

I-E Theoretical Studies of Electron Dynamics

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, electric conduction, and also chemical reaction. Despite the 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 revealed the dynamics in detail.

I-E-1 Photoinduced Electric Currents in Ring-Shaped Molecules by Circularly Polarized Laser Pulses

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We have theoretically demonstrated that circularly polarized laser pulses induce electric currents and magnetic moments in ring-shaped molecules Na₁₀ and benzene. The photoinduced electric currents are simulated in real space and real time within a time-dependent local density approximation. It has been found that the electric currents are induced efficiently and persist continuously even after the laser pulses were switched off provided the applied laser frequency is in tune with the dipole resonance frequency for each molecular system. The electric currents are definitely revealed to be a second order nonlinear optical response. The ring currents inevitably cause the magnetic dipole moment, so that the molecules are magnetized. The circularly polarized laser pulses induce the electric currents and the magnetic moment much more effectively than by using static magnetic fields.

I-E-2 An Efficient Numerical Method for Exciton States in Quantum Boxes

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We have developed an efficient numerical method for exciton states in thin quantum boxes. In our numerical method, the exciton wave function is expanded in terms of coordinate eigenstates on each grid point. This method is found to be much more efficient and promising for calculating the exciton states than the standard configuration-interaction (CI) approach. In the CI approach, the wave function is expanded in terms of single-particle electron and hole eigenfunctions. Then, the computations of the matrix elements of the Hamiltonian (Coulomb potential) require multidimensional numerical integrals. Thus, the CI approach needs huge computational costs due to the multidimensional integrals. It is practically difficult to apply the CI approach to the studies of multi-exciton states, dynamics of excitons, and excitons in complex microstructures. To overcome the drawback, we alternatively use the discrete variable representation (DVR) as the basis set for the wave function. The DVR is a coordinate eigenfunction localized on each grid point associated with the Gaussian quadrature rule. Taking the advantage of the DVR, the matrix of the multidimensional Coulomb integrals can be reduced to the diagonal matrix with single point values. Consequently, the computational time for the matrix elements decreases sharply. The matrix of the kinetic energy is also sparse. Then, we can deal with a large number of bases by using the Lanczos diagonalization. We obtained energy, eigenfunction, and electron-hole separation of the exciton for various widths L of the quantum box. Our numerical method has high potentialities for studying properties of bi- and tri-excitons in various microstructures.

I-F Electronic Structure Theory of Quantum Dissipative Systems

I-F-1 Electronic Structure Theory of Adsorbate-Surface Systems

YASUIKE, Tomokazu; NOBUSADA, Katsuyuki

In the conventional cluster model, the model cluster, which is constructed by subtracting a subsystem from the whole adsorbate-surface system, is isolated. The isolated cluster implicitly has the artificial boundary condition that the wave function should be zero at the edge of the cluster. Such an inaccurate boundary condition leads to discrete energy spectra, although adsorbate-

surface systems must have continuous ones. In the present work, we circumvent this problem by introducing the absorbing boundary condition (ABC) into the model cluster. The ABC model cluster was found to precisely reproduce the exact density of states (DOS) of a 1D periodic potential model. The improvement of DOS leads to an appropriate description for the adsorbate-surface chemical bonding. Moreover, it was also shown that the ABC model cluster allows us to reveal the dynamical properties such as an adsorbate-surface electron transfer rate and a lifetime of adsorbate electronic states.

I-F-2 Electronic Structure Calculations at Constant Chemical Potential toward the Application to Electrochemistry

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We have developed the method of quantum chemistry calculations based on Mermin's finite temperature density functional theory (FT-DFT) to describe the electronic structures of molecular systems interacting with an electron reservoir. On the basis of the Kohn-Sham (KS) formalism of FT-DFT, the FT-KS equation is derived in a very similar form to the equation at zero-temperature. In the FT-KS equation, the exchange-correlation potential is intrinsically a function of temperature, and the occupation numbers are associated

with the Fermi-Dirac distribution. We practically approximate the exchange-correlation potential by the hybrid B3LYP functional given at zero-temperature. Then, the FT-KS equation can be solved by exploiting the same algorithm in the standard DFT calculations except that the effects of the temperature and the chemical potential are taken into account through the fractional occupation numbers. The numerical scheme for solving the FT-KS equation mentioned above was implemented in the quantum chemistry program GAMESS and applied to the reaction, $\text{Ag}^{2+} + e^- \rightleftharpoons \text{Ag}^+$ in aqueous solution. To estimate the effects of the aqueous solvent, the polarizable continuum model (PCM) was employed. The radii R of the cavities in PCM were adjusted to reproduce the experimental data of the hydration free energies.

I-G Electronic Structures and Photochemical Properties of Nanometer-Sized Metal Clusters

Nanometer-sized metal clusters provide interesting physicochemical properties such as optical response, catalysis, and reactivity, which are significantly different from those in corresponding bare metal clusters or bulk metals. We have investigated the electronic structures and the photochemical properties of monolayer-protected metal clusters with special emphasis on describing metal-molecule interactions.

I-G-1 Theoretical Investigation of Optimized Structures of Thiolated Gold Cluster $[\text{Au}_{25}(\text{SCH}_3)_{18}]^+$

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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 Au_{25} core clusters protected by 18 methanethiolates. The most probable optimized structure consists of a 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 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.

plexes $\text{Au}_n(\text{SCH}_3)_n$. The complexes were found to be stable structures in the form of a circular ring. The characteristic Au-S interaction plays an important role in forming such a unique ring structure. The ring structure also provides interesting photochemical properties that are rather different from those of similar-sized gold-methanethiolate clusters.

I-G-2 Gold-Thiolate Nanoring: Electronic Structure and Photochemical Properties

NOBUSADA, Katsuyuki

We have studied the electronic structure and the photochemical properties of gold-methanethiolate com-