
# DICP Symposium on Theoretical and Computational Chemistry

Dalian, China

August 16-19, 2011

## Organizer

**Center for Theoretical and Computational Chemistry**

## Chairs

**Dong Hui Zhang & Keli Han**

## Sponsors

**Dalian Institute of Chemical Physics, CAS**
**State Key Laboratory of Molecular Reaction Dynamics**
**State Key Laboratory of Catalysis**

# Symposium Program

## Tuesday 16th August

14:00-21:00 Arrival and Registration, Bay Shore Hotel Dalian

18:00-20:00 Reception Dinner, 25th floor, Bay Shore Hotel Dalian

## Wednesday 17th August

07:00-08:00 Breakfast, 25th floor, Bay Shore Hotel Dalian

08:10 Bus to DICP

**Session A:** Wednesday Morning, DICP auditorium

**Chair: Dong Hui Zhang** ,Dalian Institute of Chemical Physics

08:30-09:00 Opening Speeches

09:00-09:35 A1: **George C. Schatz**, Northwestern University, USA
*Modeling soft material self assembly: peptide amphiphiles and DNA-linked materials*

09:35-10:10 A2: **Keiji Morokuma** , Kyoto University, Japan
*Exciting World of Theoretical Studies of Chemical Reactions – From Gas Phase Reactions to Nano Structures, Catalysts, and Enzymatic Reactions*

10:10-10:40 Group Photo and Tea Break

**Chair: Guozhong He**, Dalian Institute of Chemical Physics

10:40-11:15 A3: **Yun-Dong Wu**, Peking University, China
*Force Field Development based on Amino Acid Rotamer Distributions*

11:15-11:50 A4:**Toshihiro Kawakatsu**, Tohoku University, Japan
*Dynamic Self-Consistent Field Theory and Its Applications to Mesoscopic Structures in Polymer and Surfactant Systems*

11:50-12:25 A5: **Jinlong Yang**, University of Science and Technology of China
*Toward Atomic Details of Graphene Growth on Metal Surfaces: Theoretical Studies*

12:30-13:45 Lunch, DICP Staff Canteen

**Session B:** Wednesday Afternoon, DICP auditorium

**Chair:** **Wei-Xue Li**, Dalian Institute of Chemical Physics

14:00-14:35 B1: **Matthias Scheffler**, Fritz-Haber-Institut, Germany
*The random phase approximation for the electron correlation energy and beyond*

14:35-15:10 B2: **Xin Xu**, Fudan University, China
*Development of New Density Functionals for Accurate Descriptions of Nonbond Interactions*

15:10-15:45 B3: **GuanHua Chen**, The University of Hong Kong
*First-principles Liouville-von Neumann Equation for Open Systems*

15:45-16:05 Tea Break

**Chair:** **Wei Wu**, Xiamen University

16:05-16:40 B4: **Zhigang Shuai**, Tsinghua University, China
*Quantum chemistry for opto-electronic properties of organic materials*

16:40-17:15 B5: **Shuhua Li**, Nanjing University, China
*New coupled cluster methods for potential energy surfaces*

17:25 Bus to Bay Shore Hotel Dalian

18:30 Banquet Dinner, 4th floor Bay Shore Hotel Dalian

## Thursday 18th August

07:00-08:00 Breakfast, 25th floor, Bay Shore Hotel Dalian

08:10 Bus to DICP

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**Session C:** Thursday Morning, DICP auditorium

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**Chair: Wei Zhuang**, Dalian Institute of Chemical Physics

08:30-09:05 C1: **John D. Weeks**, University of Maryland, USA
*Screening, Structure and Simulation of Coulomb Systems: The Long and Short of It*

09:05-09:40 C2: **Ray Luo**, University of California, Irvine, USA
*Free energy simulations with continuum solvation models: How well do they stand up in biomolecular simulations?*

09:40-10:15 C3: **Yi Qin Gao**, Peking University, China
*Effects of spatial confinement and cosolvents/cosolutes on liquid water structure and dynamics-A preliminary study*

10:15-10:35 Tea Break

**Chair: Hongjun Fan**, Dalian Institute of Chemical Physics

10:35-11:10 C4: **Jing Ma**, Nanjing University, China
*Simulations of Solutions and Amorphous Solids by Using Fragmentation Quantum Chemical Calculations*

11:10-11:45 C5: **Hong-Xing Zhang**, Jilin University, China
*Design and applications of transition metal complexes in manifold functional materials*

11:45-12:20 C6: **Zhong-Zhi Yang**, Liaoning Normal University, China
*Molecular Face Model*

12:30-13:45 Lunch, DICP Staff Canteen

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**Session D:** Thursday Afternoon, DICP auditorium

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**Chair:** **Weiqiao Deng**, Dalian Institute of Chemical Physics

14:00-14:35 D1: **William H. Miller**, University of California, Berkeley, USA
*Semiclassical Theory of Electronically Non-Adiabatic Dynamics*

14:35-15:10 D2: **Stuart C. Althorpe**, University of Cambridge, UK
*Instanton calculations of rates and tunnelling splittings in water clusters and ice*

15:10-15:45 D3: **Jiushu Shao**, Beijing Normal University, China
*Derivation of Exact Master Equation with Stochastic Formulation*

15:45-16:05 Tea Break

**Chair:** **Zhigang Sun**, Dalian Institute of Chemical Physics

16:05-16:40 D4: **Yi Luo**, University of Science and Technology of China, China
*Inelastic Electron Tunneling in Molecules*

16:40-17:15 D5: **Millard H. Alexander**, University of Maryland, USA
*Theoretical simulation of the relaxation of methylene in collisions with He*

17:15-17:50 D6: **Daiqian Xie**, Nanjing University, China
*Potential energy surfaces and dynamics of $NH_2$*

18:00 Bus to Bay Shore Hotel Dalian

18:30-20:00 Dinner, 25th floor, Bay Shore Hotel Dalian

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## Friday 19th August

07:00-08:00 Breakfast, 25th floor, Bay Shore Hotel Dalian
08:10 Bus to DICP

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**Session E:** Friday Morning, DICP auditorium

