北京大学
PEKING UNIVERSITY

AI与凝聚态物理

陈 基

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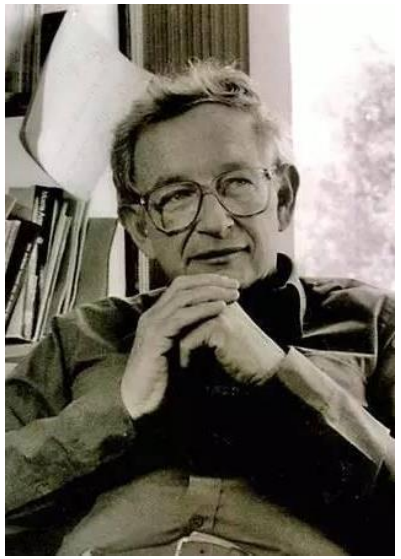
物理与人工智能课程讲座

凝聚态物理

凝聚态物理是研究大量微观粒子（原子、电子、离子等）通过相互作用凝聚形成的宏观物质体系的物理性质与规律的学科。

1972 **More Is Different:** Broken symmetry and the nature of the hierarchical structure of science.



Philip Anderson

多者异也

according to the idea: The elementary entities of science X obey the laws of science Y.

X	Y
solid state or many-body physics	elementary particle physics
chemistry	many-body physics
molecular biology	chemistry
cell biology	molecular biology
•	•
•	•
•	•
psychology	physiology
social sciences	psychology

凝聚态物理

物理学革命结束后物理学研究的状态

结果：在电子、原子核稳定存在的时间尺度内，以它们为研究对象，单体问题清楚了！也就是氢原子清楚了，复杂一些的原子还没有，分子也没有，更别说凝聚态（当时还没有诞生）。

下一步

1. 就世界组成的认识方面，满足这些，就是把量子力学用到具体问题的研究中。

1. 根据问题与现象，分为：磁学、热学、声学、光学、力学等。
   根据研究对象，分为：原子体系、分子体系、固体（早期主要是金属）等。

2. 不满足原子这个层面，探索更基础的结构。

2. 促成了30、40年代核物理研究的巨大进展。

来自李新征

凝聚态物理

物理学革命结束后物理学研究的状态

还原论
(Reductionism)

我需要研究清楚这个世界的基本构成单元。基于这个知识，我可以理解整个世界。

粒子物理、高能
(温伯格)

核能、国防等

演生论
(Emergence)

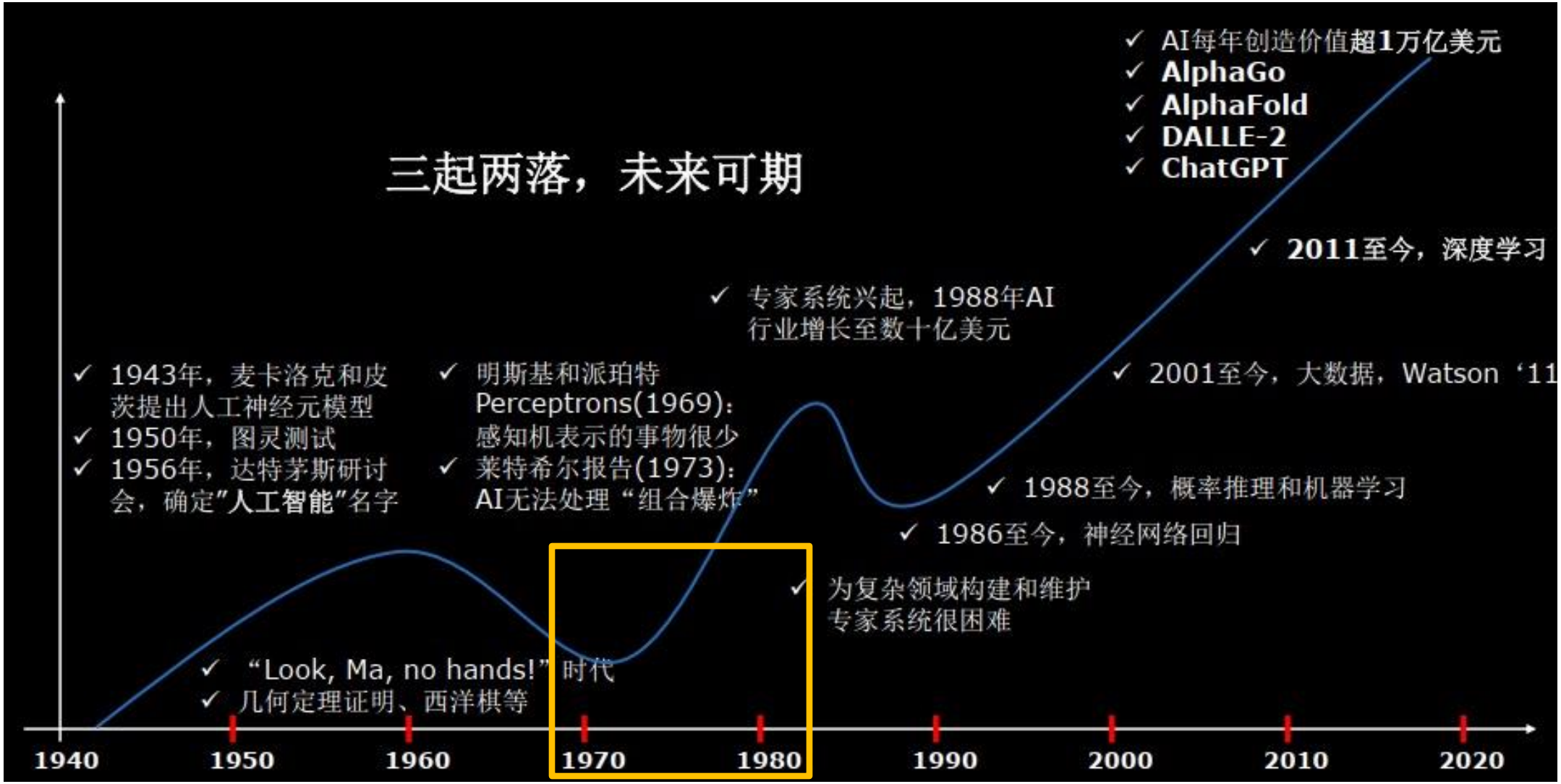
简单的构成单元可以通过相互作用构造出世间万象。重要的东西都是演生的。

凝聚态物理
(安德森)

