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Computational chemistry on catalyst technology and international collaboration

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Abstract

The computational simulation of a system with multiple molecules (molecular assemblies) is an important area to be developed. This paper presents an outline of recent advances in computational chemistry, especially focusing on catalyst research and development. It also views a project taking place through international collaboration.

1. Introduction

This paper presents recent activities in molecular computation in chemical technologies, the so-called 'industrial computational chemistry' issue, to which the author has been committed for the last 5 years.

The following items are dealt with:

(1) Our industrial activities in computational chemistry.
(2) An outline of our investigations in computational chemistry on catalyst research and development.
(3) Potential future themes.
(4) Looking at computational chemistry as industrial technology.
(5) Viewing a computational chemistry project, the so-called 'Shugo-tai Project'.

2. Background and motivation

Background is dealt with in the following four points:

(1) The chemical industry will take up a key position in creating new materials in the next century.
(2) Computational chemistry represents the major tool for future material development.
(3) Time and also enormous investments will be necessary to generate common facilities in this field.
(4) Computational chemistry will play a major technical role in the global environment and safety resolutions.

If this is so, the following questions will arise:

(1) What can you elucidate with computational chemistry?
(2) How can you draw up a plan for material development and improvement?

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(3) What kind of technology and tools are necessary to be shared publically and internationally?

The author has been committed to this problem and has worked for more than five years for ASPRONC.

3. The work project at ASPRONC

3.1. 47 Companies (57 scientists and engineers)

In the Spring of 1991 we created a technology investigation group, with the general title "Industrial Computational Chemistry", under The Association for Progress in New Chemistry (ASPRONC), which is a subsidiary organization of The Ministry of International Trade and Industry (MITI).

From the outset 47 companies participated in the project and more than 30 faculties from a variety of Japanese universities also cooperated.

Stage 1 (June 1991–April 1992) [1]

Investigations took place through the use of computational chemistry to try to find out how we can apply future material developments as a common technical tool to the chemical industry:

(1) Looking at the experimental side: (1) ceramics, (2) catalysts, (3) polymers, (4) dyes, and (5) organic compounds.
(2) Looking at the logical structure of prediction and the design of material.
(3) Looking at computational technology and systems.
(4) Planning material prediction/design system structure.
(5) Future 'musts.'

Stage 2 (June 1992–April 1994) [4]

(1) Technical investigation on molecular assembly problems — 'Shugo-tai' [2–4].
(a) Theories, mathematical modelling, and computation schemes. Three categories: small size molecules, polymers, and catalysts.
(b) System of technological structure, such as molecules, parameters, material properties, etc.

(2) Seeking and designing work to set up a national project.
(a) Primal drawing of material technology infrastructures.
(b) Setting polymers and catalysis as future targets, in terms of molecular assemblies.
(c) Investigating academic activities.
(d) Investigating the state-of-the-art technology in the chemical industry.
(e) Investigating potential themes for 'future musts'.
(f) Investigating systems of the governmental project.
(g) Designing a project of molecular assemblies, the 'Shugo-tai Project'.

Stage 3 (June 1994–April 1996)

(1) Technical workshops on catalysts, polymer modeling and parameter verification methodologies, etc.
(2) National project design.

4. Investigations applied to catalyst research as in Stage 1 [1]

Focusing on catalyst research, from our investigations over a wide range of materials, the following is given as a brief summary. Note that some items were sent to us with skeptical scopes. We thank the contributors for the items: Prof. Y. Morooka, Prof. N. Koga, Prof. A. Miyamoto, Prof. T. Hattori, and Dr. T. Itoh.

