

ワークショップ  
「複雑物質系の分子理論の発展」  
名古屋大学東山キャンパス ES総合館・ESホール  
令和6年3月14日

# “複雑物質系の分子反応理論を目指して” “Toward the Theory of Molecular Reactions in Complex Material Systems”



長岡正隆  
Masataka Nagaoka



名古屋大学 情報学部/大学院情報学研究科  
自然情報学科 複雑システム系/複雑系科学専攻  
(名大情報文化学部/大学院人間情報学研究科  
平成10年7月採用)



## Outline

- § 1 At the Beginning
- § 2 Toward “Fukui’s Lab”!  
~From physics to chemistry!~
- § 3 Go on ! “Nobel Prize” !
- § 4 Nagaoka Lab Starts ! A Departure ! ?  
What we have done before leads to  
what we have started “newly”!  
~A private version of ‘recent chemistry’~
- § 5 Evolving! Toward the Complexity
- § 6 Concluding Remarks  
~Are we carrying on the spirit of Fukui’s lab?~
- § 7 Acknowledgments

JOURNEY  
“DEPARTURE”

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reasons, the  
images are not  
displayed.



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## § 1 At the Beginning

:01





## No "Blueprints" Left Behind, but Connecting "Hearts and Minds": The night high school students burn the giant dragon they spent six months building"

Daisuke Shimizu 2023, Jul. 1st 08:00



"Students spend more than half a year creating a **huge dragon object** and erect it on the ground for the festival. They **dismantle** it and **burn** it at an evening festival. ...

This is a traditional event that has been handed down for nearly half a century at Nagano Prefectural **Suzaka High School** in Suzaka City. The school's emblem is the Miyama Gentian, (Rindo in Japanese), and there is a nearby mountain called **Garyu-zan**, so the students create objects at the "**Rindo Festival**" (cultural festival) using the **dragon** as a symbol. This tradition began in 1967.

### Half a century ago, a physics teacher said

It has a thick timber skeleton, and in some years it exceeds 10 meters in height. However, the blueprints have not been handed down to the next generation, and the words of a **physics teacher**, a licensed architect, who played a central role in designing the framework 50 years ago, are still spoken today: "**Don't leave the blueprints, burn them**". The leader of this year's dragon production: "That's the interesting part and the good part. It is **not the paper (blueprints) but the feelings that connect us.**"



### NHK Documentary Series Ningen Document

\*For copyright reasons, the images are not displayed.

"Make a Dragon Thrust into  
the Sky: Nagano Suzaka High  
School Cultural Festival"  
(2006.9.8)

## Brief Personal History

era BC	77(S52)0322 Grad. Suzaka High Sch	06(H18)10	JST*Core Research for Evolutionary Science and Technology: <b>CREST</b> "Research Development of Multiscale Simulation of Aggregation Reaction Systems"
	82(S57)0316 Grad. Fac. Eng. KU.	07(H19)04	Minor ailment
	84(S59)0314 Completed MC, KU.	08(H20)12	"Ready-to-Use Manual for Molecular Simulation Beginners" Published!
	87(S62)0311 Completed DC, KU.*JSPS: Japan Society for the Promotion of Science	12(H24)05	<b>MSCRS2012</b> (JST International)
	88(S63)0410 JSPS*Fellow (IFC)	13(H25)10	JST*Core Research for Evolutionary Science and Technology: <b>CREST</b> "Establishment of Computational Molecular Technology towards Macroscopic Chemical Phenomena"
	91(H03)0407 Deputy Chief RO (IFC)	14(H26)04	<b>StudyCamp2014</b>
	93(H05)0605 <b>US-Belgium Summer Tour</b>	15(H27)12	<b>PACIFICHEM2015</b>
	97(H09)0901 Chief RO (IFC)	16(H28)04	<b>MSCRS2016</b> (JSPS Japan-Brazil+NU)
	98(H10)0100 Leaving (Prof. Fukui Passed away)	17(H29)04	Prof. (Fac. and GS. of Informatics)
	98(H10)0710 Assoc. Prof. of GS. <b>Change to NU</b> of Human Informatics, NU	18(H30)09	Kanreki (60 <sup>th</sup> BD)
	JST*Computational Science and Technology Specific Research and Development Promotion Project: <b>ACT-JST</b> "Study on Non-equilibrium and Non-stationary Dynamics of Aggregation Reaction Systems"	20(R02)12	<b>PACIFICHEM2020</b>
	Birth of Lab Ncube!	23(R05)03	<b>StudyCamp2022</b>
	02(H14)03 Conference <b>CRN<sup>3</sup></b> (Clarifying Non-equilibrium non-stationarity characteristic of chemical reaction phenomena) (Grant-in-aid: C)		
	02(H14)09 Prof. (Human Info)		
	03(H15)04 Prof. (Info. Sci.)		
	04(H16)04 21st Century COE "Computational Science Frontiers"		



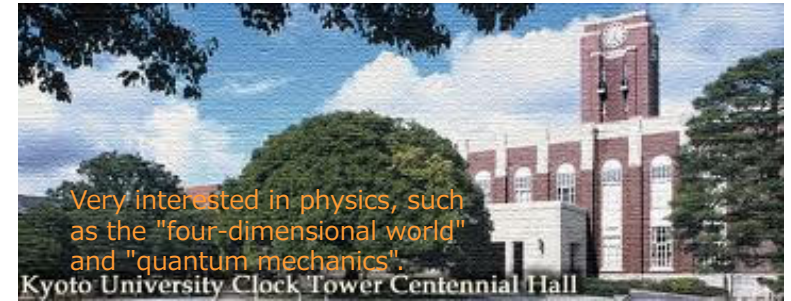


## § 2 Toward "Fukui's Lab"! From Physics to Chemistry!

## Entered Kyoto University (1978)



**Hideki Yukawa:** First Japanese to win the Nobel Prize in Physics (1949).



<https://www.kyoto-u.ac.jp/ja/about/facilities/campus/clocktower>



**"Traveler: The Autobiography of Hideki Yukawa"** (Kadokawa paperback, 1960)

**CLOSE ENCOUNTERS**  
OF THE THIRD KIND  
We are not alone.

**STAR WARS**

Episode 4/A New Hope

Galaxy Express 999

For copyright reasons, the images are not displayed.

## Entered Kyoto University (1978, BC21)

B1

Evening News 1978.7.27



Birth of Test Tube Baby (July, UK)



**STAR WARS**

Episode 4/A New Hope

Galaxy Express 999

"Candies" disbanded (April, Korakuen)(Back to being normal girls!)

NHK 2023 morning drama "Boogie Woogie" starts on Oct. 2nd, featuring heroine **Ms. Shuri**, a child of **Ms. Ran Itoh**, a member of "Candies".

For copyright reasons, the images are not displayed.

## Entered Kyoto University (1978, BC21)

B1

Evening News 1978.7.27



Birth of Test Tube Baby (July, UK)



In front of Club House of "Kyoto University Symphony Orchestra" (north of Higashiyama-Konoe intersection) (The club house was destroyed by fire on Oct. 31, 1996)

**STAR WARS**

Episode 4/A New Hope

Galaxy Express 999

"Candies" disbanded (April, Korakuen)(Back to being normal girls!)

All Kyoto tram lines were discontinued in the September!

For copyright reasons, the images are not displayed.



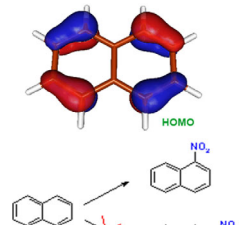
# The 1981 Nobel Prize in Chemistry Awarded to Prof. Fukui! (1981, BC17) B4



<https://www.kyoto-u.ac.jp/contentarea/ja/issue/kurenai/documents/25.pdf>



シリーズ映画第5作(1967)



"It's October 19, 1981, 9:50 p.m. The phone rings. My husband casually stands and picks up the telephone in the hallway, while my daughter and I are glued to **Seann Connery's "007,"** which is in its climax. ... I look over at him and see a slightly reddish expression, an angry look in his eyes, and a rare blood vessel on his neck. ... While I was wondering what was going on, I was distracted by the action of **"007,"** when suddenly the following words appeared on the TV screen in the form of a news bulletin: **"Professor Kenichi Fukui of Kyoto University won the Nobel Prize."**" (text by Prof. Fukui's wife)



[https://people.chem.ucsb.edu/kahn/kalju/chem109C/FMO\\_Theory.html](https://people.chem.ucsb.edu/kahn/kalju/chem109C/FMO_Theory.html)

# Hooray for Prof. Fukui! (811020) B4



<https://flyteam.jp/photo/854929>



For copyright reasons, some images are shown in low resolution or are not displayed.

ANN NEWS

"Nobel Prize in the Showa Era – Japan's First Nobel Prize in Chemistry: Kenichi Fukui"

# Fukui Lab's Year-End Party 1981 (811226) B4



福井研究室忘年会(元田中「天寅」にて)  
1981年12月26日(土)

At the 1981, Year-End Party (in "Ten-Tora" (a Japanese pub (Izaka-ya)) (Moto-Tanaka, Kyoto)) Sat., Dec. 26, 1981

Tastes loved by Nobel Prize-winning professors

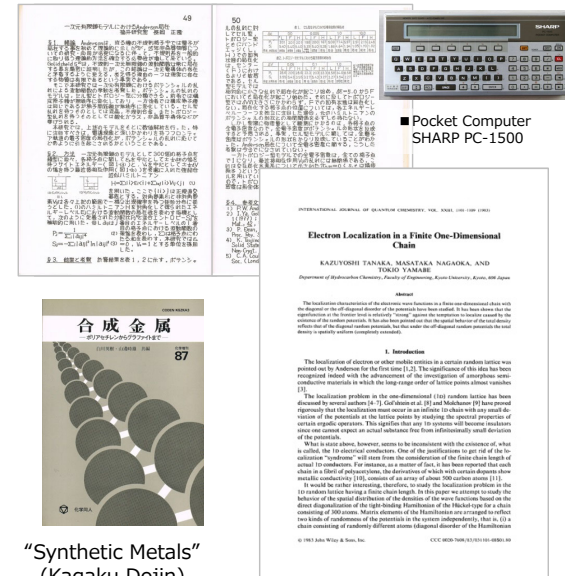


# A Last Student of Prof. Fukui ('82 Spring) B4

Bachelor's Thesis: "Anderson Localization in One-dimensional Finite Chain Models"



After the presentation of graduation theses at the entrance of building of Department of Hydrocarbon Chemistry (Taken on Mar. 11, 1982)



"Synthetic Metals" (Kagaku Dojin)





# A Last Student of Prof. Fukui ('82 Spring) B4

Bachelor's Thesis: "Anderson Localization in One-dimensional Finite Chain Models"



■ The total electron density does not change in non-diagonal disorder! !

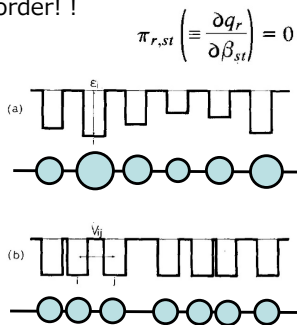


Fig. 1. Potential and one-dimensional chain diagram (a) diagonal disorder and (c) off-diagonal disorder

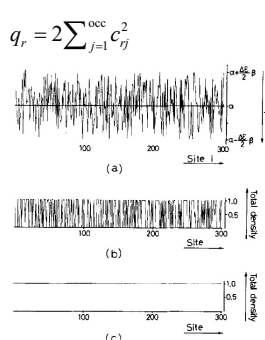


Fig 2. (a) Potential and total electron density (b) diagonal disorder and (c) off-diagonal disorder

■ The atom-bond polarizability (Coulson & Longuet-Higgins, 1947)

$$\pi_{r,st} = \frac{\partial q_r}{\partial \beta_{st}}, \quad \pi_{st,r} = \frac{\partial p_{st}}{\partial \alpha_r}$$

• C.A. Coulson, H.C. Longuet-Higgins, *Proc. R. Soc. Londn*, **A192**, 16 (1947)



C.A. Coulson  
(1910-1974)  
Oxford大('45-'47)  
King's College London  
(?47-'??)



H.C. Longuet-Higgins  
(1923-2004)  
Cambridge大('54-'67)  
Edinburgh大('67-'74)

# The Last Party (Farewell Party)! (820320) B4

The current "Tozanso" appears to have been newly built in 2008. Beg for information!



# The Last Party (Farewell Party)! (820320) B4

The really last snapshot as Fukui lab!



# Brief Personal History



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87(S62)0311 Completed DC, KU. **ICSM'86**  
88(S63)0410 JSPS\*Fellow (IFC)  
91(H03)0407 Deputy Chief RO (IFC)  
93(H05)0605 **US-Belgium Summer Tour**  
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98(H10)0100 Leaving (Prof. Fukui Passed away)  
98(H10)0710 Assoc. Prof. of GS, **Change to NU**  
of Human Informatics, NU  
JST\*Computational Science and  
Technology Specific Research and  
Development Promotion Project:  
**ACT-JST** "Study on Non-equilibrium  
and Non-stationary Dynamics of  
Aggregation Reaction Systems"  
Birth of "Three "Non"s" !!  
Conference CRN3 (Clarifying Non-equilibrium non-stationarity characteristic of chemical reaction phenomena)  
(Grant-in-aid: C)  
Prof. (Human Info)  
Prof. (Info. Sci.)  
21st Century COE  
"Computational Science Frontiers"

06(H18)10 JST\*Core Research for Evolutionary Science and Technology: **CREST** "Research Development of Multiscale Simulation of Aggregation Reaction Systems"  
07(H19)04 Minor ailment  
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20(R02)12 **PACIFICHEM2020**  
23(R05)03 **StudyCamp2022**

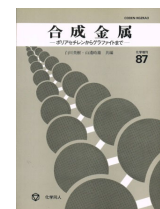






D3

~"1986 International Conference on Science and Technology of Synthetic Metals"~



Reception:  
Holyday Inn Kyoto

Banquet:  
Kyoto Hotel



Prof. Akira  
Yoshino

CMC Publishing, 2004

## "The Story of Lithium-Ion Batteries"

リチウムイオン  
電池物語

研究の楽しさ！  
開発の know how！  
現代版偉人伝？

グループフェロー  
吉野 彰 著

シーエムシー出版



D3

**Ultra Seven :**  
Episode 14  
"Ultra Guard to  
the West (Part I)"  
(1968)



## Ultra Seven

国立京都国際会館  
KYOTO INTERNATIONAL  
CONFERENCE HALL



### Ultra Seven

Episode 14 – *"Ultra Guard to the West (Part 1)"*  
Battle scene between Ultra Seven and King Joe at the Rokko  
Defense Center

For copyright reasons, the images are not displayed.



D3

**Ultra Seven :**  
Episode 14  
"Ultra Guard to  
the West (Part I)"  
(1968)



**Ultra Seven**  
Blu-ray

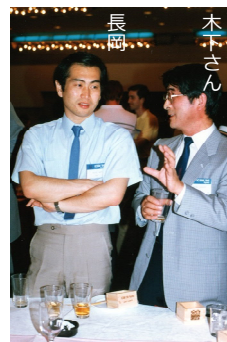
国立京都国際会館  
KYOTO INTERNATIONAL



BCS Theory of Superconducting



シュリーファー博士



木下さん



Whose  
bag?



Inn "Shibata"  
(しばた荘)  
Guest room



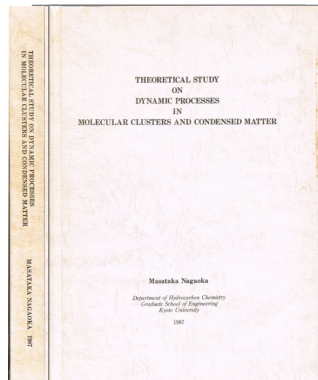
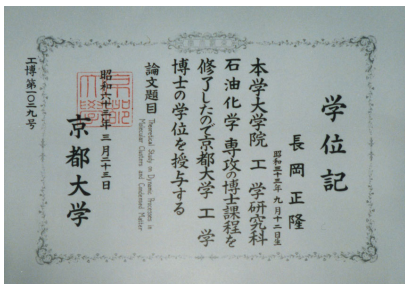




# My Inception of Doc. Degree (Dr.Eng.)



Dr. Yasunori Nishijima, the 21st President of Kyoto University, hands him his doc. degree.



Title: Theoretical Study on Dynamic Processes in Molecular Clusters and Condensed Matter

In March 1988, I completed my doctoral studies at the Graduate School of Engineering, KU, and was awarded a doctorate in engineering.



Prof. G.G. Hall  
(one of the sub-examiners)



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93(H05)0605 US-Belgium Summer Tour  
97(H09)0901 Chief RO (IFC)  
98(H10)0100 Leaving (Prof. Fukui Passed away)



Prof. Fukui  
awarded at  
Institute for  
Fundamental  
Chemistry



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JOURNEY  
"DEPARTURE"

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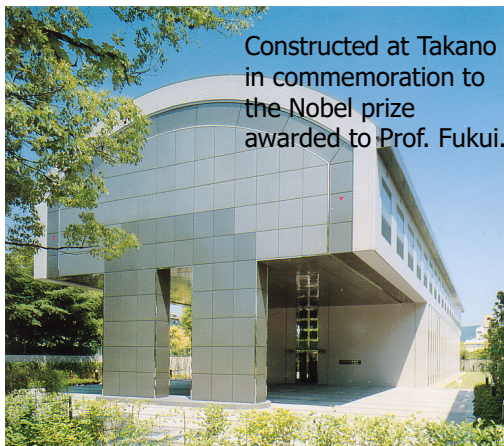


## § 3 Go on ! "Nobel Prize" !

:01



# Institute for Fundamental Chemistry (880401) ((Present) Fukui Institute for Fundamental Chemistry, Kyoto University)



Constructed at Takano in commemoration to the Nobel prize awarded to Prof. Fukui.

