Abstracts of Congress and Plenary Lectures

2CL

Interplay Between Experiment and Theory

Yuan-Tseh Lee
Academia Sinica, Taiwan

During the past 100 years, our understanding of chemistry has changed quite substantially. First, the laws of thermodynamics allowed us to elucidate, chemical equilibrium and chemical properties based on fundamental laws of nature. Then, the advances made early in the twentieth century in the understanding of the laws of mechanics governing the motion of microscopic particles, enabled us to explore molecular structures and chemical changes, solely based on quantum mechanics. However, because of the complexity of chemical system we are dealing with, neither theoretical investigation nor experimental pursuit alone have been shown to be adequate in advancing the basic understanding of chemistry. During the past fifty years, with the advancement of sophisticated experimental methods and high speed electronic computation, the interplay between experiment and theory has become more important and more fruitful.

In this lecture, my personal perspective as well as some examples will be given to illustrate the interplay between experiment and theory during the last forty years, especially in the field related to chemical dynamics. Some discussion will also be made on the important challenges human society is facing today for our survival on the surface of the earth.

2PL

Theoretical Studies of Chemical Reactions – Gas Phase Reactions to Nano Structures, Catalyses, and Enzymatic Reactions in Ground and Excited Electronic States

Keiji Morokuma
Fukui Institute for Fundamental Chemistry, Kyoto University, Kyoto 606-8103, Japan and Cherry L. Emerson Center for Scientific Computation and Department of Chemistry, Emory University, Atlanta, GA 30322, U.S.A.

The chemical reaction which creates, destroys, reorganizes chemical bonds to produce new compounds is the most important subject of chemistry. I have been absorbed by this exciting world of chemical reactions from the beginning of my career for more than fifty years, since a hand-powered calculator was used to solve Hückel secular equations for frontier electron densities of simple aromatic hydrocarbons. Theoretical/computational studies have come a long way and are now playing the central role in understanding the mechanism and dynamics of chemical reactions and in helping designing more useful chemical reactions and catalysts. The theory can study not only the reaction of the ground state of molecules in gas phase but also reactions of excited electronic states as well complicated reactions of complex molecular systems. The information theoretical/computational studies can provide is often complementary to the information experimental studies provide, and research on chemical reactions is becoming impossible without strong collaboration between theorists and experimentalists.

I will discuss a few examples of recent theoretical/computational studies performed in my group on chemical reactions. The areas to be covered include A. efficient and automatic determination of reaction pathways; B. self-assembly reactions of small carbon clusters to form fullerenes and carbon nanotubes with or without transition metal catalysts; C. homogeneous catalyses in solution and in the confined space created by protein, D. reactions of metalloenzymes with active site models and in protein environment, and E. chemical and biochemical processes involving excited electronic states.

4PL-1

Understanding Nucleation Phenomena at Large Metastability: From Gas-Liquid Transition to Metastable Solids and Polymers

M. Santra, R. S. Singh, S. Chakrabarty and B. Bagchi*
Solid State and Structural Chemistry Unit,
Indian Institute of Science, Bangalore – 560 012.
(http://www.liquid.sscu.iisc.ernet.in)
*Email: bbagchi@sscu.iisc.ernet.in

Abstract

We have revisited the apparently well-studied problem of nucleation and growth of a stable phase inside a parent metastable phase, particularly near the spinodal curve. We have undertaken extensive computer simulation studies to probe the molecular mechanism for the onset of instability in a wide range of systems (both for 2 and 3 dimensional Lennard-Jones fluid and nearest neighbour Ising model). We have constructed the multidimensional free energy surface of nucleation as a function of multiple reaction coordinates [1]. While the classical Becker-Döring (BD) picture of homogenous nucleation, that assumes the growth of a nucleus by single particle addition, holds good at low to moderate supersaturation, the formation of the new stable phase becomes more collective and spread over the whole system at large supersaturation. As the spinodal curve is approached from the coexistence line, the nucleation free energy barrier, as a function of the size of the *largest liquid-like cluster*, disappears at a supersaturation (well below the thermodynamic spinodal limit) that we term as kinetic spinodal [2]. Very close to the kinetic spinodal the free energy surface becomes quite flat and the critical nucleus grows by diffusion on a barrierless surface. We have developed an alternative formalism to treat nucleation at large supersaturation by introducing an extended set of order parameters in terms of the kth largest liquid-like clusters, where k = 1 is the largest cluster in the system, k = 2 is the second largest cluster and so on [2]. We shall also discuss nucleation of metastable solids and collapsed state of polymers.

