

Lubrication Chemistry Viewed from DFT-Based Concepts and Electronic Structural Principles

Li Shenghua*, Yang He and Jin Yuansheng

State Key Laboratory of Tribology, Tsinghua University, Beijing 100084, P.R. China

Tel.: +86 (10) 62772509, Fax: +86 (10) 62784691, E-mail: lish@pim.tsinghua.edu.cn

URL: <http://www.pim.tsinghua.edu.cn/sklt/sklt.html>

*Author to whom correspondence should be addressed.

Received: 16 April 2003 / Accepted: 16 October 2003 / Published: 26 December 2003

Abstract: Fundamental molecular issues in lubrication chemistry were reviewed under categories of solution chemistry, contact chemistry and tribochemistry. By introducing the Density Functional Theory(DFT)-derived chemical reactivity parameters (chemical potential, electronegativity, hardness, softness and Fukui function) and related electronic structural principles (electronegativity equalization principle, hard-soft acid-base principle, and maximum hardness principle), their relevancy to lubrication chemistry was explored. It was suggested that DFT, theoretical, conceptual and computational, represents a useful enabling tool to understand lubrication chemistry issues prior to experimentation and the approach may form a key step in the rational design of lubrication chemistry via computational methods. It can also be optimistically anticipated that these considerations will gestate unique DFT-based strategies to understand sophisticated tribology themes, such as origin of friction, essence of wear, adhesion in MEMS/NEMS, chemical mechanical polishing in wafer manufacturing, stress corrosion, chemical control of friction and wear, and construction of designer tribochemical systems.

Keywords: Lubrication chemistry, DFT, chemical reactivity indices, electronic structural principle, tribochemistry, mechanochemistry.

Introduction

Probing adhesion, friction, wear, and lubrication at the molecular level has accelerated progress in the science of tribology. Possible topics include mechanisms of energy dissipation, stick-slip motion,

tribochemistry and tribofilm formation, lubrication by nanoscale films or at high pressures, the nature of contact between macroscopically rough surfaces as well as its time evolution, micromachines, new approaches for measurements at molecular scales, and application of fundamental concepts and first principles toward improved materials and technological design. Owing to the atomic or molecular nature involved in these subjects, both physicists and chemists have begun exploring quantum mechanics (QM) and quantum chemistry (QC) to understand the fundamental physics and chemistry in the practical tribosystems or tribochemical systems. The approach is supposed to help engineer or design tribosystems or tribochemical systems in terms of QM and QC.

Thanks to the role of chemistry in understanding adhesion [1,2], controlling friction [3], influencing wear [4], and improving (boundary) lubrication [5], the concept of tribochemical design, or mechanochemical design in the broader sense, was elaborated based on tribochemistry and mechanochemistry concepts and principles [6,7]. As is currently recognized, tribochemical or mechanochemical processes are initiated and facilitated by exo-excited electrons [8,9,10], and all of chemistry is driven by the give and take of electrons [11], so it comes as no surprise that the Lewis acid-base theory and the hard-soft acid-base concept have been successively introduced to understand the complicated chemistry in tribology and tribochemistry. In the endeavor, a great leap has been made since chemical hardness was quantified with the Density Functional Theory (DFT). Instead of the wave function in conventional QC methodologies, DFT adopted electron density of chemical systems as an alternative, based on which many important concepts of chemical reactivity have been derived.

From QM to QC, and from wave function functional theory (WFT) to DFT, physicists have been more and more involving themselves into the traditional realms of chemists. In fact, physicists are developing better oils and lubricants that promise to improve the fuel efficiency of cars and reduce greenhouse-gas emissions [12]. In application of QC algorithms to lubrication chemistry, Dr. Yamaguchi of Chevron has led a group devoting to develop antiwear models of zinc dithiophosphates based on their local charges calculated by *ab initio* QC [13,14]. In her widely lectured subject, *Quantum Mechanics and the Automobile*, Dr. Chaka of Lubrizol has demonstrated that nowadays DFT is already used by the chemical industry to illuminate chemical processes underlying the performances of lubricants and additives [15]. Actually, QM and QC in general is becoming sources of practical tools increasingly adopted by both the physics and the chemistry community in exploring the atomic or molecular nature of tribological events. For example, in order to calculate friction coefficient at an engineering level, a hierarchy scheme including three areas of tribological phenomena, thermal, chemical and mechanical, has been plotted that symbolizes the transition from the atomistic approach to the engineering level [16]. To use the power of microscopic modeling to gain new insights into macroscopic friction processes and, ultimately, to solve technological problems, Goddard [16] suggested "hierarchy of modeling tribological behavior" that can be done from quantum-level studies to engineering design. At each level, the precise parameters include chemistry and thermochemistry of the deeper level.

DFT-Based Chemical Reactivity Indices and Electronic Structural Principles

A chemical system is any collection of nuclei and electrons. It may be an atom, a molecule, an ion, a radical or several molecules in a state of interaction. The physical and chemical behaviors of a chemical system can be described by DFT, a form of quantum mechanics or quantum chemistry that uses the one-electron density function instead of the more usual wave function [17,18]. In DFT, two basic parameters of importance to chemistry are introduced, one being electronic chemical potential (μ) and the other absolute or chemical hardness (η) [19,20]. Chemical potential measures the escaping tendency of an electron cloud, while chemical hardness determines the resistance of a species to lose electrons. Both μ and η are global properties at the ground state in the sense that they characterize the species as a whole, i.e., they are molecular but not orbital properties. The exact definitions of these two quantities [17,21] are

$$\mu = -\chi = \left(\frac{\partial E}{\partial N} \right)_{V(r)} \quad (1)$$

and

$$\eta = \frac{1}{2} \left(\frac{\partial \mu}{\partial N} \right)_{V(r)} = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right)_{V(r)}, \quad (2)$$

where E is the electronic energy of the concerned chemical system, N is the number of electrons, and $v(r)$ is the potential due to the nuclei, plus any external potentials. For atomic species, the chemical potential is the negative of Mulliken electronegativity (χ), which can alternatively be called absolute electronegativity.

Using the method of finite difference, an operational and approximate definition of μ and η are

$$-\mu = \chi = (IP + EA) / 2, \quad \eta = (IP - EA) / 2 \quad (3)$$

where IP is the ionization potential and EA is the electron affinity of the system. Within the validity of Koopmans' theorem for closed shell species, the frontier orbital energies are given by

$$-\varepsilon_{HOMO} = IP, \quad -\varepsilon_{LUMO} = EA \quad (4)$$

Therefore, on the orbital basis, we can write

$$-\mu = \chi = (\varepsilon_{LUMO} + \varepsilon_{HOMO}) / 2, \quad \eta = (\varepsilon_{LUMO} - \varepsilon_{HOMO}) / 2 \quad (5)$$

A schematic representation of all these parameters can be embodied in the orbital energy diagram in Figure 1. It offers a most graphic and concise way of defining what is meant by electronegativity and chemical hardness. Obviously, hard species has a large LUMO-HOMO gap and soft species a small one. Figure 2 is a simplified account of the electronic band structures of solids by the fundamental DFT-derived concepts, which presents inherent coherence of chemical hardness, LUMO-HOMO gap between the anti-bonding and bonding molecular orbitals of molecules, as called by chemists, and the band gap between the conduction and valence energy bands of solids (E_g), as dubbed by physicists.

