CMD WORKSHOP – OSAKA
September 2 - 6, 2019

# *Introductory Lecture on Computational Materials Design*

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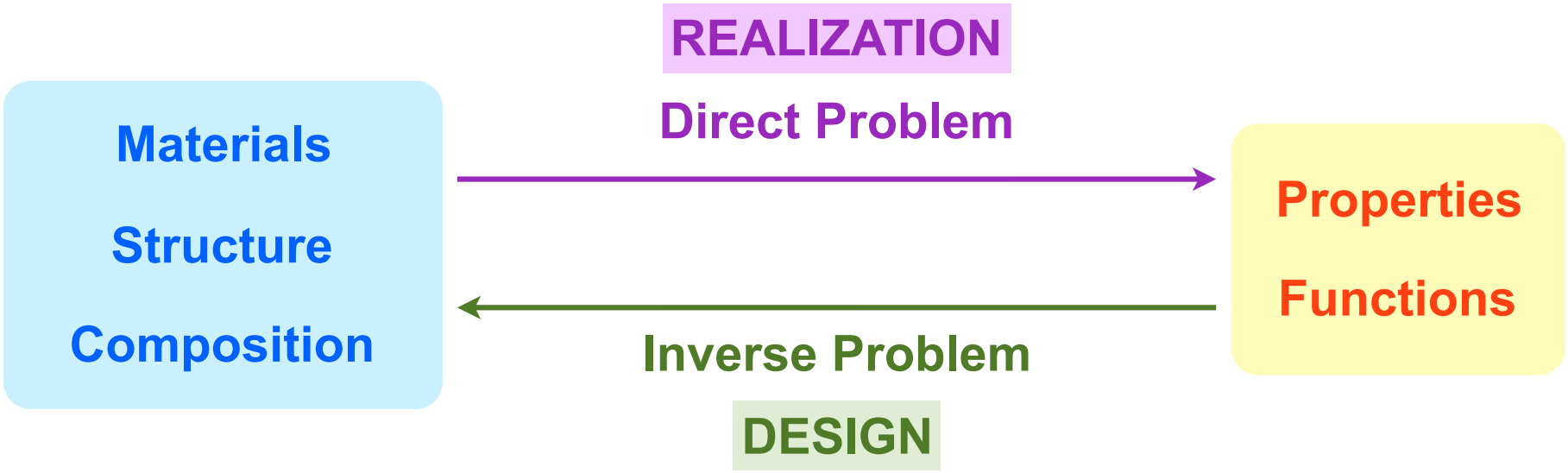
OSAKA UNIVERSITY

# OUTLINE

- Materials Design
- Computational Materials Design: CMD®
- History of the CMD® Workshop
- First-Principles Calculation
- Special Features of the Present CMD® Workshop

# Materials Design

- Goals
  - Discovery of novel materials with desired property/function
  - Optimization of property/function that known materials already possess
- An Inverse Problem of Realization



# Computational Materials Design: CMD®

- **CMD® is the theoretical design/optimization of materials with desired property/function. Specifically, CMD® involves the efficient use of computational techniques to conduct calculations based on the basic quantum theory.**

- **Key Developments of Emerging CMD®**
  - **Quantum Theory of Electrons**
  - **Computational Techniques: Methods, Algorithms, and Codes**
  - **High-Performance Computers**

- **The purpose of the CMD® Workshop is to provide the fundamental knowledge and techniques needed to enable materials design by computations.**