References:

1. P. Bhimalapuram, S. Chakrabarty and B. Bagchi, *Phys. Rev. Lett.* **98**, 206104 (2007); S. Chakrabarty, M. Santra and B. Bagchi, *Phys. Rev. Lett.* **101**, 019602 (2008); M. Santra, S. Chakrabarty and B. Bagchi. *J. Chem. Phys*. **129**, 234704 (2008).

2. M. Santra, Rakesh S. Singh and B. Bagchi, *J. Stat. Mech*. P03017 (2011); M. Santra and B. Bagchi, *Phys. Rev.* E, **83**, 031602 (2011).

4PL-2

Short-time frictional solvent effects on conical intersection dynamics for a model photoisomerization

Joao Pedro Malhado^{a}, Riccardo Spezia^{b} and James T. Hynes^{a,c}

a CNRS UMR 8640, Departément de Chimie, Ecole Normale Supérieure, 24 rue Lhomond, 75231, Paris, FR
b CNRS UMR 8587, LAMBE, Université d'Evry, Bd. F. Mitterrand, 91025 Evry, FR
c Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309, USA

It is now well appreciated that conical intersections (CIs) often provide an efficient, ultrafast nonadiabatic transition route from an excited electronic state to the ground state for photochemical reactions [1]. Accordingly, much effort---both theoretical and experimental---has been devoted to their study. Our previous efforts in this area [2,3,4] have focused on constructing an approximate model description aimed at elucidating and describing the influence of a solvent (and ultimately a more complex protein environment) on CI structure and dynamics in a photoreaction context. Of particular interest to us are photoreactions in which significant intramolecular charge transfer in the chromophore results in strong coupling to a polar environment. The template for our efforts has been a two valence bond, three coordinate description of the *cis-trans* photoisomerization of a model protonated Schiff base (PSB), itself a model for retinal, of interest in connection with vision. In this talk---after a brief review of salient features of the basic model and prior relevant results such as minimum energy paths and inertial, non-dissipative trajectory results---we will describe our most recent results [5] addressing the inclusion in the model of short-time 'friction', describing energy and momentum transfer effects on the CI and photoisomerization dynamics. These effects are modeled via a generalized Langevin description of dynamical frictions on the PSB intramolecular twist and bond length alteration coordinates and on a nonequilibrium dielectric continuum solvent coordinate. Two model solvents are examined, acetonitrile and water, which are characterized by different solvent time-scales. Nonadiabatic trajectories were generated via Tully's molecular dynamics with quantum transitions, fewest switches algorithm [6]. The important influence of the solvent-dependent generalized friction on the path to the solvent coordinate-induced seam of CIs from the Franck-Condon excitation region, on the location of the nonadiabatic transitions to the ground electronic state, and on the *trans* or *cis* ground state product distribution will be described.

[1] See e.g. B.G. Levine and T. J. Martinez, *Ann. Rev. Phys. Chem.*, **58**, 613 (2007).

[2] I. Burghardt, L.S. Cederbaum and J.T. Hynes, *Faraday Discuss.*, **127,** 395 (2004). For earlier efforts on CI *ground* state reaction effects, see D.Laage, I. Burghardt, T.Sommerfeld and J. T. Hynes, *J. Phys. Chem. A*, **107,** 11271 (2003).

[3] R. Spezia, I. Burghardt and J.T. Hynes, *J. Molec. Phys.*(Robb Issue), **104**, 903 (2006).

[4] I.Burghardt and J.T. Hynes, *J. Phys. Chem. A*, **110**, 11411 (2006).

[5] J. Malhado, Thesis, ENS (2009); J. Malhado, R. Spezia and J.T. Hynes, *J. Phys. Chem. A*, in press, 2010. **DOI:** 10.1021/jp106096m

[6] J. C. Tully, *J. Chem. Phys.,* **93**, 1061 (1990).

