

# VISTA Seminar

## Seminar 69

**May 15, 2024**

**10:00 am – 11:30 am EDT / 3:00 – 4:30 pm BST London / 4:00 pm –  
5:30 pm CEST Paris / 10 pm – 11:30 pm CST Beijing**

### **TOC:**

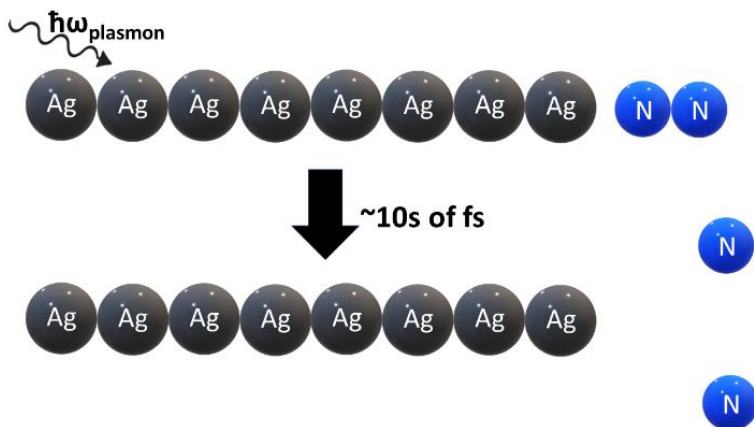
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## Time-Dependent Density Functional Theory Studies of Electron Dynamics in Plasmonic Systems

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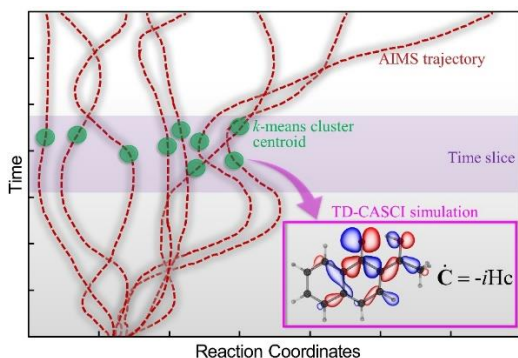


Plasmonic systems such as silver nanoparticles are of interest for applications such as nanoantennas and plasmon-enhanced photocatalysis. In order to fulfill this potential, we must understand how energy flows throughout the system and how energy transfers between two nanoparticles or between a nanoparticle and adsorbate. In this work, we present our studies that employ real-time time-dependent density functional theory (RT-TDDFT) to examine plasmon decay and electronic energy transfer processes. Using Ehrenfest dynamics, we examine electron-nuclear dynamics in systems such as silver nanowires and acenes, which display collective effects akin to those in nanoparticle systems. We investigate the propensity for non-linear excitations in tetrahedral silver nanoparticle systems. We discuss the ability of plasmonic excitation in nanoparticle systems to activate bonds in small molecule adsorbates, which can lead to photocatalysis.

# Simulations of Ultrafast Spectroscopy Observables Using the GPU-accelerated Time-dependent Complete Active Space Configuration Interaction Method

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The accurate measurement and simulation of the dynamics of ultrafast processes in photoactive systems have been the focus of much recent interest. Transient absorption (TA) spectroscopy is a state-of-the-art technique for investigating ultrafast dynamics due to its excellent temporal resolution and applicability to a diverse class of systems. The interpretation of the TA spectrum (TAS) is indirect due to the energy-time uncertainty and the projection of a large number of active degrees of freedom onto an observable with fewer dimensions which results in significant information loss. It highlights the critical need for a theoretical method which directly simulates the experiment by calculating both dynamics and the relevant observables. We combined the non-adiabatic molecular dynamics (NAMD) simulations with our GPU-accelerated Time-dependent Complete Active Space Configuration Interaction (TD-CASCI) method to simulate the dynamics and TAS of the photoactive molecules. Our direct configuration interaction approach in TD-CASCI eliminates the need to build, store, or diagonalize the Hamiltonian matrix and is based on *on-the-fly* calculations. The recasting of the time-dependent Schrodinger equation in the symplectic form and the GPU-accelerated implementation of the propagation algorithm enables the extension to large molecules and configuration spaces. The GPU acceleration also allows running thousands of TD-CASCI simulations on time-resolved NAMD trajectories with affordable computational costs.

We applied our methodology to simulate the dynamics and TAS of the 1'-Hydroxy-2'-acetonephthone (HAN) and Salicylideneaniline. TAS was computed using the time-resolved geometries from the snapshots of NAMD simulations. For each molecule, TAS was simulated by running a total of 40,000 individual TD-CASCI simulations (1.8 ns of electron dynamics) using 13440 geometries selected from the NMD trajectories. The simulated TAS exhibited remarkable agreement with the corresponding experimental Cavity-Enhanced TAS. Our approach enables independent simulation of TAS for trajectories evolving within distinct electronic states and propagating along specific decay pathways. These studies demonstrate the robustness of our approach in scenarios involving multiple competing relaxation pathways, or in cases where NAMD simulations alone pose challenges.

## How to connect

Alexey Akimov is inviting you to a scheduled Zoom meeting.

Topic: VISTA, Seminar 69

Time: May 15, 2024 10:00 AM Eastern Time (US and Canada)

Join Zoom Meeting

<https://buffalo.zoom.us/j/94410222526?pwd=TVhhQUpuU29GV1hiSzFKSWNnU2hLQT09>

Meeting ID: 944 1022 2526

Passcode: 591862