# Quantum Theory of Electrons

- **Band Theory for Crystalline Solids**

  **→ Condensed Matter Theory**

- **Molecular Orbital Theory for Molecules**

  **→ Quantum Chemistry**

# Quantum Theory of Electrons in Solids — Band Theory

## Quantum Mechanics in 1920s

# The 5th Solvay Conference 1927.10
# “Electrons and photons”

https://en.wikipedia.org/wiki/Solvay_Conference

# Quantum Theory of Electrons in Solids — Band Theory

## Quantum Mechanics in 1920s

**(1920s – 1930s) Dawn period: Bloch, Brillouin, Wigner, Seitz, Wannier, Slater, Kohn, Hellmann, Feynman, …**

**(1940s – 1950s) Development period I: Herring, Slater-Koster, Phillips-Kleinman, Korringa-Kohn-Rostoker, …**

**(1960s) Application period: Ashcroft, Heine, Harrison, Yamashita-Wako-Asano, …**

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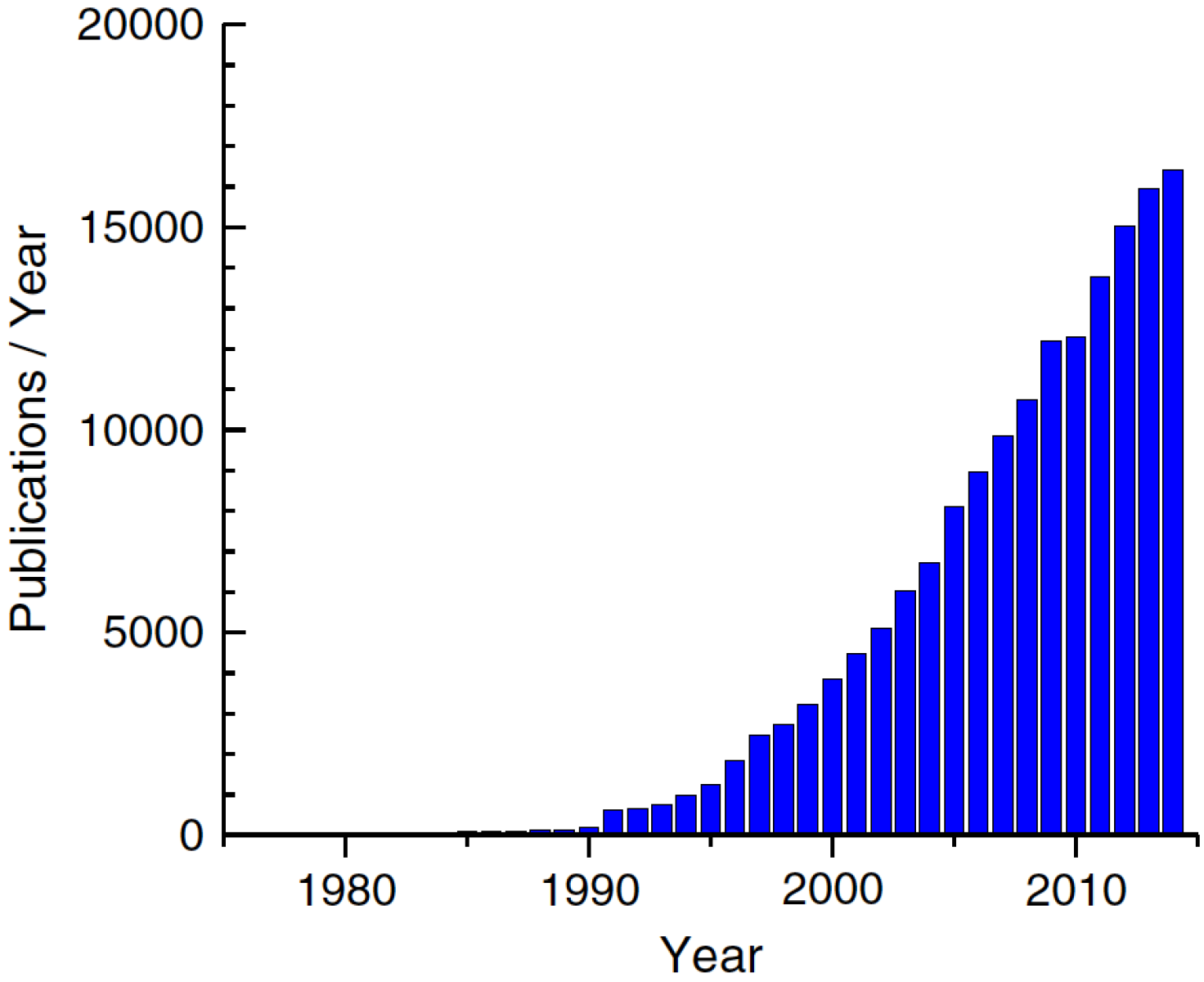
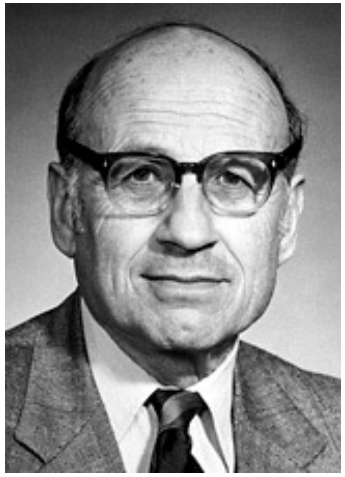


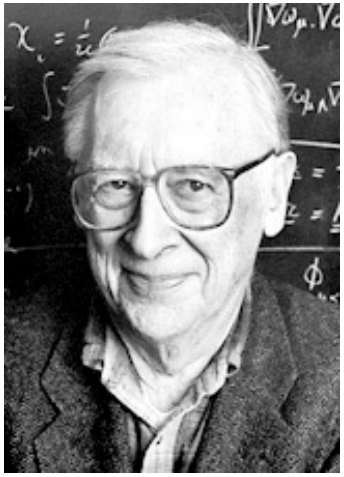

**Number of publications per year (1975–2014) on topics ("density functional" or "DFT"), according to the Web of Science Core Collection (February 2015)**

