Development of computational method aiming to design novel reagents for elements separation

November 18th 2021

National Research and Development Agency

Japan Atomic Energy Agency

Sector of Nuclear Science Research, Nuclear Science and Engineering Center

Nuclear Chemistry Division, Research Group for Radiochemistry
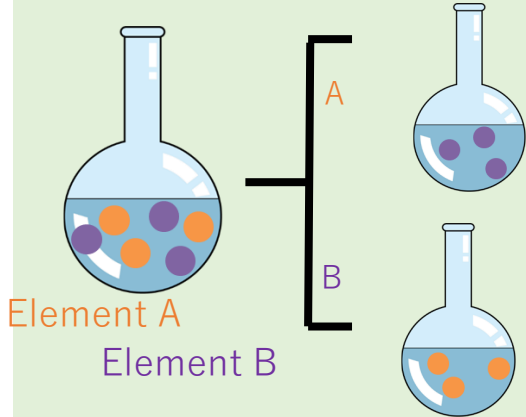
Researcher   KANEKO Masashi

Reprocessing and recycling by element separation
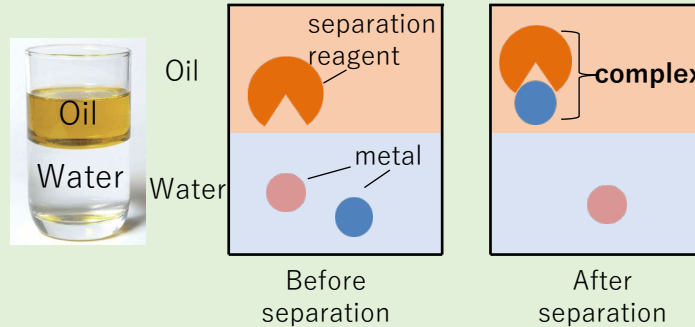
Importance of element separation

This stability is important!

Image of element separation

Element A
Element B

Element separation by solvent extraction (SX)

Complex: Reactant between metal and reagent

Oil
Water

separation reagent
metal
Before separation

complex

After separation

Catalyst
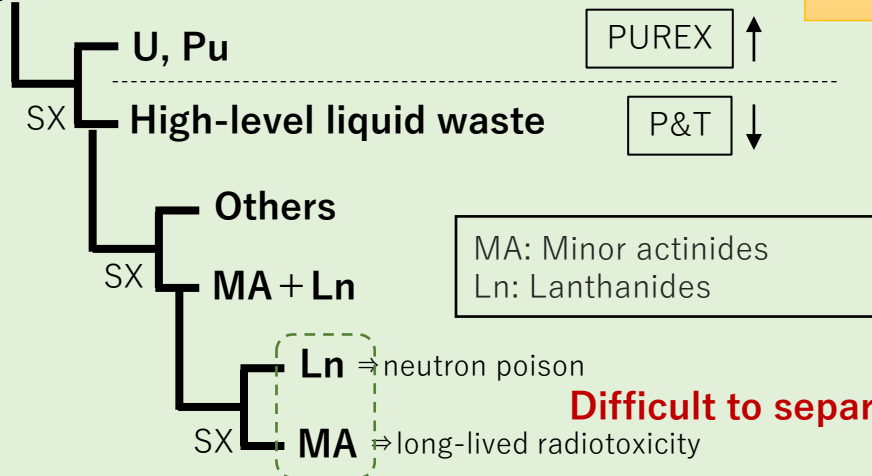Rare-metal
Magnet
e-waste
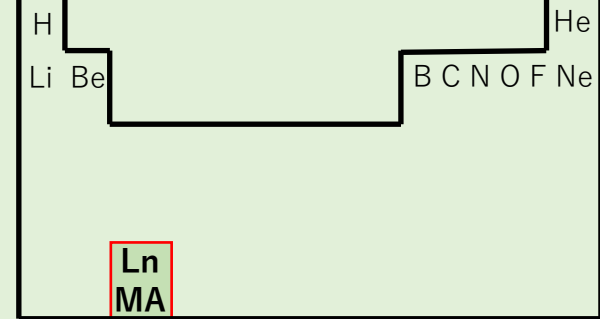Battery

Element separation in nuclear science

Partitioning and Transmutation (P&T) technology is to separate elements in HLLW discharged from the reprocessing plant depending on intended use to transmute Long-lived nuclides to short-lived or stable ones