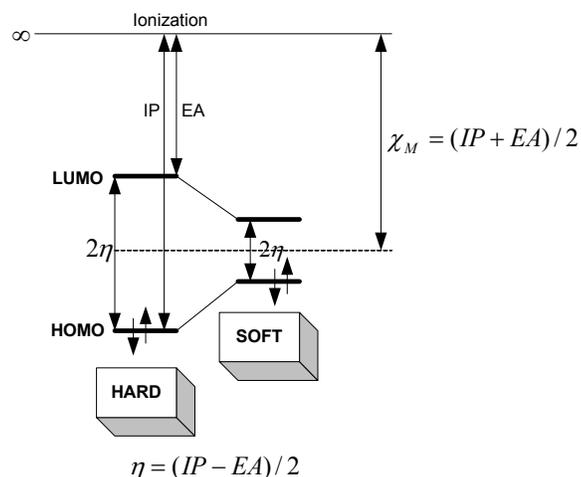


Figure 1. DFT-derived descriptors and orbital energy diagram.

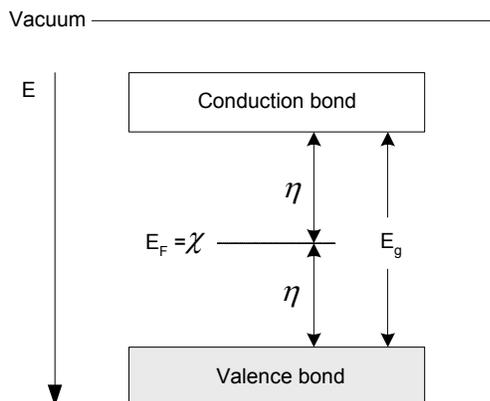


Figure 2. Schematic diagram of electronic band structures of solids.

It is natural to define, for any species, the global softness S as the inverse of global hardness [22],

$$S = \frac{1}{2\eta} = \frac{1}{2} \left(\frac{\partial N}{\partial \mu} \right)_{v(r)} . \quad (6)$$

All the above parameters are global properties in the sense that they characterize the species as a whole. On the other hand, the frontier electron densities, $\rho(r)$, proposed by Fukui are local properties; they differentiate one part of a molecule from another and serve as reactivity indices. The density functional expression of this idea is the Fukui function, $f(r)$, as defined [23] below:

$$f(r) = \left(\frac{\partial \rho(r)}{\partial N} \right)_{v(r)} \quad (7)$$

A chemical species participates chemical reactions either as an electrophile (or an electron acceptor), a nucleophile (or an electron donor), or an amphiphile. Correspondingly there exist three

Fukui functions that have approximate relations with the normalized frontier orbital electronic densities [24].

$$f^-(r) \approx \rho_{HOMO} \quad \text{measures reactivity toward an electrophilic reagent.} \quad (8)$$

$$f^+(r) \approx \rho_{LUMO} \quad \text{measures reactivity toward a nucleophilic reagent.} \quad (9)$$

$$f^0(r) \approx \frac{\rho_{HOMO} + \rho_{LUMO}}{2} \quad \text{measures reactivity toward a radical reagent.} \quad (10)$$

At the equilibrium, chemical potentials, or absolute electronegativities within a chemical system, equal everywhere, while absolute hardness is a function of position. According to Sanderson's electronegativity equalization principle, when two systems, A and B, are brought together, electrons will flow from that of lower χ to that of higher χ until the chemical potential reaches an equilibrium. As a first approximation, the fractional number of electrons transferred, ΔN , is given by

$$\Delta N \approx \frac{(\chi_A - \chi_B)}{2(\eta_A + \eta_B)} \approx \frac{\Delta\chi}{2\sum\eta}, \quad (11)$$

or

$$\Delta N \approx \frac{(\mu_B - \mu_A)}{2(\eta_A + \eta_B)} \approx -\frac{\Delta\mu}{2\sum\eta}. \quad (12)$$

Thus, the electron transfer is driven by $\Delta\chi$, but resisted by the sum of η 's. Since molecular interactions involve other interactions besides electron transfer, ΔN is not the total change of electrons, but is still useful in determining the initial orbital interaction between A and B, and in serving as an approximation for the bond strength [25]. For the hard-hard interactions, $\sum\eta$ can be very large; thus, ΔN becomes too small, and the interaction will be dominated by the electrostatic interaction instead of electron (charge) transfer. On the other hand, for the soft-soft interaction, $\sum\eta$ can be rather small and ΔN will be larger.

The DFT refinement of global and local chemical reactivity indices have effectively improved the usefulness of Electronegativity equalization principle (EEP), Hard-soft acid-base (HSAB) principle and Maximum hardness principle (MHP), and greatly facilitated their applications in organic and inorganic reactions. One recent but significant extension of absolute electronegativity, chemical hardness and the HSAB principle in terms of molecular chemistry was made by Lee [25] who, after depicting electronic work function (ϕ) and average energy gap (E_g^{Av}) in terms of solid physics, developed a similar equation for solid contacts.

$$\Delta N \approx \frac{\Delta\phi}{\sum E_g^{Av}} \quad (13)$$

This formula was applied to adhesions between a wide spectrum of solid surfaces of metal, semiconductors and insulators with satisfactory explanations.

Review of Historical Cases

Quantum chemistry is a subdiscipline subject of quantum mechanics dealing with chemistry issues. DFT, theoretical, conceptual and computational, has during the past two decades or so become an active domain of QC. From time to time, its traces in highlighting lubrication physics, mechanics and chemistry issues have been spotted. All these attempts are striving to seek fundamental understandings of physical and chemical mechanisms behind complicated lubrication phenomena observed.

Application of General Quantum Chemistry

Application of general quantum chemistry in lubrication chemistry has invariably been concentrated on finer characterization of the tribosystem elements (tribosurfaces, lubricant basestocks and tribo-additives) and more fundamental understanding of their interactions. Some representative examples are:

- 1) Applying molecular dynamics to conduct simulation study of the non-equilibrium chemistry on the diamond and covalent interfaces, and to elucidate the relations between free radical chemistry and wear, including H-abstraction reactions of chemically adsorbed molecules, radical recombination, instantaneous surface adhesion and debris formation [26].
- 2) Employing computational chemistry algorithms to mimic the chemical degradation mechanisms of perfluoropolyether lubricants on the surfaces of metals, e.g. Al, and metallic oxides, and to design combinatorial systems of surface-lubricant-additive that meet requirements of sophisticated lubrication systems [27].
- 3) Based on the radical anionic model of multi-ring aromatics, semi-empirical molecular orbital theory was applied to calculate the effect of substituted groups on the electronic affinity of polybenzylthioether as a gas phase lubricant, for decreasing the temperature at which it decomposes to form frictional polymers under boundary lubrications [28].
- 4) Using DFT to determine the electronic structure of MoS₂ related to the lubricating properties and the activation energy. A good agreement has been found between theoretical predictions and experimental results [26a].