4PL-3

A Computational Approach to the Study of Free Radical Chemistry

Leo Radom

School of Chemistry and Centre of Excellence for Free Radical Chemistry and Biotechnology, University of Sydney, Sydney, NSW 2006, Australia

Radicals are ubiquitous in chemistry and biology. Because they are reactive species, they are often difficult to study experimentally and therefore theory has a potentially useful role to play in their characterization. However, there are also challenges for theory, particularly in the form of so-called spin contamination. In recent years, we have been involved in formulating theoretical procedures that provide an improved description for radicals. We have also been using such procedures to investigate the structures, stabilities and reactivities of radicals. Highlights from this research will be presented.

5PL-1

Quantum Chemistry in Schrödinger Accuracy

Hiroshi Nakatsuji
Quantum Chemistry Research Institute (QCRI) and JST CREST
Kyoto, Japan (h.nakatsuji@qcri.or.jp)

Quantum principles represented by the Schrödinger equation and Dirac-Coulomb equation have vast and strong quantitative predictive powers. However, this was not realized for over 80 years, because we did not have a general method of solving these equations in high accuracy. However, recently, this author has found such method [1-3] and one major subject of our QCRI has been to develop efficient methodology. To make theoretical quantum science to be truly predictive, we have to establish accurate and useful method of solving these equations for our common molecular systems.

The accuracy and reliability of our methodology were well established for rather small atoms and molecules. For few-electron systems, like helium, we could give numerical proof on how accurate is our methodology, not only for ground state [4] but also for excited states [5], and not only for energy, but also for wave function itself, like local energy, cusp, and other properties [6]. This was so not only for non-relativistic Schrödinger case, but also for relativistic Dirac-Coulomb case [7]. It was further extended to non-BO case [8]. Though this was done mostly using variation principle where we have to calculate analytical integrals, we have also proposed LSE (local Schrödinger equation) method [9] which is integration-free method and completely general for any analytical functions that are generated automatically by the Hamiltonian of the system (free complement methodology). Further, we have introduced useful local sampling method, anti-symmerization method, and from-atom-to- molecule idea. These methods certainly contributed to increase the atomic and molecular size to which our theory is applicable.

Here, we will introduce some new ideas and formulations on this line of research and show some computational results.

References
[1] Nakatsuji, JCP 113, 2949 (2000); Nakatsuji, Davidson, JCP 115, 2000 (2001).
[2] Nakatsuji, Ehara, JCP 117, 9, (2002); 122, 194108 (2005)
[3] Nakatsuji, PRL 93, 030403 (2004), PRA, 72, 062110 (2005)
[4] Kurokawa, Nakashima, Nakatsuji, PRA, 72, 062502 (2005); Nakashima, Nakatsuji, JCP, 127, 224104 (2007); 128, 154107 (2008); Kurokawa, Nakashima, Nakatsuji, PCCP, 10, 1 (2008); Nakatsuji, Nakashima, Adv. Theor. Atom. Mol. Systems, B 47 (2009)
[5] Nakashima, Hijikata, Nakatsuji, JCP, 128, 154108 (2008).
[6] Nakashima, Nakatsuji, PRL, 101, 240406 (2008); Nakatsuji, Nakashima, IJQC, 109, 2248 (2009); Bande, Nakashima, Nakatsuji, Chem. Phys. Lett., 496, 347 (2010).
[7] Nakatsuji, Nakashima, PRL, 95, 050407 (2005). Ishikawa, Nakashima, Nakatsuji, JCP, 128, 124103 (2008)
[8] Hijikata, Nakashima, Nakatsuji, JCP, 130, 024102 (2009).
[9] Nakatsuji, Nakashima, Kurokawa, Ishikawa, PRL, 99, 240402 (2007)

6PL-1

Looking at the world from a coupled-cluster perspective

Rodney J. Bartlett,[1] S. Ajith Perera,[1] M. Musial,[1] P. Verma,[1] M. Strassberg[1]
[1]*Quantum Theory Project, Departments of Chemistry and Physics, University of Florida, USA*

In this talk we will address the broader context of coupled-cluster (CC) theory in chemistry. The theory offers an approach to a new correlated orbital theory (COT) that has similar computational demands to density functional theory (DFT) but is built upon the premise that the one-particle spectrum of a molecule, its principal ionization potentials and electron affinities should be right. Approximations to these equations can be made to provide the computational advantages of an effective one-particle theory.