Spent nuclear fuel

U, Pu — PUREX ↑

SX — **High-level liquid waste** — P&T ↓

Others

SX — **MA＋Ln**

MA: Minor actinides
Ln: Lanthanides

Ln ⇒ neutron poison

Difficult to separate

SX — **MA** ⇒ long-lived radiotoxicity

Periodic table of elements

H
Li Be
He
B C N O F Ne

Ln
MA

Similar property makes them to be separated

Acceleration of separation reagents development by computational science
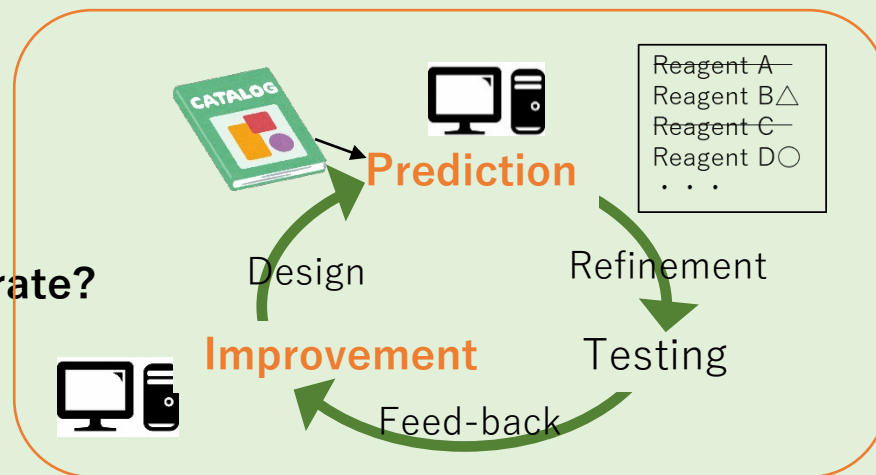
Conventional method

Reagent A ⟶ Test ➡ ×
Reagent B ⟶ Test ➡ △
Reagent C ⟶ Test ➡ ×
Reagent D ⟶ Test ➡ ○
Reagent E ⟶
Reagent F · · ·

Trial-and-Error

➡ Time-consuming

How does it accelerate?