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**Chair: Guohui Li**, Dalian Institute of Chemical Physics

08:30-09:05 E1: **John Zeng Hui Zhang**, East China Normal University, China
*Modeling protein dynamics with electrostatic polarization*

09:05-09:40 E2: **Zhipan Liu**, Fudan University, China
Electro-/Photo-catalytic water splitting with periodic DFT-MPB approach

09:40-10:15 E3: **Zhonghuai Hou**, University of Science and Technology of China
*Phase transition on complex networks: Coarse-grained simulation methods and nucleation kinetics*

10:15-10:35 Tea Break

**Chair: Keli Han**, Dalian Institute of Chemical Physics

10:35-11:10 E4: **Jiali Gao**, University of Minnesota , USA
*Quantum Mechanical Approaches to Biomolecular Simulations: From a Single Electron to Fully Solvated Proteins*

11:10-11:45 E5:**Hao Hu**, University of Hong Kong, China
*Developments and applications of ab initio QM/MM methods for the modeling of solution and enzyme reactions*

11:45-12:20 E6: **Qiang Cui**, University of Wisconsin-Madison, USA
*Approximate methods for biological systems - QM/MM and coarse-grained models*

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12:30-13:45 Lunch, DICP Staff Canteen
13:45 Bus to Bay Shore Hotel Dalian
14:30-17:30 Free time/Excursion
18:15 Bus to Restaurant
18:30 Farewell Dinner

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# Abstracts

# Modeling soft material self assembly: peptide amphiphiles and DNA-linked materials

**George C. Schatz**
*Northwestern University, Evanston IL 60201*

In this talk I describe research in my group concerning two self-assembly projects: the formation of cylindrical micelle structures from peptide amphiphiles (a collaboration with Sam Stupp) and the formation of gel-like materials composed of DNA-linked gold nanoparticles (a collaboration with Chad Mirkin). In both of these studies, a combination of atomistic and coarse-grained molecular dynamics methods has been used, as well as simple models, to understand both the mechanism of self-assembly process and the structural and thermodynamic properties of the self-assembled material that is produced. In the case of the peptide amphiphile assembly, I show how different levels of coarse-graining lead to different levels of understanding of the formation process and of the micelle structures that result. Of particular interest are recent results where my group has obtained an atomic level description of the micelle structures, enabling a detailed understanding of the quality of several levels of coarse-graining. For the DNA-linked gold particles, my group has developed a coarse-grained model of DNA (based on de Pablo's earlier work) that provides understanding of cooperative melting effects. Also, atomistic simulations show the role of osmotic pressure effects that dictate DNA density, and they provide insight about the correlation of base-pair composition and structural properties of the aggregate and crystalline materials.

**A2**

# Exciting World of Theoretical Studies of Chemical Reactions – From Gas Phase Reactions to Nano Structures, Catalysts, and Enzymatic Reactions

**Keiji Morokuma**[1,2]

[1] *Fukui Institute for Fundamental Chemistry, Kyoto University, Kyoto 606-8103, Japan*

[2] *Cherry L. Emerson Center for Scientific Computation and Department of Chemistry, Emory University, Atlanta, GA 30322, USA*

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 recent examples of our recent theoretical/computational studies on A. efficient determination of reaction pathways; B. self-assembly reactions of small carbon clusters to form fullerenes and carbon nanotubes; C. homogeneous catalysis, D. reactions of metalloenzymes in protein environment, and E. chemical processes involving excited electronic states of biomolecules

# Force Field Development based on Amino Acid Rotamer Distributions

**Yun-Dong WU, Fang JIANG, and Wei HAN, Cheuk-Kin WAN**

*School of Chemical Biology and Biotechnology, Peking University Shenzhen Graduate School, Shenzhen, and College of Chemistry, Peking University, Beijing*

We have recently obtained local conformational distributions ($\phi$, $\psi$, $\chi_1$) of the twenty natural amino acid residues based on statistics of a protein coil library, simultaneously considering backbone conformation and side-chain rotamers.[1] We show that current all-atom force fields such as AMBER-FF03 and OPLS-AA/L cannot well reproduce these distributions, indicating rooms for improving these force fields. Combining statistics and quantum mechanics calculations, we show that local conformational free energy surface of various amino acid residues can be modeled by the combination of that of alanine with the influence of sidechains in individual rotameric state. We have applied the strategy to the development of a united-atom protein force field coupled with coarse-grained solvent (PACE).[2] This PACE force field is able to fold a series of short peptides into their native structures.[3] It has also been successfully applied to the study of diphenylalanine aggregation.[4] We have also applied the strategy to modifying the parameters of OPLS-AA/L. The modified OPLS force field significantly improves the local conformational features.[5] It not only folds short peptides into native structures, but also produces much improved melting profiles of secondary structures. *The research is supported by the Research Grants Council of Hong Kong (663509).*

**References**:

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3. Han W.; Wan, C. K.; Wu, Y.-D. *J. Comput. Theor. Chem.* **2010**, *6*, 3390-3402.
4. Han, W.; Xiong, H.; Wu, Y.-D. Manuscript in preparation.
5. Jiang F., Han, W.; Wu, Y.-D. Submitted for publication.

**A4**

# Dynamic Self-Consistent Field Theory and Its Applications to Mesoscopic Structures in Polymer and Surfactant Systems

**Toshihiro Kawakatsu**

*Department of Physics, Tohoku University, Sendai 980-8578, Japan*

Multi-component polymeric materials such as polymer blends and block copolymers often show nano-scale domain structures induced by microphase separation. Self-consistent field (SCF) theory is a powerful tool to characterize the equilibrium structures of these nano-domains and is nowadays widely used. However, the usage of the SCF theory is mainly limited to equilibrium properties. On the other hand, dynamical extensions of the SCF theory is quite important in studying dynamical properties of the nano domains, for example formation of non-equilibrium domain structures or the rhelogical properties of phase separated dense polymer systems. For this purpose, we developed dynamic version of the SCF theory by introducing the microscopic chain dynamics and/or external force field such as an electric field or a constraining potential. Application of the dynamic SCF theory are discussed. We also discuss several extensions of the SCF theory by coupling it with other simulation techniques, such as phase field theory or molecular dynamics simulations.