为材料、化学等学科提供基础

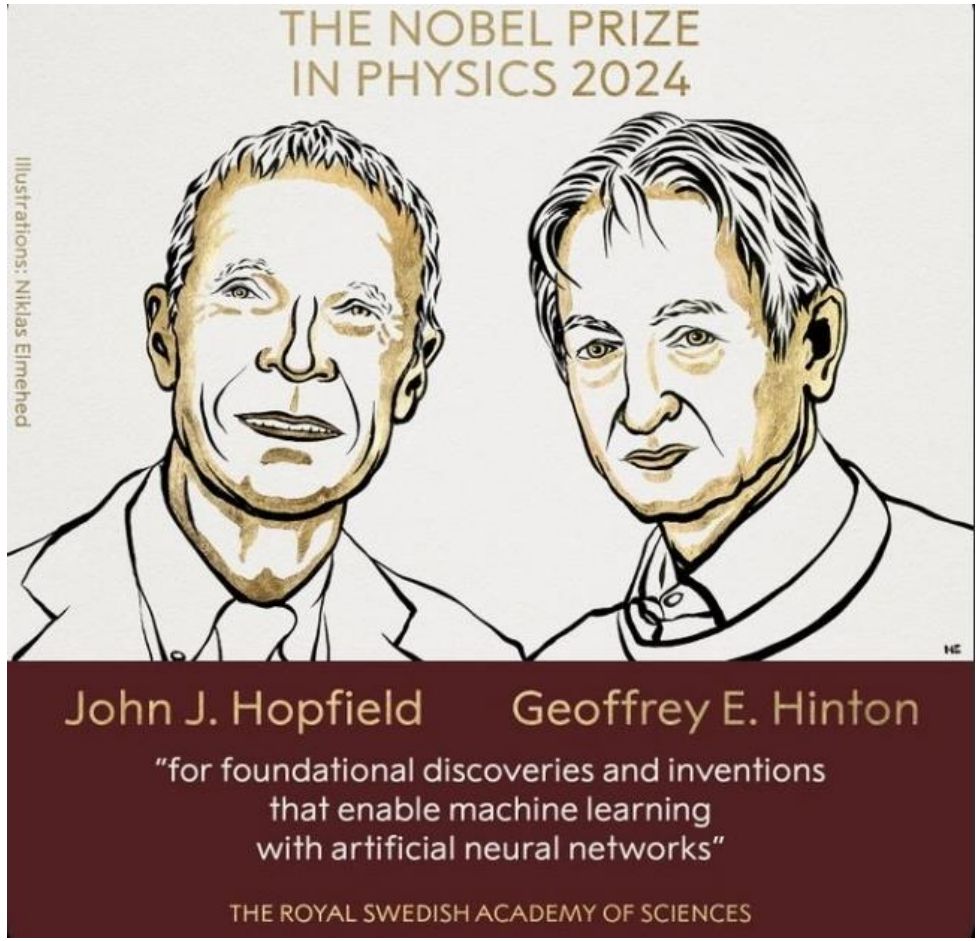
来自李新征

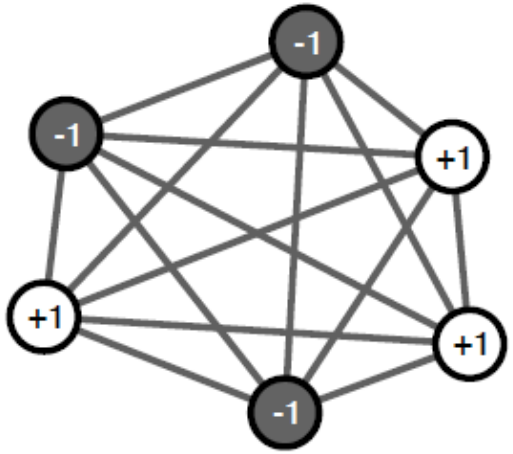
凝聚态物理与AI



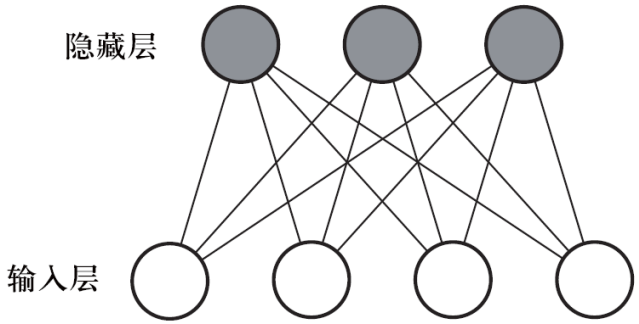
来自马滟青

凝聚态物理 for AI





Hopfield网络 （1982）

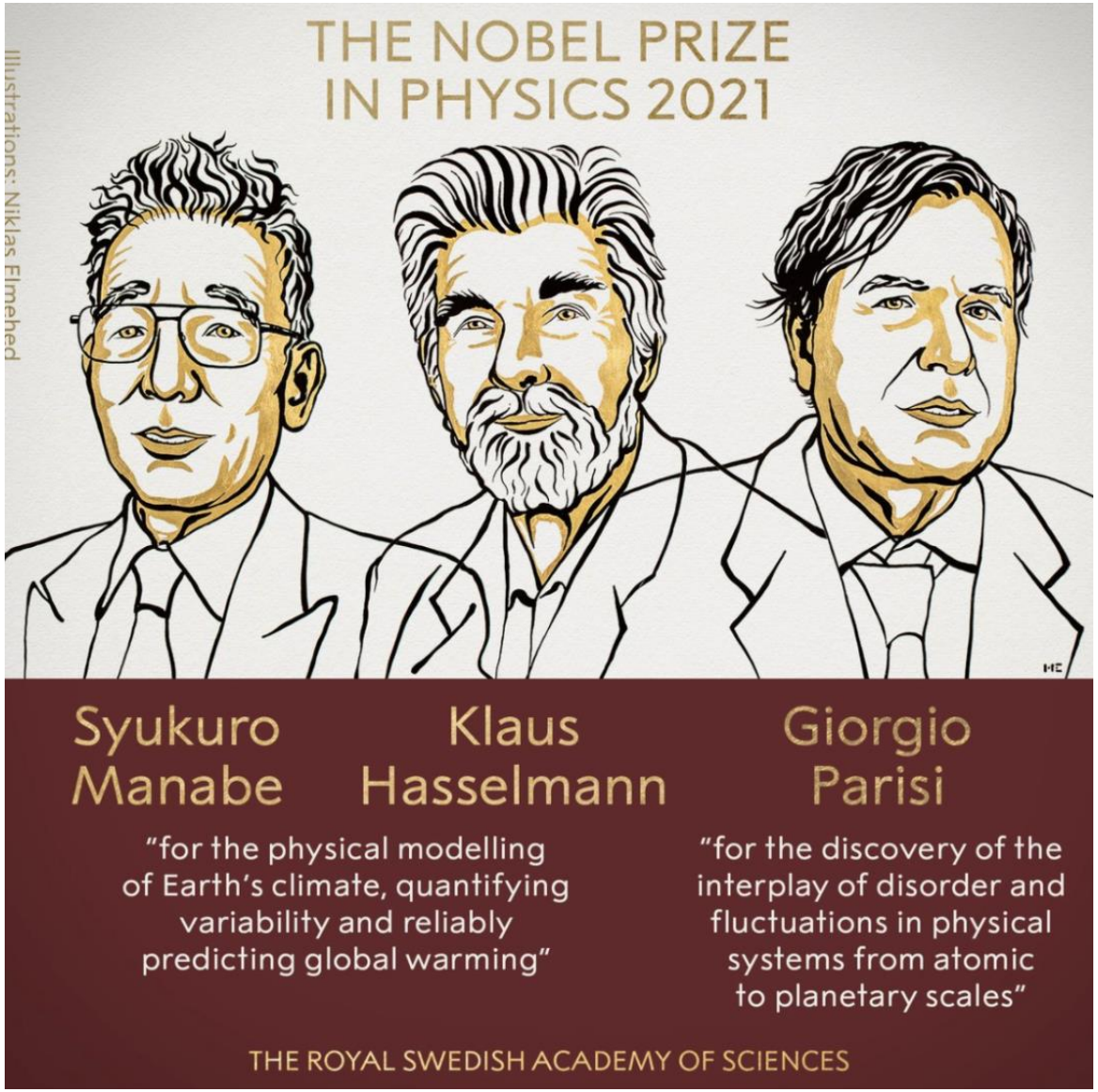


玻尔兹曼机（1985）

自旋玻璃模型

$$\mathrm{H} = -\sum_{<i,j>} J_{ij}\sigma_i\sigma_j$$

凝聚态物理 for AI



乔治·帕里西（Giorgio Parisi）获得2021年诺贝尔物理学奖最主要的工作是“发现了从原子到行星尺度的物理系统中无序和波动的相互作用”。

其中最主要的工作是1980年左右一系列对自旋玻璃的研究工作，他提出了复本对称破缺的概念并将其应用到Sherrington-Kirkpatrick自旋玻璃模型中，给出了平衡态的解。

他的工作对与理解神经网络的复杂行为和动力学特性，例如神经网络中的信息存储、检索机制和神经网络的优化都有重要的意义。

凝聚态物理 for AI