Application of DFT-Based Concepts and Principles

Until recently, many equilibrium thermodynamics concepts and principles have been suggested to account for tribochemical events. Among them, ideas based on Lewis acids and bases theory and Pearson's hard and soft acids and bases (HSAB) principle are relatively more popular in the tribochemistry literature. It is recognizable that tribochemical reactions, like thermochemical ones, are occurring via electron exchange, transferring and sharing. Therefore it is not unusual for tribochemists to resort to the Lewis acids and bases theory and relevant concepts and principles for interpreting triboevents caused by mechanochemical reactions of tribosurfaces and lubricant species which are acting, respectively, as electron donors and acceptors and thus assume varied chemical hardnesses or softnesses. A brief summary of such applications can be chronologically enumerated in Table 1.

Table 1. Applications of Lewis acid-base concepts and principles in tribochemistry [9,13,14,29-37].

Reference	Description
Mori <i>et al.</i> (1987)	Describing adsorption activity of organics on fresh steel surfaces by hard and soft acid and base concepts and HSAB principle.
Kajdas (1995)	Modeling tribochemical reactions based on low-energy electron emission from tribosurfaces and a generalized NIRAM-HSAB action mechanism.
Fischer <i>et al.</i> (1995)	Characterizing solid tribosurfaces with Lewis acids and bases theory and frontier molecular orbital theory.
Mansuy (1995)	Investigating effect of Lewis acid-base interactions between ZDTP and n-dodecylamine on the composition of ZDTP tribochemical films.
Matin <i>et al.</i> (1995-2000)	Illustrating interactions in binary additive system, formation of ZDTP tribochemical films, synergism in MoDTC/ZDTP and MoDTC/calcium borates, and transfer of tribochemical film by Lewis acids and bases concept and HSAB principle, chemical hardness and MHP.
Bhatia <i>et al.</i> (1999)	Elucidating tribochemical reactions of PFPE on magnetic head/disk interface by catalysis of Lewis acids.
Li (2000)	Attempting Bond valence matching principle and Saville's rule for understanding formation thermodynamics of inorganic and organic species yielded from ZDTP on rubbing steel surfaces.
Zhang <i>et al.</i> (2001)	Employing electronegativity, electron affinity and ionization potential of functional antiwear additive elements (S, P) from ZDTP to account for their preferential residence on tribocoating surfaces of varied mechanical and chemical nature.

ZDTP: Zinc Dithiophosphate; MoDTC: Molybdenum Dithiocarbamate

The effectiveness of Lewis acids and bases concepts and related principles in understanding tribochemistry implies the high potentiality of applying DFT and chemical hardness directly to describe tribochemical systems. In fact, they have already witnessed utilizations in the qualitative description and quantitative analysis of tribochemical phenomena. One example is the investigation of the protective films formed by organic molecules on metal surfaces under boundary lubrications by employing DFT to calculate the adsorption energy of methanol, ethylene, acetone and dimethyl ether on the clear Al surfaces [38]. Another example is employing the chemical hardness model to predict the double layer tribochemical films generated by ZDTP (polymeric long-chain zinc polyphosphates and the short-chain phosphates of transitional metals), suggesting the tribochemical reactions between zinc polyphosphates and iron oxides based on the HSAB principle, explaining the antiwear mechanism of ZDTP and forecasting the decomposition of long-chain zinc polyphosphate [32,33].

Application of Chemical Hardness and the HSAB Principle for Antiwear Films

The antiwear mechanisms of ZDTP, of all common antiwear additives, have gained the most extensive investigations in light of analytical data on its thermal films and tribochemical films. Among

the few applications of electronic structural principles to lubrication chemistry, the unique contribution of Martin's school merits special comments for their delicate use of chemical hardness and the HSAB principle in understanding the formation mechanisms of tribochemical films yielded by ZDTP and others.

Martin *et al.* first used the HSAB principle to exploit the transfer films generated by molybdenum dithiophosphate (MoDTP) which are composed mainly of an amorphous phosphate glass containing flexible and highly dispersed MoS₂ single sheets [39]. The HSAB principle was found to be useful in explaining the observed two chemical reactions, one being that between the phosphates present in the tribofilm and the native oxide layer on the tribosurface, and the other being the chemical reactions between the MoS₂ sheets and the nascent metal surface left after the removal of the oxide layer. When it comes to explain the role of ZDTP in eliminating abrasive wear due to the presence of transition metal oxide species in boundary lubrication, the HSAB principle was again suggested to understand a set of tribochemical reactions between the polyphosphates and the oxides [32a]. The model predicts a layered tribofilm with the presence of polymer-like zinc metaphosphate overlying a mixed-transition-metal phosphate glass. Based on the chemical hardness concept, a model envisaging the formation of metal sulphides embedded in the phosphate matrix was also proposed, and was used to predict the interactions between ZDTP and other additives in motor oils.

Due to the usefulness of the HSAB principle in explaining the formation chemistry of tribofilms of single antiwear additives, it was later applied to the binary antiwear systems and the ternary systems containing both antiwear and detergent additives. For example, in the presence of MoDTC/ZDTP, a two-step tribochemical reaction is generally observed. First, phosphate from the interfacial film is transferred to the oxide on the tribosurfaces, and after an induction period of a few cycles, pure MoS₂ single sheets are transferred to the tribosurface and the phosphate is eliminated as wear debris from the contact zone. The chemistry of the transfer phenomena is modeled using the HSAB principle [33a]. When investigating the synergistic tribochemical interactions between antiwear ZDTP, friction modifier MoDTC and detergent overbased calcium borate (OCB) in mild wear conditions under boundary lubrication, besides the HSAB principle, the chemical hardness concept and the maximum hardness principle were introduced to interpret the tribochemical reaction that yields a tribofilm composed of non-oriented MoS₂ sheets (friction modification) embedded in a carbon-rich phase and a mixed Zn/Mo polyphosphate glass (antiwear) [32b,40]. Another example is the investigation of the two-layer structure of the ZDTP film, in which a chemical hardness model was developed to predict the formation of the layered tribofilm, and a tribochemical reaction between zinc polyphosphate and iron oxides species was proposed according to the HSAB principle [33b].

Some features of applications of DFT-based concepts and principles in lubrication chemistry can be summarized as follows:

- 1) Use of DFT approaches, DFT-based chemical reactivity descriptors and electronic structural principles in lubrication chemistry is almost exclusively confined to qualitative illustration of the

formation chemistry of tribochemical films, antiwear (S, P) and extreme pressure (Cl, N) lubricious films in particular, with one documented citation of the HSAB principle for explaining the effect of “solubility” of ZDTP and MoDTC in bulk solution of lubricants on their friction reduction.