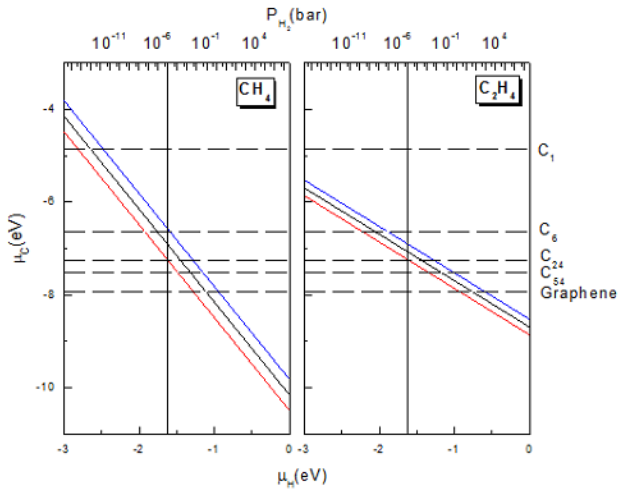
# Toward Atomic Details of Graphene Growth on Metal Surfaces: Theoretical Studies

**Ping Wu, Wenhua Zhang, Zhenyu Li, Jinlong Yang**

*Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei 230026, China*

*jlyang@ustc.edu.cn*

Graphene is an important material with many unique properties and a great application potential. A promising way to produce wafer-size graphene is chemical vapor deposition (CVD) on metal surfaces. To improve sample quality, it is important to understand the atomic details during graphene CVD growth. In this talk, some relevant elementary processes on Cu and Ir surfaces have been studied from first principles. Although diffusion of atomic carbon on Cu (111) surface is almost barrierless, coalescence of carbon atoms on the surface is found to be hampered by an intermediate bridging-metal structure. The fact which makes things more complicated is that thermodynamic analysis indicates that the main species on the Cu surface during graphene growth is not the simplest atomic carbon. Therefore, $C_xH_y$ species should be explicitly considered for initial stage growth of graphene on Cu surface. On Ir surface, steps make an important role in grapheme growth.




## References

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[2] Wenhua Zhang, Ping Wu, Zhenyu Li, and Jinlong Yang, *First-principles thermodynamics of graphene growth on Cu surface*, http://arxiv.org/abs/1101.3851.

**B1**

# The random phase approximation for the electron correlation energy and beyond

**Matthias Scheffler**
*Fritz-Haber-Institut der Max-Planck Gesellschaft, Berlin (Germany)*

The random phase approximation to the ground state correlation energy (cRPA) in combination with exact exchange (EX) has brought Kohn-Sham density functional theory one step further towards a universal, "general purpose first principles method". Indeed, at this level the exchange-correlation functional is uniquely defined, in contrast to, for example, GGA or hybrid functionals. We also discuss two systematic correction terms beyond the cRPA: renormalized single excitations (RSE) and second order screened exchange (SOSEX). [1, 2] Both corrections notably improve upon the tendency of EX+cRPA to underbind. Surprisingly, *reaction barrier heights* obtained using EX+cRPA based on a KS reference are remarkably accurate. The EX+cRPA+SOSEX+RSE functional lives up to the challenge of providing an equal level of accuracy for reaction energies and reaction barrier heights. Overall it gives the most balanced performance, which makes it applicable to a wide range of systems and chemical reactions.

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2) J. Paier, X. Ren, P. Rinke, G. E. Scuseria, A. Grueneis, G. Kresse, and M. Scheffler, to be published.

# Development of New Density Functionals for Accurate Descriptions of Nonbond Interactions, Thermochemistry, and Thermochemical Kinetics

**Igor Ying Zhang, and Xin Xu***

*Department of Chemistry, Fudan University, China*
*(xxchem@fudan.edu.cn)*

Density functional theory (DFT) has become the method of choice for first principles quantum chemical calculations of the electronic structure and properties of many chemical systems. Based on the number of occurrences of functional names in the journal titles and abstracts analyzed from the ISI Web of Science (2007), B3LYP is by far the most popular density functional in chemistry, representing 80% of the total of occurrences of density functionals in the literature, in the period 1990-2006.

Is B3LYP good for everything? There is growing evidence, showing that B3LYP (1) degrades as the system becomes larger, (2) underestimates reaction barrier heights, (3) yields too low bond dissociation enthalpies, (4) gives improper isomer energy differences, (5) fails to bind van der Waals systems, etc.

How can we go beyond B3LYP? Recently, we developed a doubly hybrid functional, XYG3, based on the adiabatic connection formalism and the Görling-Levy coupling-constant perturbation expansion to the second order (PT2). The new functional was shown to surmount the known difficulties of B3LYP, leading to a general functional with more predictive power for molecular systems of main group elements.

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**B3**

# First-principles Liouville-von Neumann Equation for Open Systems

**GuanHua CHEN**
*Department of Chemistry*
*Centre of Theoretical and Computational Physics*
*The University of Hong Kong*

Holographic electron density theorem states that the electron density function of a subsystem has one-to-one correspondence with the local potential v(r,t). Based on this, a rigorous first-principles time-dependent density-functional theory is developed for open system. The environment can be electrodes, phonons and other electrons. A series of numerical algorithms have been proposed. Applications to quantum transport and non-radiative decay of electronic excitations have been successful and will be presented.