<https://www.iqms.org/deceased/hall.php>

On April 1st, 1988, I moved to the Institute as a researcher to welcome Prof. Fukui who was supposed to be inaugurated as Director on June 1.



Tea-ceremony room  
(Calligraphy: Toko Shinoda)



Research laboratories (2F)

# First Get-together (3F Pantry)(880601We)

基礎化学研究所開所後の業務予定表			
館住所: 〒606 京都市左京区京野町開所3-4-4 TEL: 075-711-7708 (代表)			
月	日	曜	行事その他の予定
5.10	火		藤井美奈子さん(74歳)採用(月、火、木)
5.19	金		東京事務所開所
5.17	火		長瀬家移理事、朝倉事務局長就任
5.27	金		建物受渡し
5.27	金		福井先生の荷物搬入(京都工芸繊維大学より)
6.1	水		職員組合会、緑の説明等 於丹後子さん(74歳)採用
6.3	金		写真撮影(日本経済新聞社) 18:00 写真撮影(日本経済新聞社) 18:30 シンパシー(金銭、終3階食堂) 2:00 福井先生(京都工芸繊維大学) (6月1日に確定)
6.4	土		11:00 福井先生、山邊先生、京都市訪問(挨拶)
6.14	火		Prof. and Mrs. J. M. Thomas来訪 (Director and Assistant Professor, the Royal Institution of Great Britain) (留会: 館内学号 TEL: 771-7113)
6.14	火		2:00 基礎化学研究所訪問 4:00 Prof. Thomas 京大にてセミナー(分子工学、基礎化学利用)
6.17	金		12:00 理事会(於 東京パレスホテル)
6.22	水		Dr. Anita Enflo来日(京大招へい外国人学者) (留会: 京大国際学生館 TEL: 771-3443)
6.22	水		山邊先生米国出張(1250' 80, Santa Fe, New Mexico, U.S.A. 参加)
7.12	水		Prof. and Mrs. Emily E. Hershbach来日 (Prof. of Chemistry, Rutgers Univ.) (留会: 館内学号 TEL: 771-7113)
7.12	水		Prof. Hershbach 京大にてセミナー(分子工学、基礎化学利用)
7.23	土		

We entered the brand-new building without even a single pencil of stationery and said, "Yo, let's get started!" I entered the building and helped Dr. Fukui bring in his luggage and other items.



# Commemorative Photo on the Opening Day of IFC (880601, We) (without honorifics)



On June 1, 1988, after a dinner in the third floor pantry (cafeteria), we had a briefing session, a commemorative photo, and completed the first major event of the first day with Dr. Fukui.

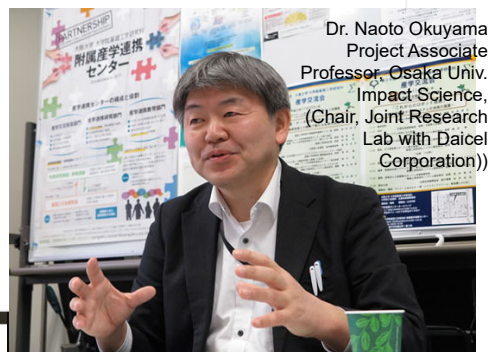
# The Institute is... At the Institute, ...

From "Green and Cultural Kyoto" (KBS)  
Interview with Professor Kenichi Fukui

\*For copyright reasons, the images are not displayed.



## In Laboratory 102 (1991).



Dr. Naoto Okuyama  
Project Associate  
Professor, Osaka Univ.  
Impact Science,  
(Chair, Joint Research  
Lab with Daicel  
Corporation))

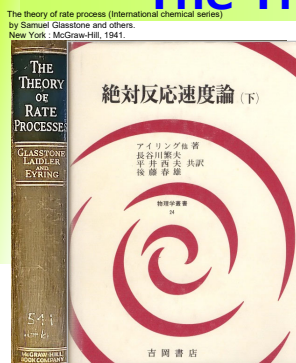
\*For copyright reasons, the images are not displayed.

## In the director's office (1991)



34

## Research Motivation #1: “The Theory of Rate Processes” (A standard theory)



### Words in “§ 8 Reactions in the liquid phase”

“The treatment of absolute reaction rate theory in solution is, in principle, the same as that in the gas phase. . . . There is some uncertainty, however, concerning partition functions of molecules in the liquid phase, and so it has been found more convenient to treat reactions in solution from a less fundamental point of view”. (H. Eyring et al., 1935)

### Gas reaction:

$$k = \frac{k_B T}{h} \cdot K^\ddagger = \frac{k_B T}{h} \cdot \frac{F_\ddagger}{F_A F_B \cdots} e^{-E_0/RT} \rightarrow k = \frac{k_B T}{h} \cdot K^\ddagger = \frac{k_B T}{h} \cdot \frac{c_M^\ddagger}{c_A c_B \cdots} = \frac{k_B T}{h} \cdot K_0^\ddagger \frac{\alpha_A \alpha_B \cdots}{\alpha_M^\ddagger}$$

Ratio of partition functions.

True equilibrium constant

### <Awareness of the issues>

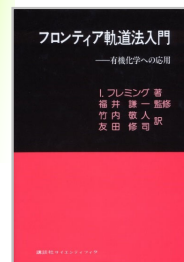
Solution reactions should also be treated from a fundamental viewpoint !!

→ The Theory of Absolute Reaction Rate using Partition Functions in the Liquid Phase !!

Includes surface reactions and enzymatic reactions!

## Research Motivation #2: “Two Ts: Temperature and Time”

Introduction to Frontier Orbital Theory  
by I. Fleming  
Supervised by Kenichi Fukui  
Translated by Taketo Takeuchi and Shuji Tomoda  
Kodansha, 1978



### Fukui Theories { 1. Frontier orbital theory 2. IRC theory

“In many cases, frontier orbital theory is effective also in solution reactions, but it must sometimes be corrected due to dynamic motion of reactant and solvent molecules. In frontier orbital theory, it is because an orbital is defined by electronic state theory at a static nuclear rearrangement. Moreover, the intrinsic reaction coordinate (IRC) theory is also a theory of the reaction pathway on which a reactant system changes at an infinitely slow speed (“one center of a reaction” (words of Fukui)).” (Monthly Journal “Chemistry” Prof. Fukui’s mourning number)

“Likewise, solvent effects (which is usually make themselves felt in the entropy of activation term) are also well known to be part of the explanation of the principal of hard(硬) and soft(軟) acids and bases. Arguments based on the interaction of frontier orbitals are powerful, as we shall see, but they must not be taken so far that we forget these very important limitations.”

(I. Fleming, “Frontier Orbitals and Organic Chemical Reactions”, (1976))

### < My Awareness of the Issues >

In both Fukui theories, there is no explicit dependence on the concepts of two “T”s (T and t)!!

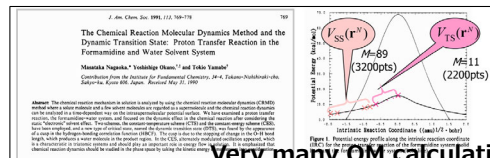
→ I want to create a theory directly depending on the two “T”s!!







# Reaction Energy Transfer Mechanisms in Solution Reactions: Heuristic Potential Functions for Chemical Reactions



**Very many QM calculations along the reaction coordinate**

MN, Y. Okuno & T. Yamabe, JACS, 113, 769 (1991)

反応座標での配置分配関数

$$Z_r = N_r^{-1} \sum_i e^{-\beta E_i} = N_r^{-1} \sum_i e^{-\beta E_i} \sum_j e^{-\beta E_j} = N_r^{-1} \sum_j e^{-\beta E_j} \sum_i e^{-\beta E_i}$$

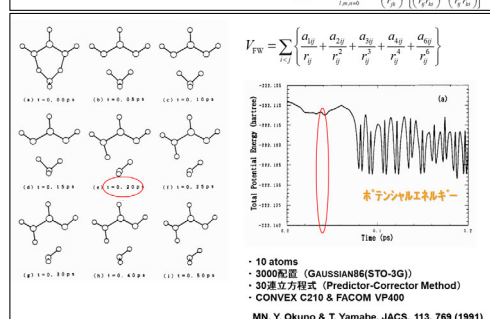
二体ポテンシャル関数

$$V = \sum_{i,j} V_{ij}(r_{ij}) = \sum_{i,j} \left( \frac{a_{ij}}{r_{ij}} + \frac{b_{ij}}{r_{ij}^2} + \frac{c_{ij}}{r_{ij}^3} + \frac{d_{ij}}{r_{ij}^4} + \frac{e_{ij}}{r_{ij}^5} + \frac{f_{ij}}{r_{ij}^6} + \frac{g_{ij}}{r_{ij}^7} + \frac{h_{ij}}{r_{ij}^8} + \frac{i_{ij}}{r_{ij}^9} + \frac{j_{ij}}{r_{ij}^{10}} \right)$$

評価関数  $\alpha_i$ : 重み関数 (=10.0) ( $s=1 \sim M$ )

$$\Delta_i = N_i^{-1} \sum_j [E_i(R_{ij}) - V_i(R_{ij}; \alpha)] \times (1 + \alpha_i \cdot \exp(-\Delta E_i / k_B T))$$

$\Delta_i = M^{-1} \sum_{j=1}^M \Delta_i$   $\Delta E_i = E_i - E_0$  ( $> 0$ )



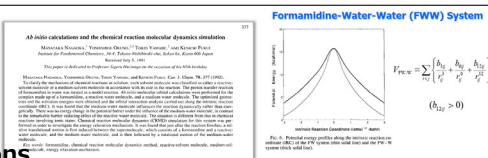
MN, Y. Okuno & T. Yamabe, JACS, 113, 769 (1991)

10 atoms

3000配置 (GAUSSIAN86(STO-3G))

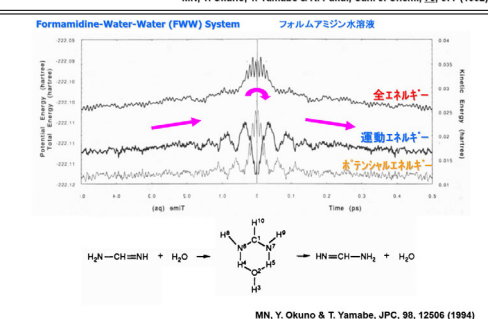
30連立方程式 (Predictor-Corrector Method)

CONVEX C210 & FACOM VP400



MN, Y. Okuno, T. Yamabe & K. Fukui, Can. J. Chem., 70, 377 (1992)

Fig. MCs and total atomic charges of FW(TS) and W(SS).

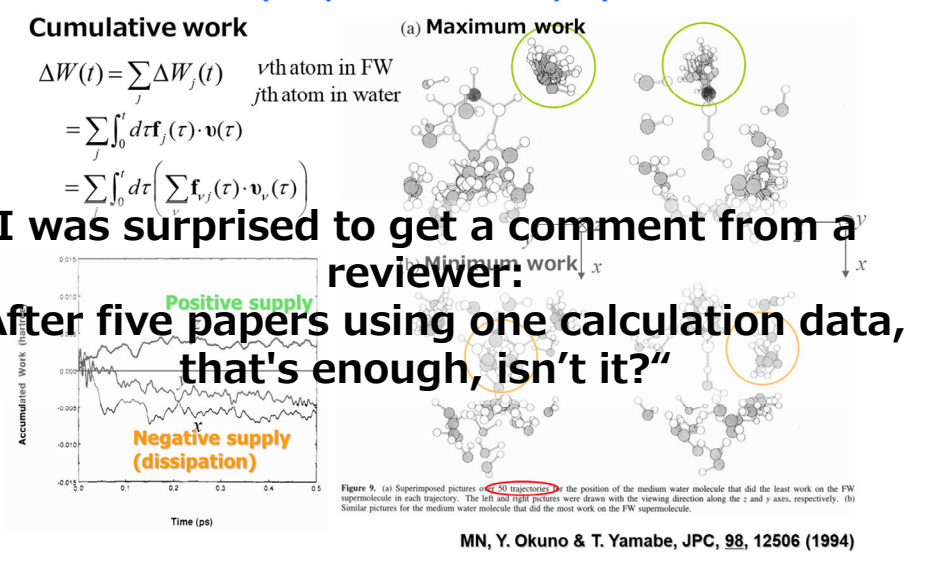


MN, Y. Okuno & T. Yamabe, JPC, 99, 12506 (1994)



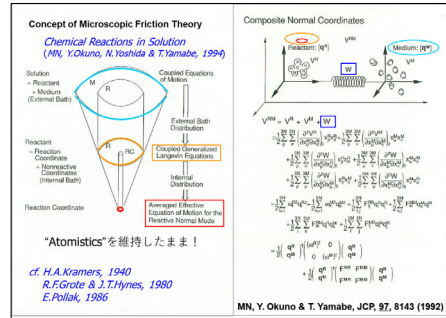
# Reaction Energy Transfer Mechanisms in Solution Reactions: Heuristic Potential Functions for Chemical Reactions

## Reaction energy transfer mechanism in solution reaction (component work analysis)



## Molecular Friction Theory: Chemical Reactions and Brownian Motion

**Any simple essential theory?**



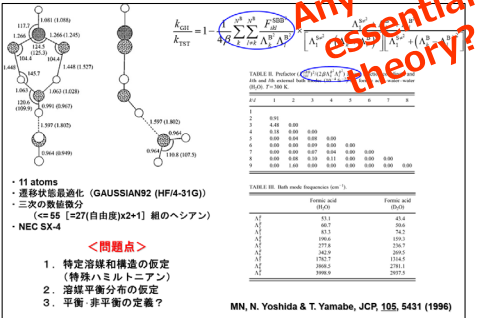
MN, Y. Okuno & T. Yamabe, JCP, 97, 8143 (1992)

MN, Y. Okuno, N. Yoshida & T. Yamabe, IJQC, 51, 519 (1994)

MN, N. Yoshida & T. Yamabe, JCP, 105, 5431 (1996)

Atomistics and statistics

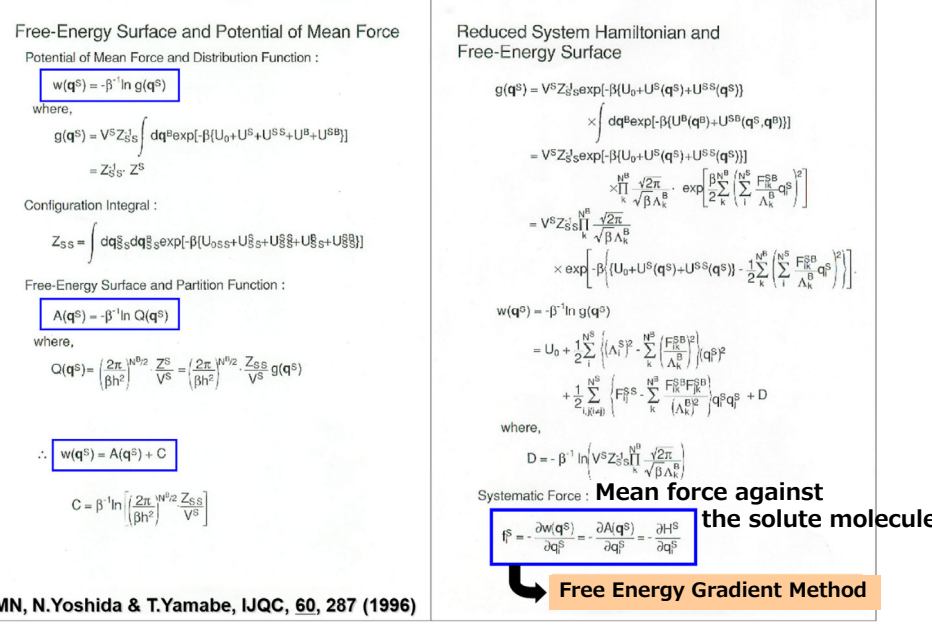
Reduction of computational cost



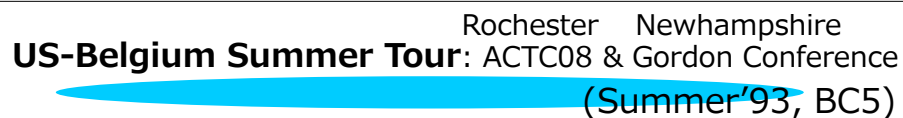
MN, N. Yoshida & T. Yamabe, JCP, 105, 5431 (1996)



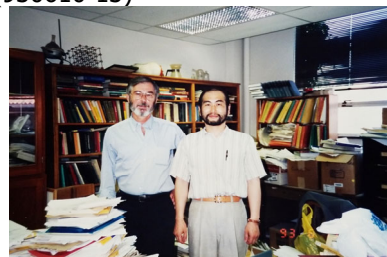
## Molecular Friction Theory and Free Energy Surface







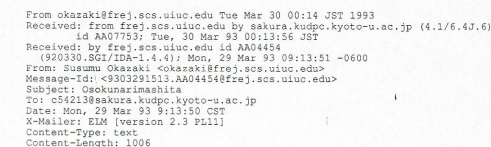
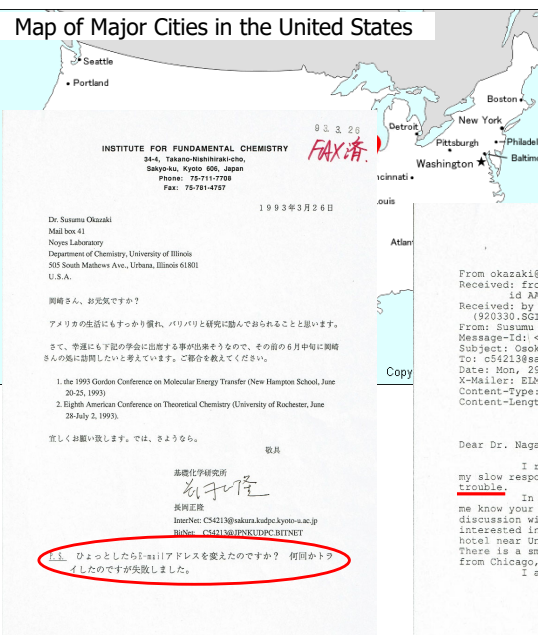
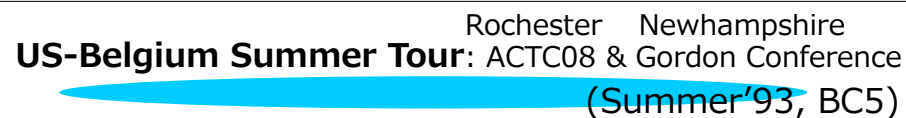
W.A.GoddardIII Lab (CALTECH) Visit  
(930610-13)



J.T.Hynes Lab (Colorado U@B) Visit  
(930613-16)



Collapse of the 55-year regime and birth of the  
Hosokawa administration (general election 930718)



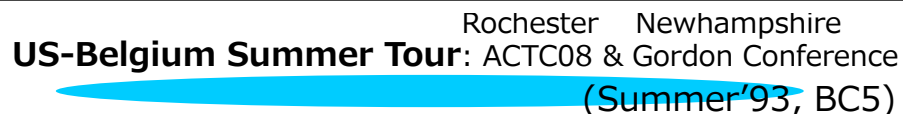
Mar. 29, 1993

Dear Dr. Nagaoka

I received your facsimile on Friday in the last week. I'm sorry for my slow response. This is because I waited for the recovery from the computer trouble.