- 2) More qualitative elucidation has been made of tribochemical film formations with chemical hardness and by the HSAB principles, and very little use has been witnessed of other DFT-based chemical reactivity indicators and electronic structural principles in lubrication chemistry. Among the conceptual DFT applications in the field, more global parameters than their local counterparts have been explored.
- 3) Rather limited computational DFT cases have been available that are targeted on the components of tribochemical systems, i.e., almost no DFT characterization of tribochemical systems has been attempted.

To sum up, only preliminary, sparse and superficial explorative endeavors have so far been made of DFT, its chemical reactivity descriptors and electronic structural principles in lubrication chemistry, which leaves so many virginal frontiers in the realm to be exploited.

Challenges in Lubrication Chemistry in View of DFT

Lubricants are remarkable fluids. To be more remarkable, lubricants have to meet different challenges [15], as numerated in Table 2.

Surprisingly, two of the major driving forces behind the development of lubricants are fuel economy and environment benefit. These challenges are more reflected on and can be effectively confronted by the designer additives. Molecular characterization and computation of candidate additive molecules can bridge additive chemistry and its engineering-level requirements. In order to develop lubricants that satisfy the demands of less frequent drain intervals, lower or even zero emissions and further reduction of losses due to friction, physicists, chemists and engineers need to understand the performances of lubricants in more detail. One major challenge is to incorporate chemistry into physical models to combat oxidation and chemical degradation of oils for extended service interval. Another challenge is to understand the physics and chemistry in the boundary lubrication region [12] and molecular lubrication modes, which are the focus of the current endeavor.

Table 2. Challenges of the future for lubricants.

Lubricant types	Critical challenges
Passenger car engine oils	Fuel economy / Low or zero emissions
Heavy-duty engine oils	Extended service interval
Automotive gear oil	Durability
Automatic transmission fluids	Shear stability
Hydraulic fluids	High pressure
Base oil	Pour point depressants/Biodegradability

Challenges from Tribomaterials, Lubricants and Additives

It is estimated that approximately 60 percent of advanced technical work is focused on energy efficient and environmental technologies [3]. For automotive tribology, its challenges for the 21st century in terms of tribomaterials, lubricants, and additives can be summarized as follows, in which DFT will have roles to play:

- 1) Development of environmentally friendly and eco-compatible lubricants, and improvement of thermal and oxidative characteristics of renewable, biodegradable lubricant basestocks, and enhanced understanding of friction-reducing additive chemistry. For example, use of QM/QC methods can be attempted to design structurally novel wear inhibitors to replace Zn dithioalkylether phosphates, or to select alternative tolerant elements to substitute Zn and P in ZDTP, to develop ashless, sulfur and phosphorus-free engine oils, and to design new corrosion inhibitors to replace imidazolines.
- 2) Investigation of compatibility between lubricant basestocks and additives, and study of basestock and additive chemistry to cater for light-weight materials technology and durable, low-friction surface coatings, such as aluminum and magnesium alloys, titanium alloys and intermetallics, ceramics, and metal-matrix composites.
- 3) Mechanism study of tribochemical compatibility among advanced coatings, low-viscosity base oils and friction modifiers (Mo series and organic esters) in the presence of simulated combustion products and biofuels (methanol, ethanol and other biomass-derived fuels). Hierarchical modelings starting from QC simulation of the most elementary triboelements, tribomaterials, lubricant basestocks and tribological additives, will pave viable routes leading to fundamentally chemical solutions to the issue.
- 4) Development of virtual laboratory test methods to screen high performance lubricants at competitive costs.

Challenges from Boundary Lubricants and Tribochemistry

For all the predictable challenges just stated, molecular computation, characterization and design from fundamental chemistry points of view should be kept at matching paces. DFT, theoretical, conceptual and computational, can be an enabling tool affordable to expedite realization of the set goals.

In boundary lubricants and tribochemistry, one challenge is to seek more desirable functional elements of triboadditives that should be compatible with tribomaterials of varied chemistry origins. There are many tribotest cases and practical applications suggesting the compatibility between triboadditives and tribomaterials [36]. Selection of ZDTP series can be cited as an example here. ZDTP (zinc dialkyldithiophosphate or zinc diaryldithiophosphate) is widely used as an anti-wear additive in engine oils to protect heavily loaded parts, particularly the valve train mechanisms (e.g., camshaft and cam followers) from excessive wear. ZDTP is also an effective oxidation inhibitor. But

oils containing ZDTP should not be used in engines that employ silver alloy bearings. All car manufacturers now recommend the use of dialkyl ZDTP in engine oils for passenger car service.

In terms of tribo-technology interactions, the two key issues in engine tribology are chemomechanical effects and materials (including coatings). The chemomechanical effects, or chemomechanical tribology or tribomechanical chemistry, can combine mechanisms of chemical activity and mechanical stresses at surfaces for deeper understanding of tribochemistry [41].

In more detail, some challenges in boundary lubricants and tribochemistry can be enumerated as follows [16,42]:

Definition of Surface Reaction Sites. Tribochemistry is much different from thermochemistry and contact (catalytic) chemistry. It follows for the most part what mechanochemistry observes. For an understanding of what changes the surface to produce different chemical reaction paths under rubbing conditions, the crystallinity (lattice imperfections, surface registry, amorphous vs crystalline), the surface active sites, either exoelectrons or dangling bonds, and their specific influences on specific model compounds have to be quantitatively determined.

Formation of Lubricating Films. Under what conditions (i.e., starting materials and reactions) will an effective film of specific constituents be thermodynamically and kinetically favorably formed? What are the basic processes and mechanisms of film degradation? What are the molecular structural effects on film formation in terms of functional groups, reactivity, chain length, cross-linking tendencies, and even self-assembling tendencies? DFT-based solutions are expected to identify the processes (mechanical and chemical) by which mechanical or frictional energy transforms solid/liquid/gas interactions into surface films and third bodies, and also to ascertain the mechanical and chemical contributions to the breakdown of tribochemical films.

Film Formation Modeling. Can molecular dynamic calculations be used to simulate the effect of the surface energy, active sites, defect sites, unpaired electrons, dangling bonds on reactivity and film formation? To solve these problems, algorithms or computation simulations need to be developed on the nm/femtosec scale (quantum-level simulations) and then are extended to $\mu\text{m}/\mu\text{sec}$ scale. One important issue in this endeavor is to make certain what kinds of chemistry, e.g. the modes of energy dissipation (vibrational, rotational, electronic) will take place under temperature jump (flash) and stress strain conditions.

It can be expected that, if we can understand the origins of the chemical reactions that occur under lubricated conditions, we will be in a position, for the first time, to understand the basic steps of lubrication. The understanding of how surfaces react with lubricants and the ability to control the lubrication process will afford much better design practices for lubrication chemistry. The information will also allow intelligent monitoring of device durability under service conditions. Many new materials are currently being explored for various components, yet the lubrication requirements and state of the surfaces are not clearly understood. Having the basic knowledge will significantly improve introduction rate of the new materials as well as system performance and efficiency.

