-shaped macromolecules which when they spin make bacteria move forward).

Molecular motors are molecules that can perform net mechanical work using energy absorbed from an external source, this mechanical work can either be translational or rotational. A rotary motor must be able to complete a 360-degree unidirectional rotation, clockwise (CW) or counter-clockwise (CCW), around a bond connecting the different parts of the motor. The rotary motion is controlled by the molecular chirality, determining the preferred direction [1]. For example, a total 360-degree rotation can be obtained by consecutive photoisomerization steps (see Figure 3).

The first step towards molecular machinery was taken by a French research group led by the chemist Jean-Pierre Sauvage in 1983, when they constructed a molecular chain with two ring-shaped molecules held together by a weaker mechanical bond (see Figure 1). This made it possible for the rings to move relative to one another more freely than in the presence of a strong covalent bond, which is a hallmark of molecular motors.

Another significant result in Sauveage’s work was that in previous attempts to create mechanically interlocked molecules, researchers had achieved a yield of a few per cent at best. Because of the method which utilizes a copper ion in the synthesis (see Figure 1), the yield now increased to 42 per cent which gave new life to the field of topological chemistry. Here, we also wish to shine light on the fact that in the 1950s and 1960s there had been reports from several research groups regarding the synthesis of molecular chains, however the amount produced were very small and the methods far too complex.

Another scientist who also constructed molecular motors from weakly bound subunits is Fraser Stoddart, who with his research group in 1991 built an open ring with a positive charge and long rod with a negative charge. From the Coulomb attraction between the open ring and the rod Stoddart was able to thread the ring on to the molecular axle. He had now created, also with high yield, a ring-...
shaped molecule that is mechanically attached to the axle. When adding heat, the ring was able to jump back and forth between two electron-rich parts of the axle (see Figure 2). In 1994 his research group had this movement under control which in previous attempts had been random.

**Figure 2**: Schematic representation of Fraser Stoddart’s molecular machine.

Importantly, the rotary motion by molecular motors cannot be random, because then the motors will rotate with equal probability in either direction (CW or CCW). Therefore, the discovery by Ben L. Feringa in 1999 of a way to achieve unidirectional rotary motion was a significant breakthrough.

Feringa’s design of a first-generation light-driven molecular motor, a so-called overcrowded alkene, is composed of two flat chemical structures that are joined with a double bond between two carbon atoms (see Figure 3). When the molecule is exposed to a pulse of ultraviolet light, one of the motor halves rotates relative to the other around the central double bond by 180 degrees, followed by a thermal stabilization step of the molecule. With the next light pulse the molecule rotates yet another 180 degrees, followed by a second thermal stabilization step, thus completing a full revolution.

**Figure 3**: First-generation overcrowded alkene motor developed by Ben Feringa. The lower half of the motor is referred to as a stator, usually adsorbed on to a surface, and the upper half is referred to as a rotor. The two halves are defined in such way to describe the function of each half and the relative rotary motion between them.
However, the first motor of this kind wasn’t exactly fast due to the rate-determining thermal steps, which occurs on much longer timescales than the photoisomerization steps, but Feringa’s research group optimized them so that in 2014 the motor could rotate at a speed of 12 million revs per second. Here, it should be noted that the overall rotary speeds and efficiency of light-driven molecular motors are strongly dependent on energy input, quantum yield, medium effects and surface confinement (The quantum yields of the photochemical steps are equal to the number of reactive photons divided by the total number of photons absorbed) [2].

To overcome the barriers in the thermal isomerization processes of the first-generation light-driven rotary motors, second-generation motors were designed to achieve more uniform rotation. By uniform rotation we imply that the rate with which the two thermal barriers are overcome have been significantly increased, and that both thermal steps in the rotational mechanism are completed within approximately the same time, which previously had not been the case.

In the second-generation motor design, the lower stator half is derived from a symmetric tricyclic unit which makes the thermal barriers nearly the same in both rotary half cycles, thus reducing the effort to accelerate the overall rotation rates. The difference in the design of stator and rotor can be done in a selective fashion to favour various functions. Ben Feringa’s research group found application for these motors and were able to use them to spin a 20-micrometer long glass cylinder (10,000 times bigger than the molecular motor itself), and in 2011, built a four-wheel drive nanocar. These three scientists, Sauvage, Stoddart and Feringa, later received the 2016 Nobel Prize in Chemistry for their ground-breaking contribution to the development of molecular machinery [3].