In any case, it is a good news that you can visit here. Please let me know your visiting schedule when it is fixed. I can arrange your discussion with Peter G. Wolynes and a few other researchers who are interested in chemical reaction. And if you need, I can also reserve your hotel near University. Urbana-Champaign is about eighty mile south of Chicago. There is a small airport (Champaign airport) in this town and several flights from Chicago, New York, and other important cities are available.

Sincerely,  
Susumu Okazaki



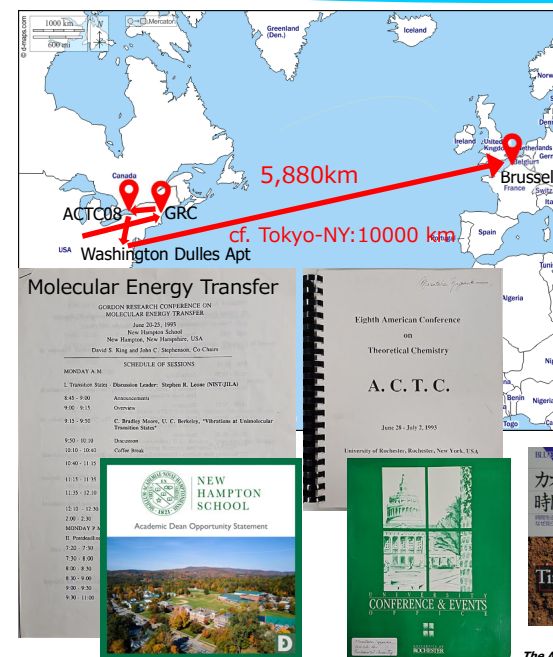
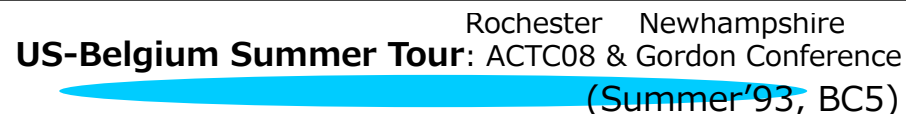
P.Wolynes Lab(Illinois U@UC)  
Visit 930620 (930616-20)



N.Makri Lab (Illinois U@UC)  
Visit 930618



TACC2023(Prof. N.Makri)230905



I.Pregogine Lab (ULB) Visit  
(930705-11)

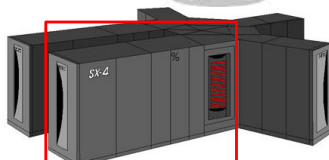


*The Arrow of Time Seen from Chaos*  
Shuichi Tasaki Kōdansha, 2000



[illegible]

T.Sekimoto (関本忠弘)  
NEC Chairman(Then)  
(IFC trustee)



[https://www.fmslib.com/benchmarks/bench\\_nec4.htm](https://www.fmslib.com/benchmarks/bench_nec4.htm)



<https://www.hpcwire.jp/archives/9428>  
T.Watanabe (渡辺 貞)  
General manager of  
HQ of supercomputer  
sales promotion (Then)  
(2009 Japan Academy prize)



Like this atmosphere!



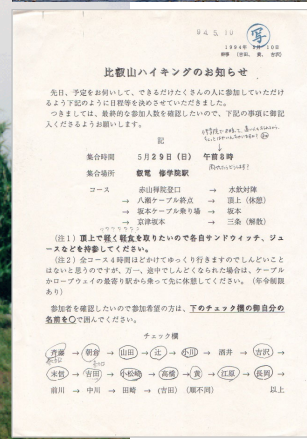
Previous Project Leader and Deputy Director, Next Generation  
Supercomputer Development and Implementation Directorate, RIKEN

Fig. 11.11


Legendary (9)




Prof. Fukui always carried a “walking stick” that was given to him by an acharya on Mount Hiei.





紀元前BC

77(S52)0322須坂高等学校卒業 

82(S57)0316京大工石化卒業 

84(S59)0314同院修士 修了

87(S62)0311同院博士 修了 

88(S63)0410JSPS\*研究員(基礎化研) 

91(H03)0407基礎化研 副主任研究員

97(H09)0901同上 主任研究員

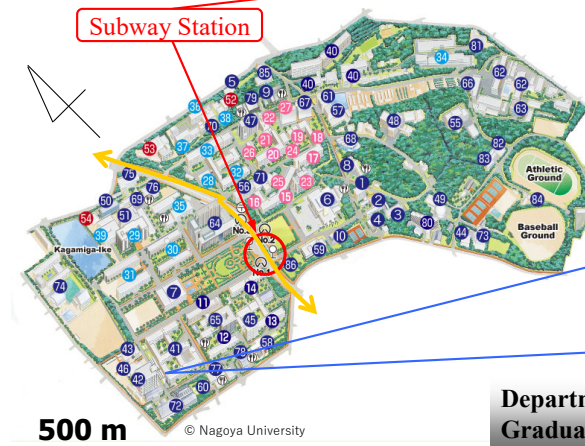
98(H10)0600同上 退所(福井先生 他界)



To  
 Nagoya University

after ~10 years in IFC.

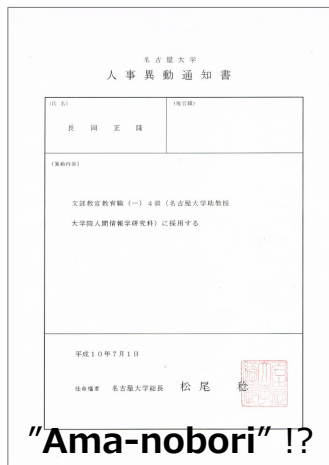
Autumn



**Department of “Natural Informatics”  
Graduate School of “human Informatics”  
at that time!**



# Graduate School of Human Informatics, Nagoya University. Appointed! ('980701, AD0)



"Ama-nobori" !?

-- an opposite command  
from private sector to  
governmental.



[https://www.sun-hp-bm-sgi-unix-workstations-for-sale/wp-content/uploads/1227512570\\_ban\\_octane.jpg](https://www.sun-hp-bm-sgi-unix-workstations-for-sale/wp-content/uploads/1227512570_ban_octane.jpg)  
<https://unixhq.com/systems/sgi-octane/>



## Outline

- § 1 At the Beginning
- § 2 Toward "Fukui's Lab"! ~From physics to chemistry!~
- § 3 Go on ! "Nobel Prize" !
- § 4 Nagaoka Lab Starts ! A Departure ! ?  
What we have done before leads to  
what we have started "newly"!  
~A private version of 'recent chemistry'~
- § 5 Evolving ! Toward the Complexity
- § 6 Concluding Remarks  
~Are we carrying on the spirit of Fukui's lab?~
- § 7 Acknowledgments

JOURNEY  
"DEPARTURE"

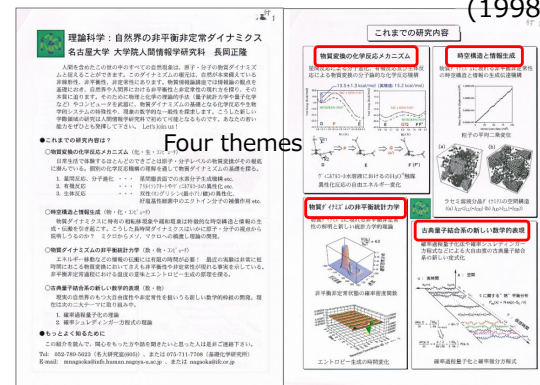
For copyright  
reasons, the  
images are not  
displayed.

## § 4 Nagaoka Lab Starts ! A Departure !?

## Graduate School of Human Informatics, Nagoya University. Employed! ('980701, AD0)



Four themes



(1998)

- Chemical reaction mechanism of materials transformation
- Space-time structure and information generation
- Non-equilibrium statistical mechanics of matter dynamics
- New mathematical expressions for classical quantum-coupled systems

(2024)

- From kinetic to nonequilibrium systems
- From isolated reactions to solution chemical reactions
- From elementary reactions to complex chemical reactions
- From molecules to life phenomena
- From parallel computing to multiscale information processing
- Industrial application by interplay between experiments and theoretical calculations





# Free energy gradient method (1998)

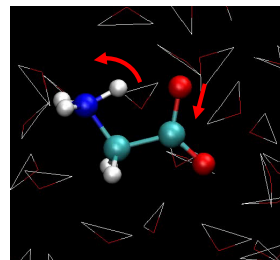
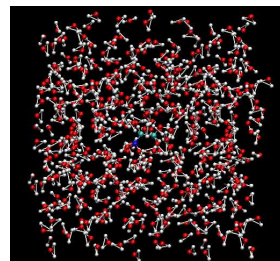
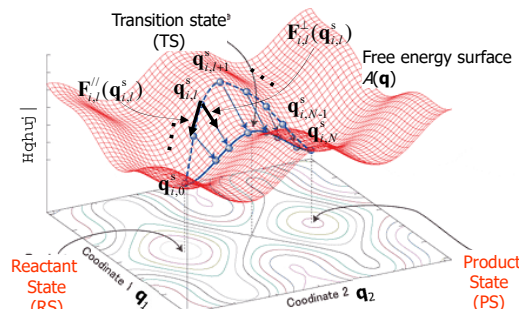
A method to study the shape of molecules and their reactions in solution

■ A method to find out what shape the molecules in solution

Dyhdjdh#  
irufh#  
lq#zoxwrg

$$\mathbf{F}_{i,l}^{\text{FE}}(\mathbf{q}_{i,l}^s) = -\frac{\partial A(\mathbf{q}_{i,l}^s)}{\partial \mathbf{q}_{i,l}^s} = -\left\langle \frac{\partial V_{\text{SB}}(\mathbf{q}_{i,l}^s)}{\partial \mathbf{q}_{i,l}^s} \right\rangle_i \approx 0,$$

■ Free energy  $A(\mathbf{q}_{i,l}^s) = -k_B T \ln Z(\mathbf{q}_{i,l}^s) \quad l=0, \dots, N$



Ex. Isomerization of glycine in aqueous solution

Q IR 10\rvkigd/PQ ) #1\ /Iqwd#1d# xdgwpx #Fkhp 1/ 435 /# 535 #4 << ; ,#

Q Wdnhqnd /# IN ldp xud /# IN r | dqr /# Wdvdg# # Q /# Wkhruf# khp 1# fwi /# 63 /# 48 +5344 ,#



# Reaction free energy and activation free energy

that the free energy gradient method enables to obtain for the first time



Dr. N.Okuyama

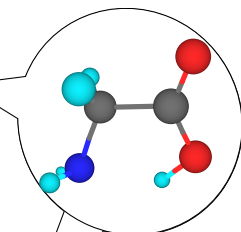
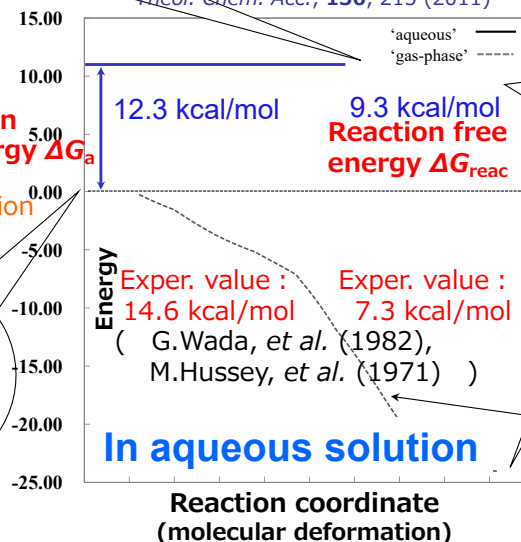
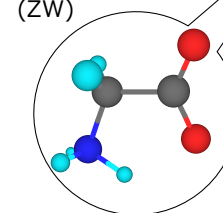
• N.O. Yoshida, MN & TY, *J. Chem. Phys.*, **113**, 3519 (2000)  
• N.Takenaka, Y.Kitamura, Y.Koyano, T.Asada & MN, *Theor. Chem. Acc.*, **130**, 215 (2011)

Neutral form (NF)

"Activated state on the free energy surface"

Activation free energy  $\Delta G_a$

Strong Stabilization  
Zwitterionic form (ZW)



Energy curve obtained from previous calculations (Contradictory to experiment!)

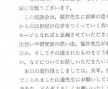
# Journal『Chemistry(化学)』Memorial Special Issue – The Legacy of Prof. Fukui – ('98, BC0, in 39)



若手化学者 師を語る  
福井謙一先生が遺したもの



Shogoin Goten-So (Kyoto): The round table meeting was held on Jan. 30, '98.



若手化学者 師を語る  
福井謙一先生が遺したもの



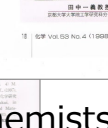
Shogoin Goten-So (Kyoto): The round table meeting was held on Jan. 30, '98.



若手化学者 師を語る  
福井謙一先生が遺したもの



Shogoin Goten-So (Kyoto): The round table meeting was held on Jan. 30, '98.



若手化学者 師を語る  
福井謙一先生が遺したもの



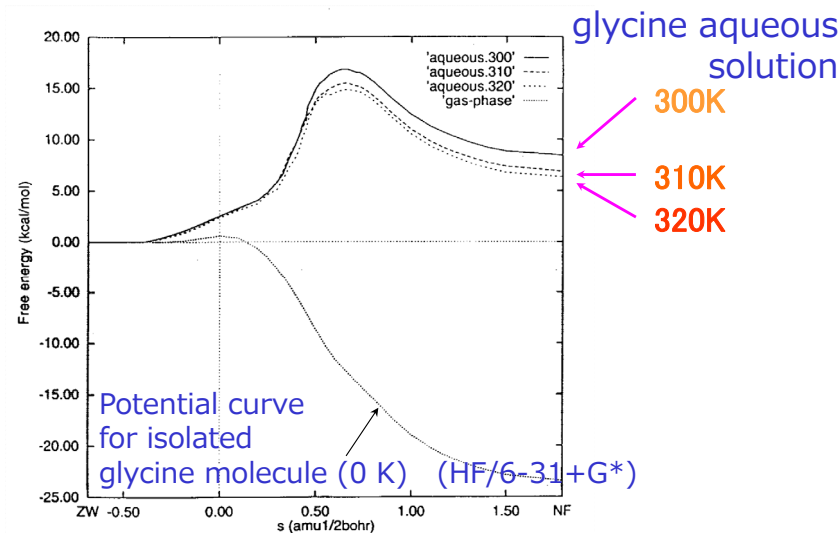
Shogoin Goten-So (Kyoto): The round table meeting was held on Jan. 30, '98.

Young chemists

talking about the mentor!

# Temperature Dependence of Activation Energy

Temperature dependence can also be obtained from free energy calculations!  
(Information that cannot be obtained from QM calculations!)



Potential curve for isolated glycine molecule (0 K) (HF/6-31+G\*)

MN, N.Yoshida, T.Yamabe, *JPC A*, **102**, 8202 (1998).