Challenges from Nano-Lubrication

Effective lubrication can be accomplished “by design” based on the so-called first principles of lubrication. Different lubrication regimes have their characteristic first principles [16,43,44], as outlined below.

- 1) Fluid lubrication (Hydrodynamic and Elastohydrodynamic Lubrications): determining what atomic scale behavior influences liquid lubrication, and how changes in phase or chemical composition influence wear, and designing of contact geometry and controlling of operating parameters to produce sufficient fluid pressure to prevent the surfaces from direct contacts. Under fluid lubrication, it is the mechanical forces occurring in the bulk lubricants that dominate the tribosystems. And so mechanical force responsiveness of lubricant molecules is of primary significance.
- 2) Boundary lubrication: using chemistry to generate sacrificial surface chemical films to protect the surfaces from shear stresses from rubbing and abrasion. Under boundary lubrication, it is the chemical forces between the lubricant (basestocks and additives) molecules and the tribomate materials that prevail in the tribosystems. One closely related subject is designing molecular or formulation chemistry to self-recondition or regenerate worn tribosurfaces in the course of lubrication.
- 3) Nano-lubrication: using sophisticated molecular engineering techniques currently available to construct monolayer films to control adhesion, stiction, friction, and wear of surfaces coming into contact at the micro/nano-scale. These films should be of, among others (non-volatile, oxidation and thermal decomposition resistant), good adhesion and cohesion, and self-repairing or self-regeneration. Under nano-lubrication, it is the physical forces and tribochemical interactions between the specific lubricant molecules (e.g., PFPE, X-1P) and/or the surfaces (e.g., single and polycrystalline silicon, silicon nitride, silicon carbide, Nickel, diamond-like carbon, and hydrogenated carbon films) that govern the tribosystems.

Whether boundary lubrication for tribochemical systems or molecular lubrication for nano-tribological systems, they are serving for new challenges posed by new technologies, such as adiabatic diesel engines, MEMS/NEMS (microsystems or micromachines), sensors and actuators. These systems are chemistry in nature and their first principles of lubrication are always related to molecular interactions. So it is logical in principle to employ DFT derived chemical reactivity parameters and related electronic structural principles to characterize these systems, to interpret their behaviors for lubrication, and in turn to *design* tribochemical or nanotribological systems of anticipated macro-, micro/nano-tribological performances.

Exploration of DFT-Based Strategies in Lubrication Chemistry

Lubrication chemistry in general presents itself on macro and micro/nano-levels. Lubrication issues of chemistry nature, such as adhesion, chemical friction and atomic-scale wear, which are

commonplace in the advanced tribosystems such as micromachines and magnetic recording storage media, belong to the latter and will be discussed in separated papers. This article concentrates on the former, which is chemically categorized into solution chemistry, contact chemistry and tribochemistry.

Solution Chemistry

Liquid lubricants are generally mixtures of a series of chemical compounds of surfactants and high-molecular weight polymers molecularly dissolved or colloiddally suspended in mineral or synthetic base stocks. These specific compounds are additives, which represent from 0.1%-30% of formulated oil volume. General formulation of lubricant solutions is such a chemically balanced package of these surface and bulk active chemical species where no undesirable interactions arise. Any introduction of foreign chemicals will disturb the fine equilibria already established and does harm to the desired functioning owing to additive interaction chemistry and additive depletion chemistry. This may explain why no arbitrary blending of the so-called “snake oil additives” should be made by reckless end-users.

The overall performance of an oil can be improved by introducing additives on the condition that the basestocks are well refined, and appropriate amount and kind of additives are blended. An additive can be chemically different when serving for specific functions, as described in Table 3.

One important consideration for molecular chemistry of additives is incompatibility of lubricants originated from additive package, lubricant formulation and mixing. Lubricant producers do not always use the same additive to accomplish the same goal. Oils for similar applications but produced by different manufacturers may be incompatible due to the additives used. Interactions occurring among the individual additives of different chemical identities in the additive package result in addition, synergism or antagonism, which are characterizing the physical and chemical compatibility among additive components. When incompatible fluids are mixed, the additives may be consumed or depleted due to chemical reaction with one another. The resulting oil mixture may be deficient of essential additives and therefore unsuitable for the intended applications. Some oils, such as those used in turbine, hydraulic, and gear applications are naturally acidic, while other oils, such as motor oils and transmission fluids, are alkaline. Acidic and alkaline lubricants are evidently incompatible.

Table 3. Molecular chemistry of additives.

Category	Surface protecting	Performance enhancing	Lubricant protective
Function	prevent wear, corrosion, or rust by forming adsorptive or reacted protective films.	make the oil perform in a desired manner for specific applications.	protect the lubricant itself.
Chemistry	tribo-additives (oiliness, friction reduction, antiwear, extreme pressure); rust & corrosive inhibitors; detergents & dispersants.	viscosity index improvers; pour point depressants; demulsifiers.	oxidation inhibitors; antifoaming agents.

There are two types of solution chemistry that occur in the bulk phase of liquid lubricants and acquire the most attention. One is the additive-additive interaction chemistry, and the other is the additive-basestock interaction chemistry. Depending on situations in question, the former brings about additive-additive matchability problems: addition, synergism or antagonism, and the latter generates additive-basestock compatibility problems: improving existing properties of base oils (e.g., antioxidants, corrosion inhibitors, antifoam agents and demulsifying agents), suppressing undesirable properties of base oils (e.g., viscosity index improvers and pour point depressants), or imparting new properties to base oils (e.g., extreme-pressure additives, detergents and metal deactivators).

In the additive-additive interaction chemistry, one classical instance is the antagonisms between ZDTP and succinimide dispersant additives that have been observed to occur at two levels [33b]: (i) chemical interaction in the bulk lubricant and (ii) competition to surface adsorption. The ^{31}P NMR study of chemical interactions in the bulk have indicated an acid-base reaction between nitrogen from the amine organic chain (soft base) of the succinimide dispersant and zinc atom in the ZDTP antioxidant (soft acid). Owing to some steric hindrances, this can prevent ZDTP from being adsorbed onto the tribosurfaces and the tribofilms could hardly be formed in such situations. Another study demonstrated the modification of the composition of ZDTP tribofilm due to the presence of nitrogen.

Categorized into the additive-additive interaction chemistry mode are almost all the additives in the commercial additive packages. There are many intra-actions of additive molecules in the bulk that belong to the additive-basestock interaction chemistry. Some representative examples are the self-assembling of the dispersants into micelle for fine dispersion of soot particles, the effective solubility of tribological additives such as ZDTP, MoDTC and MoDTP, and viscosity index improvers. Attachment of pour point depressants onto wax crystals generated by large aliphatic species/moieties in the basestock can be regarded as another version of additive-basestock interaction chemistry.