伊辛模型 $$H = -J\sum_{<i,j>}\sigma_i\sigma_j - h\sum_i \sigma_i$$

模型：它假设整个体系可以分为分立的格点，每个格点具有一定的自旋。整个体系的性质主要由相邻格点之间的自旋交换相互作用和每个格点上自旋受外磁场的作用决定。

背景：19 世纪末，物理学家已观察到铁磁体（如铁、镍）在高温下会失去磁性，低温下恢复磁性，但无法从微观层面解释。当时统计力学已能描述理想气体等简单系统，但面对磁体材料这样的“大量粒子通过相互作用形成集体行为”的复杂系统，缺乏简洁的数学模型。

历史：1920年，Ernst Ising在其博士论文（在导师Wilhelm Lenz的指导下）提出，并实现了一维模型的求解。1944年，昂萨格完成了二维模型的求解。1952年，杨振宁、李政道 基于伊辛模型的研究提出李-杨零点理论。

凝聚态物理 for AI

自旋玻璃模型 $$H = -\sum_{<i,j>} J_{ij}\sigma_i\sigma_j$$

自旋玻璃模型是凝聚态物理中描述**无序磁性系统**的经典模型。

自旋玻璃：合金中由于杂质的存在导致相邻自旋间的交换相互作用是**随机且竞争的**，这种“相互作用竞争”使系统无法形成规则有序结构，低温下呈现独特的“玻璃态”（类似玻璃的非晶无序，无长程磁有序）。