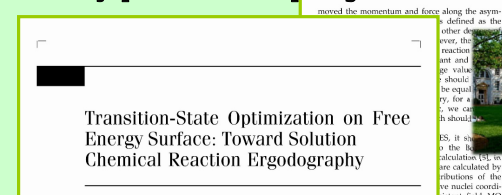


We proposed

Iuhh#Ighuj | #Udg hqwP hwkrg#4<<;



Wkh#Uj lqcd#dshu#vvhqwdghdv# #khruhwdeav#



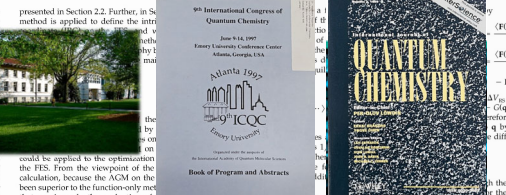
NAOTO OKUYAMA-YOSHIDA,<sup>1\*</sup> MASATAKA NAGAOKA,<sup>1</sup> TOKIO YAMABE<sup>2</sup>

<sup>1</sup>Institute for Fundamental Chemistry, 34-4, Takano-Nishihara-cho, Sakyo-ku, Kyoto 606, Japan  
<sup>2</sup>Division of Molecular Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan

Received 10 June 1997; revised 17 April 1998; accepted 21 April 1998

**ABSTRACT:** To obtain a transition state (TS) in solution chemical reaction, a new TS optimization method has been proposed on a multidimensional free energy surface (FES). Analogue to the method for the Born-Oppenheimer potential energy surface method, the FES, which can be calculated by molecular dynamics method and the free energy perturbation theory. Furthermore, on the basis of the method, we have proposed the definition of the intrinsic reaction coordinate (IRC) on the FES. According to not only the estimation of the computational demand but also the comparison of the numerical accuracy, we conclude that our method should be more efficient than such other methods that utilize only the free energy. Finally, it is discussed that the TS optimization and the IRC on the FES should become very important tools to develop a new research field called solution chemical reaction ergodography. © 1998 John Wiley & Sons, Inc. *J Comput Chem* 19: 95–103, 1998

**Keywords:** transition-state optimization; free energy surface; intrinsic reaction coordinate; solution chemical reaction ergodography



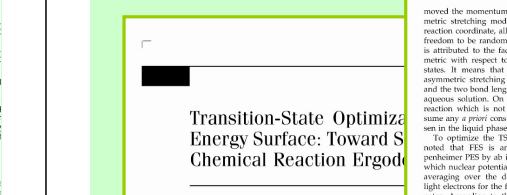
NAOTO OKUYAMA-YOSHIDA,<sup>1\*</sup> MASATAKA NAGAOKA,<sup>1</sup> TOKIO YAMABE<sup>2</sup>

<sup>1</sup>Institute for Fundamental Chemistry, 34-4, Takano-Nishihara-cho, Sakyo-ku, Kyoto 606, Japan  
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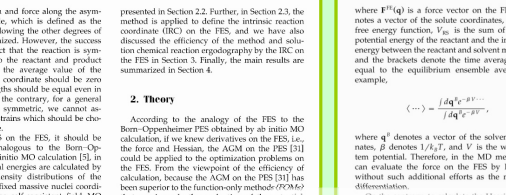
NAOTO OKUYAMA-YOSHIDA,<sup>1\*</sup> MASATAKA NAGAOKA,<sup>1</sup> TOKIO YAMABE<sup>2</sup>

<sup>1</sup>Institute for Fundamental Chemistry, 34-4, Takano-Nishihara-cho, Sakyo-ku, Kyoto 606, Japan  
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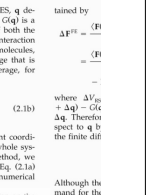
NAOTO OKUYAMA-YOSHIDA,<sup>1\*</sup> MASATAKA NAGAOKA,<sup>1</sup> TOKIO YAMABE<sup>2</sup>

<sup>1</sup>Institute for Fundamental Chemistry, 34-4, Takano-Nishihara-cho, Sakyo-ku, Kyoto 606, Japan  
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**Keywords:** transition-state optimization; free energy surface; intrinsic reaction coordinate; solution chemical reaction ergodography



NAOTO OKUYAMA-YOSHIDA,<sup>1\*</sup> MASATAKA NAGAOKA,<sup>1</sup> TOKIO YAMABE<sup>2</sup>

<sup>1</sup>Institute for Fundamental Chemistry, 34-4, Takano-Nishihara-cho, Sakyo-ku, Kyoto 606, Japan  
<sup>2</sup>Division of Molecular Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan

Received 10 June 1997; revised 17 April 1998; accepted 21 April 1998

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**Keywords:** transition-state optimization; free energy surface; intrinsic reaction coordinate; solution chemical reaction ergodography

# Badajoz Group developed an Effective FEG Method! — the FEG method via Average Solvent Electrostatic Potential (ASEP)/MD method —

JOURNAL OF CHEMICAL PHYSICS VOLUME 118, NUMBER 1 1 JANUARY 2003

## Geometry optimization of molecules in solution: Joint use of the mean field approximation and the free-energy gradient method

I. Fdez. Galván, M. L. Sánchez, M. E. Martín, F. J. Olivares del Valle, and M. A. Aguilar  
Departamento Química-Física, Universidad de Extremadura, Avda de Elvas s/n, 06071 Badajoz, Spain

(Received 17 June 2002; accepted 7 October 2002)

The average solvent electrostatic potential/molecular dynamics (ASEP/MD) and the free-energy gradient methods are applied together with the multidimensional geometry optimization of



F.J. Olivares del Valle and M.A. Aguilar, et al., *J. Chem. Phys.* **118**, 255 (2003)

# San Paulo Group developed another Effective FEG Method! — the influence of the solvent-induced electronic polarization on the <sup>15</sup>N magnetic shielding of pyridine in water —

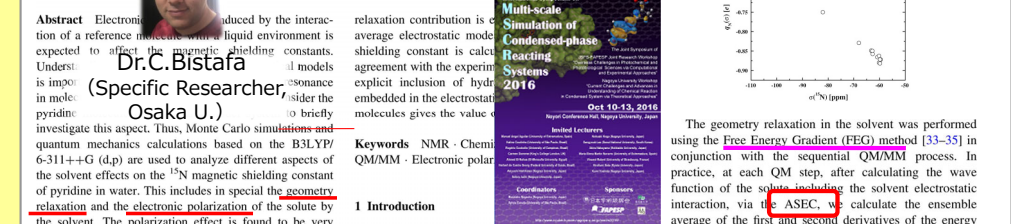
Theor Chem Acc (2012) 131:1220 DOI 10.1007/s00214-012-1220-0

## A simple analysis of the influence of the solvent-induced electronic polarization on the <sup>15</sup>N magnetic shielding of pyridine in water

Rodrigo M. Gester · Herbert C. Georg · Tertius L. Fonseca · Patricio F. Provasi · Sylvio Canuto

Received: 13 February 2012 / Accepted: 4 April 2012 / Published online: 4 May 2012 © Springer-Verlag 2012

**Abstract** Electronic polarization induced by the interaction of a reference molecule with a liquid environment is expected to affect the magnetic shielding constants. Understood in this context, the influence of the solvent-induced electronic polarization on the <sup>15</sup>N magnetic shielding of pyridine in water is investigated. This includes in particular the relaxation contribution to the average electrostatic model shielding constant is calculated in agreement with the experimental data. The explicit inclusion of hydrogens embedded in the electrostatic model gives the value of



R.M.Gester, H.C.Georg, T.L.Fonseca, P.F.Provasi, S.Canuto, *TCA*, **131**, 1220 (2012)



# Yang's Group developed also a FEG Method !



— the FEG method via

QM/MM Minimum Free-Energy Path (QM/MM-MFEP) Method

**JCTC** Journal of Chemical Theory and Computation

**QM/MM Minimum Free-Energy Path: Methodology and Application to Triosephosphate Isomerase**

Hao Hu, Zhenya Lu, and Wei Yang\*

Department of Chemistry, Duke University, Durham, North Carolina 27708

Received July 21, 2006

**Abstract:** Structural and energetic changes are two important characteristic properties of a chemical reaction process. In the condensed phase, studying these two properties is very challenging because of the great computational cost associated with the quantum mechanical calculations and phase space sampling. Although the combined quantum mechanics/molecular mechanics (QM/MM) approach significantly reduces the amount of the quantum mechanical calculations and facilitates the simulation of solution-phase and enzyme-catalyzed reactions, the required quantum mechanical calculations remain quite expensive and extensive sampling can be achieved routinely only with semirelativistic quantum mechanical methods. QM/MM simulation restricted to narrow regions of the potential transition state, or the minimum energy path, is often performed with the QM/MM-free energy path. In this paper, we propose a new method to determine the QM/MM reaction coordinate by using free-energy perturbation calculations at obtained with the QM/MM-MFEP method depend on path, which is based on local conformations difficult to obtain in practice. To overcome the need to further enhance the sampling of the free energy of the system as a function of reaction coordinate, we propose a new method to determine the QM/MM reaction coordinate by using free-energy perturbation calculations at obtained with the QM/MM-MFEP method. The free-energy gradient method, with free-energy gradient in hand, we further perform the search for the reaction path on steepest descent. This method thus efficiently locates the reaction coordinate, with structural information and enzyme reactions, with structural information. To further incorporate the dynamic information, we develop the reaction path potential (RPP) for the minimum free-energy path. The RPP is a comprehensive and accurate treatment and in enzymes with ab initio QM/MM methods, first step of the reaction of the enzyme with previous studies.

**Connection to Previous Studies of Sampling the Free Energy Surface.** The idea of representing the structural and thermodynamic properties of a molecular system in terms of the PMF surface of a few variables is a quite general idea in statistical mechanics.<sup>5,80</sup> Past simulation study often focused on building the PMF surface in simulations through various techniques such as umbrella sampling,<sup>29</sup> free-energy perturbation,<sup>81</sup> and thermodynamic integration.<sup>76</sup> Only recently, it was proposed to explore the phase space of the system by directly walking the PMF surface.<sup>55</sup> Several groups have extended the theory and the simulation techniques and have also reported several example applications to different reaction systems.<sup>48–50,78</sup> The work reported here should still be regarded as an important further improvement and enrichment of the idea because of several key differences between this work and those reported previously.

**The FEG Method**

**Our papers**

(51) Hirao, H.; Nagai, Y.; Nagakura, M. Transition-state optimization by the free energy gradient method: Application to aqueous-phase Menschutkin reaction between ammonia and methyl chloride. *Chem. Phys. Lett.* **2001**, *344*, 350–356.

(52) Okuyama-Yoshida, N.; Nagakura, M.; Yamabe, T. Potential energy function for intramolecular proton transfer reaction of glycine in aqueous solution. *J. Phys. Chem. A* **1998**, *102*, 285–292.

(53) Okuyama-Yoshida, N.; Katsuka, K.; Nagakura, M.; Yamabe, T. Structure optimization via free energy gradient method: Application to glycine zwitterion in aqueous solution. *J. Chem. Phys.* **2000**, *113*, 3519–3524.

(54) Nagakura, M.; Okuyama-Yoshida, N.; Yamabe, T. Origin of the transition state on the free energy surface: Intramolecular proton transfer reaction of glycine in aqueous solution. *J. Phys. Chem. A* **1998**, *102*, 8202–8208.

(55) Okuyama-Yoshida, N.; Nagakura, M.; Yamabe, T. Transition-state optimization on free energy surface: Toward solution chemical reaction ergodynamics. *Int. J. Quantum Chem.* **1998**, *70*, 95–103.

H. Hu, Z. Lu and W. Yang, *J. Chem. Theory and Comput.* **3**, 390 (2007)

# FEG Method must have influenced the of “Meta-dynamics method” !?

## Escaping free-energy minima

Alessandro Laio and Michele Parrinello\*

Centro Svizzero di Calcolo Scientifico, Via Cantonale, CH-6928 Manno, Switzerland; and Department of Chemistry, Eidgenössische Hönggerberg HCI, CH-8093 Zurich, Switzerland

Communicated by David Chandler, University of California, Berkeley, CA, July 18, 2002 (received for review May 8, 2002)

We introduce a powerful method for exploring the properties of the multidimensional free energy surfaces (FES) of complex many-body systems by means of coarse-grained non-Markovian dynamics in the space defined by a few collective coordinates. A characteristic feature of these dynamics is the presence of a history-dependent potential term that, in time, fills the minima in the FES, allowing the efficient exploration and accurate determination of the FES as a function of the collective coordinates. We demonstrate the usefulness of this approach in the case of the dissociation of a NaCl molecule in water and in the study of the conformational change of a dialanine in solution.

microscopic dynamics, to define coarse-grained dynamics in the space of the  $s$ s. In our case the definition of these dynamics is rather arbitrary and designed only to explore the FES efficiently. The dynamics is defined from the discretized evolution equation

$$\dot{s}_i^{n+1} = \dot{s}_i^n + \delta s_i^n \frac{\delta F}{\delta s_i^n} \quad (1)$$

**The FEG Method has become enough popular !!**

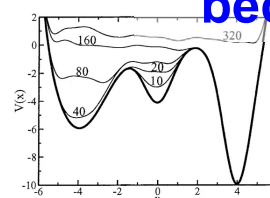


Fig. 1. Time evolution of the sum of a one-dimensional model potential  $V(x)$  and the accumulating Gaussian terms of Eq. 2. The dynamic evolution (thin line) is labeled by the number of dynamical iterations (Eq. 1). The starting potential (thick line) has three minima and the dynamics is initiated in the second minimum.

1. Carter, E. A.; Cicotti, G.; Hynes, J. T.; Krapal, R. (1989) *Chem. Phys. Lett.* **156**, 472–477.
2. Huber, T.; Torda, A. E. & van Gunsteren, W. F. (1994) *J. Comput. Sci.* **8**, 695–708.
3. Grunewald, H. (1995) *Phys. Rev. E* **52**, 2065–2066.
4. Spitz, M. & Cicotti, G. (1998) *J. Chem. Phys.* **109**, 7737–7744.
5. Voter, A. F. (1997) *J. Chem. Phys.* **106**, 4665–4677.
6. Voter, A. F. (1997) *Phys. Rev. Lett.* **78**, 3908–3911.
7. Steiner, M. M.; Gendland, P. A.; Wilkins, J. W. (1998) *Phys. Rev. B* **57**, 10236–10239.

Laio and Parrinello

PNAS | October 1, 2002 | vol. 99 | no. 20 | 12565

A. Laio and M. Parrinello, *PNAS*, **99**, 12562 (2002)

## Brief Personal History



**06(H18)1008 JST\*Core Research for Evolutionary Science and Technology: CREST "Research Development of Multiscale Simulation of Aggregation Reaction Systems"**

**07(H19)0409 Minor ailment**

**08(H20)1210 Ready-to-Use Manual for Molecular Simulation Beginners" Published !**

**12(H24)0514 MSCRS2012 (JST International)**

**13(H25)1015 JST\*Core Research for Evolutionary Science and Technology: CREST "Establishment of Computational Molecular Technology towards Macroscopic Chemical Phenomena"**

**14(H26)0416 StudyCamp2014**

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**16(H28)0418 MSCRS2016 (JSPS Japan-Brazil+NU)**

**17(H29)0419 Prof. (Fac. and GS. of Informatics)**

**18(H30)0920 Kanreki (60<sup>th</sup> BD)**

**20(R02)1222 PACIFICHEM2020**

**23(R05)0325 StudyCamp2022**

**98(H10)0700 Assoc. Prof. of GS. Change to NU of Human Informatics, NU**

**10 JST\*Computational Science and Technology Specific Research and Development Promotion Project: ACT-JST "Study on Non-equilibrium and Non-stationary Dynamics of Aggregation Reaction Systems"**

**02(H14)0304 Int. Conf. CRN<sup>3</sup> (Clarifying Non-equilibrium non-stationarity characteristic of chemical reaction phenomena) (Grant-in-aid: C)**

**02(H14)09 Prof. (Human Info)**

**03(H15)0405 Prof. (Info. Sci.)**

**04(H16)0406 21st Century COE "Computational Science Frontiers"**

**AD**

**10 Birth of Lab Ncube !**

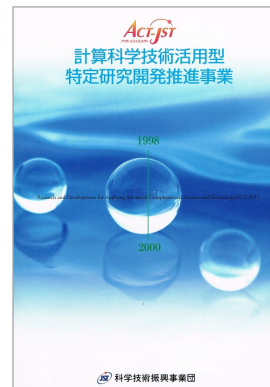
**02(H14)0304 Birth of "Three "Non"s" !!**

**02(H14)09 Prof. (Human Info)**

**03(H15)0405 Prof. (Info. Sci.)**

**04(H16)0406 21st Century COE "Computational Science Frontiers"**

## ACT-JST "Study on Non-equilibrium and Non-stationary Dynamics of Aggregation Reaction Systems" Accepted!! ('981117, AD0)



**凝集反応系の非平衡非定常ダイナミクス研究**

長岡 正隆 (名古屋大学 大学院人間情報科学研究科 助教授)

電子化学や分子動力学法などの計算科学的手法や食肉分散技術に基づき、非線形性、非平衡性、非定常性を加味した凝集系化学反応の新しい標準理論を確立。更に環境問題などに現れる現象をもっと実証的応用を行う。

図 凝集系に現れる非線形・非平衡・非定常性とその特徴

Dr. Masaki Sasai, who encouraged me to apply (Professor at the Graduate School of Human Informatics at Nagoya University at the time)

**Big occurrence !**

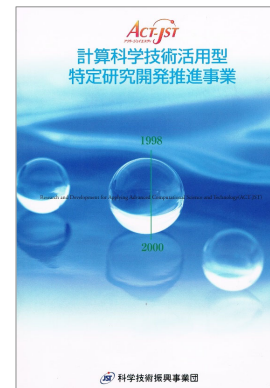


# ACT-JST "Study on Non-equilibrium and Non-stationary Dynamics of Aggregation Reaction Systems" Accepted!! ('981117, AD0)

If this project had not been adopted, history would have changed...