4.1. Requirements from the experimental side

(1) A guiding tool for discovery and prediction.
(2) Several items on catalyst research:
  (a) Water dissociation by visible light waves.
  (b) Reaction of water and CO, and controlling arbitrary selectivity.
  (c) High NO_x dissociation.
  (d) Compounds synthesis under controlling steric selectivity.
  (e) Alkane groups, and their applications.
  (f) Aromatics, their direct hydroxylations.
(3) Molecule building and catalyst design.
(4) Homogeneous catalytic gas reaction.
(5) Homogeneous catalytic liquid reaction.
(6) Catalyst surface, and computation on quantum quantities.
(7) Molecular binding to different substances, including carriers.
(8) Three-dimensional molecular configuration, and reaction selectivity.
(9) Inorganic compound catalyst (ex. Si/Al oxidation catalyst), and exploratory search.
(10) Catalyst reaction data base (ex. reactant/catalyst/product).

4.2. Requirements for tools of computational chemistry

(1) Fast computation and modelling simplification.

The Wilkinson complex is well known as an olefin hydrogenation catalyst, and it holds a very famous cyclic series of elementary reaction steps. If we wish to improve its reactivity, making a choice of an alternative metal fragment to the complex, molecular orbital (MO) will compute a series of reaction activity energies. It is quite easy to imagine that numbers of atoms and electrons are unavoidable in order to reach a huge size of computational unreality. This is a never ending story of frustration to computational scientists. As a result it is expected that some drastic simplification schemes on molecular modeling will be developed.

(2) Computer graphics and structural comparison with catalyst activity and selectivity.
(a) Atomic scale thin layer catalysts (ex. V_2O_5 with carrier TiO).
(b) Solid catalyst, its enzyme-like mechanism.

(3) Artificial intelligence (AI) of empirical knowledge.
(4) Quick accessible data base environments.

5. Investigations to catalyst research as Stage 2 [4]

5.1. A total of 254 literary works are surveyed which cover the years 1975 to 1993

(1) As catalyst categories, the following nine classifications are taken: Lewis acid, Raney, metal (transition metal; Ag, Ni, Pt, V, Pd, Re, Rh), ternary, polymerization (Ziegler–Natta, etc.), silica–alumina, silica, zeolite, interphase mobility.
(2) As for items of computational approaches, the following five are taken into consideration:
(a) Molecular approaches.
(b) Information approaches.
(c) Computer graphics (CG) and visualization.
(d) Data processing and characterization.
(e) Reaction engineering approach.

(3) The keywords used for the literature surveys were as follows: computer application, computational science, Monte Carlo, molecular dynamics, molecular orbitals, ab initio, density functional, etc.

Table 1 shows the number of literary works on computational tools in relation to catalyst categories.

Table 1
Catalytic reactions and computations

Computations \ Catalysts	Metal	Zeolite, silica, alumina/silica	Polymerization	Lewis acid	Raney acid	Hetero poly acid	Solid acid–base	Iter phase transfer	Ternary	Sum
[Molecular approach]	**56**	**27**	**24**	**25**	**5**	**5**	**11**	**2**	**0**	**155**
Molecular orbitals	35	9	21	25	5	5	11	1	0	
Density functional	3	0	0	0	0	0	0	0	0	
Molecular dynamics	7	12	1	0	0	0	0	0	0	
Molecular mechanics	1	2	0	0	0	0	0	1	0	
Monte Carlo	9	4	2	0	0	0	0	0	0	
Others	1	0	0	0	0	0	0	0	0	
[Information science approach]	**1**	**1**	**1**	**1**	**0**	**0**	**0**	**0**	2	**6**
Artificial intelligence										
Data bases		1		1						
Neural nets										
Chemometrics	1									
Others			1							
[Computer graphics & visualizations]	**3**	**14**	**0**	**0**	**0**	**2**	**1**	**0**	**0**	**20**
[Automations and optimizations]	**9**	**0**	**2**	**0**	**2**	**0**	**0**	**0**	**6**	**19**
[Reaction engineering approach]	**17**	**4**	**18**	**2**	**4**	**0**	**0**	**3**	**1**	**49**
[Others]	0	**0**	**0**	**4**	**1**	**0**	**0**	**0**	**0**	**5**
Sum	**86**	**46**	**45**	**32**	**12**	**7**	**12**	**5**	**9**	**254**
Covering period	'90/1~	'90/1~	'88/1~	'75/1~	'75/1~	'81/1~	'81/1~	'81/1~	'81/1~	'81/1~

Two of the approaches: molecular and reaction engineering are found to have remarkable rates (see Fig. 1).