In this work, we investigate the function of a potential light-driven rotary molecular motor through quantum chemical calculations performed using Hartree-Fock (HF) theory for ground states and the configuration-interaction-singles (CIS) method for excited singlet states. Specifically, we show that our motor is powered through facile photoisomerization steps around a carbon-carbon double bond (see Figure 4 for the predicted reaction of the motor). The design of the motor is motivated by recent studies in the subject of excited state aromaticity applied to molecular rotary motors [1,4].

In our motor, one of the halves contains a cyclopentadiene group (see Figure 6), which is not aromatic by itself but by adding an electron to the group it becomes a cyclopentadienyl group which fulfils the requirements of an aromatic compound. We believe that excited state aromaticity in our motor can be induced by using an amino group, a well-known electron donor group, to facilitate an electron donation to the cyclopentadiene group, here used as our electron-withdrawing group. From scan optimisation calculations of the molecule in its excited state we wish to explore whether the rotation of the molecule is unidirectional, and from bond length alternation calculations (BLA) investigate whether the cyclopentadienyl part of the molecule does exhibit aromatic properties. Thereby, we will be able to assess whether excited state aromaticity facilitates the photoisomerization steps of light-driven rotary molecular motors. The study of excited state aromaticity applied on molecular rotary motors is of interest since it has shown promise in increasing the photochemical quantum yield, although this aspect is not the priority here [1].
Aromaticity

In this chapter we will go through the fundamentals of aromaticity which is one of the cornerstones in the foundation of this thesis.

2.1 Ground state aromaticity

In the early days of organic chemistry, the word aromatic was used to describe fragrant substances such as benzene (from coal distillate) (see Figure 5) or benzaldehyde (from cherries, peaches and almonds), although it was soon realized that substances classified as aromatic differ from most other organic compounds in their chemical behaviour. Today, the association of aromaticity with fragrance has long been lost, and we now use the word aromatic to describe the class of compounds which fulfil certain criteria [5].

Aromatic compounds can be distinguished from other compounds with their properties such as being planar, cyclic and having delocalised $\pi$-electrons as prescribed by Hückel’s rule. Aromatic compounds are known to be very stable and unreactive. Hückel’s rule, formulated by Erich Hückel, asserts that ground states of planar monocyclic rings (also referred to as annulenes) containing $4n + 2$ $\pi$-electrons ($n = 0,1,2,3,...$) have closed shells of delocalized electrons, due to sp$^2$-hybridization, and substantial resonance energies. Contrarily, ground state annulenes with $4n$ $\pi$-electrons are destabilised, antiaromatic. The most commonly used example of an aromatic compound is benzene (see Figure 5) [6].

![Figure 5: Benzene with its corresponding resonance structures.](image)

There are also monocyclic species that bear either a positive or a negative charge. Some of these ions show unexpected stabilities that suggest that they are indeed aromatic ions. For example, cyclopentadiene (see Figure 6) is not aromatic but it’s possible to convert it to an anion by treatment with a moderately strong base. The resulting anion, cyclopentadienyl anion, is very stable due to sp$^2$-hybridization at every carbon and complete delocalisation [6].
Figure 6: Cyclopentadiene

2.2 Excited state aromaticity
Aromaticity have commonly been used to explain the outcome of thermal chemical reactions. Molecules prefer to adjust themselves to acquire a lower energy, stability. Compared to ground state aromaticity, excited state aromaticity hasn’t been used as much to predict the outcome of chemical reactions, especially photoinduced excited state aromaticity. Analogously to Hückel’s rule, Baird’s rule, formulated by N. Colin Baird, states that the lowest triplet state, $T_1$, of $4n\pi$ annulenes are aromatic while $(4n + 2)\pi$ annulenes are antiaromatic, this is reversed from Hückel’s rule which is for the ground state. Baird’s rule has later been generalised to conclude that annulenes with $4n + 2\pi$-electrons are aromatic in states with even total spins and antiaromatic with odd total spins, while the opposite applies to $4n\pi$ annulenes [4].

3 Quantum theory for computational chemistry
In this chapter we will go through the theory used in our calculation for ground states and excited states of our system.

3.1 The time-independent, non-relativistic Schrödinger equation
All equations are presented in atomic units.

$$\hat{H}\psi = E\psi$$  \hspace{1cm} (1)

$\hat{H}$ is the system Hamiltonian, $\psi$ is the wave function of the system and $E$ is the energy eigenvalue.