自旋玻璃的研究始于 20 世纪 60 年代末 70 年代初。

1970 年，Harry Coles首先用“自旋玻璃”一词来描述稀释合金 AuCo 的特殊磁性。

同年，Philip W. Anderson也用自旋玻璃从理论上说明 CuMn 合金的特殊磁性。

AI与凝聚态物理

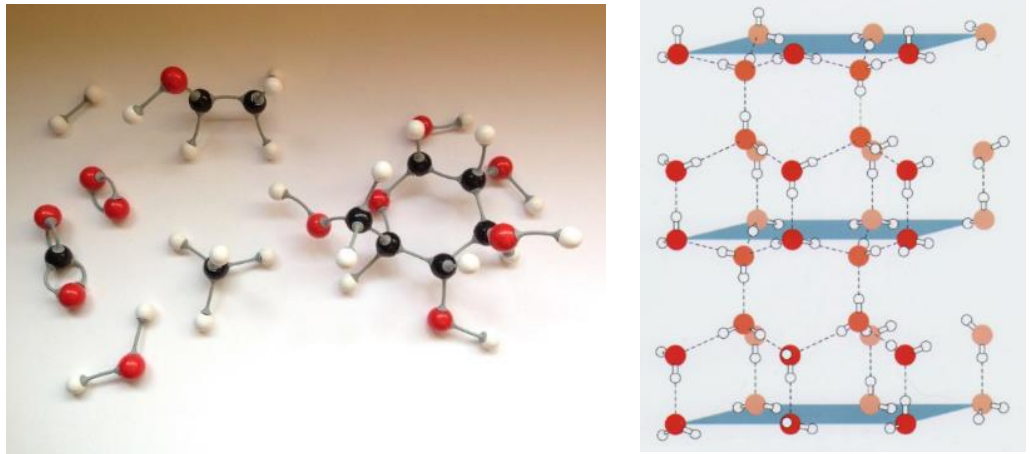
从

凝聚态物理 for AI

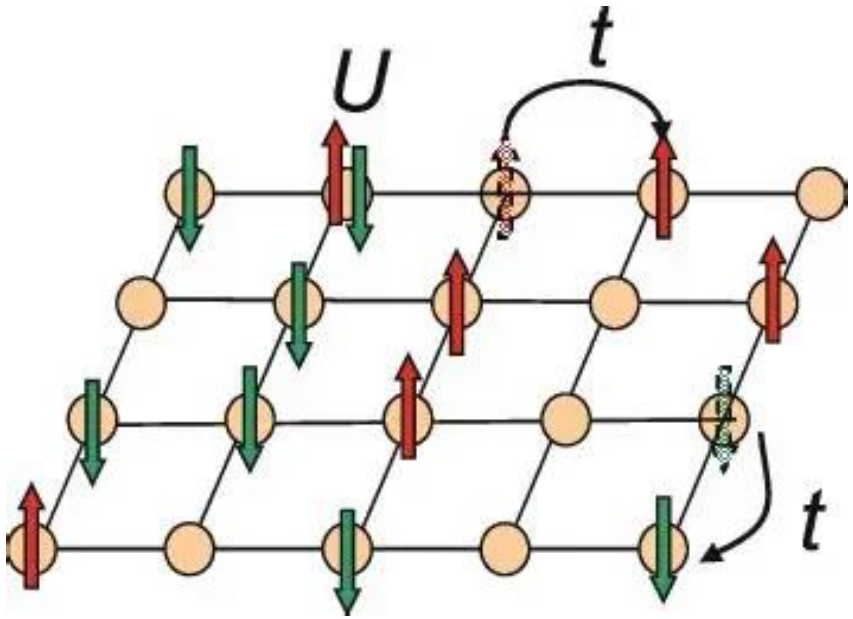
到

AI for 凝聚态物理

凝聚态物理的前沿

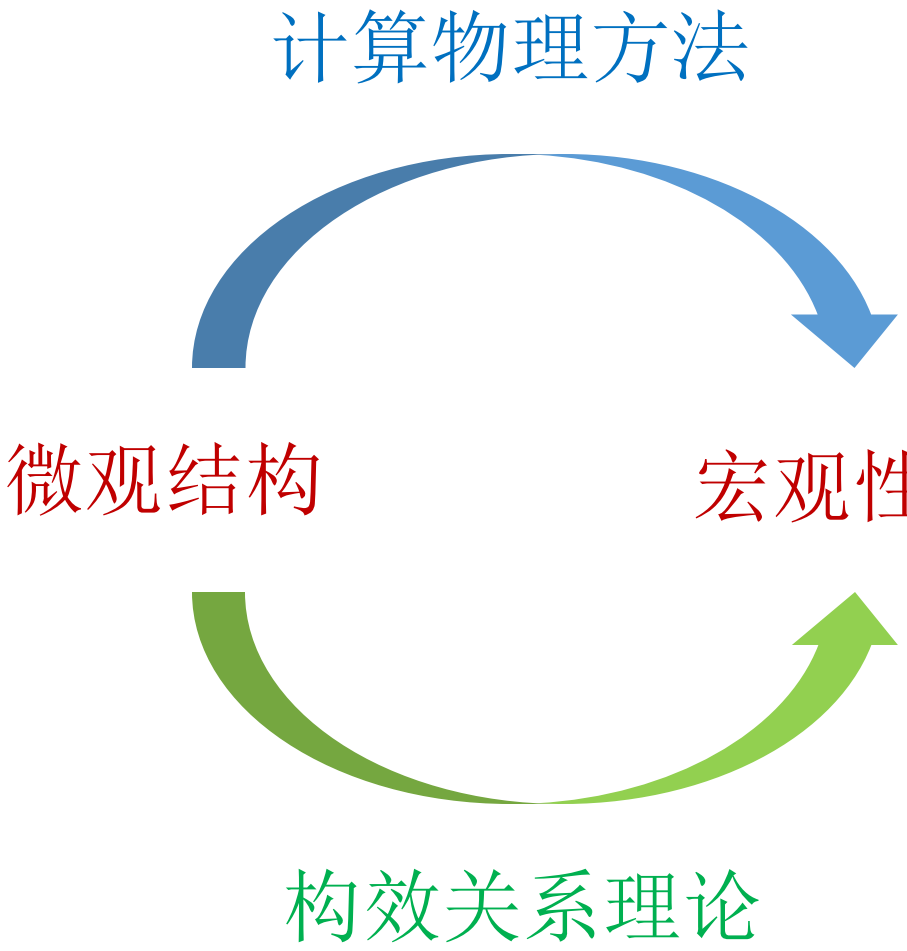


由具体原子组成的真实物质体系



量子多体模型

AI for 凝聚态物理



