Modeling of Light-Driven Heterogeneous Catalysis and Other Excited-State Processes at the Nanoscale

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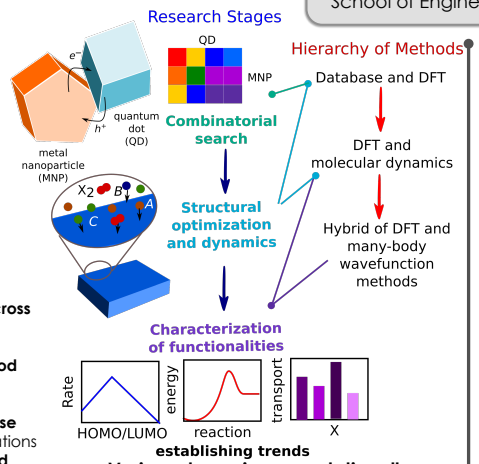
Quantum Mechanical Modeling of Solar Materials for Photovoltaic and Photochemical Applications

Research Description

Use state-of-the-art computational tools in fields where **the understanding of light-matter interactions and excited-state physics at the atomic-scale** deliver practical design principles to **accelerate the fabrication of useful, solar-driven technologies and applications**

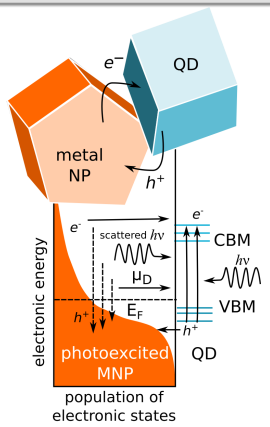
Expertise
① **visible light-driven photocatalysis**
② **nanoscale photovoltaics and charge-carrier transport across interfaces**
③ **development of density-functional-theory (DFT)-based quantum mechanical partitioning and embedding method**

Methods
① Combinatorial searches and structural discovery: **database mining** augmented with quantum mechanical **DFT** simulations
② Desirable functionalities identified and quantified: **DFT and formally exact many-body wavefunction methods**
③ Establish figures of merit and trends to guide future searches



Various stages in computationally designing functional materials using different levels of theory

Tandem Quantum Dots and Plasmonic Nanoparticles for Photovoltaics



Electronic coupling in a tandem metal nanoparticle (MNP) and quantum dot (QD) system

Objective

Study the physics and chemistry associated with combining plasmonic MNPs and semiconducting QDs to achieve highly efficient photovoltaic materials

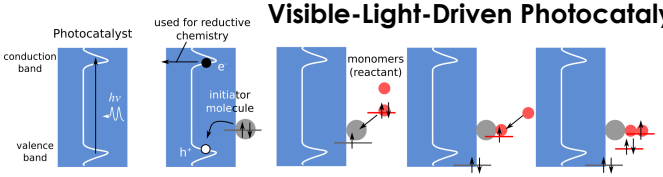
MNPs (tunable light-scattering and absorption) and **QDs (tunable band gaps)** have their own unique optical properties → photovoltaic devices with enhanced absorption profiles

Possible combinations include earth-abundant plasmonic MNPs: Cu and Al, with widely available QDs: CdSe, CdTe, and ZnS

Strategy

① **Combinatorial search**: QDs' optical gap and light scattering properties of MNPs (**experimental** and generated **DFT**-based theoretical **databases**)
② Study **local exciton generation, resonance energy transfer, and charge-carrier transport** across the MNPs and QDs (see Figure on the left): **DFT** and accurate **correlated wavefunction** methods

Visible-Light-Driven Photocatalysis



Sequence of events leading to light-induced heterogeneous polymerization

Objectives

① Explore the possibility of **directly using light-generated, energetic charge carriers in semiconductors to catalyze reactions**, with emphasis on **organic chemistry reactions**
② Study ways to **increase the lifetimes** of light-generated **energetic electrons and holes to facilitate catalysis** (prevent recombination)
③ **Reactions** to study include **polymerization chemistry**, **C-H bond activation, and water splitting**, to name a few.