In almost every catalyst category, the molecular approach, especially MO, was carried out. However, the use of the information science approach was still quite seldom.

As for catalyst classes, metal, polymerization, and Lewis acid dominate. Polymerization (53.3% to molecular approaches, 40.0% to reaction engineering), Lewis acid (78.0% to molecular, 6.25% to reaction engineering), metal (65.1% to molecular, 19.8% to reaction engineering).

5.2. *Key items of catalyst technology and literature features of the state-of-the art computational approaches*

In order to make an analysis of the recent achievements from a computational approach, we set up the key items from the point of view of catalytic technology. We investigated features on how computational approaches are carried out in each of the catalyst categories.

(1) Key items

(a) Catalyst synthesis and catalyst composition design: component choices and their compositions, additive effects, synthetic procedures, and pre-processing effects.

(b) Reaction mechanisms: active sites. Selectivities: adsorptive, reaction paths, shape selectivities, steric effects.

(c) Characterizations: surface properties and active sites, acid site, base site characteristics, impurities effects.

(d) Engineering: catalyst life.

(2) Features

(a) Silica–alumina, silica, and zeolite: computer graphics approaches are very important in connection with the validation of molecular

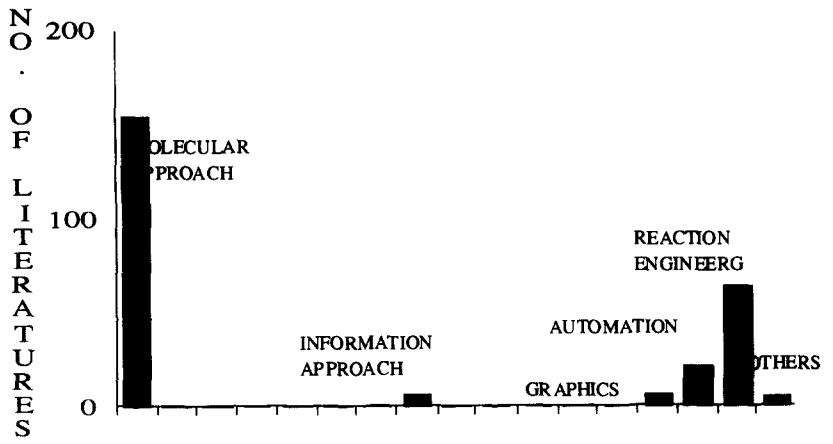

Fig. 1. Applied tools for catalyst computations (256 literature sources).

Table 2
Potential themes to "Shuhgo-tai" problems

Polymers
(*Original Proposer*; *Prof. Masao Doi, Nagoya Univ.*)
D-1 System Architecture of Linkages between Visco-elastic Properties and Molecular Characteristics
D-2 Simulation Technology for Designing Polymer Alloy Structure
D-3 Modelling and Simulation Methodology to Fracture Mechanics
D-4 Molecular Interaction at Meso-scale Surfaces

Catalysts
(*Original Proposer*; *Prof. Akira Miyamoto, Tohoku Univ.*)
M-1 Novel Separation Design of Hydro-carbon through Molecular Sieve Materials
M-2 Organic Template Molecules to design Formation of Shape-Selective Catalyst
M-3 Ti and ZSM-5 with V, on Mechanism of their Selective Oxidation, and Hydroxydation
M-4 Bio-mimetic Catalyst with Enzyme-like Characteristics
M-5 Recycle-free Catalyst, and its Engineering Design Methodology
M-6 Dynamics of Ultrafine Metal Particles on Surface Carrier, and Mechanism of Catalyst Degradation
M-7 Development of High Conversion Catalyst for CO_2 Source Hydro-carbon Synthetic Process
M-8 Investigation to High Performance Reduction Scheme of NO_x under Environment of O_2 existing and Theoretical Propositions to Experimental Sides
M-9 Development of Catalyst Virtual Reality System
M-10 Development of Expert System for Candidate Zeolite Reaction Path
M-11 Methane Partial Oxidation, and Synthesis of Methanol
M-12 Density Functional Method to Mechanism of Composite V_2O_5 Catalyst Surface
M-13 Zeolite, as Potential Features as a Reactor Cell of Fine Chemicals Synthesis
M-14 Photo Chemical Catalyst System and Development

