

Theory for Optical Near-Field Response 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,” according to Maxwell’s equations. 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* light-matter (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 dynam-

ics 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 based on minimal coupling Hamiltonian with Coulomb gauge. On the other hand, 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. We have achieved the parallelized calculations with more than 660,000 cores in the K computer (Kobe RIKEN), which is one of the worldwide leading supercomputers.

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).
- Y. Kubota and K. Nobusada, “Exciton–Polariton Transmission in Quantum Dot Waveguides and a New Transmission Path due to Thermal Relaxation,” *J. Chem. Phys.* **134**, 044108 (8 pages) (2011).

1. Massively-Parallel Electron Dynamics Calculations in Real-Time and Real-Space: Toward Applications to Nanostructures of More Than Ten-Nanometers in Size¹⁾

A highly efficient program of massively parallel calculations for electron dynamics has been developed in an effort to apply the method to optical response of nanostructures of more than ten-nanometers in size. The approach is based on time-dependent density functional theory calculations in real-time and real-space. The computational code is implemented by using simple algorithms with a finite-difference method in space derivative and Taylor expansion in time-propagation. Since the computational program is free from the algorithms of eigenvalue problems and fast-Fourier-transformation, which are usually implemented in conventional quantum chemistry or band structure calculations, it is highly suitable for massively parallel calculations. Benchmark calculations using the K computer at RIKEN demonstrate that the parallel efficiency of the program is very high on more than 60,000 CPU cores. The method is applied to optical response of arrays of C₆₀ orderly nanostructures of more than 10 nm in size. The computed absorption spectrum is in good agreement with the experimental observation.

The present computation is one of the largest first-principles calculations of photoinduced electron dynamics in nanostructures. It is highly expected that nanostructures of up to ~50 nm in size with a quantum confinement effect are promising materials in developing next-generation quantum devices with valuable functions. The first-principles calculations of excitation dynamics in such huge nanostructures are really unprecedented in molecular and material science. The present computational approach paves a new way of theoretically designing these devices at a real nanoscale.

2. First-Principles Computational Visualization of Localized Surface Plasmon Resonance in Gold Nanoclusters²⁾

We have studied the cluster-size dependence of localized surface plasmon resonance (LSPR) for Au_n clusters of up to $n = 1414$ (3.9 nm in diameter) by performing first-principles photoinduced electron dynamics calculations. The maximum cluster size is unprecedentedly large in comparison with those addressed in previous, fully quantum mechanical, calculations of optical response in real cluster systems. The computations enable us to see that LSPR gradually grows and its peak position redshifts (blueshifts) with increasing (decreasing) cluster size. These computed results are in good agreement with experimental observations. The localized surface charge distributions are visualized in real space, vividly illustrating the conduction electrons oscillate in a collective manner. From the visualization, LSPR has proven to be discernible at $n \sim 146$, although the optical responses for Au_n ($n \leq 146$) are still

mostly in a quantum regime because a quantum confinement effect remains predominant. The charge oscillation occurs in two regions, the outermost surface region and the inner region. The surface charge responds in synchronization with the applied laser field, whereas the inner charge oscillates locally around each gold atom in a direction opposite to the surface charge distribution. This is clear evidence of a screening effect caused by the d-electrons. The present quantum mechanically accurate description of LSPR in gold nanoclusters provides valuable information when utilizing the properties of LSPR in developing plasmonic functional devices.

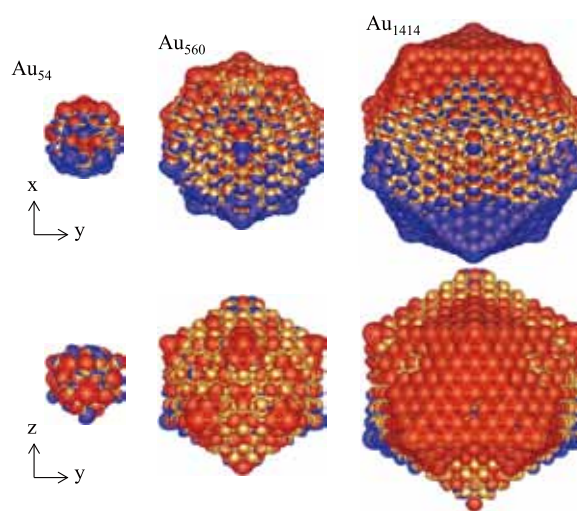


Figure 1. Photoinduced densities of LSPR for Au_n ($n = 54, 560$, and 1414).

3. Nonsuperatomic [Au₂₃(SC₆H₁₁)₁₆][−] Nanocluster Featuring Bipyramidal Au₁₅ Kernel and Trimeric Au₃(SR)₄ Motif³⁾

We report the X-ray structure of a cyclohexanethiolate-capped [Au₂₃(SR)₁₆][−] nanocluster (counterion: tetraoctylammonium, TOA⁺). The structure comprises a cuboctahedron-based bipyramidal Au₁₅ kernel, which is protected by two staple-like trimeric Au₃(SR)₄ motifs, two monomeric Au(SR)₂ and four plain bridging SR ligands. Electronic structure analysis reveals nonsuperatomic feature of [Au₂₃(SR)₁₆][−] and confirms the Au₁₅ kernel and surface motifs. The Au₁₅ kernel and trimeric staple motif are unprecedented and offer new insight in understanding the structure evolution of gold nanoclusters.

References

- 1) M. Noda, K. Ishimura, K. Nobusada, K. Yabana and T. Boku, *J. Comput. Phys.* **265**, 145–155 (2014).
- 2) K. Iida, M. Noda, K. Ishimura and K. Nobusada, *J. Phys. Chem. A* **118**, 11317–11322 (2014).
- 3) A. Das, T. Li, K. Nobusada, C. Zeng, N. L. Rosi and R. Jin, *J. Am. Chem. Soc.* **135**, 18264–18267 (2013).