

# Theory for Optical Response in Nanostructures and Application to Unified Photonic and Electronic Devices

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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) A scale of 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 spatially 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 highly suitable for massively parallelized computations. By using GCEED, we are currently computationally designing unified photonic and electronic nanodevices.

We also launched a new project of computational design of heterogeneous catalysts to develop efficient and commercially appealing ones, thus reducing the use of expensive rare catalytic metals. The simulations were carried out by using the first-principles, *i.e.*, Car-Parrinello, molecular dynamics 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).
- K. Nobusada and T. Iwasa, “Oligomeric Gold Clusters with Vertex-Sharing Bi- and Tricosahedral 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).
- M. Yamaguchi and K. Nobusada, “Indirect Interband Transition Induced by Optical Near Fields with Large Wave Numbers,” *Phys. Rev. B* **93**, 195111 (2016).

## 1. Indirect Interband Transition Induced by Optical Near Fields with Large Wave Numbers<sup>1)</sup>

Optical near fields (ONFs) have Fourier components with large wave numbers that are two or three orders of magnitude larger than those of far-field propagating light owing to their nonuniformity in space. By utilizing these large wave numbers, the ONF is expected to induce an indirect interband transition between Bloch states having different wave numbers and directly generate an electron–hole pair without electron–phonon coupling. We perform time-dependent dynamics calculations of a one-dimensional periodic potential with an indirect band-gap structure and demonstrate that the ONF definitely induces an indirect interband transition. Instead of using the general Bloch boundary condition, which is usually imposed in conventional band structure calculations, we adopt an alternative boundary condition, the Born–von Karman boundary condition<sup>1)</sup>, to appropriately treat indirect interband transitions. The calculated absorption spectra for the far-field and ONF excitations show different absorption edges and spectral patterns. We argue that this difference can be experimentally measured as evidence of the effects of the large wave numbers of the ONF.

## 2. Reducing the Cost and Preserving the Reactivity in Noble-Metal-Based Catalysts: Oxidation of CO by Pt and Al–Pt Alloy Clusters Supported on Graphene<sup>2)</sup>

The oxidation mechanisms of CO to CO<sub>2</sub> on graphene-supported Pt and Pt–Al alloy clusters are elucidated by reactive dynamical simulations. The general mechanism evidenced is a Langmuir–Hinshelwood (LH) pathway in which O<sub>2</sub> is adsorbed on the cluster prior to the CO oxidation. The adsorbed O<sub>2</sub> dissociates into two atomic oxygen atoms thus promoting the CO oxidation. Auxiliary simulations on alloy clusters in which other metals (Al, Co, Cr, Cu, Fe, Ni) replace a Pt atom have pointed to the aluminum doped cluster as a special case. In the nanoalloy, the reaction mechanism for CO oxidation is still a LH pathway with an activation barrier sufficiently low to be overcome at room temperature, thus preserving the catalyst efficiency. This provides a generalizable strategy for the design of efficient, yet sustainable, Pt-based catalysts at reduced cost.

## 3. Interface Electronic Properties Between a Gold Core and Thiolate Ligands: Effects on an Optical Absorption Spectrum in Au<sub>133</sub>(SPh-*t*Bu)<sub>52</sub><sup>3)</sup>

We analyze the electronic structures and optical absorption spectrum of Au<sub>133</sub>(SPh-*t*Bu)<sub>52</sub>, particularly in terms of

interface electronic properties between the Au core and the thiolate ligands. Computations are performed by using the time-dependent density functional theory approach in real-time and real-space that has recently been developed by our group. Local density of states analysis reveals a relationship between an icosahedral Au core and a thiolate-protected Au cluster; Au atoms associated with the edge or surface sites of the icosahedral core anchor the ligands to the core, whereas Au atoms associated with the apex sites bridge two thiolates forming –S–Au–S– bonds. We compare the optical absorption spectrum of Au<sub>133</sub>(SPh-*t*Bu)<sub>52</sub> with that of an icosahedral Au<sub>146</sub> bare cluster to clarify effects of the ligands on the optical absorption. The absorption intensity for Au<sub>133</sub>(SPh-*t*Bu)<sub>52</sub> is obviously higher than that for the bare cluster. The significant increase in the optical absorption of Au<sub>133</sub>(SPh-*t*Bu)<sub>52</sub> is attributed to mutual enhancement of electric polarizations induced both in the Au core and in the thiolate ligands. The effect of the enhancement is computationally visualized by analyzing the electric fields generated in the Au core and the thiolate ligands.

## 4. Nonlinear Optical Response Induced by a Second-Harmonic Electric-Field Component Concomitant with Optical Near-Field Excitation<sup>4)</sup>

Electron dynamics excited by an optical near field (ONF) in a two-dimensional quantum dot model was investigated by solving a time-dependent Schrödinger equation. It was found that the ONF excitation of the electron caused two characteristic phenomena: A two-photon absorption and an induction of a magnetic dipole moment with a strong third-harmonic component. By analyzing the interaction dynamics of the ONF and the electron, we explained that the physical mechanism underlying these phenomena was the second-harmonic electric-field component concomitant with the near-field excitation originating from the nonuniformity of the ONF. Despite a *y*-polarized ONF source, the second-harmonic component of an *x*-polarized electric field was inherently generated. The effect of the second-harmonic electric-field component is not due to usual second-order nonlinear response but appears only when we explicitly consider the electron dynamics interacting with the ONF beyond the conventional optical response assuming the dipole approximation.

### References

- 1) M. Yamaguchi and K. Nobusada, *Phys. Rev. B* **93**, 195111 (2016).
- 2) K. Koizumi, K. Nobusada and M. Boero, *Chem. –Eur. J.* **22**, 5181 (2016).
- 3) K. Iida, M. Noda and K. Nobusada, *J. Phys. Chem. C* **120**, 2753 (2016).
- 4) M. Yamaguchi and K. Nobusada, *Phys. Rev. A* **92**, 043809 (2015).