A related topic is the role of the random phase approximation (RPA) in defining a correlation potential for DFT. We introduce the concept of ‘coulomb attenuation” as a way to better treat the correlation problem, by first solving for Coulomb-only interactions, leaving the exchange and subsequent correlation to simpler, perturbative treatments. This new division of the correlation problem depends upon the close correspondence between CC theory and its RPA approximation limited to the sum of ring diagrams.

6PL-2

Developments of Broken Symmetry Methods Application to the $CaMn_4O_5$ Cluster at OEC of PSII Refined to 1.9 Å X-Ray Resolution

K. Kanda,[1] S. Yamanaka, [1] T. Saito, [1] Y. Umena, [2] K. Kawakami, [3] J. R. Shen, [2]
N. Kamiya, [3] M. Okumura, [1] H. Nakamura, [4] Y. Yoshioka, [5] K. Yamaguchi,[1,6]
[1]*Graduate School of Science, Osaka University, Toyonaka, 560-0043, Japan*
[2]*Graduate School of Natural Science and Technology, Okayama University, 700-8530*
[3]*Graduate School of Science, Osaka City University, Sugimoto, 558-8585, Japan*
[4]*Protein Institute, Osaka University, Suita, 560-0871, Japan*
[5]*Graduate School of Engineering, Mie University, Tsu, 514-8507, Japan*
[6] *TOYOTA Physical & Chemical Research Institute, Aichi, 480-1192, Japan*

In this lecture historical developments of broken symmetry methods at Osaka [1-4] have been briefly reviewed, particularly, in relation to electronic and spin structures of organic polydiradicals and transition-metal oxides with local spins. Past decades, manganese-oxo (Mn=O) and related manganese-oxides species [3,4] have been received great interest concerning with water splitting reaction at oxygen evolving complex (OEC) of photosynthesis II (PSII). Here, we present our recent BS UB3LYP computational results [5] on the $CaMn_4O_5$ cluster of PSII refined to 1.9 Å X-ray resolution [6] reported by Shen and Kamiya and their collaborators.

Possible electronic and spin structures of the $CaMn_4O_5$ cluster have been investigated by UB3LYP assuming the X-ray structure [6]. All the BS configurations feasible for the valence configurations of the cluster, Mn(III)xMn(IV)y (x,y = 0-4), have been constructed by the HOMO-LUMO mixing and other techniques. The spin and charge populations obtained by UB3LYP are consistent with BS configurations available. The effective exchange interactions (J) between manganese ions in the cluster are determined by our computational procedures based on the approximate projection (AP). Full geometry optimizations of the antiferromagnetic exchange-coupled states of the cluster have been performed for comparison with the X-ray result [4]. The nature of chemical bonds of the cluster is also investigated by the natural orbital analysis of the BS solutions to elucidate possible mechanisms of water splitting reaction. Implications of the present computational results are also discussed briefly.

[1] K. Yamaguchi, T. Fueno and H. Fukutome, Chem. Phys. Lett. 22, 461 (1973).
[2] K. Yamaguchi, Chem. Phys. Lett. 33, 330 (1975); 35, 230 (1975); 66, 395 (1979).
[3] K. Yamaguchi, Y. Takahara and T. Fueno, Appl. Quant. Chem, p155-p184 (1986).
[4] K. Yamaguchi et al, in Organic Peroxides (W. Ando Ed., Wiley, 1992) p1-p100.
[5] K. Kanda et al, Chem. Phys. Lett. 506, 98 (2011)
[6] Y. Umena, K. Kawakami, J. R. Shen, N. Kamiya, Nature 473, 55 (2011).