Introduction of computational science

Prediction

Reagent A
Reagent B △
Reagent C
Reagent D ○
· · ·

Design

Refinement

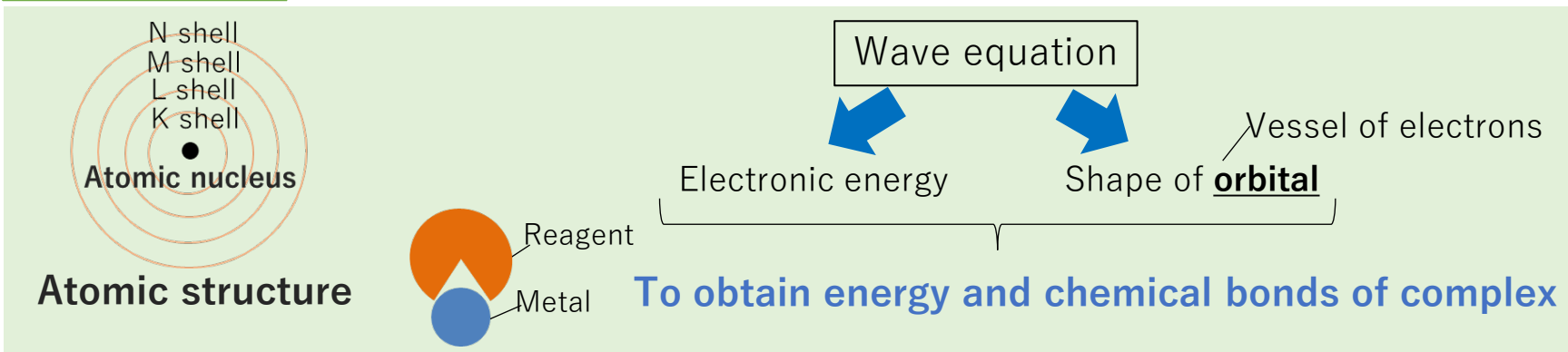**Improvement**

Testing

Feed-back
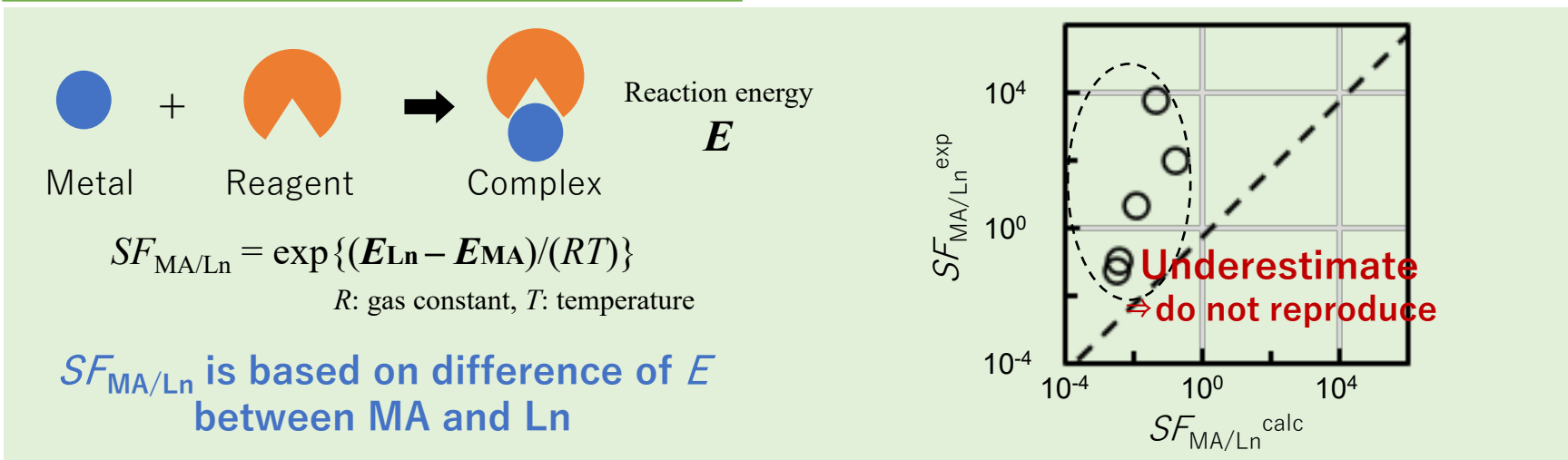
➡ Refinement and improvement

【Purpose of this study】

○ Development of prediction method of MA/Ln separation performance
○ Elucidation of separation mechanism between MA and Ln
⇒ enable us to develop novel separation reagents!

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Computational chemical method "Density functional theory" (DFT)

DFT method ⇒ to solve wave equation of electrons in atoms or molecules

N shell
M shell
L shell
K shell

Atomic nucleus

Atomic structure

Reagent

Metal

Wave equation

Electronic energy   Shape of **orbital**

Vessel of electrons

To obtain energy and chemical bonds of complex

MA/Ln separation factor ($SF_{MA/Ln}$) ⇒ Indicator of separation performance

Metal   +   Reagent   ➡   Complex

Reaction energy
E

$$SF_{MA/Ln} = \exp\{(E_{Ln} - E_{MA})/(RT)\}$$

R: gas constant, T: temperature

$SF_{MA/Ln}$ **is based on difference of** E
between MA and Ln
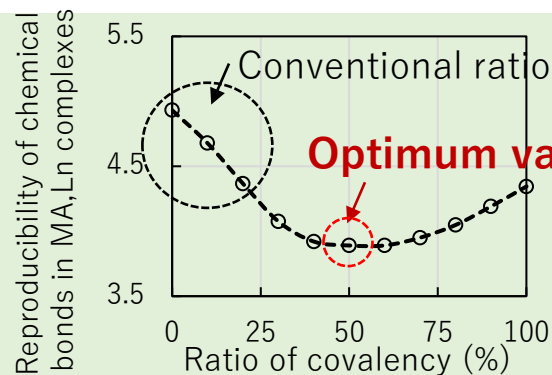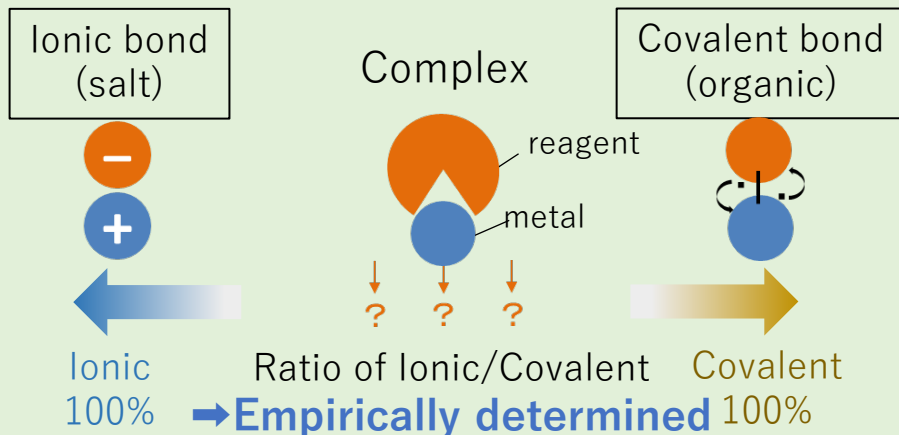