3.2 Hamiltonian operator
The general Hamiltonian to the many-body problem can be constructed using Coulombs law to describe the electrostatic potential between charged particles, and the Laplacian to describe the kinetic energy, i.e.

$$\hat{H} = -\sum_i \frac{\nabla_i^2}{2} - \sum_k \frac{\nabla_k^2}{2M_k} - \sum_i \sum_k \frac{Z_k}{r_{ik}} + \sum_{i<j} \frac{1}{r_{ij}} + \sum_{k<l} \frac{Z_kZ_l}{r_{kl}}$$ \hspace{1cm} (2)

$i$ and $j$ run over electrons, $k$ and $l$ run over nuclei. $Z_k$ is atomic number, $M_k$ is the ratio between the nuclear mass and electron mass, $r_{ab}$ is the distance between particle $a$ and $b$ and $\nabla_a^2$ is the Laplacian for particle $a$. Obs, the summation $i<j$ is to avoid double counting. The Hamiltonian can be rewritten as in a shorter notation, i.e.

$$\hat{H} = \hat{T}_e + \hat{T}_n + \hat{V}_{en} + \hat{V}_{ee} + \hat{V}_{nn}$$ \hspace{1cm} (3)

$\hat{T}_e$ and $\hat{T}_n$ is the kinetic energy operators for electrons and nuclei respectively. $\hat{V}_{en}$, $\hat{V}_{ee}$ and $\hat{V}_{nn}$ is the potential energy operator for the electron-nuclear attraction, electron-electron repulsion and nuclear-nuclear repulsion.
3.3 The Born-Oppenheimer Approximation

The term $\hat{V}_{en}$ in the Hamiltonian prevents us from writing the wave-function as a product of an electronic wave-function and a nuclear wave function, which is usually preferable. Since the mass of a proton is roughly 1836 times the mass of the electron it’s reasonable to approximate the nuclei to be fixed in space and that the electronic ‘relaxation’ with respect to nuclear motion is instantaneous. These approximations in a sense removes $\hat{T}_n$ and sets $\hat{V}_{nn}$ to be constant. Since the wavefunction is invariant to the appearance of constant terms, the total energy eigenvalue is merely shifted by $\hat{V}_{nn}$, i.e. after our calculations are done, we simply add this term to achieve the total energy eigenvalue. From these approximations we arrive to the following Hamiltonian

$$\left(\hat{H}_\text{el} + \hat{V}_{nn}\right)\psi_{el} = E_{el}\psi_{el}$$

$$(\hat{H}_\text{el}) = -\sum_i \frac{\nabla_i^2}{2} - \sum_i \sum_k Z_k \frac{1}{r_{ik}} + \sum_{i<j} \frac{1}{r_{ij}}$$

$$\hat{V}_{nn} = \sum_{k<l} \frac{Z_k Z_l}{r_{kl}} = \text{Constant}$$

The subscript ‘el’ stands for electronic and emphasizes the invocation of the Born-Oppenheimer approximation. We will hereafter drop the subscript ‘el’ since all the electronic wave functions hereafter are electronic wave functions.

3.4 Construction of Trial Wave Functions and the LCAO basis set approach

Even though there have been some simplifications to the many-body Schrödinger equation, it is still considerably troubling, mainly due to the correlation between individual electrons. A much simpler approach is needed. Consider systems with only one electron, then the electronic wave function only depends on the already fixed nuclear coordinates and the three cartesian coordinates of the single electron. If our one-electron quantum mechanical system where to contain only one nucleus then we would not need to guess a wave function since we already would have the exact solution, the hydrogen atom. The hydrogen atomic wave functions, or atomic orbitals (AO), may be useful in the construction of more complicated molecular orbitals (MO). We can construct a guess wave function, $\phi$, for our many-electron system as a linear combination of exact wave functions, $\varphi$, the hydrogen atom atomic orbitals, i.e.

$$\phi = \sum_{i=1}^{N} a_i \varphi_i$$

where the set of $N$ functions $\varphi_i$ is called the ‘basis set’, each associated with it some coefficient $a_i$. This approach is referred to as the linear combination of atomic orbitals approach (LCAO).