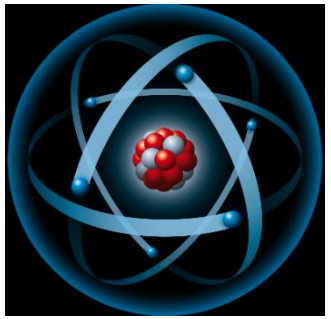
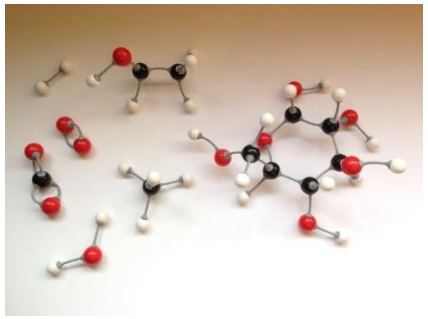
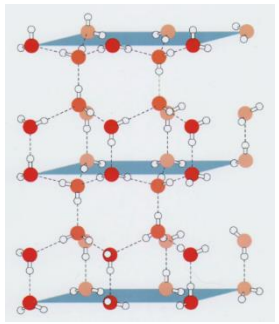
赋能

- 大数据
- 监督式学习
- 非监督式学
- 符号回归
- 深度学习
- 生成模型
- 强化学习
- 大语言模型

内容提纲

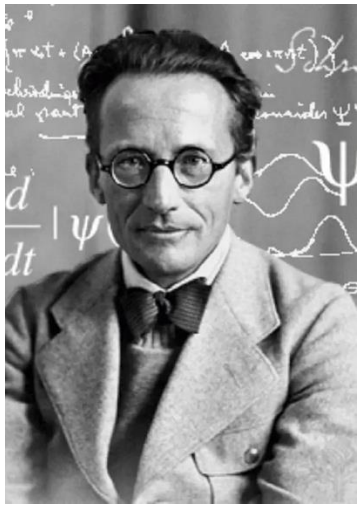
1. AI for 第一性原理计算
   A. 深度学习波函数方法
   B. 深度学习密度泛函
2. AI for 分子动力学模拟
   A. 机器学习力场
   B. 降维与聚类
3. AI for 构效关系探索