Systems and Chemical Engineering
(Original Proposer; Yuji Naka, Tokyo Institute of Technology)
N-1 System Design to Macro-Micro Material Characteristics Linkage Mappings
N-2 Polymer Product Quality Prediction Methodology
N-3 Inversion Problem Algorithms
N-4 Integrated Material Production Processing System
N-5 Modelling Technology of Fine Chemical Reaction Design
N-6 Flow Simulator with Undergoing of Reaction
N-7 Simultaneous Design Methodology of Reactor with Production Operation
N-8 Dispersion and Mixing Technology and its Evaluation

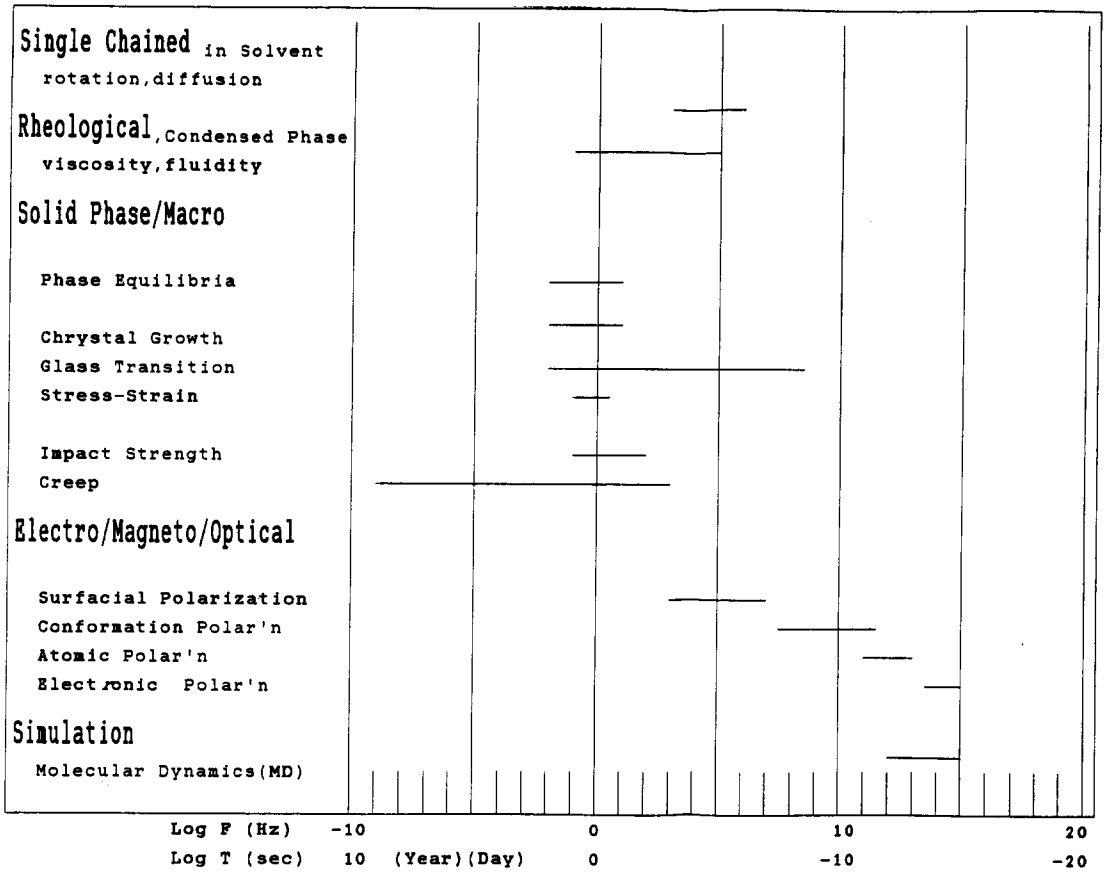

Fig. 2. Time scale of polymer technology.

dynamics (MD). Molecular orbital is in the stage of a trial application. Information approaches were not found in our surveys.