**Jones (2015)**

# The Nobel Prize in Chemistry 1998



Walter Kohn



John A. Pople

**The Nobel Prize in Chemistry 1998 was divided equally between Walter Kohn "for his development of the density-functional theory" and John A. Pople "for his development of computational methods in quantum chemistry".**

http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1998/

# Quantum Theory of Electrons in Solids — Band Theory

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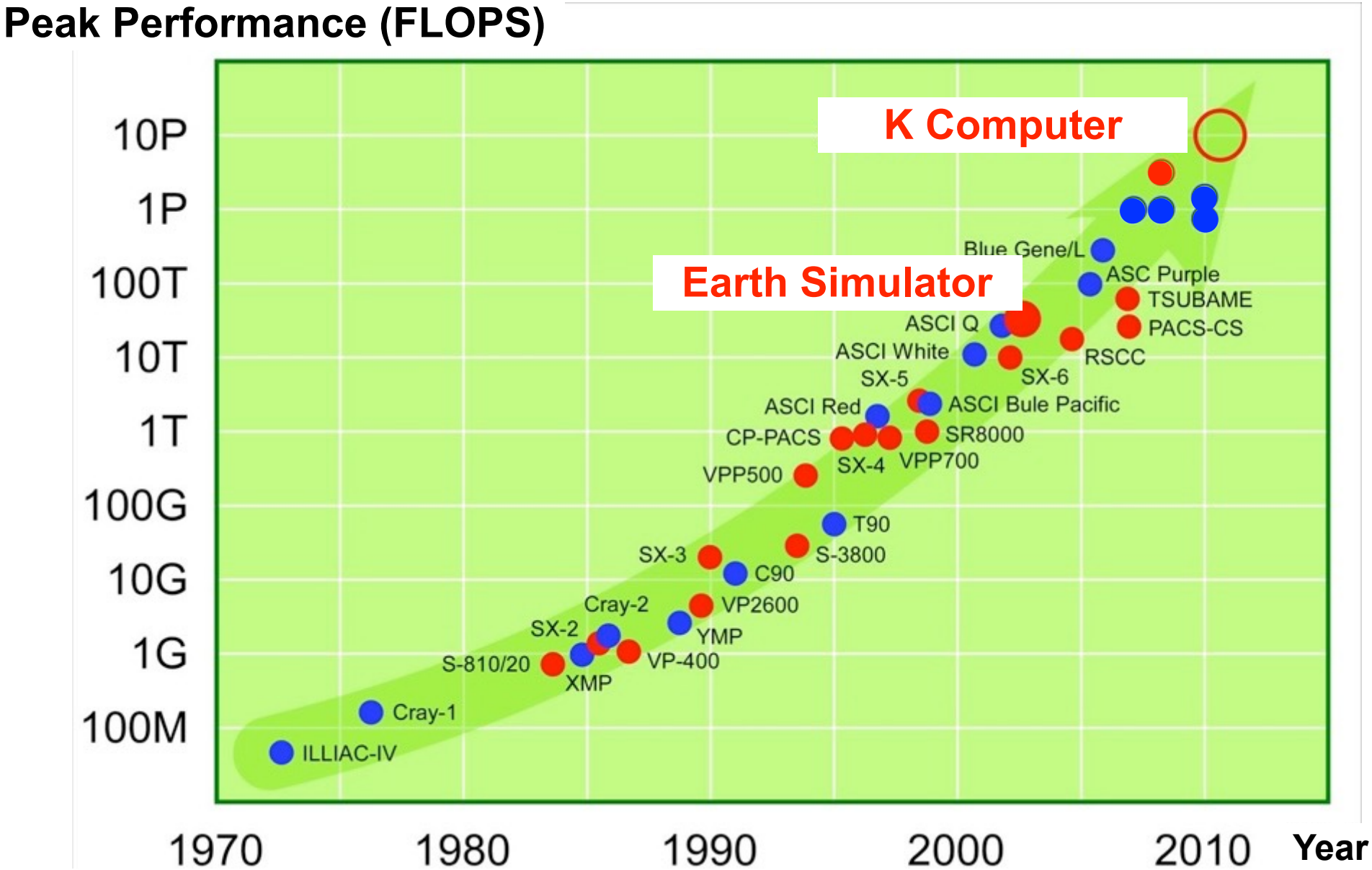
## (1964-1965) DFT: Hohenberg-Kohn, Kohn-Sham

(1970s) Development period II: Andersen, Koelling, Hamann-Schlüter-Chiang, Ihm-Zunger-Cohen, …

(1980s) Development period III: Car-Parrinello, Weinert, Vanderbilt, …

(1980s – present) First-principles calculations

# Growing Power of Supercomputers



# Computational Materials Design Workshop

- **Background**
  - **In 2001-2002, a Specialist Training Project was held at the International Institute for Advanced Studies (IIAS) in Kyoto, in the field of Information Biology. — An active effort to not merely ensure that the students acquired the target knowledge but rather to create opportunities for bilateral interchange with the instructors, with the aim of using the synergy to train a group of specialists who would become the future leaders in these areas.**
  - **Osaka University had many researchers specializing in first-principles calculations: Profs. H. Akai, H. Katayama-Yoshida, H. Kasai, and so on. They launched the "Development of methods for computational nano-materials design" computer-based project involving some other researchers in Japan under the support of JST in 2001.**
  - **Through the receipt of assistance from the JST project, the CMD® Workshop was born in September 2002 as the second IIAS specialist training project.**