# Quantum chemistry for opto-electronic properties of organic materials

**Zhigang Shuai**

*Department of Chemistry, Tsinghua University, 100084 Beijing*
*zgshuai@tsinghua.edu.cn*

Theoretical descriptions of opto-electronic properties of organic and polymeric materials fall in the interface of electronic structure and dynamics for complex system. We proposed statistical rate formalism for the organic light-emitting efficiency and emission spectrum [1], random walk simulation for charge mobility [2], and kinetic Monte Carlo approach for the power conversion efficiency for photovoltaic cells [3]. In this presentation, we focus on the nature of charge carrier, being localized or extended state, as well as aggregation effects on the light emission.

## References

[1] Qian Peng, Yuanping Yi, Zhigang Shuai, Jiushu Shao, J. Am. Chem. Soc. 2007, 129, 9333; Yingli Niu, Qian Peng, Chunmei Deng, Xing Gao, Zhigang Shuai, J Phys Chem A 2010, 114, 7817.

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[3] Lingyi Meng, et al. J. Phys. Chem. B, 2010, 114, 36; J. Chem. Phys. 2011, 134, 124102; Y Shang, et al. ; Theo Chem Acc. 2011, 129, 291.

**B5**

# New coupled cluster methods for potential energy surfaces

**Shuhua Li**

*School of Chemistry and Chemical Engineering, Institute of Theoretical and Computational Chemistry, Nanjing University, Nanjing, 210093*

In this talk, I will present our recent development on coupled cluster methods for computing global potential energy surfaces. The method we developed is called as the coupled cluster singles and doubles, with a hybrid treatment of triple excitations [denoted as CCSD(T)-h] [1]. For both RHF and UHF references, active (or pseudo-active) orbitals, which are directly related to bond-breaking processes, can be constructed automatically. With the concept of active and inactive orbitals, triple excitations can be divided into two subsets: “active” and “inactive”. The amplitudes of these two classes of triple excitations can be obtained via two different approaches. Illustrative applications show that the overall performance of CCSD(T)-h in computing potential energy surfaces is very competitive with that of CCSDT, and much better than that of the widely used CCSD(T) [2-4]. Recently, we proposed another strategy to construct active and inactive virtual orbitals, in which a smaller basis set is employed as an auxiliary basis set to split the virtual orbitals with a large basis set into active and inactive subsets. CCSD(T)-h based on the split virtual orbitals (SVO-CCSD(T)-h in short) has been applied to study the bond breaking potential energy surfaces in several diatomic molecules, and the equilibrium properties in a number of open-shell diatomic molecules [5]. For all systems under study, the SVO-CCSD(T)-h method is an excellent approximation to the corresponding CCSDT, providing considerable improvement on CCSD(T).

**References:**

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# Screening, Structure and Simulation of Coulomb Systems: The Long and Short of It

**John D. Weeks**
*Institute for Physical Science and Technology*
*and Department of Chemistry and Biochemistry*
*University of Maryland, College Park, MD USA*

Coulomb interactions from the dipoles in water or in classical models for ionic solutions cause major problems because of their slow decay, requiring, e.g., special and expensive treatment of periodic boundary conditions in computer simulations using Ewald sums. But they also cause problems at small length scales, where they can be so strong that they compete efficiently with the other strong molecular core interactions. We describe a new theoretical approach [1-6] for such systems by exactly separating the point charge Coulomb interaction into a slowly-varying long-ranged component that arises from a rigid Gaussian charge distribution with width sigma, and the remainder, which is short-ranged and can be added to the other short-ranged core interactions. When sigma is properly chosen, we show that one can account very accurately for the locally averaged effects of the long-ranged components in terms of an effective single particle potential, or "local molecular field" (LMF), making consistent use of a simple mean field approximation. We describe a new and very efficient way to solve the self-consistent LMF equation for the effective field [7].

The general theory is a mapping that relates the properties of a nonuniform system with long ranged intermolecular interactions in a given external field (arising, e.g., from charged solutes or walls) to those of a simpler "mimic system" with short-ranged intermolecular interactions in an effective or restructured field. The theory simplifies greatly when applied only to Coulomb interactions, where it provides a new view of classical electrostatics. The slowly varying component of the effective field is shown to satisfy Poisson's equation, but with a Gaussian-smoothed total charge density [4,5]. The effective field corrects long-standing problems with standard reaction field truncations of Coulomb interactions [4-7]. Characteristic phenomena such as ion pairing or the dielectric and electrostatic properties of the Simple (Extended) Point Charge (SPC/E) Model for water are quantitatively captured in the simpler mimic system.

**References:**

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**C2**

# Free energy simulations with continuum solvation models: How well do they stand up in biomolecular simulations?

**Ray Luo**

*University of California, Irvine, USA*

Continuum solvent models have become increasingly popular in biomolecular simulations. However their wide applications have revealed many limitations, such as improper balance of secondary structures, over population of salt-bridge interactions, and stability of proteins in molecular dynamics. These well-known limitations of continuum solvent models show that more developments are needed to fully establish the applications of these models in biomolecular simulations. In this talk, I will summarize our efforts to address how well these models can approximate explicit solvents. We have studied whether these models would break down when scaling from small organic molecules to typical-sized biomacromolecules. We have analyzed these models in the context of molecular dynamics simulations on simple systems such as dipeptides and peptides where conformational sampling is less challenging. We have found overall a good agreement between implicit and explicit solvents when consistent calibration and testing is performed. We have also noticed limitations in these models that require further development. Finally, I will summarize our development of next-generation continuum solvation framework in the context of the community-wide developments of polarizable force fields. Our preliminary studies show that it is possible to achieve very good agreement with quantum mechanical calculations for tested molecules when the new contiuum solvation framework is used.