(b) Metal: on adsorption and dissociation, metal cluster modelling is applied to H_2, O_2, CO, and Cl. On synthesis and engineering, and also information approaches were not uncovered there. Several are found as application MO to the adsorption problem of small size organic molecules, which have neither been treated under conjugation to the catalytic surface, nor under the transition path.

(c) Polymerization: reaction mechanism studies on Ziegler-Natta are important to this field. Especially, ethylene insertion mechanisms and their reaction paths to the catalyst are intensively studied, where the catalyst models are simplified under modification. Computer graphics are reported as already being quite powerful tools for understanding these mechanisms. Meanwhile, synthesis and engineering applications are, however, still not important.

(d) Lewis acid: reaction mechanisms, mainly to the Diels–Alder reaction, are already well studied from a molecular viewpoint, and this field is perceived to have already come in the vicinity of achieving catalyst design. Neither a synthesis study nor an engineering study were found in our surveys.

(5) Raney: this field is comparatively, less important than studies in Lewis acid. The reaction mechanisms are reported from both molecular and reaction engineering areas, but they are still in an early stage. No report of synthesis applications have been found.

The main feature of the items mentioned above is that mechanism studies are the major concern

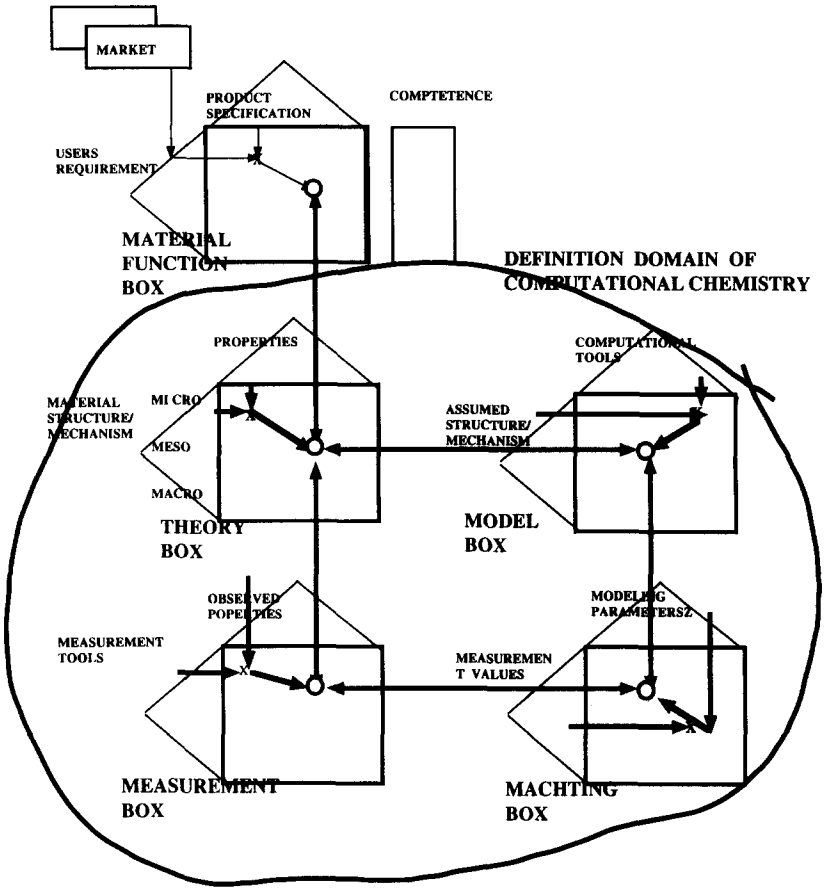

Fig. 3. Computer chemistry house box.

of each catalyst. Catalyst synthesis, except for information approaches, is relatively less important.