6PL-3

Rate of convergence of basis expansions in quantum chemistry

Werner Kutzelnigg,[1]
[1] *Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, Germany*

Traditional expansions in an orthonormal basis of the type of a Fourier series are very sensitive to the singularities of the function to be expanded. Exponential convergence is only possible, if the basis functions describe the singularities of the expanded functions correctly. Otherwise only an inverse-power-law convergence is realized, which is usually slow. Example: the slow convergence of the CI expansion due to the correlation cusp. An improved convergence, though still of inverse-power type, can be achieved, if one augments the basis by functions that describe the singularities of the wave function correctly, like in the R12 method.

Alternative: a discretized integral transformation, as in the conventional expansion of wave functions in a Gaussian basis. Such expansions are surprisingly insensitive to singularities of the wave function to be expanded (e.g. the nuclear cusp). The rate of convergence is of a new type, with an error estimate $\sim \exp(-a\sqrt{n})$, if n is the basis size. For the expansion of the hydrogenic ground state function in an even-tempered Gaussian basis, simple closed expressions for the asymptotic error can be derived. This can be generalized to the relativistic case, where the convergence is qualitatively similar to the non-relativistic one, in spite of the stronger singularity in the relativistic wave function.

References:

W. K, Int J. Quantum Chem. 51, 447 (1994);

Computational Quantum Chemistry: a Primer, by E. Cances, M. Defrancheschi, W. Kutzelnigg, C. Le Bris, Y. Maday , Handbook of Numerical Analysis,Vol. X, Elsevier 2003

W.K. J. Chem. Phys. 126, 201103 (2007) .

W.K. AIP conference proceedings, in press 2011

E-mail: werner.kutzelnigg@rub.de

6PL-4

Analysis and Control of Electronic Motion in the Time Domain

E.K.U. Gross
Max Planck Institut für Mikrostrukturphysik, Weinberg 2, 06108 Halle, Germany

This lecture is about how electronic motion can be monitored, analyzed and, ultimately, controlled, in real time. In particular:

(i) A novel approach to describe **electronic transport** through single molecules or atomic wires, sandwiched between semi-infinite leads, will be presented. The basic idea is to propagate the time-dependent Kohn Sham equations in time upon ramping up a bias between the metallic leads. In this way, genuinely time-dependent phenomena, not accessible in the standard Landauer approach, can be addressed. For example, employing an Anderson model, we demonstrate that Coulomb blockade corresponds, in the time-domain, to a periodic charging and discharging of the quantum dot [1].

(ii) With modern pulse-shaping facilities, the **control of electronic motion** is becoming more and more realistic. By combining quantum optimal control theory with TDDFT, we calculate shaped laser pulses suitable to control, e.g., the chirality of currents in quantum rings [2], the location of electrons in double quantum dots, as well as the enhancement of a single peak in the harmonic spectrum of atoms and molecules.

(iii) In all practical TDDFT calculations, approximate forms of the exchange-correlation potential need to be employed. One of the most popular approximations, the adiabatic local-density approximation (ALDA) will be analyzed as to whether the main error comes from the adiabaticity assumption, i.e. locality in time, or from the LDA, i.e. locality in space. For an exactly solvable model where the **exact adiabatic approximation** can be extracted, we find the surprising fact, that the adiabaticity assumption can be an excellent approximation even in highly intense laser fields [3].

(iv) Finally, the coupling between electronic and nuclear motion will be addressed. As a first step towards a full ab-initio treatment of the coupled electron-nuclear motion in time-dependent external fields, we deduce an exact factorization of the complete wavefunction into a purely nuclear part and a many-electron wavefunction which parametrically depends on the nuclear configuration. We derive formally exact equations of motion for the nuclear and electronic wavefunctions [4]. These exact equations lead to a rigorous definition of **time-dependent potential energy surfaces** as well as **time-dependent geometric phases**. With the simple example of the hydrogen molecular ion in a laser field we demonstrate the significance of these concepts in understanding the full electron-ion dynamics. In particular, the time-dependent potential energy surfaces are shown to represent a powerful tool to analyse and interpret different (direct vs. tunneling) types of dissociation processes.