Underestimate
⇒ do not reproduce

【Problem】 Conventional method does not reproduce $SF_{MA/Ln}$
⇒ Tuning DFT method is necessary

Tuning DFT to reproduce MA/Ln separation

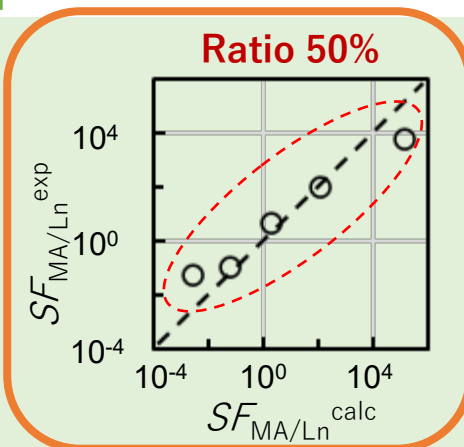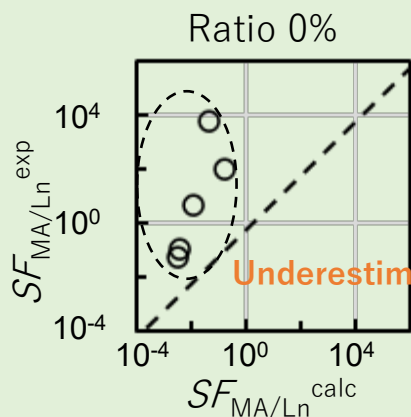## Chemical bond in complex ⇒**Remains unclear for MA, Ln complexes**

Ionic bond (salt)

Complex

Covalent bond (organic)

reagent

metal

? ? ?

Ionic 100%

Ratio of Ionic/Covalent ➡**Empirically determined**

Covalent 100%

Reproducibility of chemical bonds in MA,Ln complexes

Conventional ratio

Optimum value

Ratio of covalency (%)

World-first

Determined the optimum ratio for MA, Ln complexes

Re-estimation of $SF_{MA/Ln}$ ⇒**Change the Ionic/Covalent ratio from 0% to 50%**

Ratio 0%

$SF_{MA/Ln}^{exp}$

$SF_{MA/Ln}^{calc}$

Underestimate

Ratio 50%

$SF_{MA/Ln}^{exp}$

$SF_{MA/Ln}^{calc}$

World-first

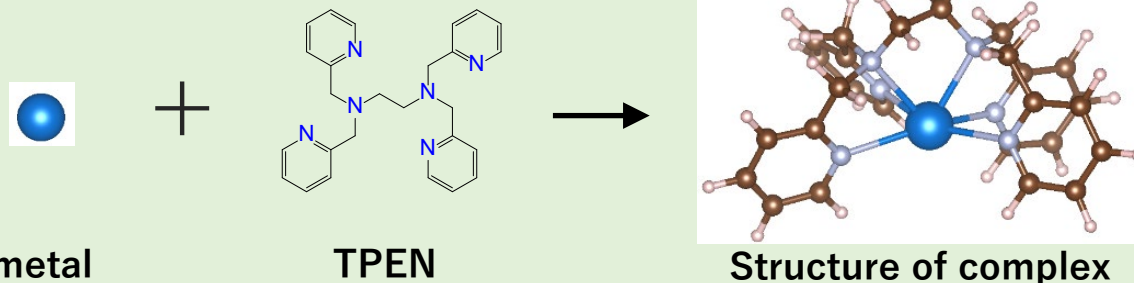**Reproduced** $SF_{MA/Ln}$

Leads to prediction of $SF_{MA/Ln}$

"Covalency" is important for MA/Ln separation
⇒Analyze the covalency in MA, Ln complexes
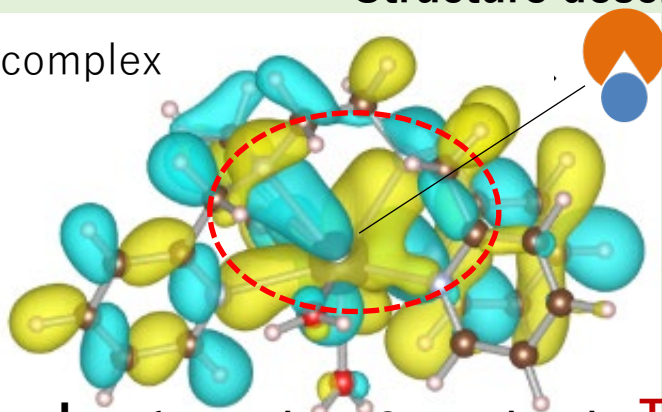
MA/Ln separation mechanism based on covalent bond

