

Personal data:

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Date of Birth and Place: 16 December 1972, Ishikawa prefecture, Japan

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Current Position: Professor,

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Educational experience:

March 1995: Bachelor of Science, Department of Chemistry, Kanazawa University.

March 1997: Master of Science, Department of Chemistry, Kanazawa University.

March 2000: Doctor of Science, Department of Chemistry, Osaka University.

Positions held:

April 2000-March 2001: Postdoctoral fellowship of Japanese Society for the Promotion of Science (JSPS fellow) (Osaka University and Kansas State University), Japan.

April 2001-December 2003: Postdoctoral fellowship of Japanese Society for the Promotion of Science (JSPS fellow, University of Tokyo), Japan.

December 2003- January 2007: Assistant Professor, Department of Applied Chemistry, School of Engineering, University of Tokyo, Japan.

February 2007- May 2008: Lecturer, Collage of Physics, Graduate School of Pure and Applied Sciences, Tsukuba University, Japan.

May 2008- July 2010: Associate Professor, Picobiology Institute, Graduate School of Life Science, University of Hyogo, Japan.

August 2010- March 2014: Associate Professor, Department of Material Sciences, School of Engineering Science, Osaka University, Japan.

March 2014-: Professor, Collage of Physics, Graduate School of Pure and Applied Sciences, Tsukuba University, Japan.

April 2016-: Professor, Center for Computational Sciences, Tsukuba University, Japan.

Research Experience and Fields:

1. April 1995 - March 1997: Kanazawa Univ. (PhD student)

Development of non-Born-Oppenheimer molecular theory

2. April 1997 - March 2000: Osaka Univ. (PhD student and JSPS fellow)

Development of multi-component density functional theory and application to proton coupled electron transfer in condensed phase.

Spin level crossing phenomena in molecular magnets.

3. April 2000 - July 2000: Osaka Univ. (JSPS fellow)

Application of Monte Carlo diagonalization method to electronic structure theory

4. August 2000 - March 2001: Kansas State Univ. (JSPS fellow)

Green's function theory based on Kohn-Sham density-functional theory

5. April 2001 - December 2003: Univ. Tokyo (JSPS fellow)
Quantum dynamics for coupled proton and electron system.
Electronic fluctuation in multi-component endohedral fullerenes by QM/MM molecular dynamics method
6. Jan. 2004 – Present
Development of quantal cumulant dynamics and application to the proton transfer reactions in DNA base pairs. Field-induced electron dynamics in biomolecules.
7. Feb. 2007 - Present
Proton and electron transfer reactions in protein environments.
8. Feb 2007 – Present
Development of first-principles molecular dynamics simulation methods using high-performance computing environments and its application to Nano-bio systems.

Awards and fellowships:

1. May 2013, 2nd Young researcher' award of Osaka University, "Dynamics Theory Including Fluctuation" (Osaka University, Japan).
2. September 2012, 5th Young scientists' prize of Japanese Society for the Molecular Science, "Dynamics Theory Including Fluctuation" (Japanese Society for the Molecular Science, Japan).
3. April 2010, Young scientists' prize, The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology (Ministry of Education, Culture, Sports, Science and Technology, Japan).
4. March 2009, 58th The Chemical Society of Japan Award for Young Chemist (Chemical Society of Japan).
5. February 2007, PCCP (Physical Chemistry and Chemical Physics) Award for Outstanding Young Scientists (Royal Society of Chemistry and Chemical Society of Japan).
6. March 2006, 86th Japanese Conference on Chemistry, presentation award for Young Scientists (Chemical Society of Japan).
7. 2001-2004, Research fellowship of Japanese Society for the Promotion of Science (JSPS Post-doctoral Fellow).
8. 1999-2000, Research fellowship of Japanese Society for the Promotion of Science (JSPS Doctoral Fellow).

Research Interest:

[1] Calculation of multi-component density functional theory.

A numerical scheme for the multi-component density functional calculation is proposed. The method is based upon the Green function techniques within the GW approximation for evaluating molecular properties in the full quantum mechanical treatment. We numerically calculate the physical properties of the individual motion in a hydrogen molecule and a muon molecule by means of this method and discuss the isotope effect on the properties in relation to correlation effects. It is concluded that the GW approximation works well not only for calculation of the electronic state but also for that of nuclear state.