[1] S. Kurth, G. Stefanucci, E. Khosravi, C. Verdozzi, E.K.U. Gross, *Phys. Rev.Lett.**104**, 236801 (2010).*
[2] E. Räsänen, A. Castro, J. Werschnik, A. Rubio, E.K.U. Gross, *Phys. Rev. Lett. **98**,157404 (2007).*
[3] M. Thiele, E.K.U. Gross and S. Kümmel, *Phys. Rev. Lett. **100**, 153004 (2008).*
[4] A. Abedi, N.T. Maitra, E.K.U. Gross, *Phys. Rev. Lett. **105**, 123002 (2010).*

7PL-1

Treatment of Vibronic Properties in Infinite Periodic Systems

Bernard Kirtman[1], Matteo Ferrabone[2], Valentina Lacivita[2], Michel Rèrat[3],
Roberto Orlando[4], and Roberto Dovesi[2]

[1]*Department of Chemistry and Biochemistry*, *University of California*,
Santa Barbara, USA
[2]*Departimento di Chimica IFM, Universitá di Torino, Italy*
[3]*Equipe de Chimie Physique, Universitè de Pau et des Pays de l'Adour*, *France*
[4]*Dipartimento de Scienze e Technologie Avanzate*,
Universitá del Piemonte Orientale, *Italy*

There are many important spectroscopic properties that are determined either entirely, or in large part, by the electronic response to nuclear displacements. Some examples are Raman intensities, static and dynamic (i.e. nonlinear optical) vibrational hyperpolarizabilities, and vibrational circular dichroism. The practical calculation of vibronic properties for infinite periodic systems, or systems that may be modeled as infinite and periodic, typically requires special considerations. We will focus here primarily on static and dynamic vibrational hyperpolarizabilities that have recently been obtained, for the first time, by the finite field nuclear relaxation (FF-NR) method. The successful implementation of this computational scheme in the CRYSTAL computer code, which utilizes Gaussian-type basis sets, will be described. B3LYP results, in particular for BN nanotubes, indicate that vibrational contributions can be as important, or much more important, than pure electronic contributions depending on the property, tensor component, optical frequency, and nanotube radius. Application of the FF-NR treatment, as well as extensions of this approach, to other systems will be discussed along with computational methods for other properties.

7PL-2

Singlet Fission

Josef Michl[1,2] and Zdeněk Havlas[1]
[1]*Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Flemingovo nám. 2, 16610 Prague 6, Czech Republic*
[2]*Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0215, USA*

Singlet fission is a little known and usually inefficient form of multiple exciton generation from a single photon. It is a spin-allowed process in which a chromophore excited into its singlet state shares energy with a nearby ground state chromophore, producing a pair of triplet excited chromophores coupled into an overall singlet. Singlet fission has been observed in a very small number of aromatic hydrocarbons, particularly tetracene and pentacene, and also in a few conjugated polymers and carotenoids, starting half a century ago. It had received little attention until very recently, when it was pointed out that if it were fully efficient, and if it were possible to achieve charge separation from both resulting triplets, the limiting theoretical efficiency of a simple photovoltaic cell would be increased from 1/3 to nearly 1/2. In order to explore the potential of the phenomenon in solar cells, a much wider selection of structures for which singlet fission is efficient is needed.

We shall describe a first-principles approach to the problem of designing molecular structures for which singlet fission is efficient. This involves developing three sets of structural design rules: (i) for finding chromophores in which the conditions $E(S_1) \geq 2\ E(T_1)$ and $E(T_2) \geq 2\ E(T_1)$ are satisfied, making singlet fission exoergic and triplet annihilation endoergic, (ii) for finding chromophore coupling that maximizes the rate of singlet fission relative to all other possible decay processes in a dimer, oligomer, or crystal, and (iii) for finding arrangements that maximize the likelihood of two independent charge separation events from a triplet pair in competition with all other decay modes. The first application of the rules produced a material that exhibited a 2005 triplet yield.