# Effects of spatial confinement and cosolvents/cosolutes on liquid water structure and dynamics-A preliminary study

**Yi Qin Gao**

*College of Chemistry and Molecular Engineering, Peking University*

In real cells, biological molecules function in a complicated environment, which is a spatially confined aqueous solution of a large number of electrolytes and small molecules. However, the effects of the spatial confinement and cosolvents/cosolutes on the structure and dynamics liquid water are far from fully understood. In this talk, I will first present some of our recent results on the simulation and theoretical studies of liquid water under hydrophobic confinement. Based on thermodynamic argument, hydrophobic confinement changes the thermal equilibrium between liquid water and its vapor, even when the confining walls are separated by long distances, up to a micrometer. It was found in MD simulations that liquid water confined between two hydrophobic plates or alkyl chain mono-layers, unlike bulk water, show an inhomogeneous density distribution and lower polarity as a solvent. We discuss the possible reasons for such an observation and its implications. In the second part of the talk, we discuss the effects of several small organic molecules and inorganic salts on the thermodynamics and dynamical, particularly rotational relaxation, of liquid water. The experimental data on surface tension of inorganic salt aqueous solutions and salt osmotic coefficient can be explained when ion cooperativity between cations and anions is taken into account, and in cosolvent/cosolute effects on protein structures, both direct and indirect mechanisms can be important.

**C4**

# Simulations of Solutions and Amorphous Solids by Using Fragmentation Quantum Chemical Calculations

**Jing Ma,* Nan Jiang, Hui Li**

*School of Chemistry and Chemical Engineering, Institute of Theoretical and Computational Chemistry, Key Laboratory of Mesoscopic Chemistry of MOE, Nanjing University, Nanjing, Jiangsu, 210093, People's Republic of China*

The energy-based fragmentation quantum mechanics (QM) calculation has been combined with the molecular mechanics (MM) to construct the fragmentation QM/MM method [1] for simulations of dilute solutions of macromolecules. We adopt the electrostatics embedding QM/MM model, where the low-cost energy-based fragmentation calculations are employed for QM part. Conformation energy calculations, geometry optimizations, and Born-Oppenheimer molecular dynamics (BOMD) simulations of oligomers in aqueous solution have been performed within the framework fragmentation QM/MM methods. The intermolecular hydrogen bonding and chain configurations obtained from the fragmentation QM/MM simulations are consistent with the conventional QM/MM method. The chain conformations and dynamics of various oligomers in aqueous solutions are investigated through the fragmentation QM/MM or fragmentation-based polarization force field [2-3] MD simulations.

The fragmentation approach is also applied to calculate the vibrational circular dichroism (VCD) spectra of the covalently bonded oligomers and non-bonded molecular aggregates of (*S*)-alternarlactam [4]. Test calculations on the molecular aggregates using fragmentation method show good agreement with the conventional QM results. The computational cost of fragmentation calculation scales linearly with the number of the molecular fragments, facilitating the future applications to a wide range of the large-sized chiral systems.

## References

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# Design and applications of transition metal complexes in manifold functional materials

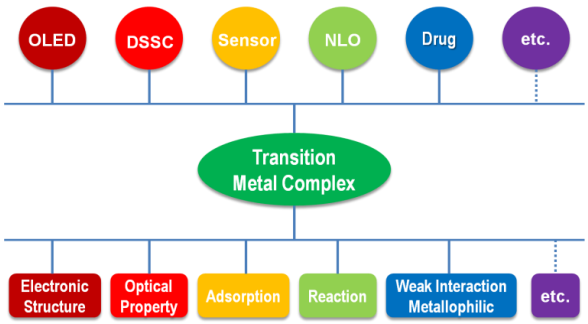
**Hong-Xing Zhang**

*State Key Laboratory of Theoretical and Computational Chemistry, Institute of Theoretical Chemistry, Jilin University, Changchun, 130023, The People's Republic of China*

For a long time, the properties of transition metal and rare earth compounds have fascinated chemists and physicists from a scientific point of view. Recently, also the enormous potential of these compounds as new materials has become evident. Applications in different fields are now established. The applications mentioned are directly related to the properties of the electronic ground state and the lower-lying excited states. Metal complexes with organic ligands or organometallic compounds exhibit outstanding features as compared to purely organic molecules.

Complexes of transition metals ($d^n$ with n=0 – 10), main group metals ($s^2$), lanthanides and actinides ($f^n$) are included in our researches. Furthermore, various types of low-lying electronic excitations can be induced by a suitable choice of the metal center and/or the ligands, such as metal-centered (MC, e.g. *d*-*d** or *f*-*f** transitions), ligand-centered (LC, e.g.π-π*), metal-to-ligand-charge transfer (MLCT, e.g. d-π*), intra-ligandcharge-transfer (ILCT) transitions, etc. In particular, the orbitals involved in the resulting lowest excited states determine the photophysical and photochemical properties and thus the specific use of the compound. Transition-metal reactions are critical in many thermodynamically feasible processes because they accelerate the reaction by opening a lower activation-energy pathway, often one that was symmetry forbidden. These metal-centered reactions consist of one or more elementary reactions such as substitution, oxidative addition, reductive elimination, migratory insertion, hydrogen exchange, β-hydrogen transfer, σ-bond metathesis, and nucleophilic addition.

Transition metal and rare earth compounds can be prepared with photophysical properties that are over a wide range user-definable. In view of the fascinating potential of these compounds, it is of substantial interest to develop a deeper understanding of their properties. Theoretical calculations are an effective way to model the physical and chemical properties of transition metal complex solids at the atomic level as a complement and guidance to experimental work. Leading scientists present modern research trends in comprehensive reviews which not only provide a deep insight into the specific subjects, but are also written in a style that enables researchers from related fields and graduate students to follow the interesting presentations.



**C6**

# Molecular Face Model

**Zhong-Zhi Yang and Dong-Xia Zhao**

*School of Chemistry and Chemical Engineering, Liaoning Normal University, Dalian, P. R. China, zzyang@lnnu.edu.cn*

The potential acting on an electron in a molecule (PAEM) is defined as the interaction energy of an electron at position $\vec{r}$ with the remaining electrons and all nuclei in a molecule.

PAEM of a series of inorganic and organic molecules were investigated using ab initio method. A molecular face (MF) [1] for a molecule, like an ID card, is defined uniquely and intrinsically, and it describes both its shape and its frontier electron dencity.

