Research Group of Quantum Chemical Engineering

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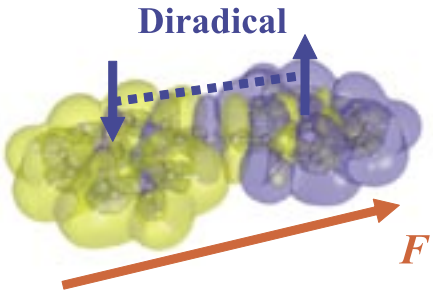
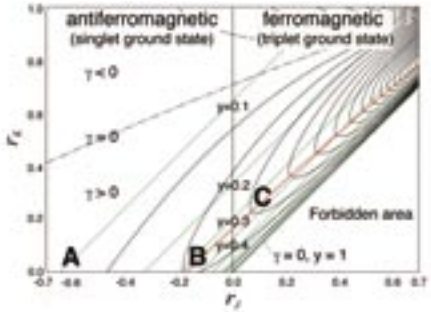
Developing Theory and Creating New Concepts in Materials Science

The research theme of Nakano Laboratory is to explore the underlying theoretical basis of various chemical and physical phenomena such as structure-property relations, spatio-temporal evolution, nonlinear responses, reaction dynamics, non-equilibrium dynamics and cooperative quantum phenomena in micro-, meso- and macro- scopic atomic/molecular systems. We develop theory, create new concepts and principles, and predict new chemical/physical phenomena in materials and biological science on the basis of classical mechanics, quantum mechanics, electromagnetics, statistical mechanics and quantum field theory. We also aim to construct new design rules for functional materials based on these fundamental principles, which will lead to a genuine breakthrough in engineering and applied science.

Theoretical Study of Open-Shell Nonlinear Optical Systems and Development of Quantum Design Principles

We construct "a theory of novel nonlinear optical (NLO) substances based on open-shell molecular systems" in intermediate/strong correlation regimes, and examine the properties of model and real systems belonging to these regimes using quantum chemistry. This study is based on our theory combined with computational prediction and is carried out in collaboration with experimentalists. The phenalenyl diradical systems, which have been predicted to show large third-order NLO properties on the basis of our theory, have turned out to exhibit one of the largest two photon absorption (TPA) cross sections in the world, and thus are expected to play a central and fundamental role in future photonic applications.



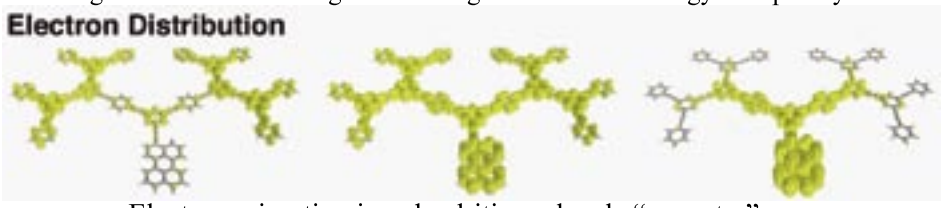


Third-order polarizability (γ) of diphenalenyl radical γ on the *J*/*U* - *K*/*U* plane and diradical character *y*

Energy Migration Dynamics and Nonlinear Optical Properties of Natural/Artificial Super- and Supra- Molecular Systems

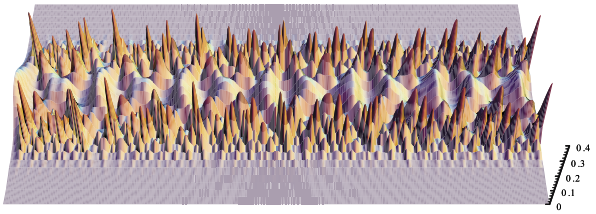
Efficient and directed transport of energy obtained by photoabsorption is observed in dendrimeric macromolecules and dendritic aggregates. This energy transport is caused by exciton (electron-hole

pair) migration from the periphery to the core region. We develop a novel treatment of such dynamics based on the quantum master equation involving exciton-phonon coupling and apply this method to the clarification of the exciton migration mechanism and its structural dependences, which will be useful for the theoretical design of efficient novel light harvesting and nano-size energy transport systems.



Electron migration in a dendritic molecule "nanostar"

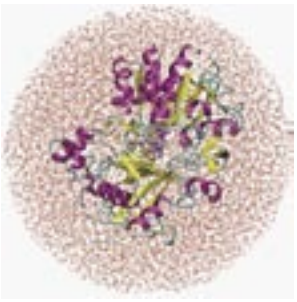
Dissipative Quantum Dynamics of Macroscopic Quantum Phenomena



Collapse–revival of the Schrödinger cat in BEC

We investigate the quantum dynamics of coupled systems composed of atoms/molecules and quantum fields such as coherent states and squeezed states, and elucidate the relationship between atomic/molecular coherency and the quantum statistics of photons. We also investigate the quantum dynamics of multi-component Bose-Einstein condensate (BEC) gas in order to clarify the mechanism of the creation of the Schrödinger cat state, i.e., the macroscopic superposition state, and its time evolution behavior such as collapse-revival. These studies on quantum open systems will be useful to develop a fundamental understanding of the boundary of classical and quantum worlds and their future application in quantum information devices.

Chemical Reactions in Condensed Phases



Clarification of reaction mechanisms in condensed phases such as biological systems is essential in order to understand the principles of life. In real biological systems, specific reaction pathways are chosen from a plurality of possible reaction pathways through the interaction between reacting substrates and surrounding proteins. To explore these mechanisms, we develop a novel quantum chemical approach combined with the theory of statistical mechanics.

References (main papers in 2007)

(1) Relationship between Third-Order Nonlinear Optical Properties and Magnetic Interactions in Open-Shell Systems: A New Paradigm for Nonlinear Optics, M. Nakano, R. Kishi et al., *Phys. Rev. Lett.* **99**, 033001-1-4 (2007).
(2) Second Hyperpolarizabilities of Singlet Polycyclic Diphenalenyl Radicals: Effects of the Nature of the Central Heterocyclic Ring and Substitution to Diphenalenyl Rings, M. Nakano, N. Nakagawa, R. Kishi, et al., *J. Phys. Chem. A* **111**, 9102-9110 (2007).
(3) Finite-Field Spin-Flip Configuration Interaction Calculation of the Second Hyperpolarizabilities of Singlet Diradical Systems, R. Kishi, M. Nakano et al., *J. Chem. Theory Comput.* **3**, 1699-1707 (2007).
(4) Theoretical Study on the Second Hyperpolarizabilities of Phenalenyl Radical Systems Involving Acetylene and Vinylene Linkers: Diradical Character and Spin Multiplicity Dependences, S. Ohta, M. Nakano et al., *J. Phys. Chem. A* **111**, 3633-3641 (2007).
(5) Novel Quantum Mechanical/Molecular Mechanical Method Combined with the Theory of Energy Representation: Free Energy Calculation for the Beckmann Rearrangement Promoted by Proton Transfers in the Supercritical Water, H. Takahashi et al., *J. Chem. Phys.* **126**, 084508-1-10 (2007).