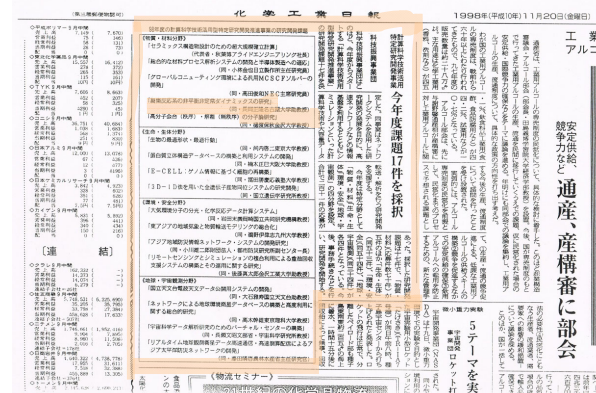
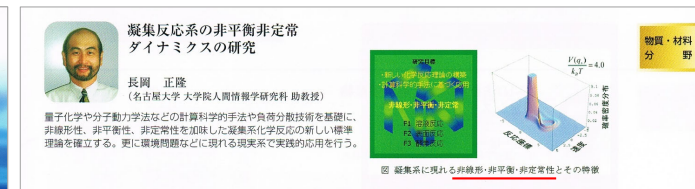


# ACT-JST "Study on Non-equilibrium and Non-stationary Dynamics of Aggregation Reaction Systems" Accepted!! ('981117, AD0)

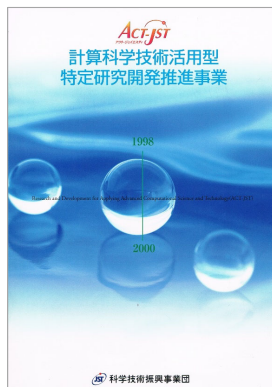


Japan Science and Technology "Corporation"

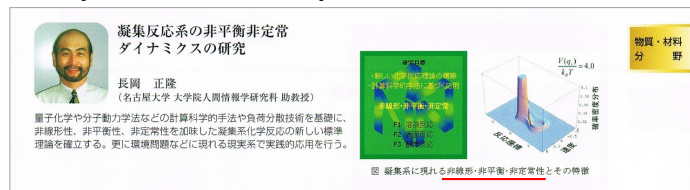
Research Period : 3 years  
Research Fee : ~150,000 kYen



# ACT-JST "Study on Non-equilibrium and Non-stationary Dynamics of Aggregation Reaction Systems" Accepted!! ('981117, AD0)



Japan Science and Technology "Corporation"



# ACT-JST "Study on Non-equilibrium and Non-stationary Dynamics of Aggregation Reaction Systems" Accepted!! ('981117, AD0)



PC Cluster (DEC (COMPAQ) )



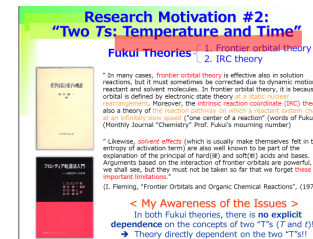
Origin200 (SiliconGraphics)



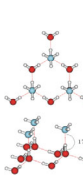
# “A Year-End Party 1999” in Sakae (’99, AD1) 栄



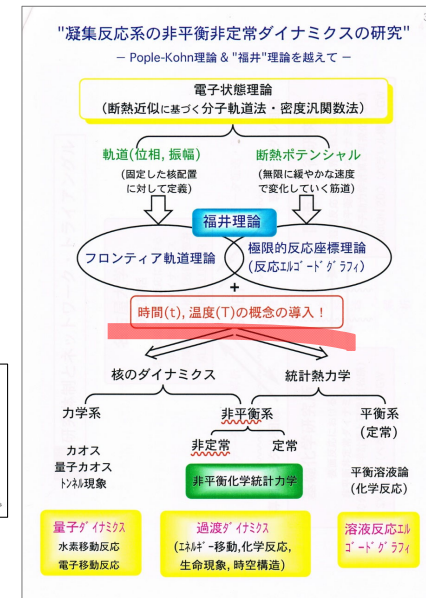
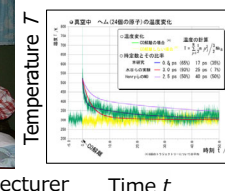
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Dr. T. Okamoto (then M2, now at HPC Systems) worked on  $T$  and  $t$  research from a theoretical and informatics point of view.

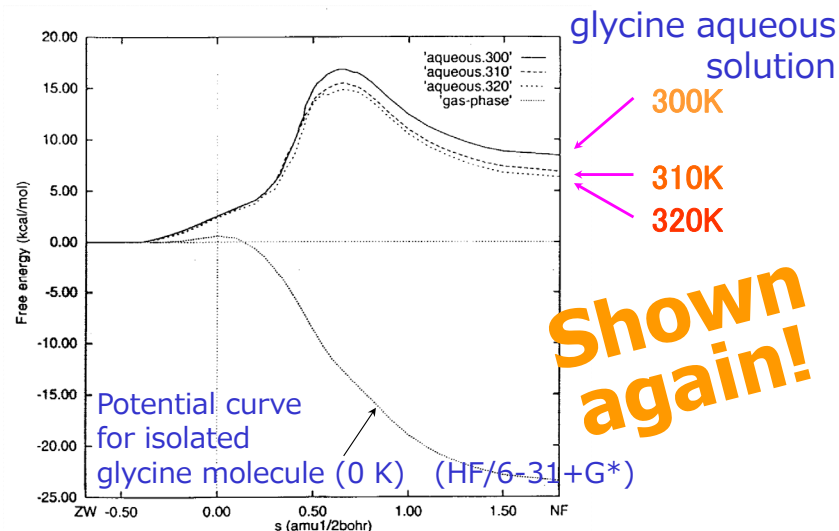


Dr. I. Okazaki (then PD, now a lecturer at Hirotsaki University) and Dr. Y. Hara (then M2, now a senior researcher at AIST) who practiced  $T$  and  $t$  research.



## Temperature Dependence of Activation Energy

Temperature dependence can also be obtained from free energy calculations!  
(Information that cannot be obtained from QM calculations!)



MN, N.Yoshida, T.Yamabe, JPC A, 102, 8202 (1998).



## Brief Personal History

77(S52)03	Grad. Suzaka High Sch	06(H18)1008	JST*Core Research for Evolutionary Science and Technology: CREST "Research Development of Multiscale Simulation of Aggregation Reaction Systems"
82(S57)03	Grad. Fac. Eng. KU.	07(H19)0409	Minor ailment
84(S59)03	Completed MC, KU.	08(H20)1210	Ready-to-Use Manual for Molecular Simulation Beginners" Published!
87(S62)03	Completed DC, KU.*JSPS: Japan Science and Technology Society for the Promotion of Science	12(H24)0515	MSCRS2012 (JST International)
88(S63)04	JSPS*Fellow (IFC)	13(H25)1016	JST*Core Research for Evolutionary Science and Technology: CREST "Establishment of Computational Molecular Technology towards Macroscopic Chemical Phenomena"
91(H03)04	Deputy Chief RO (IFC)	14(H26)0417	StudyCamp2014
93(H05)06	US-Belgium Summer Tour	15(H27)1218	PACIFICHEM2015
97(H09)09	Chief RO (IFC)	16(H28)0419	MSCRS2016 (JSPS Japan-Brazil+NU)
98(H10)01	Leaving (Prof. Fukui Passed away)	17(H29)0420	Prof. (Fac. and GS. of Informatics)
98(H10)0700	Assoc. Prof. of GS. Change to NU	18(H30)0921	Kanreki (60th BD)
10	JST*Computational Science and Technology Specific Research and Development Promotion Project: ACT-JST "Study on Non-equilibrium and Non-stationary Dynamics of Aggregation Reaction Systems"	20(R02)1223	PACIFICHEM2020
*JST: Japan Science and Tech Corporation	Birth of Lab Ncube!	23(R05)0325	StudyCamp2022
02(H14)0304	Int. Conf. CRN3 (Clarifying Non-equilibrium non-stationarity characteristic of chemical reaction phenomena) (Grant-in-aid: C)		
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03(H15)0405	Prof. (Info. Sci.)		
04(H16)0406	21st Century COE "Computational Science Frontiers"		





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## CREST "Research Development of Multiscale Simulation of Aggregation Reaction Systems"

- Coarse-graining of large-scale atomic information, development of reconstruction techniques and coarse-graining theory " ('06, AD08)

Core Research for Evolutionary Science and Technology (Japan Science and Technology Agency)

Research Director



Prof. G. Yagawa  
(Professor Emeritus, The University of Tokyo)  
(Former Professor, Toyo University)

Area Advisor



Dr. T. Watanabe  
(Project Leader, RIKEN Next Generation Supercomputer Development and Implementation Directorate at the time) and 9 others

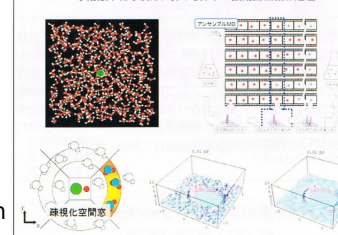


2008-2009 Japan Science and Technology Agency JST Basic Research Programs  
http://www.jst.go.jp/kisoken/

凝集反応系マルチスケールシミュレーションの研究開発  
—大規模原子情報の疎視化・再構成技法・疎視理論の開発—  
長岡 正隆 (名古屋大学大学院情報科学研究科 教授)

溶液、表面、生体高分子の非経験的分子動力学 (MD) シミュレーションで得た原子情報を疎視化・再構成する凝集反応系マルチスケールシミュレーションを実現します。具体的には、1) 疎視化技法と疎視化発展方程式、2) 最大エントロピー原理による非定常状態の再構成技法、3) 分子軌道法とMD法とを繋ぐQM/MM-インターフェースを開発し、最終的には個別事例に適用して、凝集反応系マルチスケールシミュレーション実用化基盤を確立します (Assoc. prof., Shiga U.)

非平衡非定常分布の再構成技法とアンサンブルMD法  
—水溶液中化学反応における分子の振動回転緩和過程—



Dr. T. Okamoto  
(HPC systems)



Dr. M. Takayanagi  
(Assoc. prof., Shiga U.)



Dr. N. Yamamoto  
(Prof., Chiba I.Tech.)



Dr. I. Yu  
(Assoc. prof. Maebashi IT)

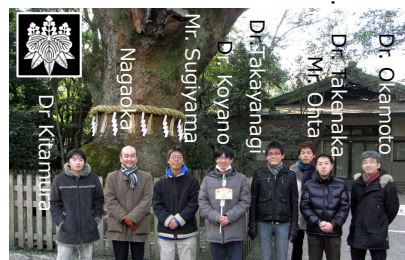
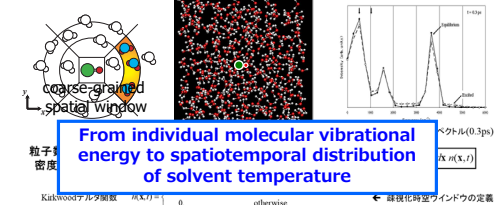
Research Period : 5.5 years  
Research Fee : ~300,000 kYen



# "Study on Multiscale Simulation of Aggregation Reaction Systems"

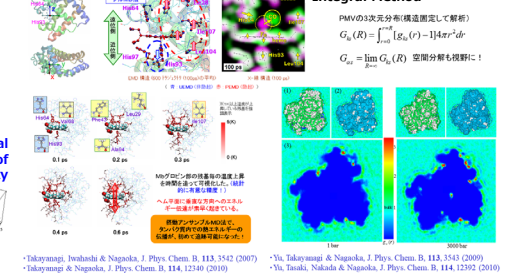
- Coarse-graining of large-scale atomic information, development of reconstruction techniques and coarse-graining theory -

■ Observation of Vibrational Relaxation Process of HF Molecules in Aqueous Solution —Real space non-equilibrium non-stationary distribution appearing in a group of water molecules around a solute molecule—



■ Prediction of the initial Process of Relaxation by the Perturbed Ensemble MD Method

■ Microscopic Elucidation of Protein Volume Para-doxes by Surface Kirkwood-Buff Integral Method



• Takamizawa, Inohara & Nagakubo, J. Phys. Chem. B, 113, 2542 (2009)  
• Takamizawa & Nagakubo, J. Phys. Chem. B, 114, 12340 (2010)  
• Y. Takamizawa & Nagakubo, J. Phys. Chem. B, 113, 1541 (2009)  
• Y. Takamizawa, Nakada & Nagakubo, J. Phys. Chem. B, 114, 12392 (2010)



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and Tech Corporation Technology Specific Research and  
Development Promotion Project:  
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04(H16)0406 21st Century COE  
"Computational Science Frontiers"

06(H18)1008 JST\*Core Research for Evolutionary Science and Technology: CREST "Research Development of Multiscale Simulation of Aggregation Reaction Systems"  
07(H19)0409 Minor ailment  
08(H20)1210 Ready-to-Use Manual for Molecular Simulation Beginners" Published!  
12(H24)0514 MSCRS2012 (JST International)  
13(H25)1015 JST\*Core Research for Evolutionary Science and Technology: CREST "Establishment of Computational Molecular Technology towards Macroscopic Chemical Phenomena"  
14(H26)0416 StudyCamp2014  
15(H27)1217 PACIFICHEM2015  
16(H28)0418 MSCRS2016 (JSPS Japan-Brazil+NU)  
17(H29)0419 Prof. (Fac. and GS. of Informatics)  
18(H30)0920 Kanreki (60<sup>th</sup> BD)  
20(R02)1222 PACIFICHEM2020  
23(R05)0325 StudyCamp2022

# "Ready-to-Use Manual for Molecular Simulation Beginners" Published ! ('081210, AD10)



Writing Process Chart

項目	担当者	担当期間	担当内容
1. 序文	長岡正隆	2008.12.10	本書の目的と使い方
2. 分子シミュレーションの基礎	長岡正隆	2008.12.10	分子シミュレーションの基礎知識
3. 分子シミュレーションの応用	長岡正隆	2008.12.10	分子シミュレーションの応用事例
4. 分子シミュレーションの発展	長岡正隆	2008.12.10	分子シミュレーションの発展事例
5. 分子シミュレーションの未来	長岡正隆	2008.12.10	分子シミュレーションの未来展望
6. 謝辞	長岡正隆	2008.12.10	本書の出版に尽力した方々への謝辞
7. 索引	長岡正隆	2008.12.10	本書の索引
8. 参考文献	長岡正隆	2008.12.10	本書の参考文献
9. 付録	長岡正隆	2008.12.10	本書の付録
10. 後記	長岡正隆	2008.12.10	本書の出版にあたっての感想



"Introduction to Quantum Chemistry" compiled by Prof. Morokuma and others in Fukui Lab.



## Brief Personal History

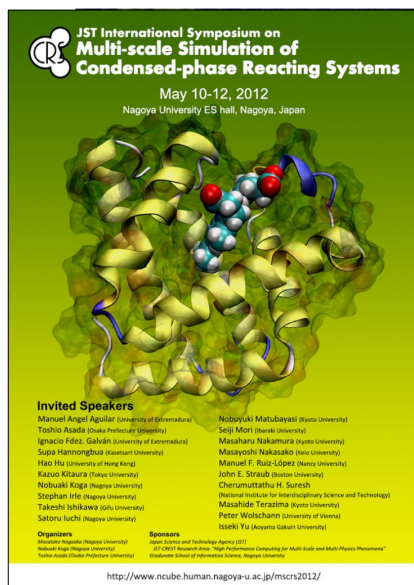
77(S52)03 Grad. Suzaka High Sch  
82(S57)03 Grad. Fac. Eng. KU.  
84(S59)03 Completed MC, KU.  
87(S62)03 Completed DC, KU. \*JSPS: Japan  
88(S63)04 JSPS\*Fellow (IFC) Society for the  
91(H03)04 Deputy Chief RO (IFC) Promotion of  
93(H05)06 US-Belgium Summer Tour Science  
97(H09)09 Chief RO (IFC)  
98(H10)01 Leaving (Prof. Fukui Passed away)  
98(H10)0700 Assoc. Prof. of GS. Change to NU  
10 of Human Informatics, NU  
\*JST: Japan Science JST\*Computational Science and  
and Tech Corporation Technology Specific Research and  
Development Promotion Project:  
Birth of ACT-JST "Study on Non-equilibrium  
Lab Ncube! and Non-stationary Dynamics of  
Aggregation Reaction Systems"  
02(H14)0304 Birth of "Three "Non"s" !!  
Int. Conf. CRN<sup>3</sup> (Clarifying Non-equilibrium non-stationarity characteristic of chemical reaction phenomena) (Grant-in-aid: C)  
02(H14)09 Prof. (Human Info)  
03(H15)0405 Prof. (Info. Sci.)  
04(H16)0406 21st Century COE  
"Computational Science Frontiers"

06(H18)1008 JST\*Core Research for Evolutionary Science and Technology: CREST "Research Development of Multiscale Simulation of Aggregation Reaction Systems"  
07(H19)0409 Minor ailment  
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12(H24)0515 MSCRS2012 (JST International)  
13(H25)1016 JST\*Core Research for Evolutionary Science and Technology: CREST "Establishment of Computational Molecular Technology towards Macroscopic Chemical Phenomena"  
14(H26)0417 StudyCamp2014  
15(H27)1218 PACIFICHEM2015  
16(H28)0419 MSCRS2016 (JSPS Japan-Brazil+NU)  
17(H29)0420 Prof. (Fac. and GS. of Informatics)  
18(H30)0921 Kanreki (60<sup>th</sup> BD)  
20(R02)1222 PACIFICHEM2020  
23(R05)0325 StudyCamp2022



# JST International Symposium MSCRS2012

## "Multi-scale Simulation of Condensed-phase Reacting Systems" ('12, AD17)



## Outline

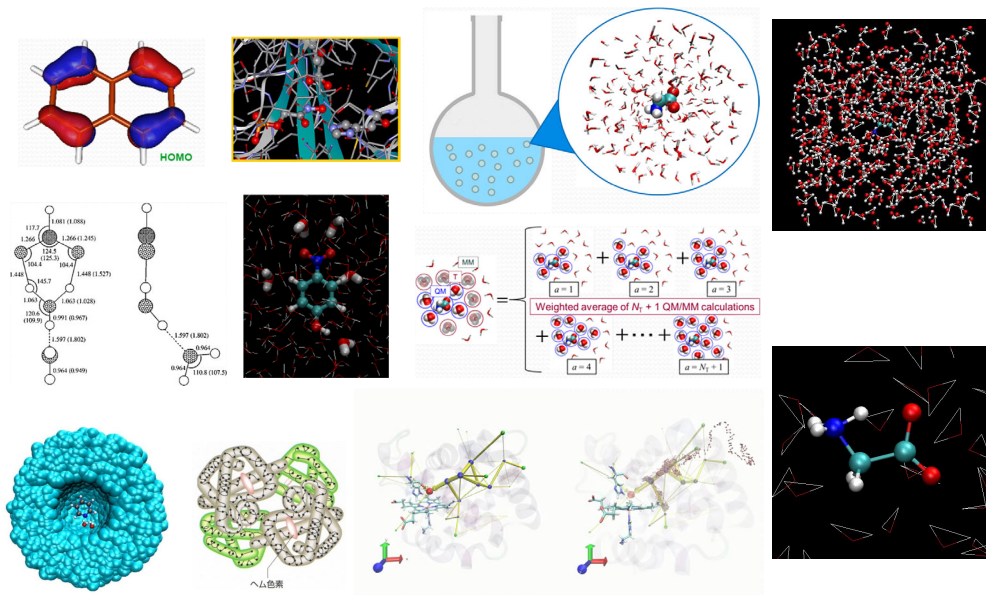
- § 1 At the Beginning
- § 2 Toward "Fukui's Lab"! ~From physics to chemistry!~
- § 3 Go on ! "Nobel Prize" !
- § 4 Nagaoka Lab Starts ! A Departure ! ?  
 What we have done before leads to what we have started "newly"!  
 ~A private version of 'recent chemistry'~
- § 5 Evolving ! Toward the Complexity
- § 6 Concluding Remarks  
 ~Are we carrying on the spirit of Fukui's lab?~
- § 7 Acknowledgments

JOURNEY  
"DEPARTURE"

For copyright reasons, the images are not displayed.