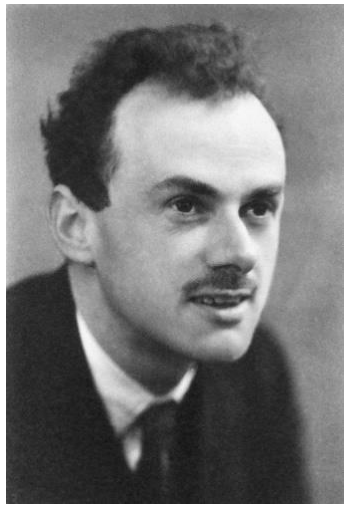
第一性原理计算

$$i\hbar\frac{\partial\psi}{\partial t} = \hat{H}\psi$$

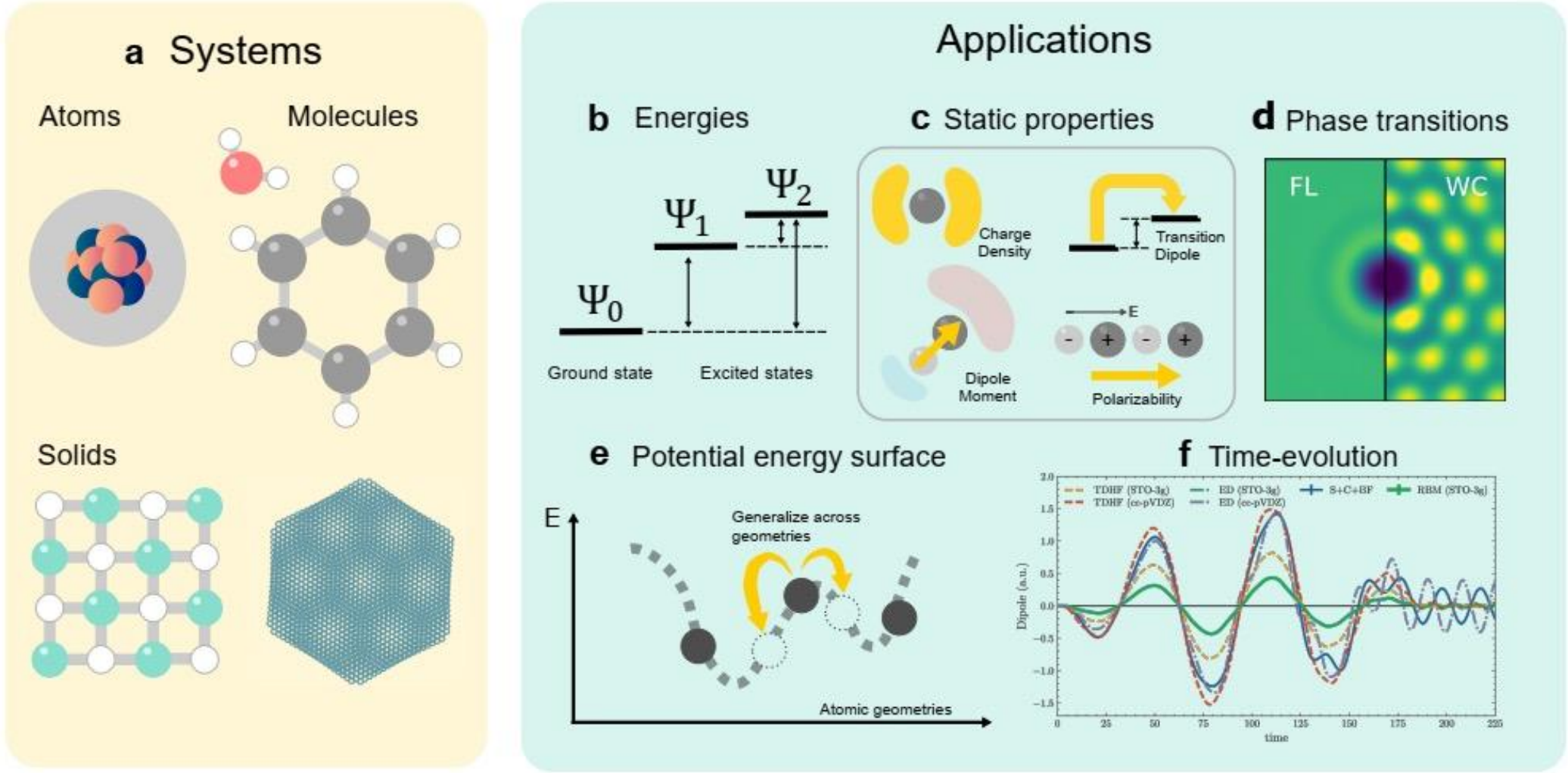

Werner Heisenberg


Erwin Schrödinger


Paul Dirac

The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.

第一性原理计算的应用


a Systems
Atoms
Molecules
Solids
Applications
b Energies
Ψ_0
Ψ_1
Ψ_2
Ground state
Excited states
c Static properties
Charge Density
Transition Dipole
Dipole Moment
E
Polarizability
d Phase transitions
FL
WC
e Potential energy surface
E
Generalize across geometries
Atomic geometries
f Time-evolution
TDHF (STO-3g)
TDHF (cc-pVDZ)
ED (STO-3g)
ED (cc-pVDZ)
S+C+BF
RBM (STO-3g)
Dipole (a.u.)
time

第一性原理计算

$$\hat{H} = -\frac{1}{2}\sum_{i}^{N_e}\nabla_i^2 - \frac{1}{2}\sum_{I}^{N_n}\nabla_I^2 - \sum_{i}^{N_e}\sum_{I}^{N_n}\frac{Z_I}{r_{iI}} + \frac{1}{2}\sum_{i\neq j}^{N_e}\frac{1}{r_{ij}} + \frac{1}{2}\sum_{I\neq J}^{N_n}\frac{Z_I Z_J}{r_{IJ}}$$

Born Oppenheimer Approximation

$$\hat{H} = \hat{H}_e(R) + \hat{H}_R(r)$$

$$\hat{H}_R = -\frac{1}{2}\sum_{I}^{N_n}\nabla_I^2 + V_{PES}(R)$$

$$\hat{H}_e(R) = -\frac{1}{2}\sum_{i}^{N_e}\nabla_i^2 + \frac{1}{2}\sum_{i\neq j}^{N_e}\frac{1}{r_{ij}} + V_{ext}(r,R)$$

第一性原理计算的核心问题：
电子结构（电子哈密顿量求解）

注：超越玻恩-奥本海默的“全量子化”计算也是凝聚态物理的前沿

第一性原理计算

The Nobel Prize in Chemistry 1998

for his development of the density-functional theory

密度泛函理论

求“电子密度分布”

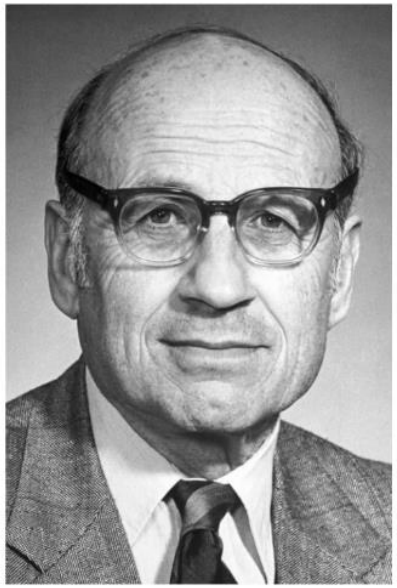


Photo from the Nobel Foundation archive.

Walter Kohn

Prize share: 1/2

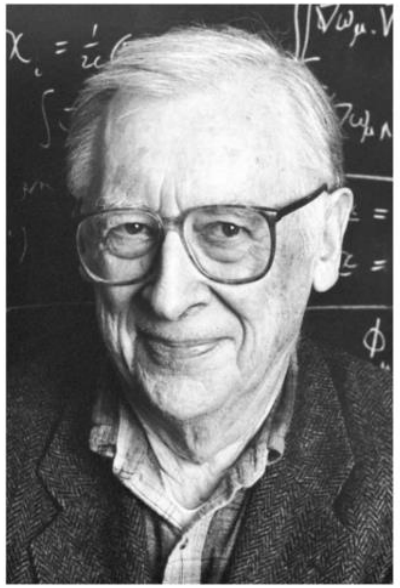


Photo from the Nobel Foundation archive.