Molecular structure of complex with high separation agent "TPEN"

metal   +   TPEN   →   Structure of complex

Covalent bond＝"Orbital overlap" ⇒Focusing on fluctuation of electrons

Structure described with orbital overlap

MA complex

Ln complex

Large overlap➡Strong bond

High stability

This difference Originates in $SF_{MA/Ln}$
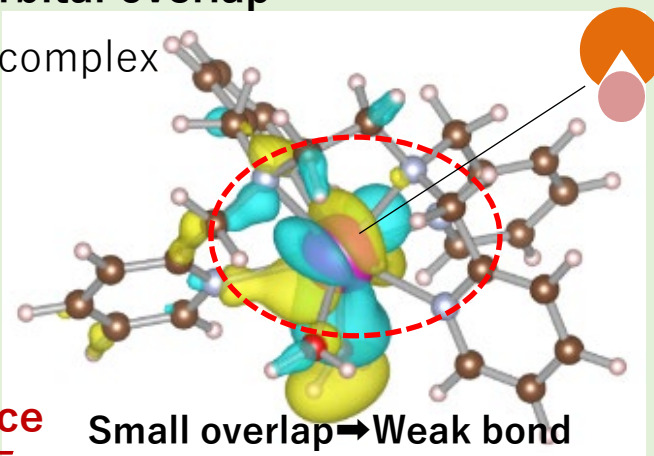
Small overlap➡Weak bond

Low stability

Strongness of orbital overlap is origin of separation mechanism
⇒Leading to design and improve reagents based on the mechanism!
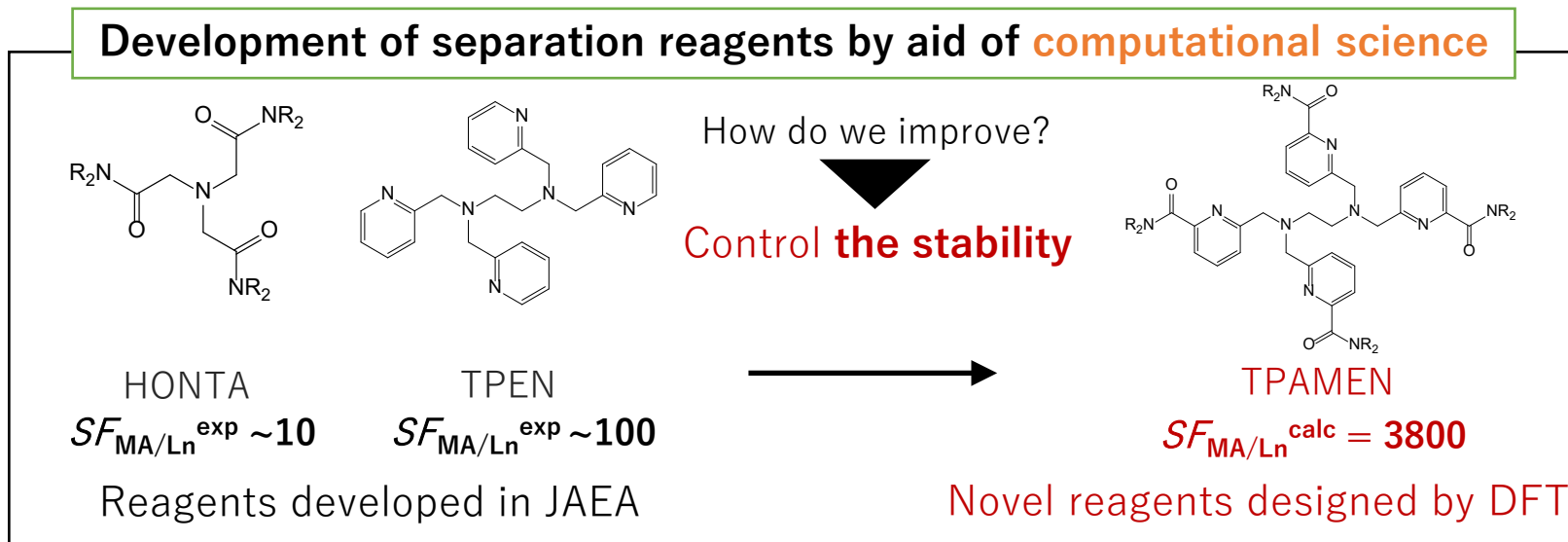
Summary