## § 5 Evolving ! Toward the Complexity

## Single molecules, elementary reactions have been primarily studied so far!

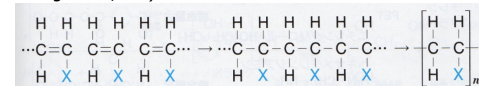




# The World is Full of Complex "Materials"!

-Our lives are surrounded by compounds of complex composition-

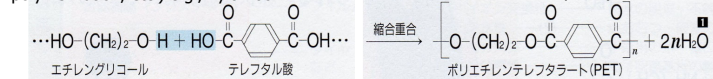
■ Synthetic resins (plastics) (thermoplastic resins, thermo-setting resins, etc.)



**Polyethylene**



■ Synthetic fibers (by condensation polymerization, addition polymerization, etc.) e.g., nylon 66

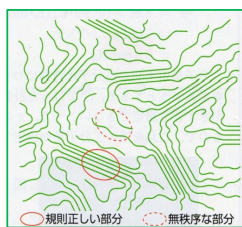


**Polyethylene terephthalate (PET) etc.**

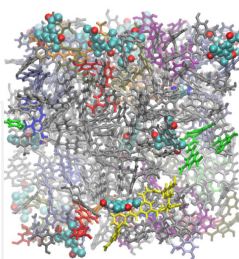
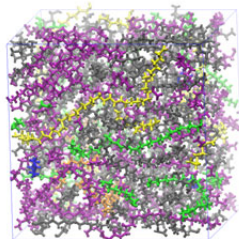
**UNI QLO Heatech Commercial**  
For copyright reasons, some images are not displayed.



Although the reaction equation is neat and tidy, in fact, polymer compounds have complex structures!



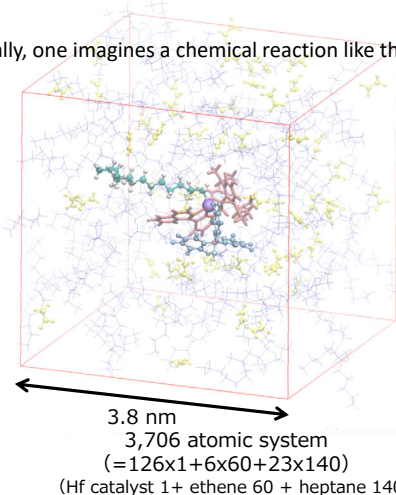
**Fig.** Structure of polymeric compounds in solids (Chemistry II, Newly Rev. Ed., p.143)



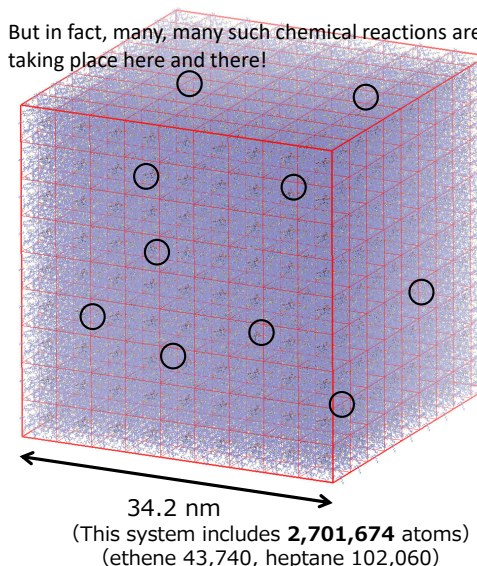
"Basic Chemistry, Newly Rev. Ed." and "Chemistry, Newly Rev. Ed." (Jikkyo Publishing) (2018)

# The image of a "chemical reaction"!? A complex reaction system is a system of random variables!

Usually, one imagines a chemical reaction like this!



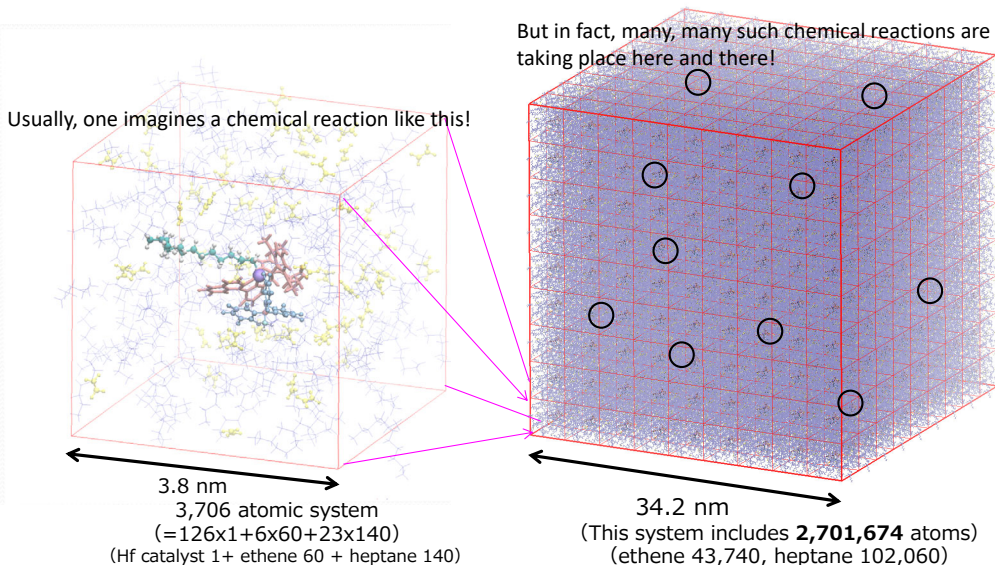
But in fact, many, many such chemical reactions are taking place here and there!



# The image of a "chemical reaction"!? A complex reaction system is a system of random variables!

Usually, one imagines a chemical reaction like this!

But in fact, many, many such chemical reactions are taking place here and there!



# Red Moon Method -Hybrid MC/MD Reaction Method- ~Molecular simulation to study compounds of complex components~



"A hybrid MC/MD reaction method with Rare event-driving Methodology of necessity"

MN, Y.Suzuki, T.Okamoto, N.Takenaka, *Chem. Phys. Lett.*, **583**, 80 (2013)

## Red Moon Method

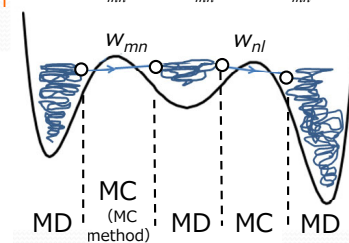
... A new simulation method

- A Hybrid MC/MD Reaction Method
- Transition rate (Metropolis method):

$$w_{mn} = \min \{1, \exp[-\beta \Delta U_{mn}]\}$$

- Reaction energy difference:

$$\Delta U_{mn} = \Delta U_{mn}^{\text{MM}} + \Delta U_{mn}^0$$



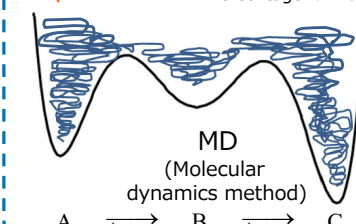
## Previous simulation methods

Newton's equations of motion:

$$\begin{cases} \frac{d\mathbf{r}^{\text{Ns}}}{dt} = \frac{\partial H}{\partial \mathbf{p}^{\text{Ns}}} \\ \frac{d\mathbf{p}^{\text{Ns}}}{dt} = -\frac{\partial H}{\partial \mathbf{r}^{\text{Ns}}} \end{cases} \quad \begin{cases} \frac{d\mathbf{r}^{\text{Nm}}}{dt} = \frac{\partial H}{\partial \mathbf{p}^{\text{Nm}}} \\ \frac{d\mathbf{p}^{\text{Nm}}}{dt} = -\frac{\partial H}{\partial \mathbf{r}^{\text{Nm}}} \end{cases}$$

Chemical Reaction (Super-rare events)

Active Molecule Percentage <~10<sup>-10</sup>



It doesn't happen very often!

Active molecule 1 vs. Inert molecules 10 billion







# CREST "Establishment of Computational Molecular Technology towards Macroscopic Chemical Phenomena" adopted! ('13, AD16)

Core Research for Evolutional Science and Technology  
Japan Science and Technology Agency

Research Director



Prof. Hisashi Yamamoto  
(Emeritus Prof. at Nagoya U., Chubu U.)  
<https://www.jst.go.jp/crest/mt/supervisor/>



Dr. M. Takayanagi  
(Assoc. prof., Shiga U.)



Dr. S. Xing

Research Period : 5.5 years  
Research Fee : ~300,000 kYen



## 概要 Outline

本研究では、多数の分子が集まった“分子凝集状態”で起こる集合化学反応の制御を目指します。そのために、ミクロに見ると非常に稀にしか起こらない化学反応（超希少現象）を、原子・分子情報も保持したまま、新しい計算分子技術を創り上げ、科学技術イノベーションを回ります。具体的には、凝集系化学反応の立体化学制御と超ナノ階層集合体の構造制御を実現して、新機能材料を設計・創成します。最終的に、マクロ化学現象シミュレーションの計算分子技術の汎用環境を実験者と協働して提供したいと夢見ています。

## Research Project Outline

This project aims at control of complex chemical reactions in the “molecular aggregation state” where a large number of molecules literally gather. For the purpose, new “computational molecular technology” will be developed, keeping atomic and molecular information, to treat such chemical reactions that do occur very rarely from the microscopic viewpoint (i.e., super-rare phenomena), then leading to a technology innovation. Realizing the stereochemical control of aggregation-state chemical reactions and the structural control of super-nano scale aggregates, new functional materials will be designed and created. We are dreaming to finally offer the general-purpose environment of the “computational molecular technology” of macroscopic chemical phenomena simulation, through collaboration with experimentalists.



Dr. Y. Suzuki



Dr. S. Saha  
(Assoc. prof. TDB U.)



Dr. Y. Kitamura  
(Assi. Prof. Shizuoka U.)

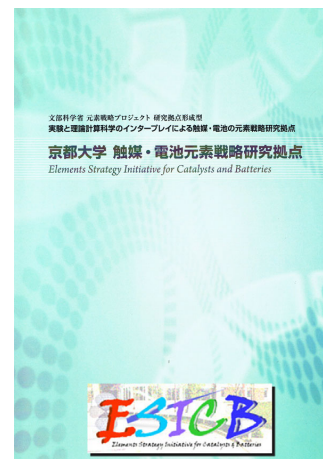


Dr. C. Bistafa  
(PD. Osaka U.)

# MEXT Participation in "Elements Strategy" & "Post "K"" Projects (Since '12, AD15)

文部科学省 (MEXT)

Ministry of Education, Culture, Sports, Science and Technology

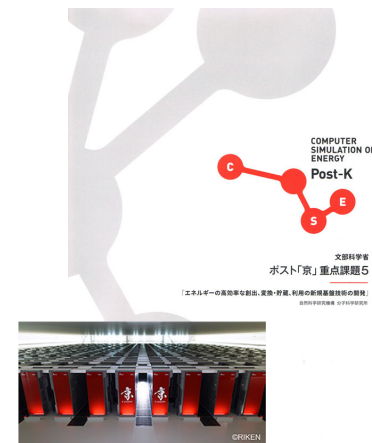


Dr. N. Takenaka  
(Lecturer, U. Tokyo)



Dr. A. Bouibes  
(Assoc. Prof. INSA Toulouse)

Elements Strategy Initiative for Catalysts and Batteries



Post "K" Project



Dr. T. Inagaki  
(Ass. Prof., Keio U.)

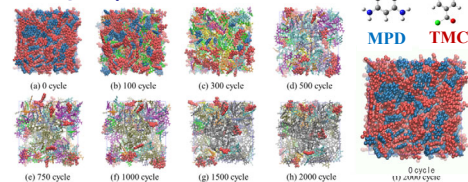


Mr. T. Fujie

## CREST "Molecular Technology" "Establishment of Computational Molecular Technology towards Macroscopic Chemical Phenomena"

Interfacial Polycondensation Reaction -Aromatic Polyamide Synthetic Fibers-

### ■ Polymerization process and molecular distributions (MPD: TMC=1:1)

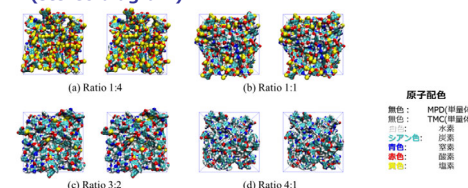


最終状態(2000サイクル)のポリマー長と数  
MPD(甲鎖): 1鎖 7鎖 8鎖 1鎖  
TMC(乙鎖): 1鎖 7鎖 8鎖 1鎖

架橋接合部(赤色)と線形接合部(青色)の分布(最終状態(2000cycle))

二官能性のMPDと三官能性のTMCの反応点の総数が等しいため、最終平衡状態では、未反応のTMC単量体が残存している。

### ■ Molecular surfaces inside an aromatic polyamide film (stereo diagram)



比率1:1, 3:2の膜では、非常に多くの高分子集合体からなる密な部分が形成されている。密な高分子ネットワークが形成。少ない集合体ボア。(実験と一致)  
・ Y. Suzuki, Y. Koyano, M. Nagaoka, J. Phys. Chem. B, 119, 6776 (2015).

### ■ Degree of polymer cross-linking (DPC) and atomic composition ratio

表. 計算値と実験値との比較

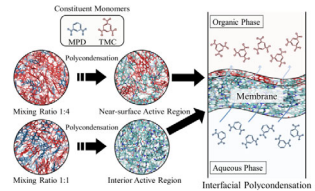
	Present <sup>a</sup>				Experimental <sup>b</sup>	
	Ratio 1:4	Ratio 1:1	Ratio 3:2	Ratio 4:1	XPS	RBS
DPC	94.3 ± 0.1	96.9 ± 0.1	99.0 ± 0.0	100.0 ± 0.0	91.7 ± 3.9	96.2 ± 0.2
%C	67.8 ± 0.1	71.6 ± 0.1	73.6 ± 0.1	74.9 ± 0.0	71.0 ± 1.6	71.0 ± 1.2
%O	25.7 ± 0.1	18.6 ± 0.1	14.2 ± 0.1	9.4 ± 0.0	26.2 ± 1.7	17.4 ± 0.4
%N	6.5 ± 0.1	9.9 ± 0.1	12.2 ± 0.0	15.6 ± 0.0	7.8 ± 1.7	11.5 ± 0.6

<sup>a</sup>Ratio=MPD(TMC), 5個のサンプルの平均値。  
<sup>b</sup>それぞれ、X線光電子分光法(XPS)と、ラザフォード後方散乱法(RBS)による結果。

- 比率1:4の結果は、X線光電子分光法(XPS)による実験値に近い傾向を示していることが分かった。
- 一方、比率1:1の計算結果は、組成比及び高分子架橋度ともに、ラザフォード後方散乱法(RBS)による実験値と良好一致を示した。

(Red Moon法のマクロ化学現象シミュレーション手法としての意義と価値)

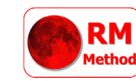
### ■ Conceptual diagram and interpretation of atomic composition ratios



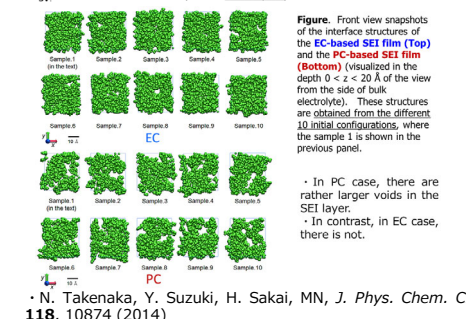
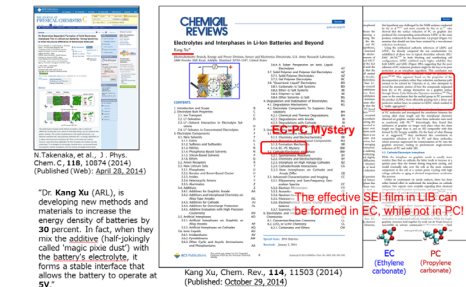
FT-30膜は、コーティング層と一部の活性層とからなる近表面活性領域(表面から~36 nmまで)と膜構造の大半を占める活性層とからなる内部活性領域(36nm以上から~92nmまで)とで構成されている。



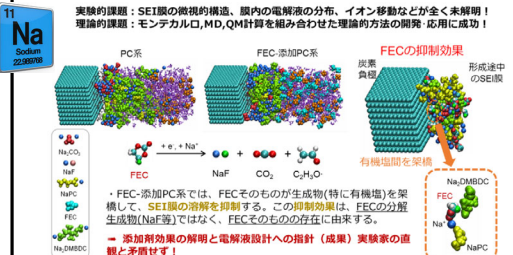
## Toward Structural Elucidation of the Solid-Electrolyte Interphase in Secondary Batteries and its Higher Capacity



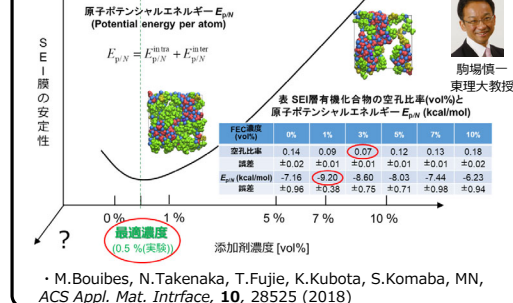
### ■ Unraveling the EC-PC Mystery



### ■ Additive Effects on SEI Film Formation in SIB



### ■ Structural stability of the organic salt layer in the SEI membrane of NaPF6/PC-based HC electrodes





# "The Joys, Angers, Sorrows, and Pleasures of Researchers in Informatics" (Planned) Prof. Arita

メニュー 情報学の研究者たちの... 作成

すべてのツール 編集 変換 電子サイン テキストまたはツールを検索

2024/02/08 10:03 情報学の研究者たちの喜怒哀楽 (長岡正隆 (物質情報学 (分子シミュレーション・データ科学)) 複雑系科学専攻 教授) | 情報玉手箱

## Candy Box of Information 情報玉手箱

名古屋大学 情報学部 大学院情報学研究科

<https://tamatebako.i.nagoya-u.ac.jp/5780/>

情報学の研究者たちの喜怒哀楽 (長岡正隆 (物質情報学 (分子シミュレーション・データ科学)) 複雑系科学専攻 教授)

Prof. Masataka Nagaoka (Materials Informatics (Molecular Simulation, Data Science))



**-When is the time you felt "joy" (or was you felt most joy)?**

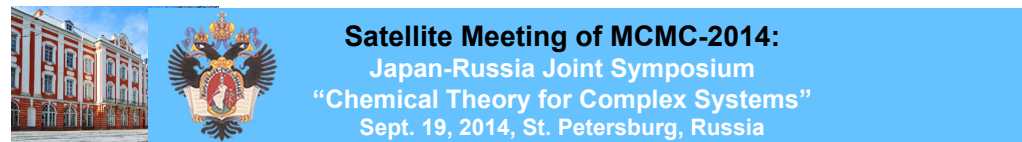
I was given a bold challenge (a "problem" outside of the problem!), "Can't your Red Moon method be used for "Li-ion batteries"? I was given this bold challenge by an outside expert in a different speciality. I felt joy when I realized that, as I worked recklessly on it, I managed to produce results that led to the elucidation of the "EC-PC Mystery"!!