[2] Anomalous phases in proton and electron transfer systems.

We investigate singly ordered phases of the charge density wave (CDW), spin density wave (SDW), and singlet superconductivity (SSC) for a pseudo one-dimensional proton and electron transfer (PET) system of the quinhydrone crystal by means of the two-band model. We perform band structure calculations of model systems, which are (i) the quinone and the p-hydroquinone model and (ii) the two semiquinones model. It is found that model (i) exhibits a nonmagnetic insulator and model (ii) manifests the SDW insulator at low temperature. Next, the conductive properties of model polymers including the deoxyribonucleic (DNA) base pairs (iii) A-T and (iv) G-C are investigated. We find that these model polymers also exhibit the SDW insulator, and the double-proton transfer reaction in the base pairs decreases the transition temperature, which is, however, much higher than room temperature.

[3] Spin level crossing phenomena of molecules.

The dependence of the magnetization of model systems on an external magnetic field has been investigated. An ab initio path integral Monte Carlo method is used to study the spin level crossing phenomena of molecules with ring structures such as those in the ferric wheel. The ab initio treatment is essential to calculate the magnetization in a system with a large contribution from next-neighbor interactions. A possible use as a molecular device for switching or molecular recognition is suggested.

[4] Electron propagator calculation based on KS reference state (Under collaboration with Prof. Ortiz's group at Auburn University)

Kohn-Sham orbitals are employed in a generalization of the 2p-h Tamm-Dancoff approximation derived for a determinantal reference state. Neglect of certain terms in the superoperator couplings between triple field operator products recovers the so-called GW approximation, which has been extensively applied in solid state physics. Further simplifications are examined as well. The performance of these approximations with several exchange-correlation potentials is assessed by comparing calculated ionization energies with the in counter parts obtained with electron propagator methods based on Hartree-Fock reference states.

[5] Relation between Green function theory and density functional theory (Under collaboration with Prof. Hirata's group at University of Florida (Now at University of Illinois, Urbana-Champaign)

We deal with two topics concerning about the single-particle Green's function (GF) theory for molecular systems. One is to derive an energy-independent and renormalized single-particle equation with a set of auxiliary renormalization equations in super-operator formalism of the GF theory. It is found that the present theory is categorized as one of the density matrix functional theories, because the resulting single-particle equation depends explicitly on a single-particle density matrix and the auxiliary renormalization equations determine it. The other is that a relation between the GF method and the non-empirical Kohn-Sham density functional theory is clarified by deriving a local and energy-independent single-particle potential from the Sham-Schluter (SS) equation, which is one of the optimized effective potential (OEP) method.

The effects of the adiabatic approximation in time-dependent density-functional theory (TDDFT) on dynamic polarizabilities and van der Waals C_6 coefficients have been analyzed quantitatively. These effects are shown to be small in the off-resonance region of the perturbation frequencies by comparing the results from the exact-exchange TDDFT employing the optimized effective potentials and the corresponding frequency-dependent kernel time-dependent optimized effective potentials TDOEP and those from the frequency-independent kernel adiabatic TDOEP (ATDOEP). We have shown the breakdown of the ATDOEP at the resonance, whereas the rigorous non-adiabatic TDOEP reproduces the exact results.

[6] Gigantic fluctuation of effective charge on encapsulated atoms in fullerenes (Under collaboration with Prof. Takatsuka at Tokyo University)

As one of the typical examples of characteristic reaction field generated in inclusion enclosure compounds, the dynamics of an endohedral metallofullerene, $\text{Be} + n\text{H}_2 @\text{C}_{60}$ ($n = 1, 2$), is studied with Be atom serving as a test probe. A very large dynamical and thermal fluctuation of electronic state of Be has been found, which is surprising since the highest occupied molecular orbital-lowest unoccupied molecular orbital gap of Be is so wide that such a large fluctuation in a low temperature is never expected. This finding demonstrates one of the special features of endohedral reaction field offered by the fullerene.

