

# Theoretical Studies of Electron Dynamics

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Electron dynamics in nanometer-sized molecules and nanostructured materials is an intrinsic process related to a number of interesting phenomena such as linear and nonlinear optical response, electrical conduction, and also chemical reaction. Despite their importance, the electron dynamics has not been understood in detail. We have developed a computational method simulating the electron dynamics in real time and real space, and elucidated the dynamics.

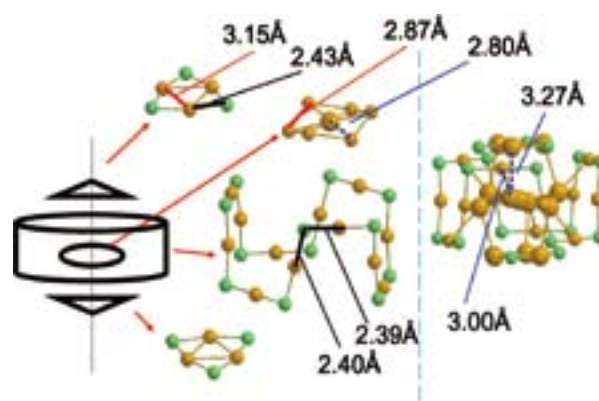
## 1. Photoinduced Electric Currents in Ring-Shaped Molecules by Circularly Polarized Laser Pulses<sup>1)</sup>

We have theoretically demonstrated that circularly polarized laser pulses induce electric currents and magnetic moments in ring-shaped molecules  $\text{Na}_{10}$  and benzene. The time-dependent adiabatic local density approximation is employed for this purpose, solving the time-dependent Kohn-Sham equation in real-space and real-time. It has been found that the electric currents are induced efficiently and persist continuously even after the laser pulses were switched off provided the frequency of the applied laser pulse is in tune with the excitation energy of the electronic excited state with the dipole strength for each molecular system. The electric currents are definitely revealed to be a second order nonlinear optical response to the magnitude of the electric field. The magnetic dipole moments inevitably accompany the ring currents, so that the molecules are magnetized. The production of the electric currents and the magnetic moments in the present procedure is found to be much more efficient than that utilizing static magnetic fields.

## 2. Theoretical Investigation of Optimized Structures of Thiolated Gold Cluster $[\text{Au}_{25}(\text{SCH}_3)_{18}]^+$

Geometric and electronic structures of a gold-methanethiolate  $[\text{Au}_{25}(\text{SCH}_3)_{18}]^+$  are investigated by using density functional theory. Three types of optimized structures are

derived from two different  $\text{Au}_{25}$  core clusters protected by 18 methanethiolates. The most probable optimized structure (FCC2) consists of a  $\text{Au}_7$  core cluster and Au-S complex-like ring clusters,  $\text{Au}_{12}(\text{SCH}_3)_{12}$  and  $\text{Au}_3(\text{SCH}_3)_3$ . The  $\text{Au}_7$  core cluster is enclosed by the  $\text{Au}_{12}(\text{SCH}_3)_{12}$  ring cluster and then the  $\text{Au}_7$ - $\text{Au}_{12}(\text{SCH}_3)_{12}$  core-ring subsystem is capped with the two  $\text{Au}_3(\text{SCH}_3)_3$  ring clusters from both sides of the top and the bottom. This structural feature is in contrast to a general notion of gold-thiolate clusters that a core gold cluster is superficially protected by thiolate molecules. The optimized structure provides a large HOMO-LUMO gap, and its X-ray diffraction and absorption spectra successfully reproduce the experimental results.