The general acid-base chemistry based on the DFT-derived concepts and principles are evidently the strategic and tactic banks that can be resorted to for understanding the two interaction chemistries, the additive-additive interaction chemistry in particular. Subjects of highly expectation possibly cover:

- 1) Application of DFT-derived concepts and related electronic structural principles to account for addition, synergism and antagonism in additive-additive interaction chemistry;
- 2) Application of the same concepts and principles to account for compatibility of additives with lubricant solutions, the synthetic basestocks in particular.

General approaches that have to be formulated or borrowed from DFT will include:

- 1) Determination of critical DFT-based reactivity descriptors for additive molecules and general basestock molecules;
- 2) Computation of such indices on the global and local scales. In the latter, the distributions of the DFT-based reactive sites should be mapped for individual additive molecules.

In the study of solution chemistry, the basestock-basestock interaction chemistry is an often ignored field but it is of significance when such properties as viscosity, viscosity index and freezing

point are considered. When these performances are of concern, dispersion (for mineral-based hydrocarbon lubricants and some synthetic based lubricants such as poly-alpha-olefins, alkylbenzenes) and other molecular interaction modes, e.g., induction and electronic exchange, should be taken into serious consideration (for many types of synthetic based non-hydrocarbon lubricants like esters). The DFT-derived concepts outlined herein fail to represent dispersion energy correctly, and thus might be of limited use in dealing with some of the basestock-basestock interaction chemistry.

Contact Chemistry

Contact chemistry distinguishes itself from tribochemistry in that it concerns with all tribosurface-related chemistries on the standpoint of no mechanical influences. Investigation of contact chemistry can borrow heavily from surface chemistry and catalysis chemistry many useful concepts and principles for direct use. As in solution chemistry, the Lewis acids-bases interaction mode assumes unique position in surface phenomena such as adsorption of additive molecules and reactions on or with the surfaces. Specific contact chemistry issues in lubrication chemistry can be studied in two broad aspects.

One aspect is the decomposition chemistry of hydrocarbon species, and polymerization (condensation) chemistry of hydrocarbon fragments. This is perhaps the least studied subject of all lubrication chemistry issues. Generally this is a chemically similar system to the catalytic cracking process of petroleum hydrocarbons in the presence of Lewis acids or Bronsted acids catalysts. A detailed comparison was once made by the author [45]. Based on the conclusions drawn and those interesting findings by Lauer *et al.* on carbonaceous gas lubrication for metal tribomates such as iron and nickel [46], a novel high temperature lubrication chemistry strategy has been conceived that employs carbonaceous mesophases and their metal (Fe, Ni, Cu)-doped derivatives to achieve faster mechano-facilitated carbonization and graphitization, which were previously proved to be effective for high temperature lubrication [47].

The other aspect of contact chemistry is the physical and chemical adsorption of additives, e.g., corrosion and rust inhibitors and metal deactivators, whose discussion is omitted as much literature can be referenced.

A plethora of experimental data in catalysis chemistry can provide instant and beneficial assistance in understanding specific contact chemistry issues in the lubrication chemistry. Thus, a similar expectation is the application of DFT-derived concepts and related electronic structural principles to account for surface adsorption, decomposition and poly-condensation of hydrocarbon fragments and additive species. For the purpose, materials chemistry and electronic state characterization and computation of active surface sites in terms of Lewis acid-base theory via electronic structural analyses are highly necessary and in great need.

Tribochemistry

Knowledge of the detailed interaction chemistry between tribosurfaces and organic species is important not only in contact chemistry but in tribochemistry as well. Contact chemistry concerns more about the catalytic chemistry of the basestocks, while tribochemistry pays more attention to the selective adsorption and reaction of tribological additives on/with tribosurfaces. In tribochemical processes, the interaction between solid surfaces and molecular species interaction plays a critical role in the formation of protective films on the tribosurfaces. In the study of Zhou *et al.* [38], the first principle DFT calculations were carried out to investigate the adsorption properties of various organic molecules on the clean Al surfaces. For example, they calculated the adsorption energies for methanol, ethylene, ketone, and dimethyl ether molecules, and found that the calculated adsorption energies were in good agreement with the experimental data (methanol > ketone > dimethyl ether > ethylene).

Generally there are two chemistry modes in the tribochemistry considerations, i.e., the additive-surface interaction chemistry and the hydrocarbon-surface interaction chemistry. These interaction chemistries, both of which are stimulated and driven by mechanical stress strains, and thus are of mechanochemistry nature. Our recent studies demonstrated the remarkable promotion of tribochemical actions to the ordering of low-order carbonaceous mesophases [11]. Table 4 presents an anatomy of traditional and modern mechanochemistry. Clearly, tribochemistry is one specific case of mechanochemistry.

Mechanochemical reactions generally refer to athermal or ultra-fast reactions occurring between solids or solids and molecules under shearing forces [48]. Under such mechanical actions, solids and molecules undergo various changes in their structures and properties, such as Zener tunneling effect, shear-induced macromolecule scission, shear-induced metallization, shear-induced phase transformation, and mechanochemical reactions [48]. Unlike the even reaction probabilities in the gaseous or liquid chemical systems, the mechanochemical reactions of solids are occurring on local sites. So local chemical reactivity indices are of more potentiality to understand the mechanochemical reactions.

The DFT-based concepts of absolute hardness or softness and Fukui function were employed to describe the global or local reactivities of solids and molecules [19]. Solids like metals, ionic and covalent crystals are macromolecular systems, and can be characterized with DFT [27]. Specific features of the mechanochemical reactions between solids or solids and molecules can be epitomized as follows, which are likewise applicable to describing tribochemical reactions in lubrication chemistry systems.

- 1) There exists an energy gap in the bonding energy spectrum in solids and molecules. Either solids or molecules are chemical systems with fixed 'hardness' that is determined by the energy gap in the energy spectrum of bonding electrons. There are different nomenclatures for such a gap depending on the chemical systems: the work function (ϕ) in metals, the forbidden band width (E_g) in non-metals (semiconductors and insulators), and the chemical hardness (η) in molecules.

Table 4. Traditional and modern mechanochemistry.

	About 'mechano'	About 'chemo'	Comparisons
Traditional	<ul style="list-style-type: none"> -hydrostatic stress state -plastic deformation -dynamic loading & relaxation -fine grinding & comminution -ultrasonic irritation -explosive shock wave 	<ul style="list-style-type: none"> -dissolution -dissociation -extractive process -polymer stress reactions -electrochemistry -solid state reactions -mechanical alloying -tribochemistry & wear -stress corrosion -synthesis of organic & inorganic compounds 	<ul style="list-style-type: none"> ▪ Macrosystems (solid-solid and solid-molecule interaction mechanochemistry) ▪ Mechanochemical effects — mechanical stresses on the course of chemical reactions and physico-chemical transformations of solids
Modern	<ul style="list-style-type: none"> -chemical bonding forces between atoms and/or molecules -molecular interaction energies (electrostatic, exchange, induction, dispersion, and other terms) 	<ul style="list-style-type: none"> -the processes of directing chemical reactions by mechanical forces on the reactants, i.e., position specific reactions (Molecular nanotechnology or machine phase chemistry) -how cells sense, respond, and adapt to physical forces (Biophysics) 	<ul style="list-style-type: none"> ▪ Chemomechanical effects — how chemical bondings or forces of chemical nature drive mechanical movements, or change mechanical states of interactive bodies in miromachines