3.5 The variational principle

Pick an arbitrary square integrable orthonormal function $\Phi$ which is an eigenfunction for the Schrödinger equation and assume we have a complete set of orthonormal wave functions $\Psi$. The function $\Phi$ can be written of some linear combination of the $\Psi_i$, i.e.
\[ \Phi = \sum_i c_i \psi_i \] (8)

One can then show that the inner product for this wave function is

\[ \langle \Phi | \Phi \rangle = \int \|\Phi\|^2 \, d\mathbf{r} = \sum_i c_i^2 \] (9)

And similarly

\[ \int \Phi \mathcal{H} \Phi \, d\mathbf{r} = \sum_i c_i^2 E_i \] (10)

Multiplying (9) with the ground state energy \( E_0 \) and then subtracting (10) with it, one will arrive to the following expression

\[ \int \Phi \mathcal{H} \Phi \, d\mathbf{r} - E_0 \int \|\Phi\|^2 \, d\mathbf{r} = \sum_i c_i^2 \left( E_i - E_0 \right) \geq 0 \] (11)

This must be greater or equal to zero since the ground state energy is the lowest energy. If we now rearrange the equation, we get that

\[ \frac{\int \Phi \mathcal{H} \Phi \, d\mathbf{r}}{\int \|\Phi\|^2 \, d\mathbf{r}} \geq E_0 \] (12)

The equation implies that as we are looking for the best wave function, \( \Phi \), to define the ground state of a system, we can judge the quality of our arbitrarily guessed wave function by the associated energy, the lower the better.

### 3.6 The Secular Equation

Evaluating the energy of our guess wave function, from eq. (12) and (7) we have

\[ E = \frac{\sum_{ij} a_i a_j \int \varphi_i \mathcal{H} \varphi_j \, d\mathbf{r}}{\sum_{ij} a_i a_j \int \varphi_i \varphi_j \, d\mathbf{r}} = \sum_{ij} a_i a_j H_{ij} \]

where we have introduced the notation \( H_{ij} \) and \( S_{ij} \) for the integrals. Once we have selected a basis set, \( \varphi \), we would like to choose the coefficients \( a_i \) to minimize the energy for all possible linear combinations of our basis functions. Since the coefficients \( a_i \) are free variables, to minimize the energy and obtain our secular equation we take the derivative of the energy with respect to its free variables, i.e.

\[ \frac{\partial E}{\partial a_k} = 0 \] (14)

for all \( k \).

### 3.7 Many-electron wave functions Hartree-product wave functions

When having a one-electron Hamiltonian, only consisting of the kinetic energy and nuclear attraction terms, the operator can be separated and be expressed as
\[ \hat{H} = \sum_{i=1}^{N} h_i \]

where \( N \) is the total number of electrons and \( h_i \) is the one-electron Hamiltonian for electron \( i \) defined as

\[ h_i = -\frac{1}{2} \nabla_i^2 - \sum_{k=1}^{M} \frac{Z_k}{r_{ik}} \]

where \( M \) is the total number of nuclei, also emphasizing that the eigenfunctions \( h_i \) must satisfy the corresponding one-electron Schrödinger equation

\[ h_i \psi_i = \varepsilon_i \psi_i \]

Because of the Hamiltonian operator being separable, its eigenfunctions can be constructed as products of one-electron eigenfunctions, i.e.

\[ \Psi_{HP} = \psi_1 \psi_2 \ldots \psi_N \]

where the subscript HP means Hartree-Product. Combining eq. (17) and (18)

\[ \hat{H} \Psi_{HP} = \left( \sum_{i=1}^{N} \varepsilon_i \right) \Psi_{HP} \]

### 3.8 The Hartree Hamiltonian

As mentioned, our Hamiltonian (eq. 15) does not include the interelectronic repulsion term which depends on all possible simultaneous pairwise interactions between electrons. Adding the repulsion term, \( V_i\{j\} \), to our Hamiltonian we get

\[ h_i = -\frac{1}{2} \nabla_i^2 - \sum_{k=1}^{M} \frac{Z_k}{r_{ik}} + V_i\{j\} \]

where \( V_i\{j\} \) represents an interaction potential for electron \( i \) with all the other electrons occupying orbitals \( \{j\} \) and may be computed as

\[ V_i\{j\} = \sum_{j \neq i} \int \frac{\rho_j}{r_{ij}} \, dr \]

where \( \rho_j = |\psi_j|^2 \) is the charge probability density associated with electron \( j \). Note that in this Hamiltonian the nuclei are treated as point charges while the electrons are treated as wave functions which have their charge spread out in space.