Potential acting on an electron in a molecule $V(\mathbf{r})$ (PAEM) was first defined. The molecular face contour is formed by all the MF points defined by : $\boldsymbol{G}(-I)=\{\mathbf{r}:V(\mathbf{r})=-I\}$, where I is the first ionization potential of the molecule. The feature of a MF is the electron density on the face contour that is calculated one by one with an ab initio method.

We have studied the molecular faces (MF) for a series of inorganic and organic molecules. As examples, the molecular faces (MF) of water and formic acid molecules are shown in Figure 1. We have also investigated the changing features of MFs for a few reaction processes which show interesting pictures.

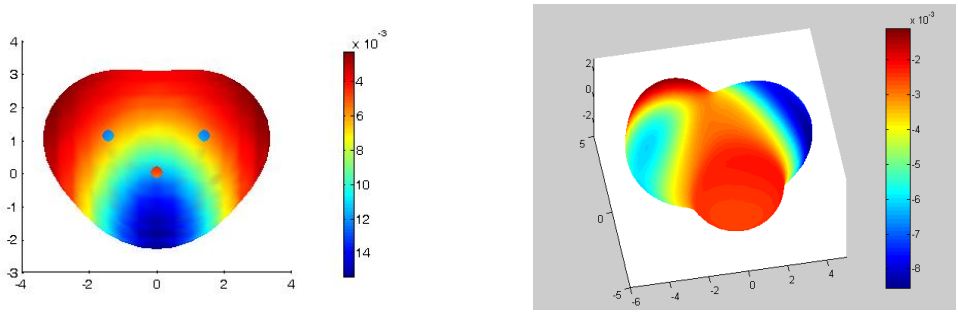


Figure 1. The molecular faces (MF) of water and formic acid molecules.

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# Semiclassical Theory of Electronically Non-Adiabatic Dynamics

**William H. Miller**
*Department of Chemistry and K. S. Pitzer Center for Theoretical Chemistry*
*University of California*
*and Chemical Sciences Division, Lawrence Berkeley National Laboratory*
*Berkeley, California 94720-1460*

The focus of my research over the last decade has been on developing semiclassical (SC) theory into a practical way for adding quantum effects to classical molecular dynamics (MD) simulations of large, complex molecular systems. A particularly interesting and important aspect of this is the ability to describe *electronically non-adiabatic processes* in a fashion that treats nuclear and electronic degrees of freedom (DOF) in an equivalent dynamical framework. This is accomplished by using a model developed by Meyer and Miller (MM) [*J. Chem. Phys*. **70**, 3214 (1979)] for replacing a finite set of electronic states of a molecular system (i.e., the various potential energy surfaces and their couplings) by a *classical* Hamiltonian involving the nuclear and (collective) electronic DOF. Much later Stock and Thoss (ST) [*Phys. Rev. Lett*. **78**, 578 (1997)] showed that the MM model is actually not a 'model', but rather a 'representation' of the nuclear-electronic system; i.e., were the MM nuclear-electronic Hamiltonian taken as a Hamiltonian *operator* and used in the Schrödinger equation, the exact (quantum) nuclear-electronic dynamics would be obtained. In recent years various initial value representations (IVRs) of SC theory have been used with the MM Hamiltonian to describe electronically non-adiabatic processes. Of special interest is the fact that although the classical trajectories generated by the MM Hamiltonian (and which are the 'input' for an SC-IVR treatment) are 'Ehrenfest trajectories', when they are used within the SC-IVR framework the nuclear motion emerges from regions of non-adiabaticity on one potential energy surface (PES) or another, and not on an average PES as in the traditional Ehrenfest model. Very recently an even more ambitious SC description of electronic DOF—one which replaces the fermionic creation and annihilation operators in the general second-quantized many-electron Hamiltonian by functions of classical action-angle variables—has been seen to provide an excellent description of transmission of electrons through a molecular junction. This opens up the possibility of being able to use classical MD simulations (of electronic and nuclear DOF) to model the many aspects of current interest in 'molecular electronics'.

**D2**

# Instanton calculations of rates and tunnelling splittings in water clusters and ice

**Jeremy O. Richardson and Stuart C. Althorpe**
*Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, UK*

This talk will explain how semi-classical instanton theory can be formulated very simply in terms of ring-polymers1-3. The approach yields the dominant 'instanton' tunneling path through a potential barrier, which, together with quadratic fluctuations around this path, can be used to calculate reaction rates or tunneling-splitting patterns. The approach is readily applied to multi-dimensional systems, including condensedphase systems with the application of periodic boundary conditions. We describe calculations of tunneling-splitting patterns in water clusters (dimer, trimer and pentamer), and investigations of the rearrangement dynamics in ice.

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# Derivation of Exact Master Equation with Stochastic Formulation*

**Jiushu Shao**

*Beijing Normal University, Beijing 100875, China*

For a dissipative system, it is shown that the influence of the environment on the system of interest is fully characterized by the bath-induced stochastic field. As a consequence, the quantum dissipative dynamics can be rigorously described by stochastic differential equations, the analogue to the traditional Langevin equation in classical mechanics.

We will report a systematic procedure for deriving the master equation of a dissipative system in the framework of stochastic description and show that the existence of a closed-form master equation depends on both the specificity of the system and the feature of the dissipation characterized by the spectral density function. For a dissipative harmonic oscillator it is observed that the correlation between the stochastic field due to the bath and the system can be decoupled and the master equation naturally comes out. Such an equation possesses the Lindblad form in which time dependent coefficients are determined by a set of integral equations. It is proved that the obtained master equation is equivalent to the well-known Hu-Paz-Zhang equation based on the path integral technique. The procedure is also used to obtain the master equation of a dissipative harmonic oscillator in time-dependent fields. A derivation of the master equation for spontaneous decay of a two-state atom will also be illustrated.

