Theoretical study of the dynamics induced by photoexcitation of atoms in superfluid helium nanodroplets

Étude théorique de la dynamique induite par photoexcitation d'atomes en nanogouttes d'hélium superfluides

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The goal of this project is to study the dynamics induced by photoexcitation of a dopant atom inside a superfluid helium nanodroplet. Helium nanodroplets are large helium clusters (typically thousand to several hundred thousand atoms) exhibiting remarkable properties : very low temperature (0.4 K), superfluidity, weak interaction with the dopant, very high thermal conductivity and very fast relaxation dynamics. This makes them an exceptional environment for dynamics studies.[1] During the past few years, several dynamics experiments have been conducted on these systems using highly sophisticated techniques : real time pump-probe experiments, velocity map imaging, ... Many of them dealt with alkali atoms or alkali earth ions because of their simple excited electronic state structure. Upon photoexcitation they tend to desorb, either as a bare atom or with one or a few helium atoms attached, due to the strong repulsion between the electronic orbital (much more diffuse in the excited state) and the surrounding helium. The process can be rather complex, since the nanodroplet can absorb and dissipate part of the recoil energy as density waves and/or atom evaporation. In addition, the helium environment can induce electronic relaxation processes which dissipate a lot of kinetic energy.

From a theoretical point of view, it is a serious challenge to study the real time dynamics of these systems because of the strong quantum effects due to the light mass of helium. Helium density functional theory (He-DFT) and its time-dependent version (He-TDDFT), which deal with the helium density rather than the many-body helium wave function, have emerged as an optimal compromise between accuracy and the ability to work with large numbers of helium atoms. However, they can only describe the dynamics following an electronic transition but not predict it, and it is unclear how to describe kinetic energy transfer to the helium density. Other methods such as zero-point averaged dynamics (ZAPD)[2] or gaussian wave packets[2] treat the helium atoms dynamics in a more approximate way, but they can predict electronic transitions and the correct kinetic energy transfer to helium when combined with a surface hopping method.[2]

We will address the puzzling case of the dynamics following photoexcitation of Ba^+. Experiments show a possible desorption of Ba^+ whereas He-TDDFT simulations could only reveal rearrangement of the surrounding helium about the excited state orbital.[3] Therefore helium-induced transitions to lower electronic states of the Ba^+ dopant are suspected, although helium is a very poor perturber. This study could provide the first *ab initio* proof of the existence of helium-induced electronic transitions, which in turn could help interpret a number of other discrepancies and controversies between experiment and theory for other dopants.

This internship will be conducted in collaboration with the team of M. Barranco and M. Pi from the University of Barcelona, who are experts in the He-(TD)DFT methods, which will be used as a reference to test the validity of the other approaches.

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[2] D. Bonhommeau *et al.* , J. Chem. Phys. **126**, 051104 (2007) ; W. Unn–Toc *et al.* , J. Chem. Phys. **137**, 014304 (2012) ; D. Bonhommeau *et al.* , J. Chem. Phys. **120**, 11359-11362 (2004).
[3] X. Zhang and M. Drabbels, J. Chem. Phys. **137** , 051102 (2012) ; Leal *et al.* , J. Chem. Phys. **144** , 094302 (2016).