Controlling the color of the light emitted by a single molecule junction: a time-dependent density functional theory (TD-DFT) study

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Statement of problem

The project proposal belongs to the field of studies dedicated to molecular electronics which has become a major research domain in recent times [1]. In the mid-90's, Joachim *et al* used the scanning tunneling microscope (STM) to measure electron transport properties through a metal/molecule/metal nano-junction (hereafter named "single molecule junction" - Fig. 1) [2,3], marking the beginning of molecular nano-electronics. Much progress has been made since that time, and nowadays, the degree of control is such that it is possible not only to assemble atoms and molecules using the tip of a scanning tunneling microscope and to measure and manipulate their electric and magnetic properties [4,5] but also to excite them to induce transitions between some of their electronic states[6], making single molecule junction promising device for the development of light source at the nanoscale [7,8]. However, the control of the frequency of the emitted light is a key point to make the single molecule junction a powerful optical device; the present project takes place within this framework: our aim is to investigate the optical properties of single molecule junctions from a theoretical point of view by resorting to time-dependent density functional theory in order to identify the main parameters influencing the light emission such as chemical composition or stress inside the molecule.

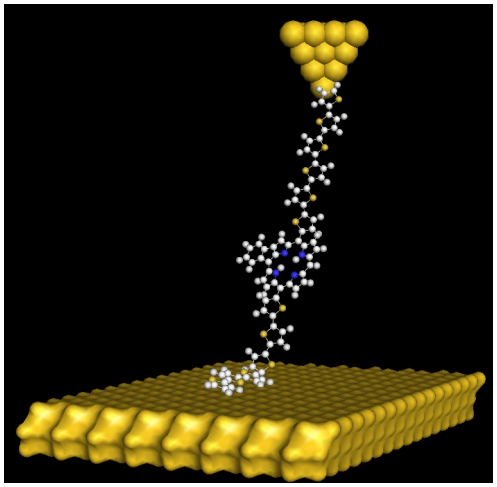

Fig.1: Single molecule junction

Description of the research work

The study of the optical properties of the single molecule junction requires (i) to consider a large number of atoms, to precisely describe the nano-junction, (ii) to take into account the diversity of interactions involved in the system (covalent bonds within the molecules, metal bonds in the electrodes, van der Waals interaction between molecules), and (iii) to calculate the optical properties of the device. We will adopt a three-step approach, involving both classical and quantum physics in order to take address all the issues above. We will consider various types of nanojunctions, chosen so as to isolate the effect of different aspects of physics that may influence the light emission. The first step will consist of a very fast structural pre-optimization of the single molecule junction by using classical molecular dynamics. The following step will be the more accurate optimization through the gradient algorithm used in approaches based on the density functional theory (DFT). The last step will consist in the calculation of the electronic structure and the optical properties of the relaxed system using the time-dependent density functional theory (TD-DFT), in the approximation of linear response, for calculating the excited states.

References

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