The goal of the calculation is to determine each one-electron wave function and thus, its corresponding energy. In the first step towards achieving our goal, in the self-consistent field (SCF) process, one guesses the wave functions for all occupied MOs (AOs in Hartree’s case) and uses these.
to construct the necessary one-electron operators $h$. The solution to each differential (eq. 17) provides a new set of wave functions, presumably different from the initial guess. The new set of wave functions are then used to determine each necessary $\rho$, this method is then repeated to obtain a still better set of wave functions. At some point, the difference between the newly and the previously determined set falls below a predetermined threshold criterion, and we refer to the final set as the ‘converged ‘SCF’ orbitals (For example, a threshold criterion might be to set the total electronic energy change to $\leq 10^{-6}$ a.u, and similar for each energy eigenvalue of the MOs). Of course, this criterion is arbitrary and the lower the threshold is the more SCF cycles are required and in turn a greater cost in computational resources. If we now simply compute $E = \langle \Psi_{HP} | H | \Psi_{HP} \rangle$

\[
E = \sum_i \varepsilon_i - \frac{1}{2} \sum_{i \neq j} \int \left| \frac{|\psi_i|^2 |\psi_j|^2}{r_{ij}} \right|^2 dr_idr_j
\]

where $i$ and $j$ run over all electrons, $\varepsilon_i$ is the energy of MO $i$ from the solution of the one-electron Schrödinger equation using (eq. 20) where we have replaced $\rho$ with the square of the wave function.

### 3.9 Electron Spin and Antisymmetry

Electrons have the intrinsic property of spin, shown by the Stern-Gerlach experiment, and are characterized by a spin quantum number. The $S_z$ spin operator has only two eigenvalues, $\pm \hbar / 2$, corresponding to two spin eigenfunctions, usually denoted as $\alpha$ and $\beta$, which are orthonormal to each other. As first shown by Dirac, the spin quantum number is a natural consequence when applying relativistic quantum mechanics to the electron. What also follows from relativistic quantum mechanics is the Pauli exclusion principle, a form of exchange interaction between fermions, which states that no two electrons can have the same set of quantum numbers. Thus, only two electrons may be placed in a MO, since there are only two possible choices remaining for the quantum number, $\alpha$ or $\beta$. What also follows from the Pauli exclusion principle is that electronic wave functions must be antisymmetric, which means that the electronic wave functions must change sign whenever the coordinates of two electrons are interchanged. A mathematical notation for the antisymmetric property of a two-electron wave function can be written as

\[
\Psi(r_1, r_2) = -\Psi(r_2, r_1)
\]

A wave function that satisfies the Pauli exclusion principle must have antisymmetric properties and is in the form of a Slater determinant. In our two-electron case we have

\[
\Psi(r_1, r_2) = \frac{1}{\sqrt{2}} [\chi_1(r_1)\chi_2(r_2) - \chi_1(r_2)\chi_2(r_1)] = \frac{1}{\sqrt{2}} \begin{vmatrix} \chi_1(r_1) & \chi_2(r_1) \\ \chi_1(r_2) & \chi_2(r_2) \end{vmatrix}
\]

$\chi_N(r) = \psi_N(r)\omega(r)$ is a spin-orbital i.e. a product of a spatial orbital and an electron spin eigenfunction, $\omega$ is either $\alpha$ or $\beta$. For $N$ electrons

\[
\Psi_{SD} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(r_1) & \chi_2(r_1) & \cdots & \chi_N(r_1) \\ \chi_1(r_2) & \chi_2(r_2) & \cdots & \chi_N(r_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(r_N) & \chi_2(r_N) & \cdots & \chi_N(r_N) \end{vmatrix}
\]
The subscript ‘SD’ means Slater-determinant. A feature of the slater determinants is the quantum mechanical exchange. Consider the interelectronic repulsion term for the wave function (Eq. 20), evaluated using two electron slater-determinant where the electrons have the same spin

$$\int \Psi_{SD} \frac{1}{r_{ij}} \Psi_{SD} d\mathbf{r} = J_{ij} - K_{ij}$$

(26)

The result implies that for a two-electron slater-determinant wave function the classical Coulomb repulsion between the electron clouds \(i\) and \(j\) is reduced by \(K_{ij}\). This is a consequence of the Pauli exclusion principle and is analogous to the reduced probability of finding two electrons with the same spin close to one another. Interestingly, this property is unique to electrons of the same spin. If one were to calculate the integral (eq. 26) again but for two electrons with opposite spin, the \(K_{ij}\) term would disappear. However, the solutions given by Slater-determinants does not account for the Coulomb correlation, which tells us that a particle is influenced by the presence of all other particles in the system. This leads to a total electronic energy difference from the exact solution of the non-relativistic Schrödinger equation within the Born-Oppenheimer approximation.