# 1st CMD Workshop at IIAS in September 2002

Morikawa Yoshida Akai Kasai Hamada Nakanishi

Kanamori Terakura

# Computational Materials Design Workshop

- **Since 2002 the 5-day Workshops have been held twice a year (spring and autumn) and the 35$^{th}$ Workshop is being witnessed here.**
  - **Total number of participants (till 34$^{th}$ WS): 1547**
    - **Grad. & Undergrad. Students: 906**
    - **University/College Staffs (incl. National Labs): 261**
    - **Researchers from campanies: 380**

**http://phoenix.mp.es.osaka-u.ac.jp/CMD/**

# Asian CMD® Workshop

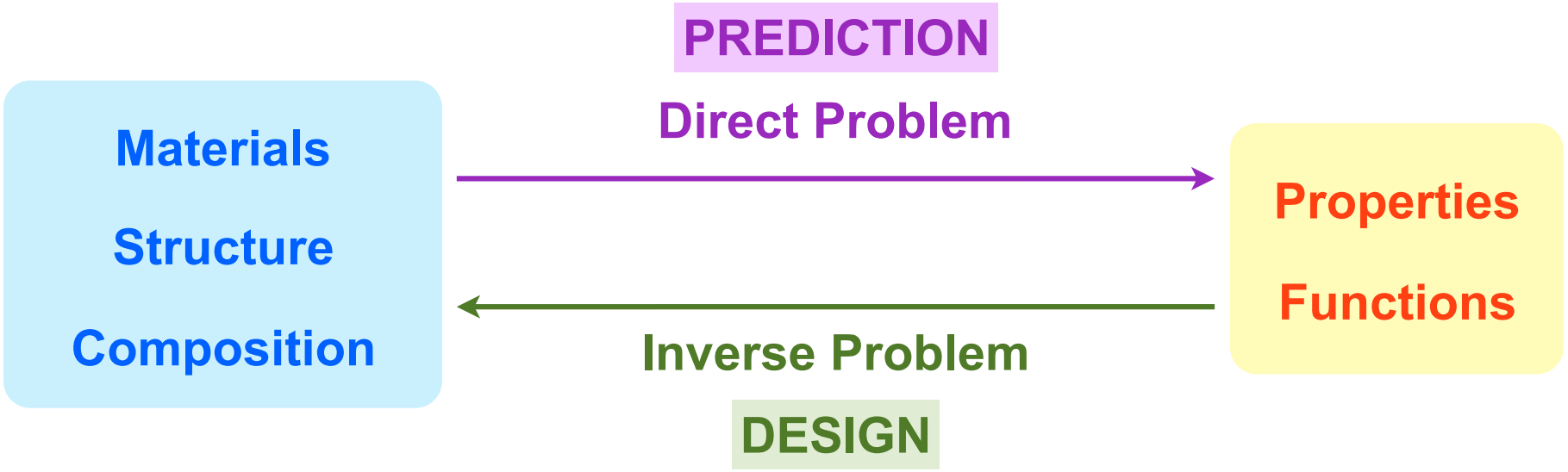
- Since around 2007, the number of foreigners attending the Workshop from Southeast Asia has increased. Most of these are graduate students studying abroad at Osaka University. This made it difficult to conduct the lectures and hands-on training in Japanese only, and not only the explanatory slides but the oral explanations came to be presented in both Japanese and English. This style of instruction has continued to these days, but it has produced problems as well.

- Interchange with people from the Southeast Asian region through the CMD® Workshop became the inspiration in 2008 for the start of Asian CMD® Workshop in Southeast Asia. In August 2008, the first Asian CMD® Workshop was held at Institut Teknologi Bandung in Indonesia. In September 2008, an Asian CMD® Workshop was held at De La Salle University in the Philippines. In the following year, Asian CMD® Workshops were held again in Indonesia and the Philippines, and in Vietnam as well. In 2010, the number of countries was expanded to four with the addition of Thailand. It has continued to be held till these days.