7PL-3

State-specific Multi-reference Coupled Cluster Formalisms: An Overview of a Suite of Recent Developments

Debashis Mukherjee
Raman Center for Atomic, Molecular and Optical Sciences
Indian Association for the Cultivation of Science
Jadavpur, Kolkata 700 032, India

In this talk, I will present an overview of some of the recent developments in State-specific Multi-reference (SS-MR) many-body formalisms. The overarching theoretical framework is the use of the Jeziorski-Monkhorst (JM) cluster ansatz for the state-specific (SS) wave operator acting on a linear combination of model functions spanning a complete active space (CAS). The JM ansatz, when used in the context of the SS formalism, induces the "redundancy problem" of the number of cluster amplitudes which exceeds the number of combining coefficients of the virtual functions present in the target state. By imposing two desirable features, from the formalism, viz. the avoidance of intruders and the maintenance of size-extensivity, essentially unique sufficiency conditions resolving the redundancy can be found. I will give a survey of not only the parent formalism (the State-specific MRCC) but also will discuss an approximant where an **I**nternally **C**ontracted treatment of the **I**nactive (**ICI)** is done to reduce the number of the most numerous amplitudes. Numerical performance of the various methods will be illustrated by example applications to challenging prototypical systems, with pronounced and varied multi-reference character. In particular, I will highlight the following insights gained from the applications (1) the parent SS-MRCC theory in the usual CCSD truncation undermines the importance of coupling of virtual functions which are doubly excited with respect to another, thereby posing both slowness of convergence of the solutions and of somewhat poor performance; (2) an extended hierarchy of truncation schemes, viz. the SS-MRCCSDt/CCSDtq, with the t/q having the same meaning as in the Adamowicz SR-MR Ansatz allows the leading missing virtual couplings and it performs very well; (3) the SS-MRCCSD scheme, with localized orbitals obtained from individual transformations on the core, active and virtual orbitals, performs spectacularly well, presumably because the vastly reduced importance of the doubles-quadruples virtual couplings; (4) the ICID-MRCCSD, with the internally contracted treatment of the inactive double excitations perform nearly as well as the parent SS-MRCCSD. The finding (3) indicates the potential importance of the SS-MRCCSD method to treat large systems in a 'local correlation' framework. The finding (4) implies that essentially the same accuracy as the parent theory can be attained if the inactive doubles are treated in a contracted manner.

8PL-1

The K Supercomputer and Recent Advances in LC-DFT

Kimihiko Hirao
Advanced Institute for Computational Science, RIKEN, Kobe, Japan

Twice a year, the world's supercomputers are ranked according to their level of performance in a listing called the TOP500. On June 20, 2011, the K computer jointly developed by RIKEN and Fujitsu was pronounced the fastest computer in the world in the TOP500 listing announced at the 2011 International Supercomputing Conference in Hamburg. The K computer came out way ahead of its competitors with a LINPACK benchmark performance of 8.162 petaflops. The K computer's achievement was wonderful news following as it did the devastation of the March 11 Great East Japan Earthquake, and reinforces Japan's strengths in science, technology and manufacturing. It is my fervent hope that the international recognition given to the K computer will help to prime Japan's recovery from the disaster. It should be noted, however, the real test of the K computer will be the results that are achieved through its use. With the emergence of petascale computing platforms we are entering a new era of modeling. Petascale computing will enable us to simulate physical processes on a scale never seen before, and approach convergence for dynamical processes never thought possible. The K computer will open up a new frontier in computational chemistry.

DFT has emerged as a powerful computational tool for the chemical systems. It is simple and conceptual. KS-DFT calculation takes about the same amount of time as a HF calculation, yet unlike HF, we get a correlated result from KS-DFT. Many of the problems of KS-DFT have mostly been a consequence of not having accurate functionals and potentials. Recently there has been considerable interest in the long-range correction (LC) DFT. In the LC scheme the exchange functional is partitioned with respect to the inter-electronic separation into long-range and short-range parts using a standard error function. The LC solves many of the problems of the conventional KS-DFT. Recently it was demonstrated that the LC satisfies Koopmans'theorem, which implies that the eigenvalues and eigenvectors connected to the Kohn-Sham equation have a strict physical meaning. Different from Hartree-Fock Koopmans ionization energy, DFT Koopmans ionization energy to some extent takes into account the relaxation and correlation effects. Recent advances in LC-DFT will be discussed.