

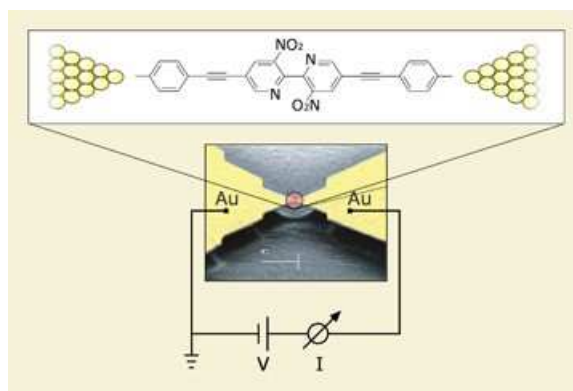
Project description

Molecular electronics and opto-electronics

1 Purpose

In recent years there has been an increasing interest in using individual molecules as nano-scale electronic devices, driven by the needs of the microelectronics industry to find alternative routes to miniaturisation. One of the most basic devices of this kind is a molecular switch. A molecular switch is a molecule that can change between states with low and high electrical conductance, as a result of an external stimulus. An obvious application of molecular switches is as binary data storage cells.

This project investigates the atomic scale mechanisms that enable the molecule to switch between the conducting and non-conducting states. The purpose is to establish a framework for searching for suitable molecules for molecular electronics, and ultimately to discover new molecules with such properties.



A molecular switch is a molecule connected between two conducting electrodes. The molecule can switch between two different states with high and low electrical conductance.¹

2 Background

Our society has come to rely on continuous progress within the microelectronics industry, where improved miniaturisation leads to faster and cheaper microelectronics every year. Miniaturisation of our current semiconductor technology cannot, however, continue much longer, as the silicon will cease to behave like a continuous material when device dimensions reach the nanometer scale. One possibility to overcome these limitations is to develop molecular electronics, where individual molecules act as electronic components such as transistors, logical gates and switches. This research proposal focuses on molecular switches.

In the search for suitable molecules for molecular switches, theoretical methods are needed to predict the electronic properties of large numbers of candidate molecules before expensive experimental studies are undertaken. These theoretical methods should solve two main tasks.

1. To calculate the electronic properties (mainly the conductance) of a molecule in a given conformation.
2. To calculate how the molecule can switch from one structural state to another (with different electronic properties) as the result of an external stimulus such as a light pulse or an electrical pulse.

While suitable theoretical methods for solving task 1 have recently been developed, and are now in use in several groups around the world (including our group at DTU),²⁻⁵ progress on task 2 is just beginning to appear in the scientific literature.⁶⁻⁸ This research proposal addresses task 2 by adapting existing theoretical tools to the study of atomic-scale changes in molecules used as electronic switches; and combines these methods with the methods for calculating electronic properties. This will establish a framework for searching for molecules that can be used as electronic switches by changing their atomic configuration with an external electrical or optical pulse.

2.1 Conductance calculations

Over the last few years one of us, Kristian Thygesen (KT), has been leading the development and maintenance of a software code for calculations of the low-bias conductance of nano-scale junctions.³ The method combines Green's function techniques with Density Functional Theory (DFT) to solve the scattering problem for electrons moving through a molecule connected to two electrodes. The combination of Green's functions and DFT is very efficient and the code can treat molecules containing up to one hundred atoms at a relatively low computational cost. The method has been used extensively to study quantum transport in a variety of different nano-scale systems including molecular junctions,^{4,5} atomic metal chains^{2,9} and carbon nanotubes,¹⁰ finding good agreement with experimental data, where available.

At present, the transport code is limited to the case of a small applied bias voltage. In this project we will remove this limitation by extending the method to treat the situation of a large bias voltage. This is of great technological importance as future nano electronic devices most likely will be operated under such conditions. In particular, this extension will allow us to study switching effects in molecules induced by voltage pulses.¹

2.2 Switching the state of a molecule

When a molecule connected to two electrodes is subjected to an electrical or optical pulse, the result can be an electronic excitation of the molecule. If this excitation leads to an atomic rearrangement in the molecule, a change in the conductance properties is possible. To investigate if such a change occurs, a number of methods may be applied, all of which requires the ability to perform quantum chemical calculations on the molecule with attached electrodes. The standard workhorse of quantum chemistry (at least for large systems as investigated here) is DFT. Unfortunately, DFT is by construction a method addressing the ground state properties of a system, and thus appears unsuitable for solving the problem at hand. Recently, however, a number of extensions to DFT have been made, allowing us to address the low-energy excited states relevant to the properties at hand. The two most interesting are Delta Self-Consistent Field^{11,12} (Δ SCF) and Time-dependent Density Functional Theory^{13,14} (TDDFT).