# Asia CMD Workshop @ UKM in 2016

# First-Principles Calculations

- **Provide a way for solving a direct problem by prediction.**



# First-Principles Calculations

★ ***Starting from first principles, equations are derived under some approximations and solved for a realistic system.***

★ ***Two main characteristics:***

- ***General-purpose*: the methods do not depend on material systems and properties to be studied**
- ***Non-empirical*: the methods do not require any experimental parameters and knowledges as input except for fundamental physical quantities (*m*, *e*, *h*)**

**We may possibly:**

➡ **Predict properties to be compared with experiments**

➡ **Understand underlying microscopic mechanisms**

➡ **Design new materials with desired property/function**

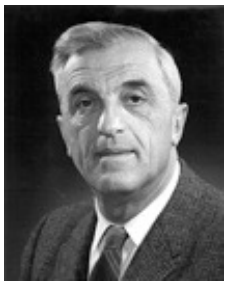
# First-Principles Calculations

- **Basic Approximations**
  - **Born-Oppenheimer Approx. → Interacting N-electron problem under external field (nuclear position: structure)**
  - **One-electron Approx. → Non-interacting problem**
    - **Local Density Approximation to Density Functional Theory**
      - ➡ **Kohn-Sham equations to be solved**

- **Band Theory for Crystalline Systems**
- **Real-Space Methods for Nanostructure Systems**

# Band Theory

- **Crystal Systems with Periodic Boundary Condition**
  - **Bloch Theorem**
    - **A one-electron quantum-mechanical state in a periodic potential can be specified with a wave vector *k*. → quantum number**

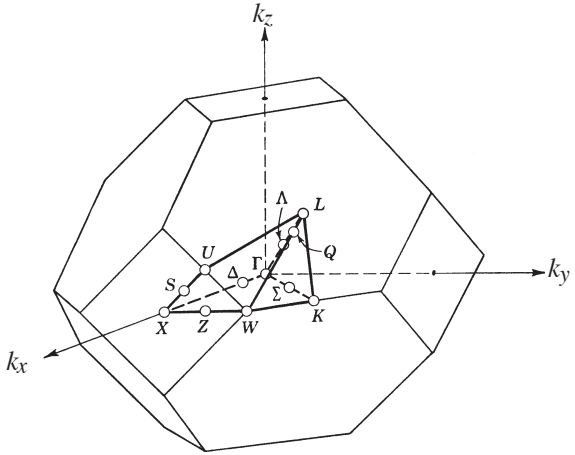


*Felix Bloch*
**1952 Nobel prize**

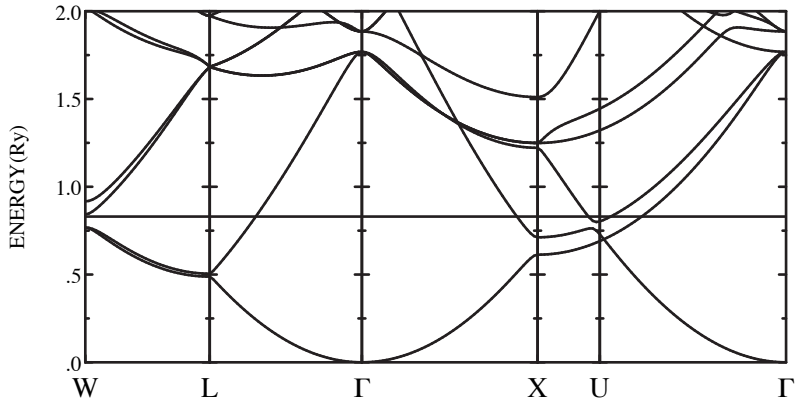
$$\left[-\frac{\hbar^2}{2m}\nabla^2 + v_{\text{eff}}(\mathbf{r})\right]\psi_j^{\mathbf{k}}(\mathbf{r}) = \varepsilon_j^{\mathbf{k}}\psi_j^{\mathbf{k}}(\mathbf{r})$$

**dispersion relation: band structure**

- **Brilloiun Zone: a volume in the k space that includes all the independent electronic states**




**Brillouin zone of fcc**




**band structure of fcc Al**

# How to Solve Kohn-Sham Eq.

- Bloch Theory → Plane Wave Representation
  - Rigorous but practically intractable
- Coulomb Singularity in Potential Terms
  - Pseudopotential method with plane waves
    - Contributions from core (nucleus and core electron potentials, and orthogonality to core electron states) are replaced by a soft (easily Fourier transformed) potential.
  - Augmentation method
    - Plane wave basis functions are augmented inside muffin-tin spheres with localized atomic-like spherical-wave functions.
  - Green's function method
    - Formulated as a multiple scattering problem and mathematically equivalent to the idea of augmentation without invoking explicit basis functions

# What We Get

- **Many kinds of physical quantities that can be directly compared with experimental observables**
  - ***Structural properties***
    - **heat of formation, phonon, elastic constants, thermal expansion, ...**
  - ***Electric properties***
    - **electric polarization, piezoelectric constants, Born charges, ...**
  - ***Magnetic properties***
    - **magnetic moments (spin and orbital), magnetic coupling, magnetoanisotropy energy, hyperfine constants, ...**
  - ***Optical properties***
    - **optical constants, absorption spectra, ...**
  - **.....**

# Structural Properties

- **Born-Oppenheimer Potential = Total Energy**

$$E(\{\mathbf{R}_n\}) = + \sum_{n>n'} \frac{Z_n Z_{n'} e^2}{|\mathbf{R}_n - \mathbf{R}_{n'}|} + E_e(\{\mathbf{R}_n\})$$