- 2) The energy gap will diminish or even close when solids or molecules are sheared. Under shearing strains, there occurs symmetry breakdown in solids and molecules resulting in the loss of the structural stability of bonding electrons. Under such circumstances, there happens the decrease of the electronic work functions of metals, narrowing of the forbidden gap between the valence and conduction bands of non-metals, and reduction of the energy gap between the bonding and antibonding orbitals of molecules [48]. All these will lead to easier transferring of the localized electrons into the conduction bands of solids or antibonding orbitals of molecules resulting in free or non-localized electrons, which greatly decreases the chemical stability of solids and molecules, and hence facilitate their mechanochemical reactions.
- 3) The potential barrier of mechanochemical reactions is the function of shearing strains. Kinetically, mechanochemical reactions can be well described by Zener tunneling effect, i.e., the transition of electrons from HOMO to LUMO. Rate of the Zener tunneling process, r , in given chemical bonding states is expressed as [48]:

$$r \approx k_0 \exp\left(-\frac{\eta}{G\gamma b^3}\right), \quad (14)$$

where η , G , γ and b^3 stand respectively for chemical hardness, local shearing modulus, shearing strain and volume of the chemical bonds. It can be seen in comparison with the reaction rate-activation energy relationship ($r \propto \exp[-E/RT]$) in thermochemistry, that progress of mechanochemical reactions depends strongly on the energy barrier expressed in E_g or $\varepsilon_{LUMO} - \varepsilon_{HOMO}$.

Thus, the expected tribochemistry subjects when dealt with the DFT-based chemical reactivity concepts and electronic structural principles may include:

- 1) Dynamic responses of chemical reactivity indices of all the involved tribo-elements under shearing;
- 2) Formation kinetics of lubricious films in terms of mechanochemistry;
- 3) Application of the frontier orbital theory and the energy gap concepts to tribomaterials and triboadditives under mechano-activation.

Success of the endeavor relies uniquely on the following DFT-based approaches or strategies in general:

- 1) Mapping of tribosurfaces in terms of DFT-based chemical reactivity descriptors;
- 2) DFT-based chemical reactivity descriptors for additive molecules and general basestock molecules, and computations of such indices both on the global and local scales;
- 3) Computation and measurement of narrowing of E_g of tribomaterials and $\varepsilon_{LUMO} - \varepsilon_{HOMO}$ of triboadditives.

Summary and Outlook

- 1) Lubrication chemistry is generally explored from solution chemistry, contact chemistry and tribochemistry. Each of the three fields needs involvement of DFT-based chemical reactivity indices and related electronic structural principles from different angles and to varied extents.
 - a) For the solution chemistry, as all chemistry is occurring between lubricant basestocks and additives on the molecular scale, all of the current DFT-based molecule-targeted chemical reactivity indices and related electronic structural principles, either global or local and either qualitative or quantitative, can be adopted with highly expectations. They are anticipated to be of particular significance in understanding and prognosticating varied complicated additive-additive interaction modes.
 - b) Contact chemistry concerns with heterogeneous catalytic chemistry involving adsorption and reaction of reactive atoms and functional groups, molecules and free radicals of lubricant basestocks and additives on either tribo- or non-tribo surfaces of metals/alloys and ceramics. Success of DFT application to contact chemistry, given the fine DFT characterization of lubricant molecules, depends on its provision of chemical reactivity parameters of solid tribomaterials, particularly tribocoating surfaces of different physical, chemical, mechanical and metallurgical properties.
 - c) The core of tribochemistry is mechanochemical interactions of lubricant basestocks, tribological additives and tribomate surfaces under time-dependent, excited states, and external shearing stress fields. It is the most complicated branch of DFT applications to lubrication chemistry, and devotion to it will surely breed smarter tribochemical systems of high efficiency and low emissions. Non-equilibrium mechanochemistry and advanced computational DFT will have to be integrated for dynamic illustration and molecular chemistry understanding of tribochemical events and underlying mechanisms.
- 2) DFT is being developed in theoretical, conceptual and computational aspects, and the latter two will be of more direct and imminent potentiality in understanding lubrication chemistry issues, the tribochemistry in particular. Concretely it can be stated as follows.
 - a) On the theoretical DFT level, it is necessary to develop formalism of density functionals of tribo-elements in lubrication chemistry systems: model compounds of mineral basestocks or specific compounds of synthetic basestocks, critical additive species, and conventional solid tribomaterials and advanced tribological coatings whose characters can be more proactively designed.
 - b) On the conceptual DFT level, more chemical reactivity indicators of local and quantitative nature should be sought for chemically mapping the tribo-elements in lubrication chemistry systems besides empirical or semi-quantitative global hardness or softness. And on the other hand, not only HSAB principle but also EEP and MHP based on the DFT-derived chemical reactivity indicators should be exploited for illustrating the interactions among the tribo-

elements in lubrication chemistry systems.

- c) On the computational DFT level, algorithms are greatly needed for finer quantitative characterization of chemical and mechanochemical reactivity of the tribo-elements in lubrication chemistry systems.

With effective merging of these aspects, an essential chemical understanding of both traditional and modern lubrication chemistry issues on the atomic or molecular level can be well expected. Designer lubrication chemistry systems will then be no longer a concept but can be engineered, tailored and maintained under proactive chemical control. And ultimately DFT-based solutions may be procured to the atomic level tribochemistry questions, such as “If we want to control friction and we have the ability to precisely modify the chemistry and structure of surfaces, what chemical and physical properties would we give to the first few hundred angstroms of a metal or ceramic?” [16]