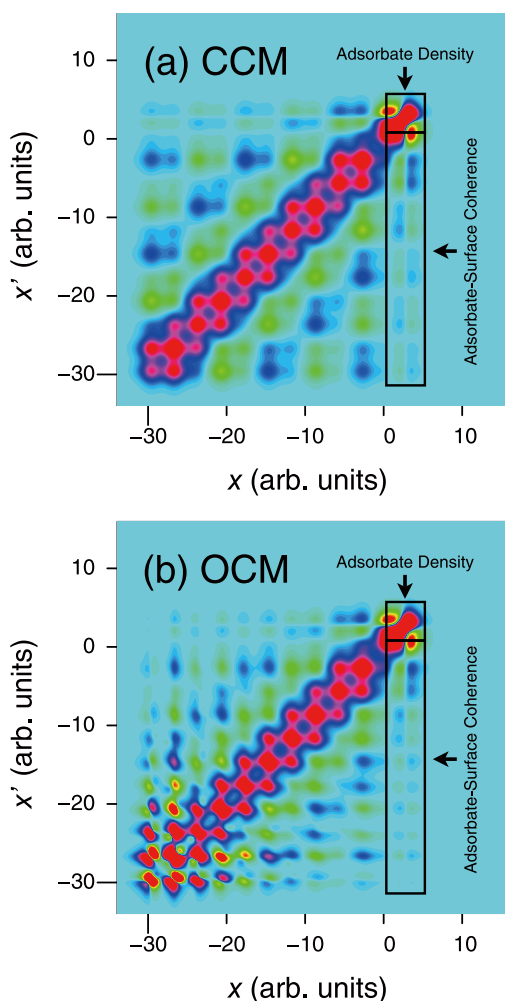
**Figure 1.** Fractionalized subsystems of FCC2 and their bond distances.<sup>2)</sup>

## 3. Efficient Numerical Method for Calculating Exciton States in Quantum Boxes<sup>3)</sup>

We have developed an efficient numerical method for exciton states confined in quantum boxes. The exciton wave function is expanded in terms of discrete variable representation basis functions. Our numerical approach has proved to be computationally much less demanding in comparison with the conventional configuration-interaction one.

#### 4. Open-Boundary Cluster Model for Calculation of Adsorbate-Surface Electronic States

We have developed a simple embedded-cluster model approach to investigate adsorbate-surface systems. In our approach, the physically-relevant subsystem is described as an open-quantum system by considering a model cluster subject to an outgoing-wave boundary condition at the edge. This open-boundary cluster model (OCM) is free from artificial waves reflected at the cluster edge, and thus the adsorbate properties computed with the OCM are almost independent of the model cluster size. The exact continuous density of states (DOS) of a 1D periodic potential model is shown to be precisely reproduced with the OCM. The accurate DOS leads to an appropriate description of adsorbate-surface chemical bonding. Moreover, the open-boundary treatment of the OCM allows us to evaluate the electron-transfer rate from the adsorbate to the surface, whereas the conventional cluster model (CCM) does not give any information about such a dynamical process.



**Figure 2.** One-body reduced density matrix in the real space representation obtained with (a) CCM and (b) OCM. The adsorbate density and the adsorbate-surface coherence are illustrated in the square and rectangle regions, respectively. The adsorption distance and the chemical potential are set to be 2.5 and  $-1.3$ , respectively.

#### 5. Finite-Temperature Density Functional Calculation with Polarizable Continuum Model in Electrochemical Environment

We present a numerical methodology to calculate electronic structures of a molecule in electrochemical environment. The methodology is based on the finite temperature density functional theory (FTDFT) and allows us to study electronic properties of a molecule at a fixed chemical potential. The approach is applied to a reaction of  $\text{NO}^+ + e^- \rightleftharpoons \text{NO}$  in chemical equilibrium. The solvent effect is taken into account by a conductor-like polarizable continuum model (C-PCM), and the size of the cavity in C-PCM is given in terms of the molecular charge so as to reproduce the experimental solvation energy of the cation. We demonstrate that the method combined with C-PCM (FTDFT/C-PCM) successfully describes the electronic structures of the molecule in electrochemical environment. Applicability of the present method to electrochemical properties is discussed in comparison with an alternative approach of statistically averaged DFT calculations.

#### References

- 1) K. Nobusada and K. Yabana, *Phys. Rev. A* **75**, 032518 (7 pages) (2007).
- 2) T. Iwasa and K. Nobusada, *J. Phys. Chem. C* **111**, 45–49 (2007).
- 3) Y. Kubota and K. Nobusada, *Phys. Lett. A* **369**, 128–131 (2007).