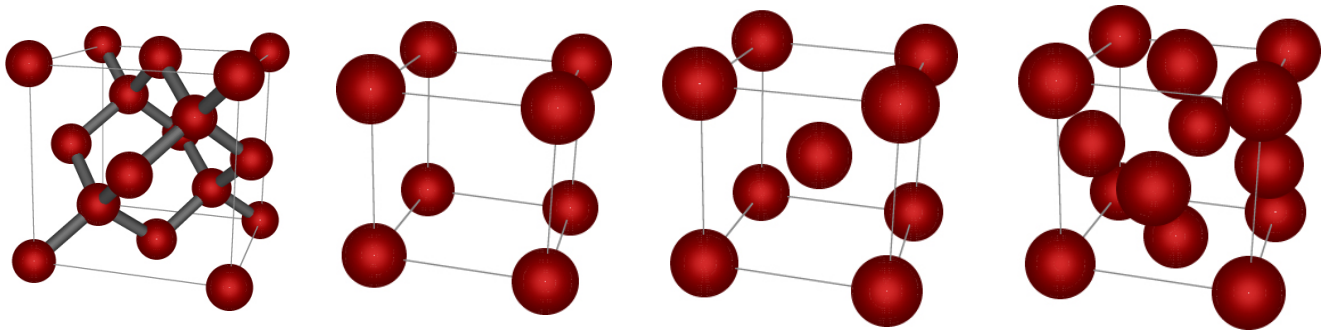
- **Atomic Forces → structural optimization, molecular dynamics**

$$\mathbf{F}_n(\{\mathbf{R}_n\}) = -\nabla_n E(\{\mathbf{R}_n\})$$

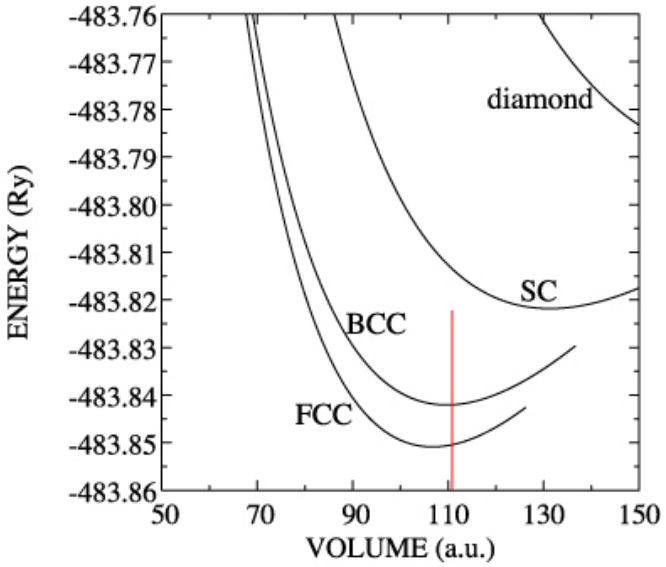
- **Force Constants → phonon, structural stability**

$$k_{n\alpha,n'\beta}(\{\mathbf{R}_n\}) = \frac{\partial^2}{\partial R_{n\alpha} \partial R_{n'\beta}} E(\{\mathbf{R}_n\})$$

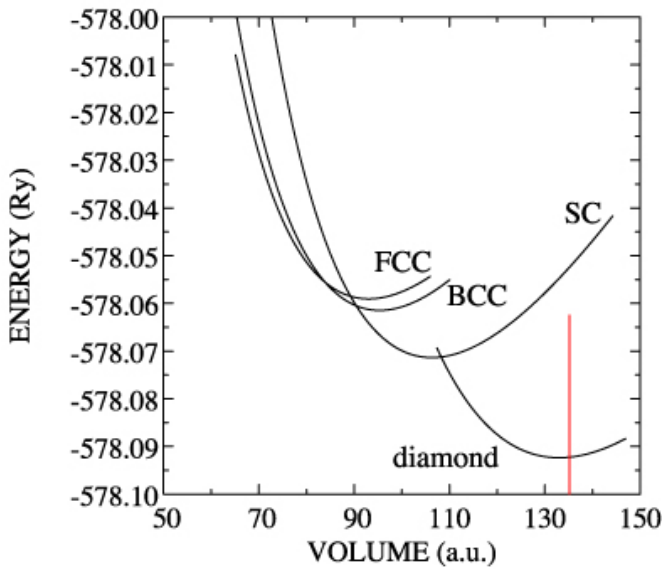
# Total Energy for a Given Structure and Composition