2.2.1 Delta Self-Consistent Field

Δ SCF is one of the simplest possible ways to extend DFT to low-lying excited states; perhaps for that reason it works remarkably well. The main idea is to occupy a Kohn-Sham single-electron orbital (or a linear combination of such orbitals) corresponding to the desired excitation, and keep this orbital occupied while iterating the electronic density to self-consistency. This represents a tremendous improvement over the traditional (but not very good) method of just using the Kohn-Sham energies of the excited orbitals corresponding to the ground state density. We have recently extended the Δ SCF formalism to cover molecules interacting strongly with a metal (e.g. a surface, or the electrodes in case of molecular electronics), and have shown that Δ SCF gives excellent agreement with experiment, and competes well with much more demanding quantum chemical methods.¹²

2.2.2 Time-dependent density functional theory

Time-dependent density functional theory (TDDFT) exists in two flavors. With *linear response TDDFT* (lr-TDDFT) it is possible to calculate the optical excitation spectrum of a system. We plan to make heavy use of lr-TDDFT to identify relevant excitations in the molecules under investigation.

With the *time-evolution TDDFT* (te-TDDFT) method, the quantum state of a system is explicitly evolved in time, enabling us to follow e.g. the response of the molecule to an external stimuli, or the decay of an excited state due to the influence of the electrodes.

Both flavors of TDDFT are available in our in-house DFT code GPAW.¹⁵

2.2.3 The motion of the atoms

The methods mentioned above mainly address the electronic structure of the switching molecule, but to model the change of atomic configuration they must be combined with methods describing this atomic motion. For this project, the most important are *Molecular Dynamics* (MD) and the *Nudged Elastic Band*^{16,17} (NEB) method. In MD, Newton's second law for the atoms is integrated directly, and the atomic motion can be followed in time. NEB is a method for finding the minimum-energy pathway between two known configurations. Both methods have long been used in the CAMD and CINF groups, and are available in our simulation software.

2.3 The research group

The project will be carried out in a collaboration between the CAMD and CINF research centers at DTU-Physics. CAMD is one of the worlds leading research centers in electronic structure theory and quantum transport calculations. One of us (KT) is leading the molecular electronics group in CAMD. CAMD develops the CAMPOS suite of molecular simulation codes used by approx 50 groups around the world.

The CINF center focuses on surface processes including surface reactions triggered by exciting the adsorbed molecule with hot electrons (electrons with an energy of a few eV above the Fermi level). To treat these phenomena, the CINF theory group headed by Jakob Schiøtz (JS) has been using and developing excited state methods that are directly applicable to this project.

CAMD and CINF have access to one of the largest supercomputer clusters in Denmark, the Niflheim cluster,¹⁸ sponsored by the Danish Center for Scientific Computing. Niflheim will be available for this project.

We will establish a collaboration with the experimental group of Dr. Sense Jan van der Molen of the Institute of Physics, Leiden University, see the enclosed letter of support. Dr. van der Molen is one of the worlds leading experts in molecular electronics, with a focus on experimental studies of light-sensitive molecular switches.

3 Research plan

Switching a molecule between two states can be regarded as a two-step process, where each step can be understood independently. First, an electronic excitation is induced into the molecule, then that excitation induces a change in the atomic configuration. This change in atomic configuration can either be a *conformational change* (i.e. a change in the three-dimensional structure without breaking or making chemical bonds) or an *internal chemical reaction*, where one or more internal chemical bonds are made or broken. Both types of changes have been shown to cause changes in the electrical conductance of molecules.^{6-8,19}

Once the mechanism leading from an electronic excitation to a change in conductance has been elucidated, it remains to be investigated how the electronic excitation can be introduced into the molecule. The most straight-forward way is to use optical excitations. Ir-TDDFT is one of several well-established methods for calculating the optical response of a molecule.¹⁴

A more technologically interesting approach is to induce the excitation electronically. By placing a finite bias across the molecule, energetic electrons will be injected into the molecule. Inducing chemical reactions with these “hot electrons” has previously been proposed to induce chemistry at surfaces²⁰. This is currently being investigated in CINF both theoretically¹² and experimentally.²¹

In the molecular switches under investigation here, the energetic electrons are not made by a special device, but the electrons become energetic due to the finite voltage across the molecule. This may directly induce forces on the atoms which can make the molecule change configuration. The finite voltage may also induce electronic excitations leading to structural changes similarly to the changes caused by optical excitations. To study these possibilities, we will extend our DFT and transport program (GPAW)¹⁵ to operate with finite voltages across the system being studied. This will allow us to study the forces on the atoms induced by the voltage. By combining these calculations with Δ SCF and TDDFT calculations we can extend the study to cover electronic excitations induced by the flowing current.

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