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**D4**

# Inelastic Electron Tunneling in Molecules

**Yi Luo**

*Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei, China*

*&*

*Department of Theoretical Chemistry and Biology, Royal Institute of Technology, Stockholm, Sweden*

Electron transport through a molecule is a dynamic process, which can be heavily affected by the local excitations of vibrational and electronic states. We have developed and applied several computational approaches to study these excitation processes in the framework of scattering theory. In this talk, I will demonstrate how accurate our methods can be for modeling inelastic electron tunneling spectra (IETS) of molecular junctions[1-3] and adsorbates[4] on a metal surface, and how to use it to determine the molecular conformation, the contact geometry and electron transport pathways. Dynamics of inelastic electron tunneling induced molecular switching is another important topic that will also be addressed[5-6].

Electroluminescence from molecules can also be observed under the excitation of inelastic electrons. We have developed a general theoretical approach based on the density matrix formalism to describe the electroluminescence from molecules near a metal surface induced by both electron tunneling and local surface plasmon excitations simultaneously[7]. It can provide explanations for several interesting new experimental observations[8].

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# Theoretical simulation of the relaxation of methylene in collisions with He

**Millard H. Alexander**
*(mha@umd.edu), LiFang Ma, Jacek Klos*
*University of Maryland, College Park, MD 20742-2021*
*Paul J. Dagdigian, The Johns Hopkins University, Baltimore, MD 21218-2685*

My talk will focus on the study of the methylene radical ($CH_2$) in the ground $X^3B_1$ and first excited $c^1\tilde{a}$ state. This work is one of the first detailed simulations of state-to-state relaxation of an asymmetric top in collisions with an atom. We have determined highly-accurate PES's for the interaction of $CH_2$(X) and $CH_2(\tilde{a})$ with He, using CCSD(T) calculations with correlationconsistent basis sets, extrapolated to the complete basis set limit. The calculations were carried out on a large grid of $CH_2$–He orientations and separation distances.

In the $\tilde{a}$ state the $2p_y$ orbital (the non-bonding orbital perpendicular to the plane of the molecule) is unoccupied. Thus, $CH_2(\tilde{a})$ behaves as an amphoteric Lewis acid/base. When He approaches perpendicular to the molecular plane, the interaction is substantially less repulsive than when He approaches in the molecular plane. To determine cross sections and rate constants we utilize our recent extension of the Hibridon program suite to inelastic collisions of asymmetric top molecules. There appear pronounced propensities in the inelastic cross sections are a consequence of the strong electronic anisotropy in the $CH_2(\tilde{a})$–He PES.

There have been a number of papers in the literature in which the relative magnitude of cross sections for rotationally-inelastic collisions of a diatomic molecule have been modeled entirely by a (negative) exponential or inverse power-law dependence on the magnitude of the energy gap. Our simulations reveal that overall, rotationally-inelastic collisions in a bent triatomic, at least in the case of $CH_2(\tilde{a})$–He collisions, cannot be fit by either an exponential or power-law dependence on the energy gap.

In its ground ($X^3B_1$) electronic state, both the in- and out-of-plane *p* orbitals are singly occupied, so that the potential for the interaction with He is much less anisotropic. Consequently, the rotational relaxation cross sections are smaller. A number of rotational levels in the v=2 and 3 bending levels of the X state are nearly degenerate with rotational levels in the v=0 level of the $\tilde{a}$ state. These few nearly degenerate levels are strongly mixed by the spin-orbit Hamiltonian. The mixed states provide "gateways" for collisional energy transfer between the X and $\tilde{a}$ states. We will explore the influence of these gateways on collisional relaxation.

**D6**

# Potential energy surfaces and dynamics of $NH_2$

**Daiqian Xie**

*Institute of Theoretical and Computational Chemistry, Key Laboratory of Mesoscopic Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China*

*Email: dqxie@nju.edu.cn*

The $N(^2D) + H_2(X^1\Sigma_g^+) \rightarrow NH(X^3\Sigma^-) + H(^2S)$ reaction plays an important role in atmospheric chemistry and in combustion. The electronic ground state of $NH_2$ is coupled non-adiabatically in collinear geometry with the excited $A^2A'$ state through the Renner-Teller interaction. The signature of the Renner-Teller coupling is well known in the absorption and emission spectra of $NH_2$. This excited electronic state of $NH_2$ correlates with the same $N(^2D) + H_2$ asymptote, but in the product side to the excited $NH(\tilde{a}^1\Delta) + H$ limit.

Recently，we develped the global potential-energy surfaces for the ground and first excited electronic state of $NH_2$ by three-dimensional cubic spline interpolation of more than 20,000 *ab initio* points, which were calculated at the multireference configuration-interaction level with the Davidson correction using the augmented correlation-consistent polarized valence quadruple-zeta basis set. The ($J$=0) vibrational energy levels for the ground ($X^2A''$) and excited ($A^2A'$) electronic states of $NH_2$ were calculated with the diagonal Renner-Teller terms. The results show a good agreement with the experimental vibrational frequencies of $NH_2$ and its isotopomers.

We also examined the influence of electronically non-adiabatic Renner-Teller coupling between the two lowest-lying electronic states of $NH_2$ on absorption spectra and state-to-state reaction dynamics. The fully Coriolis coupled quantum mechanical calculations were carried out on the recently developed $NH_2$ potential energy surfaces of both the $\tilde{X}^2A''$ and $\tilde{A}^2A'$ states. It is shown that the Renner-Teller coupling has a dramatic effect on the low-lying ro-vibrational states on the excited $\tilde{A}^2A'$ potential, but its impact on the differential and integral cross sections of the $N(^2D) + H_2 \rightarrow NH + H$ reaction is relatively minor.

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**E1**

# Modeling protein dynamics wth electrostatic polarization

**John Zeng Hui Zhang**

*State Key Laboratory of Precision Spectroscopy, Department of Physics, Institute of Theoretical and Computational Science, East China Normal University*

*Department of Chemistry, New York University*

*zhzhang@phy.ecnu.edu.cn*

Although in principle theory and computation can provide detailed description and prediction of protein's structure and dynamics at molecular level, but quantitatively reliable realization of such goal is still a very difficult task. Among many difficulties, a major one is the lack of accurate description for protein interaction. Electrostatic interaction is perhaps the most important interaction in biomolecules, but so far the molecular force fields widely used to describe protein systems lack the polarization effect. Based on the recently developed fragment quantum method for proteins, we developed polarized protein-specific force field which takes into account polarization effect of specific protein structures. Systematic studies of various protein systems demonstrated the critical effect of polarization.