With regards to the problem of the catalyst lifetime, even though this is important to the industrial side of affairs, there have been relatively few studies with the exception of some research on poisoning.

6. Extracting themes 'musts' for research projects and industrial desires [4]

In order to promote a project on computational molecular assemblies, we collected research according to the advice of specialists in three fields; 4 specialists for polymers, 14 for catalysts, and 8 for computational modelling and systems.

Table 2 lists the above themes. These items, although yet to be accomplished within a further detailed plan, lead us a step closer to an effective project.

Additional suggestions and themes are welcome to the author.

7. Computational chemistry environment: future chemical technology

Fig. 2 shows the comparison between temporal scales of polymer with current MD.

This is a sketch of the state-of-the-art in the subject showing the symbiotic temporary relationship between a molecular computation, such as molecular dynamics (MD) and polymer physical properties.

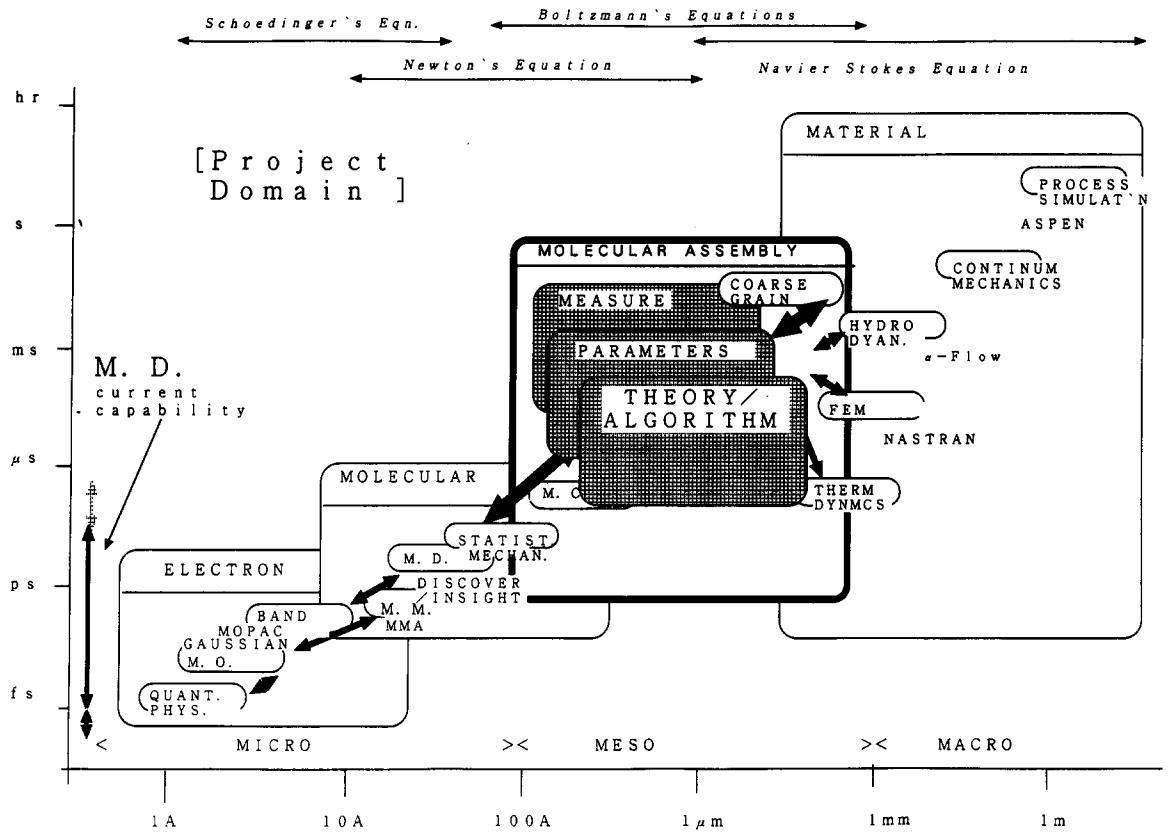

Fig. 4. Scheme for molecular assembly (Shugo-tai) development as a project domain.