John A. Pople

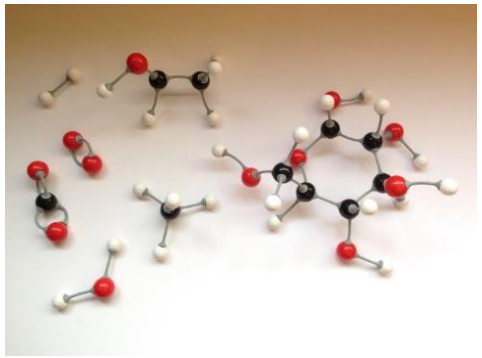
Prize share: 1/2

for his development of computational methods in quantum chemistry

量子化学方法

求“薛定谔方程的波函数”

（确定性）求薛定谔方程的波函数



$$\hat{H}\psi(r;R) = E\psi(r;R)$$

$$\hat{H} = -\frac{1}{2}\sum_{i}^{N_e}\nabla_i^2 - \sum_{i}^{N_e}\sum_{I}^{N_n}\frac{Z_I}{r_{iI}} + \frac{1}{2}\sum_{i\neq j}^{N_e}\frac{1}{r_{ij}}$$

Hartree-Fock

$$\Psi_{HF} = \frac{1}{\sqrt{N!}}\det\begin{vmatrix} \psi_1(r_1) & \psi_2(r_1) & \cdots & \psi_N(r_1) \\ \psi_1(r_2) & \psi_2(r_2) & \cdots & \psi_N(r_2) \\ \cdots & \cdots & \cdots & \cdots \\ \psi_1(r_N) & \psi_2(r_N) & \cdots & \psi_N(r_N) \end{vmatrix}$$

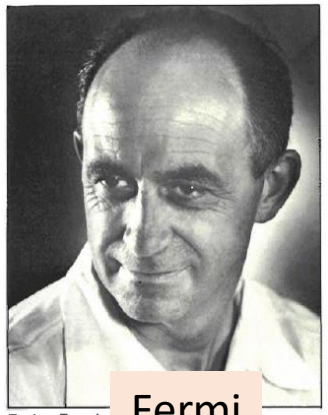
post Hartree Fock

$$\Psi_{exact} = \sum_{J=1}^{L} c_J \Psi_J$$

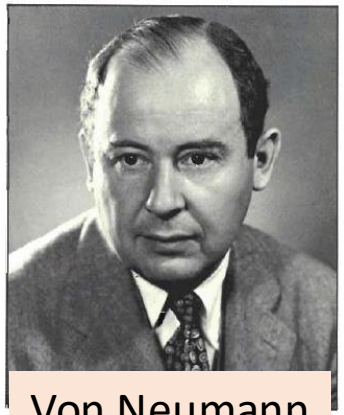
微扰法，耦合簇，组态相互作用

量子蒙特卡洛：（随机性）求波函数

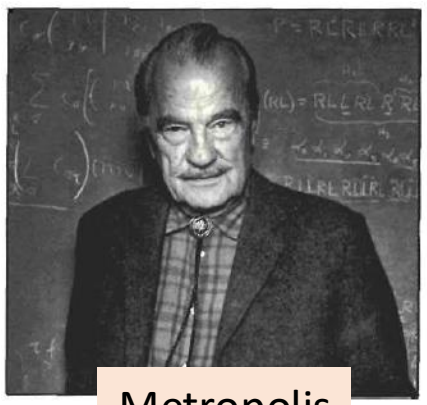
1949, Metropolis and Ulam described the idea applying Monte Carlo methods for solving Schrödinger equation.



Fermi


Von Neumann

Ulam


Metropolis

Let us indicate now how other equations could be dealt with in a similar manner. The first, purely mathematical, step is to transform the given equation into an equivalent one, possessing the form of a diffusion equation with possible multiplication of the particles involved. For example as suggested by Fermi, the time-independent Schrödinger equation

$$\Delta\psi(x, y, z) = (E - V)\psi(x, y, z)$$

could be studied as follows. Re-introduce time dependence by considering

$$u(x, y, z, t) = \psi(x, y, z)e^{-Et}$$

u will obey the equation

$$\frac{\partial u}{\partial t} = \Delta u - Vu.$$

This last equation can be interpreted however as describing the behavior of a system of particles each of which performs a random walk, i.e., diffuses isotropically and at the same time is subject to multiplication, which is determined by the value of the point function V. If the solution of the latter equation corresponds to a spatial mode multiplying exponentially in time, the examination of the spatial part will give the desired $\psi(x, y, z)$—corresponding to the lowest "eigenvalue" E.

The mathematical theory behind our computational method may be briefly sketched as follows: As mentioned above and indicated by the examples, the process is a combination of stochastic and deterministic flows.[1] In more technical terms, it consists of repeated applications of matrices—like in Markoff chains—and completely specified transformations, e.g., the transformation of phase space as given by the Hamilton differential equations.