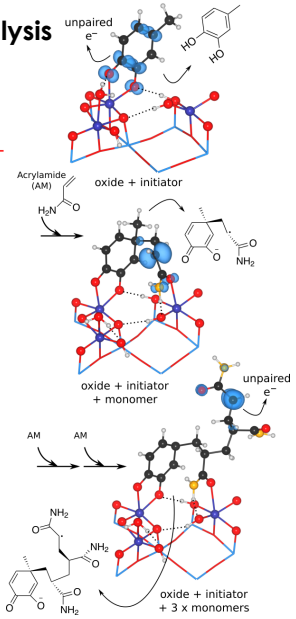
Example

Alternative avenue to **generate radical species for polymerization via light-induced decomposition of molecules on photoactive semiconductors** (*e.g.*, TiO_2, MoS_2, and GaP), whereby they are generated *in situ* and may remain immobilized on the surface

Advantages:
① radicals are surface bound : free-radical recombination processes are avoided
② unstable molecules need not be used as initiators (free radicals are generated "on the fly" using light)

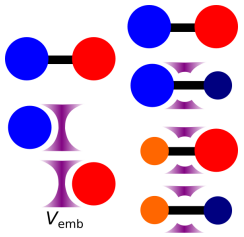
Strategy

① **Combinatorial search**: organic molecules' and semiconductors' optical gaps from **experiments** and **DFT**-based **databases**
② Study **surface excitation** and their **lifetimes** : **DFT** and accurate **correlated wavefunction** methods



DFT-predicted polymerization of acrylamide (AM) catalyzed by an oxide using a benzenediol molecule as the initiator

Capped Density Functional Embedding Theory (capped-DFET) for Covalent Systems



Covalent bond partitioning schemes in classic DFET[1] (left) and capped-DFET[2] (right)

① Model the system within periodic DFT
② Partition the system into the active-site (cluster) and the environment → choose cap of suitable valence
③ Optimize the embedding potential (V_{emb}) → maximize W, V_{emb} represents the cluster-environment interaction
④ Conduct embedded fragment calculations → both in DFT and higher-level correlated wavefunction calculations

$$W = E_{eDFT}^{cl+cap'}(\rho^{cl}) + E_{eDFT}^{env+cap''}(\rho^{env}) - E_{eDFT}^{cap'+cap''}(\rho^{cap'+cap''}) - \int V_{emb}\left(\frac{\partial E^{ref}}{\partial V_{emb}}\right)dr$$

$$\rho^{cl+cap'} + \rho^{env+cap''} - \rho^{cap'+cap''} = \rho^{ref}$$

reference total electron density matched by the sum of capped-fragment electron densities with cap contributions removed

Objective

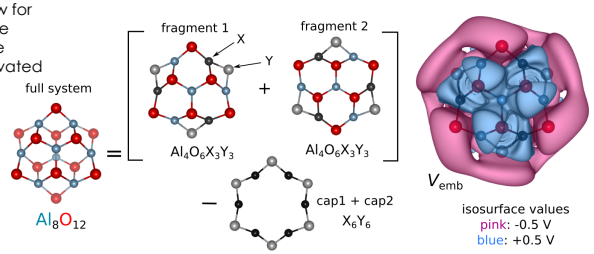
Develop and test a tool that would allow for formally exact many-body but expensive quantum mechanical calculations to be conducted to explicitly model light-activated processes in semiconductors

Will be tested and used to calculate and model:

Systems
① small inorganic transition-metal-based clusters
② organic molecules
③ covalent crystals

Properties and figures of merit
① light absorption energies
② reaction energetics

Processes
① heterogeneous catalysis
② energetic charge carrier generation and transport



LEFT: An example of the partitioning of an oxide Al_8O_{12} into Al_4O_6 fragments using the capped-DFET scheme, X and Y caps. **RIGHT: An example of a DFT-derived Vemb** for this system using X=Mg^{2+}, Y=O^{2-} capping. Fragment 1 is shown surrounded by positive and negative potentials, which redistribute its electron density.

1. Huang, C.; Pavone, M.; Carter, E. A., *J. Chem. Phys.* **2011**, *134* (15), 154110
2. Martirez, J. M. P.; Carter, E. A., to be submitted