**E2**

# Electro-/Photo-catalytic water splitting with periodic DFT-MPB approach

**Zhipan Liu**
*Department of Chemistry*
*Fudan University, Shanghai, China*

In this talk, I will present the theoretical methods we developed and utilized for studying electrocatalytic systems and also our recent results on the mechanism and kinetics of electrochemical reactions as represented by the oxygen evolution via water splitting on RuO2 [1]. Our theoretical approach can be extended to understand the mechanism of the photocatalytic water splitting on antatase TiO2 surfaces [2] and the heterogeneous catalysis of gold nanoparticles in solution [3], which are all concerned with the solid/liquid interface. The talk will give a general introduction on the theoretical tools available for studying solid/gas interface reactions and point out that the current methods are not sufficient to model reactions in electrochemistry efficiently, mainly because of the presence of the solid/liquid interface and the electrochemical potential. In the past several years, we have developed a fast transition state searching algorithm to handle the complexity of the reactions at the solid/liquid interface and also implemented a periodic continuum solvation model based on modified Poisson-Boltzmann equation in DFT-slab methods to treat the solid/liquid interface. We will show that how accurate the DFT-MPB method for treating the metal surfaces in solution and how the method can be utilized to study the kinetics in electrochemistry, such as Tafel curves and Polarization curve.

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# Phase transition on complex networks: Coarse-grained simulation methods and nucleation kinetics

**Hanshuang Chen and Zhonghuai Hou**

*Hefei National Laboratory for Physical Sciences at Microscales and Department of Chemical Physics, University of Science and Technology of China, Hefei, 230026, China*

Network physics has gained extensive research attention in the last decade[1]. In this talk, I will present our recent work on the study of phase transition on complex networks. On one hand, we have proposed a degree-based coarse graining (d-CG) approach that not just accelerates the evaluation of phase transition properties, but also satisfies the consistency conditions for both equilibrium statistical distributions and nonequilibrium dynamical flows. For the Ising model and Susceptible-Infected-Susceptible epidemic model, we introduce these required conditions explicitly and further prove that they are satisfied by our coarse-grained network construction within the annealed network approximation. We numerically show that the phase transitions and fluctuations on the coarse-grained network are all in good agreements with those on the original one[2-3]. On the other hand, we have studied the nucleation kinetics of the Ising model on complex networks, by using the forward flux sampling method. On scale-free networks, we show that the nucleus of the new phase always grows from those nodes with smaller degrees. In addition, the critical nucleus size and the free energy barrier both increase linearly with the network size, implicating that homogeneous nucleation is only releant in finite-size networks of this type. We have also studied homogeneous nucleation on modular networks, finding that the nucleation process follows a two-step mechanism and that the nucleation rate can reach a maximum at a moderate level of modularity. A simple mean field based classical nucleation theory is proposed to illustrate these simulation results[4-5].

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**E4**

# Quantum Mechanical Approaches to Biomolecular Simulations: From a Single Electron to Fully Solvated Proteins.

**Jiali Gao**
*University of Minnesota*

Atomistic simulation and modeling of biomolecular systems and quantitative analysis of protein-ligand interactions are generally performed with the use of molecular mechanical potentials, or force fields. Although the current force fields have been very successful thanks to the parameterization by many groups around the world in the past half a century, the formalisms and the functional terms have hardly changed. To increase the accuracy and predictability in biomolecular simulation and modeling, and ultimately in drug discovery, we have developed a novel theoretical framework for a fully quantum-mechanical force field, in which the functional form is based on electronic structural theory explicitly. I will present a multistate density functional theory (MSDFT) for studying chemical reactions, including proton coupled electron transfer (PCET) processes. Then, for systems that do not involve bond-making and bond-breaking processes, I will present the explicit polarization (X-Pol) theory, which relies on block-localization of molecular fragments, by separating a large molecular system such as a fully solvated protein into subsystem molecular or group fragments. In X-Pol, the total molecular wave function is approximated as a Hartree product of the antisymmetric wave functions of individual fragments. The exchange repulsion, dispersion and charge transfer effects are approximated empirically, or can be determined *ab initio*. Some recent developments and applications are illustrated including a fully solvated protein using a quantal force field.

# Developments and applications of ab initio QM/MM methods for the modeling of solution and enzyme reactions

**Hao Hu**
*University of HongKong, China*

We report our recent progress in the development of ab initio QM/MM methods, in particular, the consideration of long-range QM/MM electrostatic interactions in the simulation of reaction systems treated by periodic boundary conditions. The inclusion of long-range QM/MM electrostatic interactions allows us to computer accurate solvation free energy and redox potentials, as well as to explore the contribution of conformational dynamics in the enzymatic catalytic process. We also report our recent results on the simulation of enzyme catalysis with QM/MM methods. Specifically, we discuss how PIN1 catalyzes the isomerization of phosphorylated prolyl-peptidyl bond.

**E6**

# Approximate methods for biological systems – QM/MM and coarse-grained models

**Qiang Cui**
*University of Wisconsin-Madison,USA*

I'll briefly discuss some recent results from our computational analysis of enzyme catalysis and dynamics. On the issue of catalysis, I'll discuss how combined quantum mechanical/molecular mechanical (QM/MM) methods help resolve interesting mechanistic issues in proton pumps and/or phosphoryl transfer enzymes. Regarding enzyme dynamics, I'll mainly talk about results from coarse-grained models. In particular, I'll discuss our attempt to use coarse-grained models to interchange dynamical characteristics of mesophilic and thermophillic adenylate kinases; the methodology can be potentially applied to other allosteric systems. In the discussion of both subjects, connection to the relevant experimental observables (e.g., infrared and small angle x-ray scattering) will be highlighted.