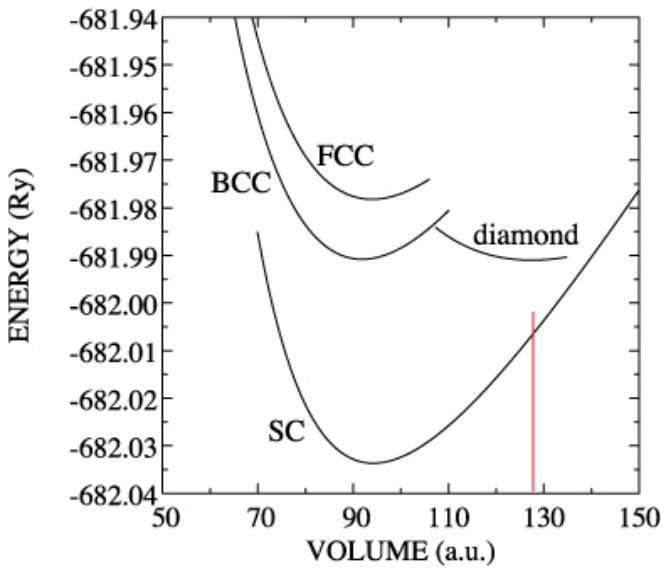
diamond simple cubic bcc fcc




Al




Si

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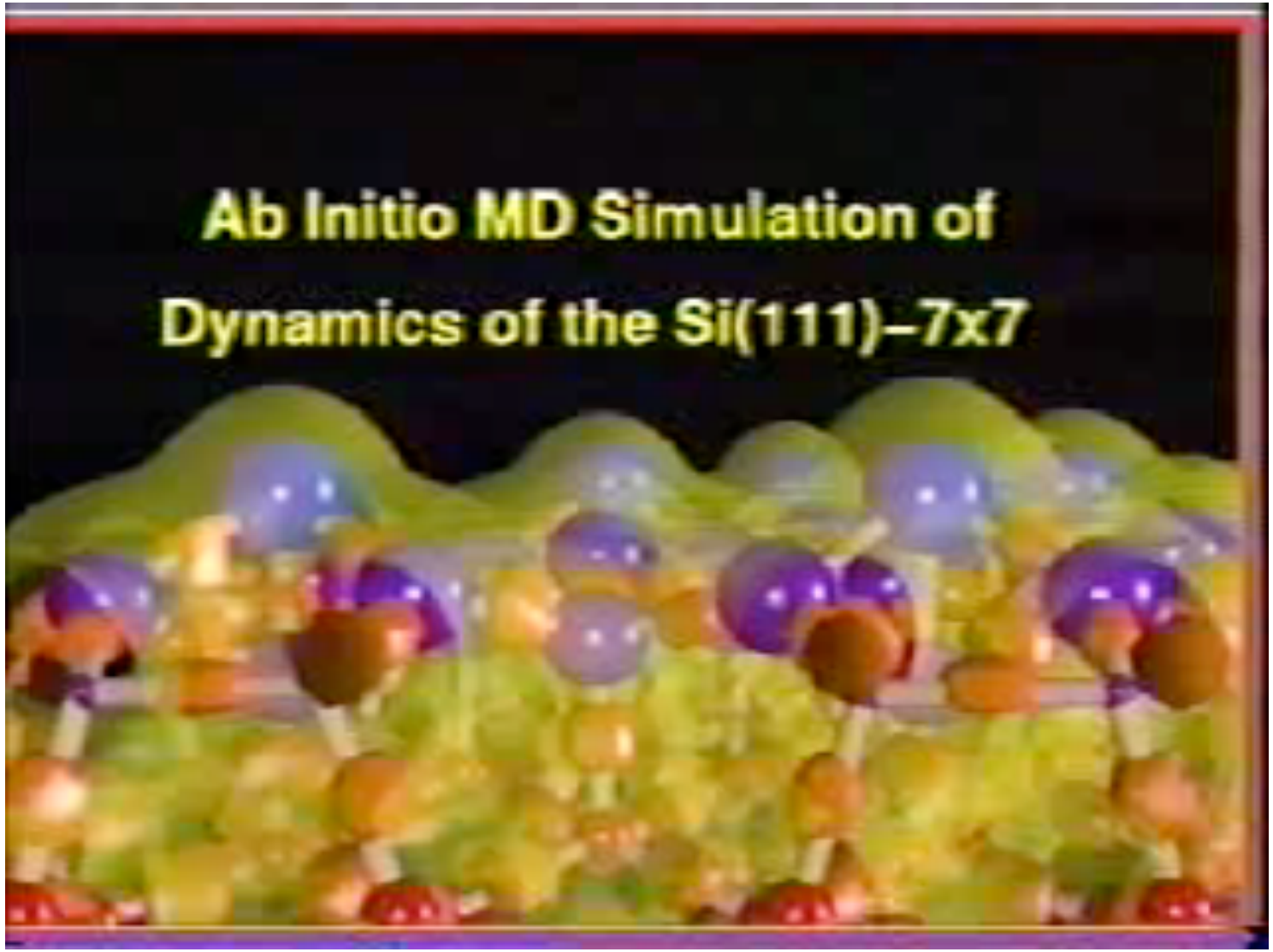
# First-Principles Molecular-Dynamics Simulation