### 3.10 The Hartree-Fock Self-consistent Field Method

The Self-consistent field (SCF) approximation. Like Hartree product orbitals, the HF MOs can be individually determined as eigenfunctions of a set of one-electron operators called Fock operator, \(f_i\). This is similar as \(h_i\) though now the interaction of each electron with the static field of all the other electrons includes exchange effects, \(K_{ij}\), on the Coulomb repulsion, this being the basis of the SCF. The final term of the one-electron Fock operator, the HF potential \(V_{HF}^{(i)}\), is \(2J_{ij} - K_{ij}\), and the \(J_{ij}\) and \(K_{ij}\) operators are defined in the fashion how one computes the integrals \(J_{ij}\) and \(K_{ij}\). The general matrix elements, \(F_{\mu \nu}\), would then be computed as such

$$F_{\mu \nu} = \left\langle \mu \left| -\frac{1}{2} \nabla^2 \right| \nu \right\rangle - \sum_{k} Z_k \left\langle \mu \left| \frac{1}{r_k} \right| v \right\rangle - \sum_{\lambda \sigma} P_{\lambda \sigma} \left[ (\mu \nu | \lambda \sigma) - \frac{1}{2} (\mu \lambda | \nu \sigma) \right]$$

(27)

$$\left(\mu \nu | \lambda \sigma\right) = \int \int \phi_{\mu}(1) \phi_{\nu}(1) \frac{1}{r_{12}} \phi_{\lambda}(2) \phi_{\sigma}(2) d\mathbf{r}(1) d\mathbf{r}(2)$$

(28)

where \(\phi_{\mu}\) and \(\phi_{\nu}\) represent the probability density of one electron and \(\phi_{\lambda}\) and \(\phi_{\sigma}\) the other. \((\mu \nu | \lambda \sigma)\) and \(\frac{1}{2}(\mu \nu | \lambda \sigma)\) is the already mentioned Coulomb interaction and exchange integrals respectively. The final summation term of \(F_{\mu \nu}\) weights the so-called ‘four-index integrals’ by the elements of the ‘density matrix’ \(P_{\lambda \sigma}\) and describes the degree to which individual basis functions contribute to the many-electron wave function, thus describing the significance of the Coulomb and exchange integrals for each basis function.

$$P_{\lambda \sigma} = 2 \sum_{\text{occupied}} a_{\lambda i} a_{\sigma i}$$

(29)

where the coefficients \(a_{\zeta i}\) denotes the normalized contribution of basis function \(\zeta\) to MO \(i\) and the factor two appears because we are only considering singlet wave functions in which all orbitals are doubly occupied. In order to obtain the necessary orbital coefficients to form the density matrix that is used in the Fock matrix elements we first guess the orbital coefficients to construct our HF-secular
equation, and then we iterate to convergence. The energy of the HF wave function can be computed in a fashion analogous to eq. (22) [7].

3.11 CIS – Configuration interaction singles

The CIS method is used to study excited states, while the theory previously mentioned refers to ground state calculations.

Given a HF wave function $\psi_{HF}$ for the ground state of the system that is single-determinantal, one can obtain an approximate wave function for a singly excited state by replacing an occupied orbital $i$ of the ground state with a virtual orbital $a$, denoted $\psi^a_i$, though the resulting wave function will have two major deficiencies. First, by replacing an occupied orbital with a virtual one will correspond more to an ionization than an excitation process. Secondly, $\psi^a_i$ is not an eigenfunction of $\hat{S}^2$ (the total electron-spin operator) and does not represent a pure spin state.