[7] Field-induced electronic ring current in biomolecules. (Under collaboration with Prof. Manz's group at Freie Universität Berlin)

The purpose of this work is to suggest a new mechanism for the induction of selective electronic ring currents in molecules: excitation by a few cycle circularly polarized UV laser pulse, within a few femtoseconds (fs). It is motivated by recent advances in laser technology which provide the tools for the present approach, from circularly polarized pulses with controlled shape in the fs to the attosecond (as) time domain. A circularly polarized ultraviolet (UV) laser pulse may excite a unidirectional valence-type electronic ring current in an oriented molecule, within the pulse duration of a few femtoseconds (e.g., $t = 3.5$ fs). The mechanism is demonstrated by quantum model simulation for $|X\rangle = |1\ ^1A_{1g}\rangle \rightarrow |E_+\rangle = |4\ ^1E_u\rangle$ population transfer in the model system, Mg-porphyrin. The net ring current generated by the laser pulse ($I = 84.5$ micro A) is at least 100 times stronger than any ring current, which could be induced by means of permanent magnetic fields with present technology.

[8] Quantal cumulant dynamics (Collaboration with Prof. Prezhdo's Group at Washington Univ.)

This work opens new frontiers in the quantum dynamics, which offers convenient way to investigate quantum isotope effect of proton transfer reactions. Y. Shigeta has formulated a novel semi-quantal method both for static and dynamic phenomena, which is called a λ quantal cumulant dynamics (QCD)[†]. The QCD is an extension of the quantized Hamilton dynamics (QHD) method, first proposed by Prezhdo, and the second order approximation of the QCD is equivalent to the well-known Gaussian wave packet theory and to the wave function-based method by means of the squeezed-coherent state ansatz. Although the QHD is limited to treating special cases, i.e. a truncated potential, the QCD is more widely applicable. The key point of the extension is the use of a position shift operator acting on the potential operator, so that one needs not truncate the potential, and it does not require separating into quantum and classical parts, as is done in the QHD method.

In particular, he has derived the coupled equation of motion (EOM) for the position, momentum, and second-order cumulants of the product of the momentum and position fluctuation operators, where the cumulants describe the quantum fluctuation around the classical variables. The EOM consists of variables and a quantal potential and its derivatives, where the quantal potential is expressed as an exponential function of the differential operator acting on the given potential. The advantages of the QCD approach over the QHD method are: (i) a systematic construction of the higher-order equations of motion is possible; (ii) there are no errors in the energy and its gradient due to the truncation of the potential; and (iii) there is no tedious derivation with respect to the

decomposition scheme in the QHD method.

To evaluate the quantal potential and its derivatives, he have proposed three possible schemes: (i) a truncation; (ii) a series summation of the analytic derivatives; and (iii) convolution schemes. If one truncates the potential up to the fourth order, then the EOM is identical to the second order QHD approach, as used by him for problems about molecular vibrations. Using the second and third schemes, one can generate quantal potential of a Morse, Gaussian, and Coulomb potentials. These techniques enable us to evaluate not only the potential but also any operator whatever one wants, such as the density operator. Thus the method gives definite density, whereas the several semi-classical dynamics methods do not.

On the basis of the QCD, he has introduced the concept of a quantal potential energy surface, where the idea of the potential energy surface is extended to taking quantum effects, such as the zero-point vibration, into account. The tunneling phenomena are observed based on the transition state analysis of the present quantal potential hyper surface. In particular, he has applied the method to investigate double hydrogen transfer reaction in DNA base pairs and revealed that the double hydrogen transferred structure of the GC pair is no longer stable due to dynamic quantal fluctuation and its deuterium isotopomer is meta-stable due to isotope effects.

[9] Reaction mechanism and physical properties of biological and bio-inspired systems (in collaboration with Prof. Negoro and Prof. Higuchi, Univ. Hyogo, Japan)

We have investigated reaction mechanisms of Cytochrome *c* Oxidase, a terminal enzyme of respiratory chain, and Nylon-oligomer hydrolase, a enzyme degrading an artificial compound on the basis of molecular dynamics and first-principles molecular dynamics simulation. Free energy profiles are estimated using Metadynamics techniques. We have suggested a possible point mutation for higher enzymatic activity than the wild type under the collaboration with experimentalists.

We have also investigated a bio-inspired systems that consist of DNA bases and metal ions such as a cis-platine DNA complex, metal-containing artificial DNAs (ADNA), and metal-coordinating mismatch DNAs (MDNA). Especially, proton transfer reactions between the bases enhanced by Pt coordination and electronic conductivity of ADNA and MDNA are focused in this project.