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

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Optical response of materials is undoubtedly essential for understanding their physicochemical properties. In conventional theoretical approaches to optical response of materials, two conditions are usually assumed:
(i) A scale of wavelength of an incident light is much longer than material size, *i.e.*, dipole approximation. Thus, a target material is well approximated by a point dipole and the dipole feels a spatially uniform electromagnetic field.
(ii) Electric polarization in a material induced by incident-light excitation inevitably generates a new electromagnetic field, referred to as an "optical near-filed." 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. Electron dynamics in nanostructures interacting with an electromagnetic field is described by the time-dependent Kohn-Sham equation, whereas electro-magnetic field dynamics is represented by the microscopic Maxwell's equations. The nonuniform LM interaction is considered 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. Very recently, we newly developed a computational program called SALMON (Scalable Ab-initio Light-Matter simulator for Optics and Nanoscience) including all the functions of the GCEED. By using the SALMON, we are currently computationally designing unified photonic and electronic nanodevices.

We also performed 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.

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 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).
- M. Noda, M. Yamaguchi and K. Nobusada, "Second Harmonic Excitation of Acetylene by the Optical Near Field Generated in a Porous Material," *J. Phys. Chem. C* **121**, 11687–11692 (2017).

1. Second Harmonic Excitation of Acetylene by the Optical Near Field Generated in a Porous Material[1]

We perform first-principles calculations of the photo-excitation dynamics of an acetylene molecule in a metal organic framework, IRMOF-10. Resonant laser excitation of the IRMOF-10 generates an optical near field (ONF) around the two benzene rings that comprise the main framework of the IRMOF-10. Interestingly, along with the ONF of frequency ω, which synchronizes with the resonant frequency of the IRMOF-10, a second harmonic (= 2ω) component of the ONF is generated. The second harmonic component effectively excites the acetylene molecule at a frequency of 2ω, although the incident laser field is in tune with ω. It is noteworthy that the second harmonic excitation is caused by spatial nonuniformity of the ONF interaction. It is completely different from the conventional two-photon excitation and is much more efficient than the two-photon excitation by several orders of magnitude.

2. Development of Theoretical Approach for Describing Electronic Properties of Hetero-Interface Systems under Applied Bias Voltage[2]

We have developed a theoretical approach for describing the electronic properties of hetero-interface systems under an applied electrode bias. The finite-temperature density functional theory is employed for controlling the chemical potential in their interfacial region, and thereby the electronic charge of the system is obtained. The electric field generated by the electronic charging is described as a sawtooth-like electrostatic potential. Because of the continuum approximation of dielectrics sandwiched between electrodes, we treat dielectrics with thicknesses in a wide range from a few nanometers to more than several meters. Furthermore, the approach is implemented in our original computational program called GCEED. Thus, the approach is capable of comprehensively revealing electronic structure changes in hetero-interface systems with an applied bias. We calculate the electronic structure of a SiO_2-graphene-boron nitride (BN) system in which an electrode bias is applied between the graphene layer and an electrode attached on the SiO_2 film. The electronic energy barrier between graphene and BN is varied with an applied bias, and the energy variation depends on the thickness of the BN film. This is because the density of states of graphene is so low that the graphene layer cannot fully screen the electric field generated by the electrodes. We have demonstrated that the electronic properties of hetero-interface systems are well controlled by the combination of the electronic charging and the generated electric field.

3. An Atomic-Level Insight into the Basic Mechanism Responsible for the Enhancement of the Catalytic Oxidation of Carbon Monoxide on a Cu/CeO_2 Surface[3]

The reaction mechanisms of CO molecules interacting with a Cu/CeO_2 surface and related morphological modifications occurring upon removal of O atoms to generate CO_2 are investigated by first-principles dynamical simulations complemented by a free-energy sampling technique. We show that the reactivity of oxygen atoms located in the first layer in the vicinity of the Cu site is remarkably high because of a reduction of the O coordination number. Moreover, we evidence that the doped Cu atoms are responsible for an enhancement of the exposure of other surrounding O atoms, even below the first surface layer, which can then easily react with CO and are gradually removed from the system in the oxidation process. The underlying mechanism responsible for such a high catalytic reactivity of the Cu/CeO_2 surface toward CO oxidation is rationalized in terms of the characteristics of the doped Cu. In fact, this copper site is responsible for providing an increasing number of O atoms participating in the catalysis by exposing subsequently all O atoms in the vicinity which are likely to react with an approaching CO. This peculiarity of the Cu atoms extends to O atoms which initially can be deeply buried up to the fourth layer underneath the surface.

4. Large Hyperpolarizabilities of the Second Harmonic Generation Induced by Nonuniform Optical Near Fields[4]

We studied the optical selection rules and hyperpolarizabilities of a second harmonic generation (SHG) induced by a nonuniform optical near field (ONF) on the basis of first-principles calculations. The excitations of the symmetric and asymmetric molecules para-dinitrobenzene (pDNB) and para-nitroaniline (pNA), respectively, were investigated according to the time-dependent density functional theory. By calculating the ONF excitation dynamics of symmetric pDNB, we demonstrated that the ONF causes the SHG even in symmetric materials because of nonuniformity of the field in space. To quantitatively evaluate the intensity of the SHG induced by the ONF, we estimated the first hyperpolarizability, $\beta(2\omega)$, of asymmetric pNA for both of the usual far-field light and ONF excitations. Our results showed that $\beta(2\omega)$ for the ONF excitation is 1–2 orders of magnitude larger than that for the far-field excitation when the distance between the source of the ONF and pNA is around 10 Å.

References
1) M. Noda, M. Yamaguchi and K. Nobusada, *J. Phys. Chem. C* **121**, 11687–11692 (2017).
2) K. Iida, M. Noda and K. Nobusada, *J. Chem. Phys.* **146**, 084706 (10 pages) (2017).
3) K. Koizumi, K. Nobusada and M. Boero, *Phys. Chem. Chem. Phys.* **19**, 3498–3505 (2017).
4) M. Yamaguchi and K. Nobusada, *J. Phys. Chem. C* **120**, 23748–23755 (2016).