In CIS, these problems are dealt with by constructing an excited state wave function $\psi_{CIS}$ in the form of a linear combination of all possible singly excited determinants

$$\psi_{CIS} = \sum_{ia} c^a_i \psi^a_i$$

It is then possible to obtain a wave function more suitable for an excited state by using variational optimization calculations for the CIS expansion coefficients $c^a_i$. Inserting the equation into the time-independent electronic Schrödinger equation then yields, after multiplication from the left by $\psi_j^b$ and integration over all electronic coordinates,

$$\sum_{ia} \langle \psi^b_j | \hat{H} | \psi^a_i \rangle c^a_i = E_{CIS} \sum_{ia} c^a_i \delta_{ij} \delta_{ab}$$

where

$$\langle \psi_j^b | \hat{H} | \psi^a_i \rangle = (E_{HF} + \epsilon_a - \epsilon_i) \delta_{ij} \delta_{ab} + (ia||jb)$$

$\epsilon_a$ and $\epsilon_i$ are the energies of spatial orbitals $a$ and $i$, respectively, and $(ia||jb)$ is an anti-symmetrized two-electron integral over spatial orbitals in standard notation.

The CIS excitation energies $\omega_{CIS} = E_{CIS} - E_{HF}$ can be calculated from the equation

$$\sum_{ia} [(E_{HF} + \epsilon_a - \epsilon_i) \delta_{ij} \delta_{ab} + (ia||jb)] c^a_i = \omega_{CIS} \sum_{ia} c^a_i \delta_{ij} \delta_{ab}$$

which in matrix notation takes the form of eigenvalue problem

$$H \mathbf{C} = \omega \mathbf{C}$$

$H$ is the matrix representation of the electronic Hamiltonian, with matrix elements $H_{ia,jb} = (\epsilon_a - \epsilon_i) \delta_{ij} \delta_{ab} + (ia||jb)$. $\mathbf{C}$ is the matrix of the CIS expansion coefficients, and $\mathbf{C}$ is the diagonal matrix of the CIS excitation energies that’s obtained by diagonalizing $H$ in the space of all singly excited determinants. CIS provides pure spin states, total excited state energies $E_{CIS}$ which are always greater than the exact total excited state energies, first and second derivatives of $E_{CIS}$ with respect to nuclear coordinates can be expressed analytically, which allows for calculation of excited state geometries and vibrational frequencies. Though CIS does not explicitly include electron
correlation. When studying valence-excited states with predominant single excitation character, CIS is usually a sufficiently accurate method for qualitative computational studies despite its shortcomings [8].

4 Method
In this chapter we will describe the methods used in this thesis. The main question we wish to answer is whether the E and Z isomers of our motor will rotate in the same direction, if at all, in the excited state, this will tell us if the rotation is unidirectional. Given that the rotation is unidirectional, we will with further calculations construct potential energy surfaces for the two isomers in the excited state, this will then give us information whether the motor can undergo facile photoisomerization or not.

The calculations were done for both isomers using the software Gaussian [9] and computational resources provided by the National Supercomputer Centre (NSC) at Linköping University. Optimisation calculations for the molecular ground state geometry were performed to achieve the lowest ground state energy using the Hartree-Fock method (HF) with the 3-21G basis set. Using CIS, the bright second excited singlet state $S_2$ was then calculated (and indeed confirmed to be bright from the corresponding oscillator strength). Excited state optimisation scan calculations with C1-C2-C3-C4 (see Figure 7) as the relevant dihedral angle were performed, first without any constraint, which means that the molecule is free to rotate in any direction. From the calculations, it was found that the molecule will rotate in a CCW fashion. By using the information from the previous calculations, we then performed scan calculations for the excited state with the dihedral angle changed in increments of 2 degrees along the photoisomerization coordinates. This was done for a total of 45 steps.

![Figure 7: E(1) and Z(2) isomers of the molecular motor under study.](image)

5 Results
The excited state optimisation calculations, without restrictions, showed the motor increasing its dihedral angle for both the E and Z isomer, which corresponds to CCW rotation. The scan steps were then chosen to increase the dihedral angle +2 degrees every step for 45 steps when doing scan calculation to construct the excited-state potential energy surfaces.
5.1 Scan calculation

**Figure 8:** Results from CIS – optimisation scan calculation of the E isomer. The figure shows how the potential energy for the molecule changes with respect to the dihedral angle. The first data point is the Franck-Condon (FC) point, which corresponds to the energy of the excited state of the ground state geometry.

![E-isomer diagram](image)

**Figure 9:** Results from CIS – optimisation scan calculation of the Z isomer. The figure shows how the potential energy for the molecule changes with respect to the dihedral angle.