References and Notes

1. Adams, L. G.; Hector, Jr.; Soegel, D. J. *et al. Adhesion, lubrication, and wear on the atomic scale.* http://ceaspub.eas.asu.edu/cms/papers/wear_review.pdf.
2. Lee, L.-H. *Fundamentals of Adhesion*; Lee, L.-H., Ed.; Plenum Press: New York, 1991.
3. Dudko, O. K.; Filippov, A. E.; Klafter, J. *et al. Tribology Lett.* **2002**, *12*, 217-227.
4. Olsson, M. *Chemical factors influencing engine wear.* http://www.himec.org/materials/himec/Pages/Material_for_nedladdning/posters_01/Martin_poster.pdf.
5. (a) Shenghua, Li; Chunhong, Zhou; Ruijun, Zhang. *et al. J. Tribology (Chinese)* **2002**, *22*, 75-80;
(b) Shenghua, L.; Yuansheng, J. *Chemodesign analysis approach to working environment in combustion chamber-piston (ring)-cylinder wall region of advanced heat engines.* Presented at 56th STLE Annual Meeting, May 20-24, **2001**, Orlando, Florida.
6. Yuansheng, Jin; Shenghua, Li. *Friction & Wear (Russian)* **2000**, *21*, 33-40.
7. Shenghua, Li; Yuansheng, Jin. *A Density-Functional Theory Description of Mechanochemical Reactions. J. Tribology (Chinese).* (in review).
8. Kajdas, C. *Tribochemistry Studied by Surface-Analytical Tools.* <http://www.nanoworld.unibas.ch/lm/nanotribo/research/tribochemistry>.
9. Mori, S. Proc. Int. Trib. Conf., Yokohama, Japan, *Satellite Forum on Tribochemistry*, **1995**, 37-42.
10. Gilman, J. J. *Science* **1996**, *274*, 65-67.
11. Xiaohao, C.; Shenghua, L.; Huaihe, S. *et al. Tribology Lett.* **2003**, *14*, 53-59.
12. Taylor, I. *Car lubricants: fact and friction.* <http://physicsweb.org/article/world/15/2/7>
13. Shaoyi, J.; Dasgupta, S.; Blanco, M. *et al. J. Phys. Chem.* **1996**, *100*, 15760.
14. Shaoyi, J.; Frazier, R.; Yamaguchi, E. S. *et al. Journal J. Phys. Chem. B* **1997**, *101*, 7702.
15. Anne, M. C. Quantum Mechanics and the Automobile. <http://www.phys.ksu.edu/paw/sc/abs/chaka.htm>.
16. Singer, I.; Pollock, H. *Epilogue to the NATO ASI on fundamentals of friction.* May 1992.

- <http://stm2.nrl.navy.mil/~wahl/epilogue.pdf>
17. Pearson, R.G. *J. Chem. Ed.* **1999**, *76*, 267-275.
 18. Parr, R.G.; Pearson, R.G. *J. Am. Chem. Soc.* **1983**, *105*, 7512.
 19. Pearson, R.G. *Proc. Natl. Acad. Sci.* **1986**, *83*, 8440.
 20. Lee, L.-H. In *Acid-Base Interactions: Relevance to Adhesion Science and Technology*; Mittal, K.L.; Anderson, H.R., Jr.; Eds.; VSP, 1991.
 21. Pearson, R. G. *Coord. Chem. Rev.* **1999**, *100*, 403-425.
 22. Geerlings, P; Proft, F. D. *Int. J. Mol. Sci.* **2002**, *3*, 276-309.
 23. Yang, W.; Parr, R. G. *Proc. Natl. Acad. Sci.* **1985**, *82*, 6723-6726.
 24. Pearson, R. G. *Chemical Hardness*; Wiley-VCH Verlag, Weinheim:Germany, 1997.
 25. Lee, L.-H. *J. Adhes. Sci. Tech.* **1991**, *5*, 71-92.
 26. (a) El Beqqali, O.; Zorkani, I.; Rogemond, F. *et al. Synthetic Metals*, **1997**, *90*, 165-172; (b) Martin, J. M.; Grossiord, C.; Mogne, T. Le. *et al. Tribology Int.* **2000**, *33*, 453-459.
 27. Zehe, M. J. <http://www.grc.nasa.gov/WWW/RT1997/5000/5140zehe.htm>
 28. (a) Sulton, D. L.; Boothe, M.; Ball, D. W. *et al. NASA Technical Memorandum* 113178, Nov. 1997; (b) Harrison, J. A.; Brenner, D. W. *J. Am. Chem. Soc.* **1994**, *116*, 10399-10402.
 29. Fischer, T. E.; Mullins, W. M. *J. Phys. Chem.* **1992**, *96*, 5690.
 30. Kajdas, C. Proc. Int. Trib. Conf., Yokohama, Japan, *Satellite Forum on Tribochemistry*, **1995**, 31-35.
 31. Georges, J. M.; Mazuyer, D.; Loubet, J.-L. *et al. In Fundamentals of Friction: Macroscopic and Microscopic Processes*, Singer, I. L.; Pollack, H. M., Eds., Kluwer Academic Publishers, 1991.
 32. (a) Martin, J.M. *Tribology Lett.* **1999**, *6*, 1-8; (b) Martin, J.M.; Grossiord, C.; Varlot, K. *et al. Tribology Lett.* **2000**, *8*, 193-201.
 33. (a) Martin J.M.; Grossiord, C.; Le Mogne, T. *et al. Wear*, **2000**, *245*, 107-115; (b) Martin J.M.; Grossiord, C.; Le Mogne, T. *et al. Tribology Int.* **2001**, *34*, 523-530.
 34. Bhatia, C. S.; Fong, W.; Chen, C. Y. *et al. IEEE Trans. Magnetics* **1999**, *33*, 910.
 35. Mansuy, H. NTIS No: DE96753703/HDM, July 1995.
 36. Shenghua, L. *Study on Tribochemodesign Based on Tribochemical Case Analyses*. Postdoctoral Report, Tsinghua University, December 2000.
 37. Ruijun, Z.; Shenghua, L.; Yuansheng, J. *et al. Science in China, Series A*, **2001**, *44*, 149-155.
 38. Hui, Z.; Tamura, H.; Takami, S. *et al. Appl. Surf. Sci.* **2000**, *158*, 38-42.
 39. Grossiord, C.; Martin J.M.; Le Mogne, T. *et al. Surface & Coatings Technology*, **1998**, 108-109:352-359
 40. Grossiord, C.; Martin J.M.; Varlot, K. *et al. Tribology Lett.* **2000**, *8*, 203-212.
 41. Holmberg, K. *Tribotechnology* 2001. <http://ltds.ec-lyon.fr/cost532/532holmbergpresentation.pdf>
 42. Hsu, S. M. *Langmuir* **1996**, *12*, 4482-4485.
 43. Hsu, S. M. Proc. of New Tribological Frontiers and Future Trends, Beijing, China, Oct., **2002**, 5-20
 44. Hsu, S. M. Proc. of New Tribological Frontiers and Future Trends, Beijing, China, Oct., **2002**, 25-37

45. Shenghua, L.; Yuansheng, J. *Chemistry (Chinese)* **2000**, *63*, 14-18.
46. Lauer, J.L.; Dwyer, S.R. *Tribol. Trans.* **1990**, *33*, 529–534.
47. Yuansheng, J.; Chunhong, Z. *Wear* **1997**, *205*, 77-87.
48. (a) Gilman, J. J. *Mater. Sci. & Techn.* **1996**, *A209*, 74-81; (b) Gilman, J. J. *Mechanochemical mechanisms in stress corrosion*. Symp. on Chemistry and Electrochemistry of Corrosion and Stress Corrosion Cracking, **2001**; (c) Gilman, J. J. *Mechanochemical mechanisms in stress corrosion*. Chemistry and Electrochemistry of Stress Corrosion Cracking: A Symposium Honoring the Contributions of Staehle, R.W., Jones, R. H., Ed.; TMS, **2001**, 3-25; (d) Gilman, J. J. Mechanisms of shear-induced solid-state reactions. *Mat. Res. Soc. Symp. Proc.* **1997**, *453*, 227-232.