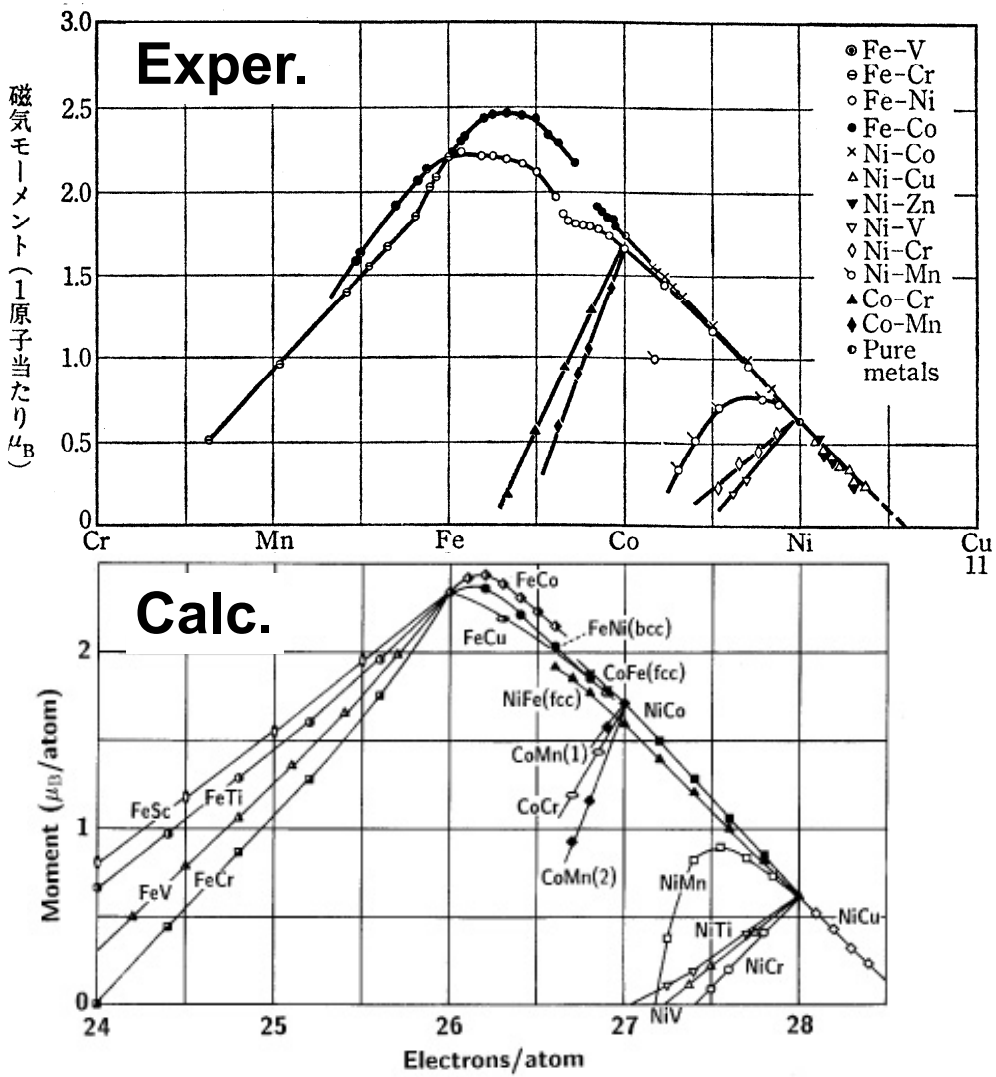
- **Si(111) 7x7 Surface**




**I. Stich *et al*. 2002**

# What We Get

- **Spin Magnetic Moments**
  - **Slater-Pauling Curve**




Dederichs et al. JMMM100, 241(1991).

**Extension to spin-density functional**

$$E = E\left[n(\mathbf{r}), m(\mathbf{r})\right]$$

**spin density**

**Spin Moment**

$$M_{\text{spin}} = 2\mu_{\text{B}} \sum_j \langle \psi_j | s_z | \psi_j \rangle$$

$$= \mu_{\text{B}} \int d\mathbf{r}\; m(\mathbf{r})$$

# 35th CMD® Workshop

- Common Lectures
  - CMD Introductory
  - Short Talks, Case Study Talks, Special Lecture
- Beginners Course
  - Machikaneyama, STATE-Senri, HiLAPW
- Advanced Course
  - A: Naniwa, ABCAP, RSPACE, Salmon
  - B: Machikaneyama, ecalj, ES-OPT
- Supercomputer Course
  - STATE-Senri
- Spintronics Course
  - Lectures and Hands-on/Machikaneyama, ecalj, ES-OPT
- Materials Informatics Course
  - CrySPY, LIDG

# Hope you enjoy the Workshop

http://phoenix.mp.es.osaka-u.ac.jp/CMD/