The quest to simulate larger and more complex systems and new computational strategies clearly need to be justified.

Fig. 3 shows a definition domain of our computational chemistry with a hand drawn circle, where computational chemistry is located in a so-called 'CC quality box', as material technology activities. These types of mappings are quite familiar to quality control technologies in a sense of sharing a view to make an effort to achievement, what and where and under what relations with others are responsible.

As a primal target, an integration of the 4 boxes are desirable to be shared for strategies of industrial technology: Theory Box (material structures vs. physical properties), Modelling Box (material structures vs. computational modelling/tools), Experiment Box (measurement tool vs. physical properties), and Matching Box (measurement tools vs. computational modelling/tools).

Fig. 4 shows a scheme for molecular assemble (Shugo-tai) development as a project domain.

8. Computational chemistry project: 'Bunshi-Shugo-tai project' (molecular assemblies) and its expecting scope

During our designing work under ASPRONC, we make an outline of the project under an application to the Science and Technology Frontier Program (ISTF) of MITI, as follows:

Its Target

(1) Development of a 'meso-scopic scale theory', which provides an adequate bridge between molecular and continuum body object on meso scale extending to:

(a) molecules (Ångstroms, and femto seconds) and

(b) continuum body (meters, and hours).

(2) Development of numerical computational algorithms to (1):
(a) Multiple bodies MD simulation algorithms.
(b) First principle molecular dynamics algorithms to very large numbers of atoms (more than 100 atoms).
(c) Ad-hoc processors, especially to MD, under parallel architecture with tips embedded algorithm (thousands times faster than the current fastest super computer).

(3) Development of technology for measurement verification of computation results.
(4) Development of potential parameters databases.

8.1. The next 10 years

Organization/administration

The strategy for cooperating with top researchers in this project is now being designed in detail.

Table 3 shows our basic ideas.

The author thinks that the 'atomic technology' project is an excellent model to be taken, especially because of:

(a) Equal partnership between government, academy, and industry, and

(b) Equal opportunity between domestic and overseas.

Any comments and suggestions are welcome from any person who is concerned with the future realizations for the Computational Chemistry.

We wish this project will become a new measure as to match us with to overseas counterparts.

Table 3
Case study to collaborations

No. 1 *Flexible and Dynamics* Equal partnership of Government, University, and Company of Domestic and Overseas and of Permanent and Visitor Members
No. 2 *Inter-disciplinary* Status Evidence as Academic Career Wide Sectors from Industries, as Material Makers, Computer Hard/Soft-ware Makers, and Material Users
No. 3 *'Same Roof' Collaboration Between* Theorist, Computation Scientist, Experimentalist, Chemical Engineer, etc.
No. 4 *Salary and Accommodations* Very Attractive
No. 5 *Rights* Patents, Publishing of Paper
No. 6 *Commercialization Promotion ofResearch Fruit*
No. 7 *Education Open*

9. Conclusions

The following items have been dealt with in this paper:

(1) Our industrial activities in computational chemistry.
(2) An outline of our investigations in computational chemistry on catalyst research and development.
(3) Potential future themes.
(4) Looking at computational chemistry as industrial technology.
(5) Viewing a computational chemistry project, the so-called 'Shugo-tai Project'.

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I would like to thank Prof. A. Miyamoto for his notable contribution to our investigations at ASPROC, particularly to our understanding of catalyst computational chemistry. We also acknowledge Prof. Yukio Yoneda for the many years which has devoted to giving leadership in a

wide range of computer applications and data bases for catalyst technology [5].

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