![Z-isomer diagram](image)

Figure 8 and 9 show the molecule rotating in the CCW direction with ease, due to the surprisingly flat potential curves. This tells us that the molecule will photoisomerize without being hindered by potential-energy barriers. However, the calculation had difficulty in converging at dihedral angles of 50 – 60 degrees. Keeping in mind that we are in the S₂ state, this is because lower states come close in energy in this region. Also, at this stage the probability whether the molecule will continue to rotate in the same direction or relax to S₀ and obtain its original geometry starts to play a bigger role.
5.3 Bond length alternation

In this work we use bond length alternation (BLA) to investigate whether the molecule exhibits aromatic properties. A small BLA corresponds to more aromatic resemblance in the molecule. BLA is the difference between the average single bond length and the average double bond length, and can be calculated as

\[
\text{BLA} = \frac{1}{3}[(C_1 - C_2) + (C_3 - C_4) + (C_5 - C_1)] - \frac{1}{2}[(C_2 - C_3) + (C_4 - C_5)]
\]

(33)

where \( C_x - C_y \) is the bond length between carbon \( x \) and \( y \) in angstrom.

![Atomic numbering for the calculation of BLA.](image)

**Figure 10:** Atomic numbering for the calculation of BLA.

![BLA plot for the E isomer](image)

**Figure 11:** BLA plot for the E isomer
The BLA plots for the E and Z isomer, Figure 11 and 12, show the BLA instantly decreasing after photoexcitation, which means that the molecule starts to exhibit aromatic like properties. By comparing the potential energy surface with the BLA plots for respective isomer, we find a clear correlation between the two. This is especially clear when looking at the first data points of each plot. Thus, the efficient photoisomerization appears to be due to excited state aromaticity.

6 Conclusion and discussion

From the calculated results we conclude that the molecular design, such that it attains or gets close to the necessary requirements in order to be considered aromatic in its excited state, has a significant impact in improving the rotary motion for this light-driven molecular motor. This is shown by the flat potential curve for both isomers.

However, one may argue for the necessity of a more detailed and complete potential curve for the isomers in order to draw such conclusions. Still, even if one was able to compute a more accurate potential surface for the motor it would not be the complete picture due to other significant factors such as the quantum yields. From the BLA calculation we see the molecule exhibiting aromatic like properties, the smaller the BLA the more aromatic like it becomes. Therefore, we draw the conclusion that an excited state aromaticity feature is present due to the significant decrease of the BLA (see Figure 11 and 12).

For further research in the subject of excited state aromaticity applied to molecular rotary motors, one might ask how a motor where both rotor and obtains aromaticity after photon absorption would perform or how it could be designed. One proposition would be to design one half to become aromatic as an anion and the other half as a cation, e.g. cyclopentadiene and cycloheptatriene respectively, through intramolecular electron transfer (see Figure 13).
Figure 13: Schematic example of a photoinduced intramolecular electron transfer between cyclopentadiene and cycloheptatriene. A molecular motor design.

Acknowledgements
I’d like to thank my supervisor Prof. Bo Durbeej for guiding me through this thesis and introducing me to the interesting field of molecular machinery.

References


Appendix

A.1 Settings and inputs

(E/Z) – isomer

- Optimization calculation
  Input in gif-file:
  \textit{opt freq=noraman HF/3-21g nosymm geom=connectivity scf=tight}

Explanation: Creating checkfile with optimised geometry for the molecule ground state \((S_0)\)
Key input: opt, HF/3-21g

- CIS calculation
  Input in gif-file:
  \textit{CIS=(Singlets,Direct,NStates=10)/3-21g nosymm scf=tight}

From out-file:
\textbf{Excited State} 2: \textbf{Singlet-?Sym} 4.9990 eV 248.02 nm \(f=1.1982\)

Explanation: Calculating 10 lowest excited singlet state, then choosing the lowest state with highest oscillator strength “f” from out-file.
Key input: CIS=(Singlets,Direct,NStates=10), 3-21g.

- Scan calculation
  Input in gif-file:
  \textit{CIS=(Singlets,Direct,Root=2)/3-21g opt=modredundant nosymm scf=tight geom=check guess=check}
  \(D 4 3 2 18 S 45 2.0000\)

Explanation: Optimising the molecule in its second excited state \((S_2)\). This is done for each 2 degrees of rotation of the dihedral angle for 45 steps, thus a total of 45 optimisation calculations and 90 degrees rotation. Here C4-C3-C2-C18 is selected for the dihedral angle calculation. Geometry is extracted from the first optimization check-file.
Key input: CIS=(Singlets,Direct,Root=2), 3-21g, opt=modredundant, D 4 3 2 18 S 45 2.0000.