

Theory for Optical Response in Nanostructures and its Application to Functional Nanodevices

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Optical response of molecules is undoubtedly essential for understanding their physicochemical properties. In conventional theoretical approaches to optical response of molecules, two conditions are usually assumed:

- (i) Wavelength of incident light is considered to be much longer than molecular size, *i.e.*, dipole approximation. Thus, a target molecule is well approximated by a point dipole and the dipole feels a uniform electromagnetic field.
- (ii) Electric polarization in a molecule induced by incident-light excitation inevitably generates a new electromagnetic field, referred to as an “optical near-field.” However, such a self-consistent light-matter (LM) interaction between electron and electromagnetic field dynamics is ignored.

Recent development of nanofabrication and nano-optical techniques requires a more general optical response theory fully taking account of *nonuniform and self-consistent* LM interactions.

We have developed a generalized theoretical description of full (nonuniform and self-consistent) LM interactions with the aim of understanding the optical near-field excitation dynamics in nanostructures of more than ten-nanometers in size. Electron dynamics in nanostructures interacting with an

electromagnetic field is described by the time-dependent Kohn-Sham (TDKS) equation, whereas electromagnetic field dynamics is represented by the microscopic Maxwell’s equations. The nonuniform LM interaction is taken into account in the vector potential and the self-consistent LM interaction is described by solving the electron and electromagnetic field coupled equations self-consistently. The coupled equations are solved numerically by using our developed computational program (GCEED: *Grid-based Coupled Electron and Electromagnetic field Dynamics*). Our computational approach is based on a finite-difference method in real-time and real-space. Since the approach employs very simple algorithms, it is very suitable for massively parallelized computations.

Very recently, we also started the theoretical studies of computational design of catalytic metal clusters supported on bulk surfaces. The simulations were carried out by using the first-principles molecular dynamics (MD) approach, *i.e.*, Car-Parrinello MD simulations. The theoretical approach allows us to treat dynamical chemical reaction processes taking account of the effects of temperature and nonequilibrium interactions between clusters and supports.

Selected Publications

- K. Nobusada and K. Yabana, “Photoinduced Electric Currents in Ring-Shaped Molecules by Circularly Polarized Laser Pulses,” *Phys. Rev. A* **75**, 032518 (7 pages) (2007).
- T. Iwasa and K. Nobusada, “Nonuniform Light-Matter Interaction Theory for Near-Field-Induced Electron Dynamics,” *Phys. Rev. A* **80**, 043409 (11 pages) (2009).
- K. Nobusada and T. Iwasa, “Oligomeric Gold Clusters with Vertex-Sharing Bi- and Triicosahedral Structures,” *J. Phys. Chem. C* **111**, 14279–14282 (2007).
- M. Noda, K. Ishimura, K. Nobusada, K. Yabana and T. Boku, “Massively-Parallel Electron Dynamics Calculations in Real-Time and Real-Space: Toward Applications to Nanostructures of More than Ten-Nanometers in Size,” *J. Comput. Phys.* **265**, 145–155 (2014).

1. Two-Photon Absorption Induced by Electric Field Gradient of Optical Near-Field and its Application to Photolithography¹⁾

An electric field gradient is an inherent property of the optical near-field (ONF). In this study, we have verified that the electric field gradient of the ONF intrinsically leads to two-photon absorption, demonstrating the optical response of a closely-placed dielectric nanoparticle and quantum dot system. The theoretical calculations were carried out by using a density matrix formalism and a classical Lorentz model. The electric field gradient of the ONF was found to cause two-photon absorption by an unusual mechanism. Furthermore, the absorption exhibits a non-monotonic dependence on the spatial arrangement of the nanosystem, completely different from that of conventional two-photon absorption induced by an intense electric field. The present two-photon absorption process was illustrated in a previous experimental observation, by reinterpreting the results of ONF photolithography. The present idea of the two-photon absorption due to the electric field gradient is not limited to the model system considered here. The idea provides a basis for fundamental optical responses in nanostructures and paves the way for the ONF excitation dynamics that are completely different from those of conventional optical response processes.

2. Reaction Pathway and Free Energy Landscape of Catalytic Oxidation of Carbon Monoxide Operated by a Novel Supported Gold–Copper Alloy Cluster²⁾

An insight into the catalytic activities of pure gold (Au_8) and gold-alloy (CuAu_7) clusters supported on either $\text{MgO}(100)$ or graphene has been undertaken in the search for an efficient, yet commercially appealing production of Au-based nanocatalysts. The present set of first-principles dynamical simulations shows that the gold and gold-copper alloy clusters destabilize to various extents on MgO but preserve their structures on the graphene support at room temperature. Consequently, the Cu atom remains embedded inside the Au cluster on MgO , whereas it can be easily exposed on the cluster surface on the graphene substrate. This feature appears to be a general key issue to trigger the catalytic reaction and discloses new perspectives for a rational synthesis of supported Au-based catalysts relying on the intrinsic chemical character of Cu which possesses a stronger affinity to oxygen than Au. Indeed, the Cu atom acts as an active site for the approach of O_2 and keeps the molecule bound to the cluster. We clarified that the catalytic oxidation of CO occurs on the graphene-supported CuAu_7 in a highly selective Langmuir-Hinshelwood type reaction, addressing the long-standing controversy about the actual reaction mechanism for this type of catalysis. Our findings contribute to the development of

efficient and commercially appealing supported alloy clusters driven by a proper choice of dopants and supports, thus reducing the use of expensive gold.



Figure 1. A first step of the Langmuir-Hinshelwood type reaction on CuAu_7 supported by graphene, obtained via Blue-Moon ensemble simulations. CO approaches the gold surface and reacts with O_2 anchored on the Cu active site, forming an intermediate for the subsequent CO_2 desorption.

3. Control of Optical Response of a Supported Cluster on Different Dielectric Substrates³⁾

We developed a theoretical approach for photo-induced electron dynamics at an interface, approximating a substrate as a dielectric continuum. Because electron dynamics is treated in real-time and real-space, the approach is applicable to various optical processes. We calculated optical absorption of Ag_n ($n = 2, 54$) supported on a dielectric substrate with a Drude-type dielectric function. Changes in ω_p and γ of the substrate differently altered the spectral peak position and intensity. By analyzing the time-dependent induced dipole and spatial configuration of induced electron density, we clarified the mechanism underlying spectral changes, relating to experimental results obtained in many research areas. Shifts in spectral peaks of Ag_2 were mainly determined by the strength of attractive and repulsive interactions with the substrate, and decreases in peak intensity were due to energy dissipation into the substrate. These peak shifts and intensity changes are related to the real and imaginary parts of $\epsilon - 1/\epsilon + 1$, respectively. We extended the approach to a nanostructure, Ag_{54} , and found another mechanism for changes in intensity, which is related to the real part of $\epsilon - 1/\epsilon + 1$. The spectral peak for Ag_{54} increases through interactions with the Ag substrate because of collective oscillations of electrons. The present method and the resulting insights contribute to a basic understanding of optical processes at an interface and to the development of optical devices that can be controlled by electronic properties of a substrate.

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