**-When is the time you feel "fun" (or was you had the most fun)?**

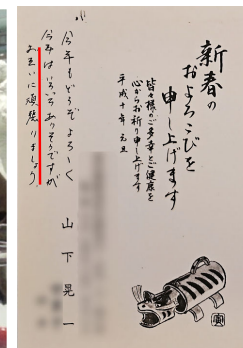
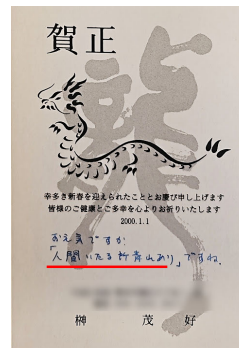
At the Ncube training camp "Study Camp", current students and graduates present their new developments with surprising ingenuity and novel sense. At the compeers, they smile and enthusiastically discuss their hardships! When I am on the sidelines of it all (a regular summer session that is not during the Corona disaster)

# Moscow Symposium "Chemical Theory for Complex Systems" ('14, AD17)



「人間至る所青山あり」(a proverb)  
"There's room for us all in the world"

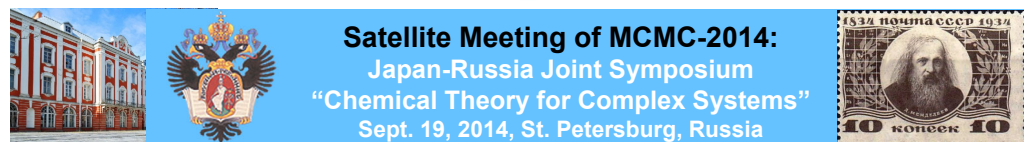
「お互いに頑張りましょう」  
"Let's do our best for each other"



New Year's cards

Get-together party at the symposium

# Moscow Symposium "Chemical Theory for Complex Systems" ('14, AD17)





**Molecular Complexity in Modern Chemistry (MCMC-2014)**  
Moscow 2014, September 12-19

Russia-Japan Joint Session of "Chemical Theory for Complex Systems"

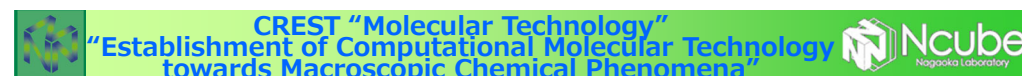
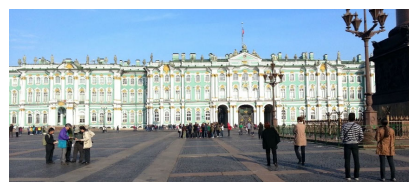
## "A Hybrid MC/MD Reaction Method with Rare Event-driving Mechanism: Atomistic Realization of 2-Chlorobutane Racemization Process in DMS Solution"

Masataka Nagaoka

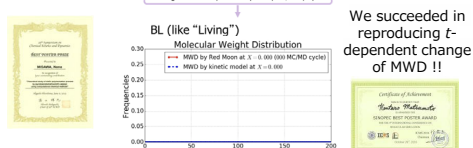
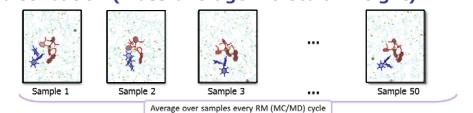
<sup>a)</sup> Graduate School of Information Science, Nagoya University, JAPAN; <sup>b)</sup> Core Research for Evolutional Science and Technology (CREST), Japan Science and Technology Agency (JST), JAPAN; <sup>c)</sup> ESICB, Kyoto University, JAPAN

• N. Takenaka, Y. Suzuki, H. Sakai, MN, *J. Phys. Chem. C*, **118**, 10875 (2014).  
• MN, Y. Suzuki, T. Okamoto, N. Takenaka, *Chem. Phys. Lett.*, **583**, 80 (2013).  
• N. Takenaka, Y. Kitamura, Y. Koyano, MN, *J. Chem. Phys.*, **137**, 024501 (2012).  
• N. Takenaka, Y. Kitamura, Y. Koyano, MN, *Chem. Phys. Lett.*, **524**, 56 (2012).  
• N. Takenaka, Y. Kitamura, Y. Koyano, T. Asada, MN, *Theor. Chem. Acc.*, **130**, 215 (2011)



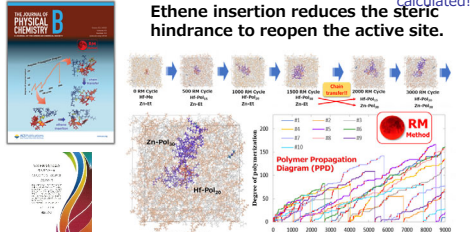
## Catalytic Polymerization and Radical Polymerization -Polyolefin Resins-

■ Time-dependent change of molecular weight distribution (mass-average molecular weight)



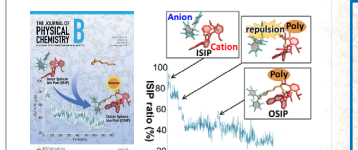
• M. Matsumoto, M. Takayanagi, Y. Suzuki, N. Koga, MN, *J. Comp. Chem.*, **40**, 421 (2019).

■ Polymer propagation diagram (PPD)



• S. Kanesato, K. Yasoshima, N. Misawa, K. Matsumoto, Y. Suzuki, N. Koga, MN, *J. Phys. Chem. B*, **127**, 7735 (2023).

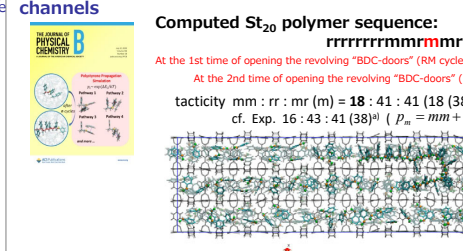
■ Polymerization reaction mechanism Two different time scales



A computational chemistry method was established to simulate copolymerization reactions and chain transfer polymerization in the 1-octene/ethene system.

• N. Misawa, K. Matsumoto, Y. Suzuki, S. Saha, N. Koga, MN, *J. Phys. Chem. B*, **127**, 1209 (2023).

■ Styrene polymerization observed between MOF channels



• Z. Rao, M. Takayanagi, MN, *J. Phys. Chem. B*, **126**, 5343 (2022)



eHfCat OCT\_ETH\_3.mp4  
A chain transfer reaction occurs at 1124 RM cycle for #9.





# Brief Personal History

77(S52)03 Grad. Suzaka High Schl  
82(S57)03 Grad. Fac. Eng. KU.  
84(S59)03 Completed MC, KU.  
87(S62)03 Completed DC, KU. \*JSPS: Japan Society for the Promotion of Science  
88(S63)04 JSPS\*Fellow (IFC)  
91(H03)04 Deputy Chief RO (IFC)  
93(H05)06 US-Belgium Summer Tour  
97(H09)09 Chief RO (IFC)  
98(H10)01 Leaving (Prof. Fukui Passed away)  
98(H10)0700 Assoc. Prof. of GS. Change to NU  
10 of Human Informatics, NU  
\*JST: Japan Science and Tech Corporation  
Birth of Lab Ncube!  
02(H14)0304 Int. Conf. CRN<sup>3</sup> (Clarifying Non-equilibrium non-stationarity characteristic of chemical reaction phenomena) (Grant-in-aid: C)  
02(H14)09 Prof. (Human Info)  
03(H15)0405 Prof. (Info. Sci.)  
04(H16)0406 21st Century COE "Computational Science Frontiers"

06(H18)1008 JST\*Core Research for Evolutionary Science and Technology: CREST "Research Development of Multiscale Simulation of Aggregation Reaction Systems"  
07(H19)0409 Minor ailment  
08(H20)1210 "Ready-to-Use Manual for Molecular Simulation Beginners" Published!  
12(H24)0515 MSCRS2012 (JST International)  
13(H25)1016 JST\*Core Research for Evolutionary Science and Technology: CREST "Establishment of Computational Molecular Technology towards Macroscopic Chemical Phenomena"  
14(H26)0417 StudyCamp2014  
15(H27)12 PACIFICHEM2015  
16(H28)0419 MSCRS2016 (JSPS Japan-Brazil+NU)  
17(H29)0420 Prof. (Fac. and GS. of Informatics)  
18(H30)0921 Kanreki (60<sup>th</sup> BD)  
20(R02)1222 PACIFICHEM2020  
23(R05)0325 StudyCamp2022



## StudyCamp2014 (Gujo-Kogen Highland) (郡上高原)(Aug.25-27, 2014)

### 1<sup>st</sup> StudyCamp

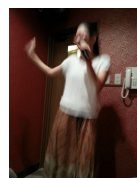
was held inspired by "OntakeMeeting2014"  
(Mar. 31-Apr. 1, 2014)

Dr. Wales Ms. & Mr.  
Dr. Yamato Me Straub

郡上高原ホテル 公益財団法人 小田村 小田村



## "StudyCamp" Starts ! ('14, AD17)



## Trying on Making Soba Noodle in Gujyo!



@StudyCamp  
Aug.26, 2014



Brown  
udon ?!  
Waiting  
for "soba"  
boiling!







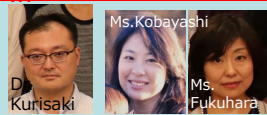




# Brief Personal History

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Birth of Lab Ncube!  
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06(H18)1008 JST\*Core Research for Evolutionary Science and Technology: CREST "Research Development of Multiscale Simulation of Aggregation Reaction Systems"  
07(H19)0409 Minor ailment  
08(H20)1210  
12(H24)0515  
13(H25)1016  
14(H26)0417  
15(H27)12 PACIFICHEM2015  
16(H28)0419 MSCRS2016 (JSPS Japan-Brazil+NU)  
17(H29)04  
18(H30)09  
20(R02)12  
23(R05)0325 StudyCamp2022



## JSPS-FAPESP International Symposium MSCRS2016 "Multi-scale Simulation of Condensed-phase Reacting Systems"

(2016年10月10-13日, AD18)



Noyori Conference Hall



Toast by Dr. Eisuke Kita, Vice-Dean of the Graduate School



## JSPS-FAPESP International Symposium MSCRS2016 "Multi-scale Simulation of Condensed-phase Reacting Systems"

(2016年10月10-13日, AD18)

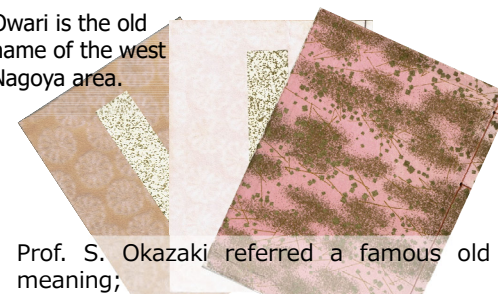


## Owari Complex Seminar & Visitors' Books

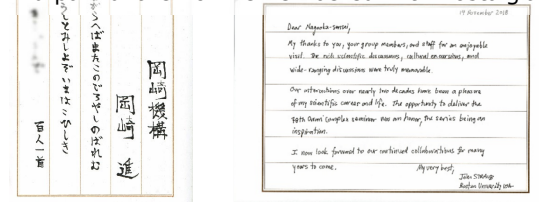
Complex ... Complex systems, Complex (chemistry), assembly, gathering place

Owari is the old name of the west Nagoya area.

The Owari Complex Seminar, which started immediately after the move, has been held 79 times!!



Prof. S. Okazaki referred a famous old poem meaning;  
If I live longer, I wonder if I will be able to remember with nostalgia the world of these days, which I feel painful now. The days that I used to find painful are now remembered with nostalgia.



左掲示  
78th OWARI COMPLEX SEMINAR  
第78回 尾張コンプレックスセミナー  
下掲のとおりセミナーを開催します。参加は自由です。多人数で参加ください。

講 師	ジョン ストラoup 先生 (ボストン大学)
SPEAKER	Prof. John E. Straoup (Boston University)
題 目	膜中におけるドメイン形成とタンパク質移動を決定する
題 名	ドメインの形成
TITLES	Probing the rules governing domain formation and protein partitioning in membrane

日 時	平成30年11月14日 (水) 15:30 - (約1時間)
DATE	Wednesday 14th Nov. 2018 15:30 - (About one hour)
場 所	情報科学研究科 1階 第1講義室
PLACE	Lecture Room 1 (1F)
連絡先	長岡 正造 (名古屋大学大学院情報科学研究科)
	内線 5623
CORRESPONDENCE	
	Mountsaka Nagasaki, Graduate School of Information, Nagoya University
	Ext. 5623



# 15th "Complex Systems Science" Seminar

A seminar series of the division of complex systems science ('23, AD25)

第15回複雑系科学セミナーのご案内 ㊦ 要領トレイ

**R** Ryotaro Koike <koike@i.nagoya-u.ac.jp>  
To 複雑系科学専攻 students

複雑系科学専攻の先生方・大学院生・研究員の皆様

生命情報講座の小冊子です。

第15回複雑系科学セミナーを以下の通り開催します。  
お忙しいことは存じますが、ぜひご参加いただければと思います。

日時：2023年9月22日(金) 17時半から1時間程度

(終了後に懇談会開催予定)

場所：情報学研究科棟1F 第1講義室

講師：生命情報講座 教授 山西芳裕

タイトル：  
人工知能とビッグデータで新薬をつくる

アブストラクト：  
近年の生命医学では、疾患に関するゲノム情報や臨床情報、生体分子に関するオミクス情報、膨大な化合物に関する生物活性情報などが得られるようになった。このようなビッグデータ時代において、人工知能・機械学習の重要性が高まってきており、データ解析から創薬や医療に繋げる役割が求められている。医薬データは、グラフ構造、木構造、文字列、テンソルなど様々なデータ構造を取り、情報科学的にも複雑な課題が多い。本セミナーでは、疾患、遺伝子、タンパク質、化合物に関する多様なビッグデータを融合解析し、創薬や医療における様々な課題を解決するための機械学習アルゴリズムの研究を紹介する。創薬模様の探索、化合物スクリーニング、シナジー創薬学、細胞直接変換、医薬品分子構造設計などへの応用例をいくつか紹介する。



## § 5 Concluding Remarks ~Are we carrying on the spirit of Fukui's lab?~



## Outline

- § 1 At the Beginning
- § 2 Toward "Fukui's Lab"! ~From physics to chemistry!~
- § 3 Go on! "Nobel Prize"!
- § 4 Nagaoka Lab Starts! A Departure! ? What we have done before leads to what we have started "newly"! ~A private version of 'recent chemistry'~
- § 5 Evolving! Toward the Complexity
- § 6 Concluding Remarks ~Are we carrying on the spirit of Fukui's lab?~
- § 7 Acknowledgments

JOURNEY  
"DEPARTURE"

For copyright reasons, the images are not displayed.

## Attitude of studying in the opposite direction Value the fundamentals, and strive to learn widely

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 24, NUMBER 4 APRIL, 1952  
A Molecular Orbital Theory of Reactivity in Aromatic Hydrocarbons

Koseki, Koichi, Tadashi Shimizu, and Shiro Huzar  
Faculty of Engineering, Kyoto University, Kyoto, Japan  
(Received October 29, 1951)

In the search for a quantitative correlation between reactivity and electronic configuration of aromatic hydrocarbons, the electronic density, as such carbon atom, of the highest occupied orbital in the ground state of the molecule is calculated for many of the C<sub>6</sub>H<sub>6</sub> system. Comparing the result of such calculation with the known reactivity of aromatic hydrocarbons, we find that the position at which the electron density is highest is usually associated with the electrophilic or nucleophilic reactivity.

In the present paper it is shown that the electronic density of the highest occupied orbital in the ground state of the molecule is a decisive factor in the reaction of aromatic hydrocarbons. The electronic density of the highest occupied orbital in the ground state of the molecule is calculated for many of the C<sub>6</sub>H<sub>6</sub> system. Comparing the result of such calculation with the known reactivity of aromatic hydrocarbons, we find that the position at which the electron density is highest is usually associated with the electrophilic or nucleophilic reactivity.