【**Conclusion**】
DFT method is applied to
➡reproduce MA/Ln separation performance
➡elucidate the separation mechanism based on covalency

【**Spreading effect**】
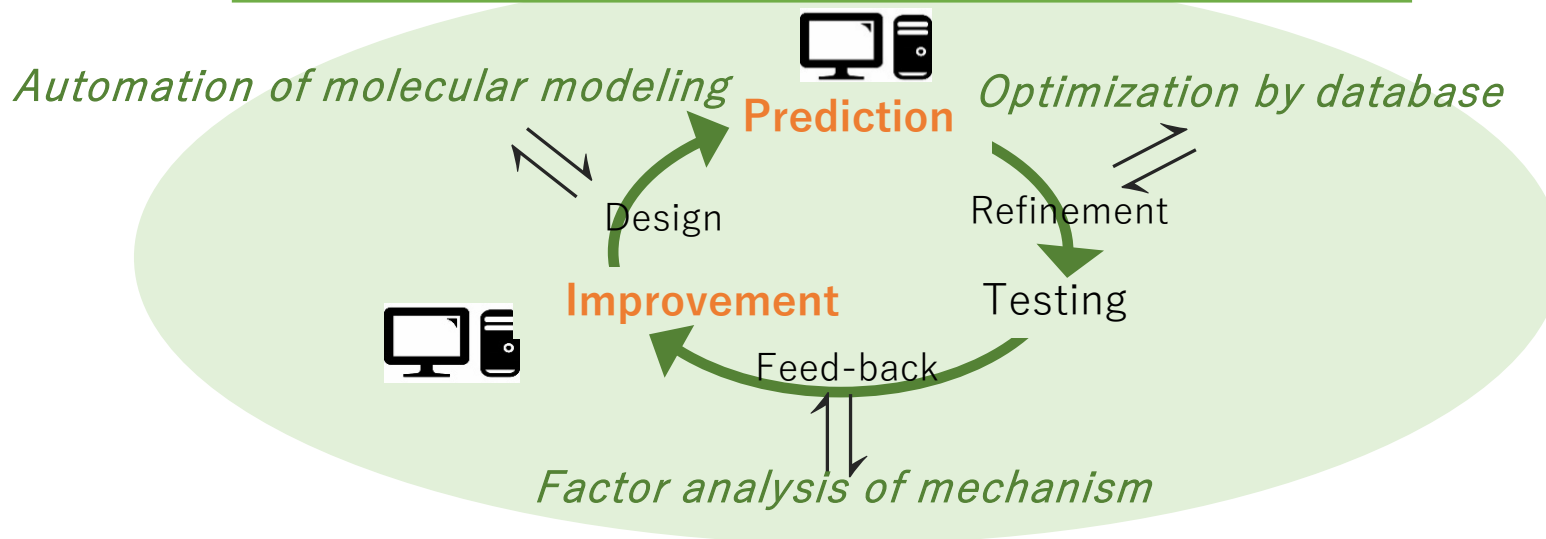Designing and prediction of novel reagents based on the mechanism
➡support the development of separation reagents with high performance

Development of separation reagents by aid of computational science

How do we improve?

Control **the stability**

HONTA
$SF_{MA/Ln}^{exp} \sim 10$

TPEN
$SF_{MA/Ln}^{exp} \sim 100$

Reagents developed in JAEA

TPAMEN
$SF_{MA/Ln}^{calc} = 3800$

Novel reagents designed by DFT

Novel reagents development with high separation performance!

Introduction of computational science and "AI"

Automation of molecular modeling

Prediction

Design

Improvement

Refinement

Testing

Feed-back

Optimization by database

Factor analysis of mechanism

Nuclear Science	From HLLW	
	Actinide separation	Platinum-group metal separation

| Spin-Off | Ex) RI for medical use
Ac: α-ray source
⇒Ac/Th,Ln separation | Ex) Rare-metal recovery
Pd: Catalyst for autobobile
⇒Pd/Pt separation |

Applicability to element separation for other scientific fields!