INTRODUCTION  
CONSIDERABLE progress has been made of late years in the quantum-mechanical treatment for planning the chemical reactivity of organic compounds. Especially, the problem of predicting the reactivity of an organic molecule in a particular reaction has been solved in many cases by the use of the molecular orbital method. In the case of aromatic hydrocarbons, the electronic density of the highest occupied orbital in the ground state of the molecule is a decisive factor in the reaction of aromatic hydrocarbons. The electronic density of the highest occupied orbital in the ground state of the molecule is calculated for many of the C<sub>6</sub>H<sub>6</sub> system. Comparing the result of such calculation with the known reactivity of aromatic hydrocarbons, we find that the position at which the electron density is highest is usually associated with the electrophilic or nucleophilic reactivity.

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Koseki Publishing

"To study hard together a subject that does not seem to be related to the path you are trying to follow, or, more extremely, to study in the opposite direction. ..."

"We never know when or in what form what we have learned will be useful. If we compare learning to a plant, the underground stems of individual studies are connected to each other in unexpected ways."

"Students today have too much to learn compared to my time. Given this, one might argue against such idealism. But, knowing this, I would like to emphasize. To be creative, narrow study is not beneficial. We must study broadly at all costs." (「The Creation of "Study"」 (1984))

In connection with the naming of the frontier orbital theory, he wrote in his book that he studied quantum basic mechanics, which was the most advanced basic science at that time, and wondered if he could apply it.



"Lithium Diffusion in  $\text{Li}_x\text{CoO}_2$  Electrode Materials"

Professor Ryoji Noyori  
Laboratory of Chemistry, School of Chemistry, Kyoto University  
1-5 Katsura Site  
Chiyoda-ku, Tokyo 101

Re: O70534

Dear Professor Noyori:

Thank you very much for the letter of March 27, 1998 from Professor Akira Miyamoto. Since the original manuscript was submitted to the Chemical Society of Japan in the last November, but they sent comments in January. By the same reason, we would like to answer your comments in English.

We have considered and incorporated reviewer's comments. I enclose two copies of our revised manuscript with a separate note detailing the changes we have made. The changes are also indicated with a line-marker in one of the copies attached. I believe that the revised manuscript has been significantly improved along the lines which the reviewer suggests. The revised version includes Fumihito Mohri as a new author because he has greatly contributed to computations and the revising work. I also enclose a floppy disk including text (Mac, MSWord 5.1a). We are very happy that this paper will appear in the Bulletin of the Chemical Society of Japan.

Your kind management is greatly appreciated in advance.

Best regards,

Rajwanti Yoshizawa

Dr. Kazumi Yoshizawa  
On behalf of Prof. Takao Yamabe

Department of Molecular Engineering, Kyoto University  
Sakyo-ku, Kyoto 606-8501, Japan  
Fax: +81-75-751-7279

© 1998 The Chemical Society of Japan

Bull. Chem. Soc. Jpn., 71, 2229-2257 (1998) 2259

### Lithium Diffusion in $\text{Li}_x\text{CoO}_2$ Electrode Materials

Gerhard Nemp, Masataka Nagaka, Kazumi Yoshizawa, Fumihito Mohri, and Takao Yamabe\*

Institute for Fundamental Chemistry, 36-4 Takano Nishikubo-cho, Sakyo-ku, Kyoto 606-8501

\*Department of Molecular Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501

(Received December 1, 1997)

The maximum energy migration path and the minimum barrier height of lithium diffusion are discussed for the layer compound  $\text{LiCoO}_2$ . The Universal Free Field (UFF) is applied for an  $\text{LiCoO}_2$  model compound. Molecular dynamics simulations with additional imposed dynamics results, performed at a microcanonical ensemble, point out that the lithium migration between the  $\text{CoO}_2$  layers takes place by ion hopping from one octahedral site to the adjacent one via an interstitial embedded site. The barrier height of lithium migration is estimated to be 28.7 kJ/mol (0.30 eV) for the original layer distance of 2.8 Å. A potential energy profile for molecular dynamics calculations is calculated. The observation that the repulsive van der Waals interaction between  $\text{Li}^+$  and neighboring  $\text{O}^{2-}$  ions is the most important contribution to the barrier height is consistent with the fact that the activation energy of lithium diffusion is very sensitive to the layer distance, within the experimentally observed values.

In the last two decades, an uncountable number of various insertion compounds have been investigated with respect to their use as possible electrode materials in rechargeable lithium ion batteries.<sup>1-10</sup> Such kinds of ion batteries are interesting for battery use in computer systems, for example. In particular, transition metal oxides<sup>11-13</sup> and chalcogenides<sup>14-16</sup> consisting of layer structures or two-dimensional frameworks with tunnel systems insert remarkably amounts of lithium.

Up to now, for consumer applications the most promising cathode material for solid state lithium ion batteries is  $\text{LiCoO}_2$ ,<sup>17</sup> since this compound shows a high theoretical energy density of 766 Wh/kg.<sup>18</sup> The use of  $\text{LiCoO}_2$  in commercial lithium ion batteries<sup>19</sup> has initiated intensive research efforts in this field.<sup>20-22</sup> Recently, beside the original lithium ion battery<sup>20-22</sup> including a  $\text{LiCoO}_2$  cathode and an amorphous carbon anode, many so-called "rocking chair" cells in which both electrodes are lithium intercalation compounds are under development. One important example of these new types of cells consists of lithium  $\text{TiO}_2$  (anode) as the anode and  $\text{LiCoO}_2$  or  $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{O}_2$  as the cathode.

$\text{LiCoO}_2$  structural type, in a typical layer compound form, is a typical layer compound formed by stacking sheets consisting of  $\text{CoO}_2$  octahedra. The octahedra in one layer share six edges, resulting in a monolayer of  $\text{CoO}_2$  within one octahedral layer. The stacking sequence of the  $\text{CoO}_2$  layers is ABCABC, leading to a trigonal unit cell with space group  $R\bar{3}m$ . Therefore,  $\text{LiCoO}_2$  can also be regarded as a lipid derivative of the  $\text{CoO}_2$  structure type. The empty octahedral sites between the  $\text{CoO}_2$  layers are statistically

likely to be occupied with lithium ions. The crystal structure of  $\text{LiCoO}_2$ , also adopted in  $\text{LiVO}_2$ ,<sup>23</sup>  $\text{LiCoO}_2$ ,<sup>24</sup> and  $\text{LiNiO}_2$ ,<sup>25</sup> is shown in Fig. 1 (orthorhombic unit cell). Interestingly, the distance between the  $\text{MD}$  octahedron layers is larger in  $\text{LiCoO}_2$  than in the other  $\text{LiMO}_2$  oxides. This fact is regarded as an important reason why a higher  $\text{Li}^+$  mobility is observed in  $\text{LiCoO}_2$  than in the other oxides.<sup>26</sup> Recently  $\text{CoO}_2$ , the end member of the  $\text{LiCoO}_2$  solid solution, was also characterized by its X-ray diffraction in a deintercalated cell by complex lithium intercalation.<sup>26</sup> Even so, the technologically interesting region of lithium

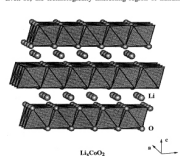


Fig. 1. Crystal structure of the layer compound  $\text{LiCoO}_2$  ( $0.5 < x < 1$ ). All possible sites of lithium insertion are shown ( $\text{LiCoO}_2$ ). In the lower lithium content, the same sites are occupied statistically.

\* Present address: Institut für Anorganische Chemie der LMU München, München, D-80333 München, Germany.

## 「Study on gelation by bonding between multifunctional grouping unit」

1964



"I (Dr. Yamabe) was assigned to the laboratory of Prof. Fukui as a graduation research student in April 1958, with the intention of studying quantum chemistry, but for some reason I was assigned to be directly supervised by Prof. Fukui for the time being. The subject was not quantum chemistry, but a "theoretical study on the gelation phenomenon of polymers with a special isocyanurate (isocyanurate ring) bonding mode," which had nothing to do with the other members, and Prof. Fukui asked me to develop from statistical mechanics what he had already been working on from kinetics." (「Rakuho(洛陽)19」(2010))

1960  
JOURNAL OF POLYMER SCIENCE  
VOL. XIV, PAGES 305-312 (1960)

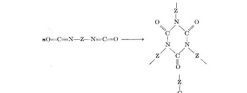
### A Theory of Gel Formation with Terfunctional Internit Junction

KENICHI FUKUI and TAKAO YAMABE, Faculty of Engineering, Kyoto University, Kyoto, Japan

#### INTRODUCTION

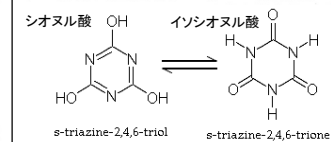
The way in which high polymeric substances are formed from monomeric units may be classified according to the number of functional groups involved in the formation of an internal junction. Each case may be referred to as polymerization by  $\text{ho}$ ,  $\text{ter}$ ,  $\text{quater}$ , ..., multifunctional internal junction, respectively. The simplest case, polymerization by difunctional internal junctions, is, most familiar, and almost all of the known polymerizations or polycondensations, for instance, vinyl polymerization, or the formation of polymers, and polyesters, belong to this group.

Recently, polymerizations of a novel type, in which three functional groups of three different monomeric units unite together to form an internal junction have come to our attention.<sup>1-3</sup> This type of polymerization may be called polymerization by terfunctional internal junction. The examples are illustrated as follows, where the internal junctions are the isocyanurate ring and s-triazine ring, respectively. Many other reactions of the same type may also be considered.



The theory of polymeric gel formation due to bifunctional internal junction has been established by Flory<sup>4</sup> and Stockmayer,<sup>5</sup> and many other

1963  
日本化学会誌 第83巻第3号 (1963)



多官能基異性化反応によるゲル化現象の理論  
(横井 謙三 博士論文)

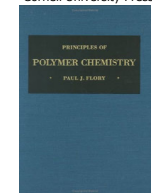
(昭和34年10月)

この報告は、著者が京都大学において、1958年4月から1960年3月までの間に、博士課程で研究した内容である。この研究は、著者が京都大学において、1958年4月から1960年3月までの間に、博士課程で研究した内容である。この研究は、著者が京都大学において、1958年4月から1960年3月までの間に、博士課程で研究した内容である。

1. 緒言  
2. 実験  
3. 結果と考察  
4. 結論  
5. 参考文献  
6. 謝辞  
7. 発表論文目録  
8. 抄録

著者: 山手 謙三 (Yamabe Kenji)  
所属: 京都大学工学部  
学位: 工学博士 (1963)

Cornell University Press



P. J. Flory  
「Polymer Chemistry」  
(1953)

第8章 線状高分子の分子量分布  
二官能基性単位間結合  
第9章 非線状高分子の分子量分布とゲル化理論  
三官能基性枝分れ高分子

拡張1: 巨環\*なしの三官能基性単位間結合  
拡張2: (拡張1) + 二官能基性単位間結合  
拡張3: 巨環ありの三官能基性単位間結合  
\*巨環 (macroring)



「Rakuho(洛陽)19」  
(2010)

## Establishment of Computational Molecular Technology towards Macroscopic Chemical Phenomena ~Complex chemical reactions, stereospecificity, aggregate structure~



A hybrid MC/MD reaction method with a rare event-driving mechanism: Atomistic realization of 2-chlorobutane racemization process in DMF solution

Masataka Nagaka<sup>a,b,\*</sup>, Yuichi Suzuki<sup>a</sup>, Takuya Okamoto<sup>a</sup>, Norio Takenaka<sup>a,b</sup>

<sup>a</sup> Graduate School of Information Science, Nagoya University, Gokiso-cho, Chikusa-ku, Nagoya 466-8601, Japan

<sup>b</sup> NICS, Kyoto University, Yoshida-cho, Sakyo-ku, Kyoto 606-8501, Japan

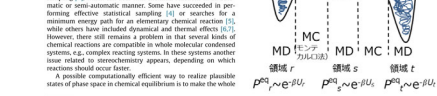
ARTICLE INFO  
ABSTRACT  
A "new" efficient method

We demonstrate a new hybrid MC/MD reaction method with a rare event-driving mechanism as a practical model reaction simulation of large-scale chemical reaction systems. Application of the method to 2-chlorobutane molecules in N,N-dimethylformamide (DMF) molecules starting in the optical pure state (100% ee) has found to successfully provide such an atomistic state with 40% ee.

1. Introduction  
It has long been known that in diffusion in solids and chemical reactions, etc., many dynamical systems require the overestimation of their time to obtain well-defined phase space regions [1-3], e.g., 100,000,000 in the initial state of  $\text{H}_2$  dissociation reaction at 273 K. The transition between these stable regions typically occur due to infrequent or activated events of their duration [1-3]. With traditional molecular simulations, it is difficult to determine the long-term properties and stereochemical characteristics that depend on an ensemble in such rare events.

A number of simulation methods have been developed to overcome this difficulty, such as generalized ensemble [4], metadynamics [5], transition path sampling [6], and action-based path sampling [7], which can deal with chemical reactions in an automatic or semi-automatic manner. Some have succeeded in providing effective statistical sampling [8] or accurate free energy barrier [9] for an elementary chemical reaction [10], while others have included dynamical and thermal effects [11]. However, there still remains a problem in that several kinds of chemical reactions are comparable in whole molecular condensed systems, e.g., complex reacting systems. In these systems another issue related to stereochemistry appears, depending on which reactions should occur faster.

A possible computationally efficient way to realize plausible states of phase space in chemical equilibrium is to realize the whole system transition between relatively stable regions in the stable phase states that are divided by transition state regions, and to apply a stochastic approach to judge whether the state after a rare transition occurrence might be adopted. A similar idea was previously introduced to treat gas phase chemical equilibria [12] and later applied to more complex chemical systems [13-15].

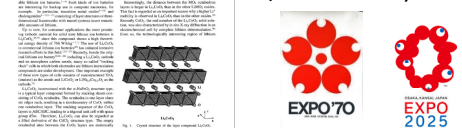


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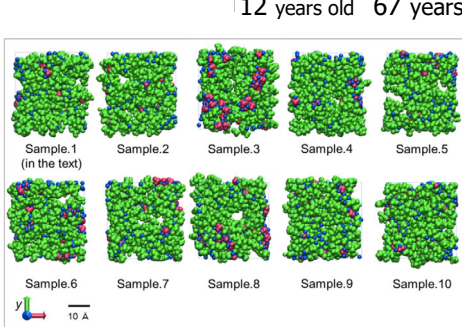
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When, 6 years old 62 years old!



When, 12 years old 67 years old!



## "Backpropagation Method"

- A method for efficiently computing the derivative of the evaluation function -

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LETTERS TO NATURE

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### Learning representations by back-propagating errors

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We describe a new learning procedure, back-propagation, for networks of neurone-like units. The procedure repeatedly adjusts the weights of the connections in the network so as to minimize a measure of the difference between the actual output vector of the net and the desired output vector. As a result of the weight adjustments, internal 'hidden' units which are not part of the input or output come to represent important features of the task domain, and the regularities in the task are captured by the interactions of these units. The ability to create useful new features distinguishes back-propagation from earlier, simpler methods such as the perceptron-convergence procedure.

There have been many attempts to design self-organizing neural networks. The aim is to find a powerful synaptic modification rule that will allow an arbitrarily connected neural network to develop an internal structure that is appropriate for a particular task domain. The task is specified by giving the desired state vector of the output units for each state vector of the input units. If the input units are directly connected to the output units it is relatively easy to find learning rules that iteratively adjust the relative strengths of the connections so as to progressively reduce the difference between the actual and desired output vectors. Learning becomes more interesting but

more difficult when we introduce hidden units whose actual or desired states are not specified by the task. (In perceptrons, there are 'feature analysers' between the input and output units that are not true hidden units because their input connections are fixed by hand, so their states are completely determined by the input vector; they do not learn representations.) The learning procedure must decide under what circumstances the hidden units should be active in order to help achieve the desired input-output behaviour. This amounts to deciding what these units should represent. We demonstrate that a general purpose and relatively simple procedure is powerful enough to construct appropriate internal representations.

The simplest form of the learning procedure is for layered networks which have a layer of input units at the bottom; any number of intermediate layers; and a layer of output units at the top. Connections within a layer or from higher to lower layers are forbidden, but connections can skip intermediate layers. An input vector is presented to the network by setting the states of the input units. Then the states of the units in each layer are determined by applying equations (1) and (2) to the connections coming from lower layers. All units within a layer have their states set in parallel, but different layers have their states set sequentially, starting at the bottom and working upwards until the states of the output units are determined.

The total output vector  $y_j$  is a linear function of the outputs,  $y_j$ , of the units that are connected to  $j$  and of the weights,  $w_{ij}$ , on these connections

$$y_j = \sum_i y_i w_{ij} \quad (1)$$

Units can be given biases by introducing an extra input to each unit which always has a value of 1. The weight on this extra input is called the bias and is equivalent to a threshold of the opposite sign. It can be treated just like the other weights.

A unit has a real-valued output,  $y_j$ , which is a non-linear function of its total input

$$y_j = \frac{1}{1 + e^{-x_j}} \quad (2)$$

\* To whom correspondence should be addressed.

H.C. Longuet-Higgins (1923-2004)

Cambridge U. ('54-'67)

Edinburgh U. ('67-'74)



A little further, while learning  
the fundamentals carefully and extensively!

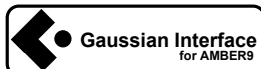


Ncube changed the mode for the time being!  
Thank you very much  
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## Collaborators and Students:

- N.O.-Yoshida (DR) • I.Okazaki (DR) • Y.Hara (DR)
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  - I.Kurisaki (DR) • N.Takenaka (DR) • Y.Suzuki (DR)
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- (Other OBs & OGs and outer Coworkers)



Thank you for your attention!



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