量子蒙特卡洛

Initial wavefunction
DFT, HF, etc…

$\Psi_{HF}(r)$

→ Wavefunction ansatz
Slater-Jastrow, etc…

$\Psi_{SJ}(r)$

→ Wavefunction
optimization with VMC

$\Psi_{SJ}^{opt}(r)$

→ Fixed-node DMC

E_0^{DMC}

量子蒙特卡洛中如何“拟设困境”和“符号问题”？

- VMC结果直接依赖于“拟设”
- DMC结果通过节点面间接依赖于“拟设”

以上问题的本质是波函数（和波函数节点面）的表达能力问题？

内容提纲

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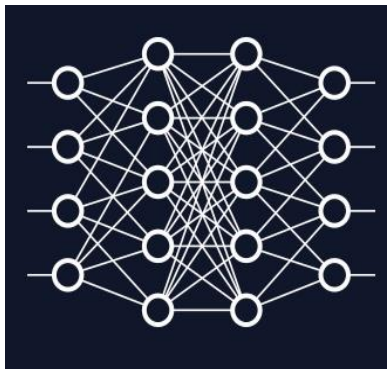
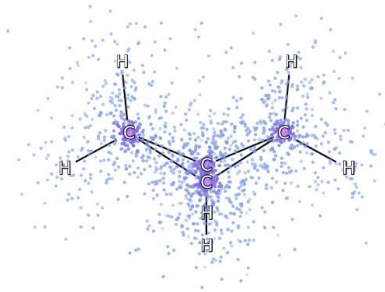
   B. 深度学习密度泛函
2. AI for 分子动力学模拟
   A. 机器学习力场
   B. 降维与聚类
3. AI for 构效关系探索

深度学习波函数

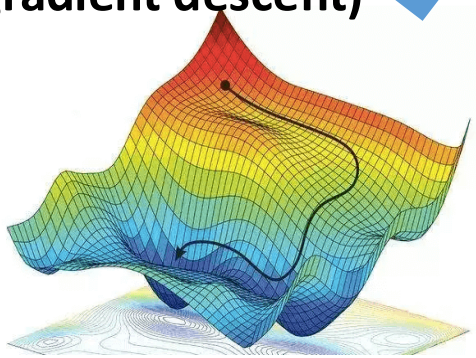


Neural network
wavefunction ansatz

Integration to obtain energy
(Monte Carlo)



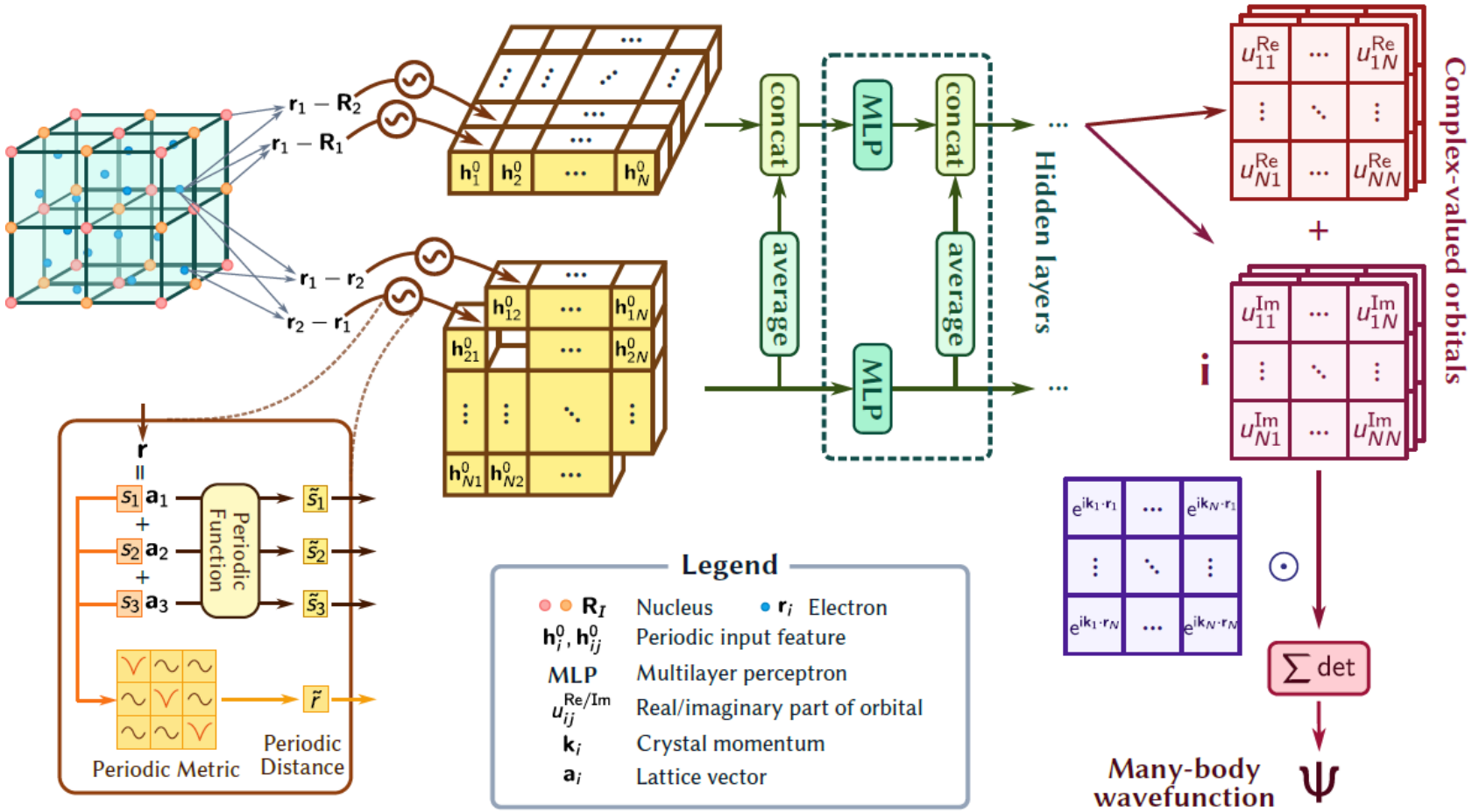
Computing the gradient of wavefunction
parameters to the energy



Wavefunction optimization
(Stochastic gradient descent)

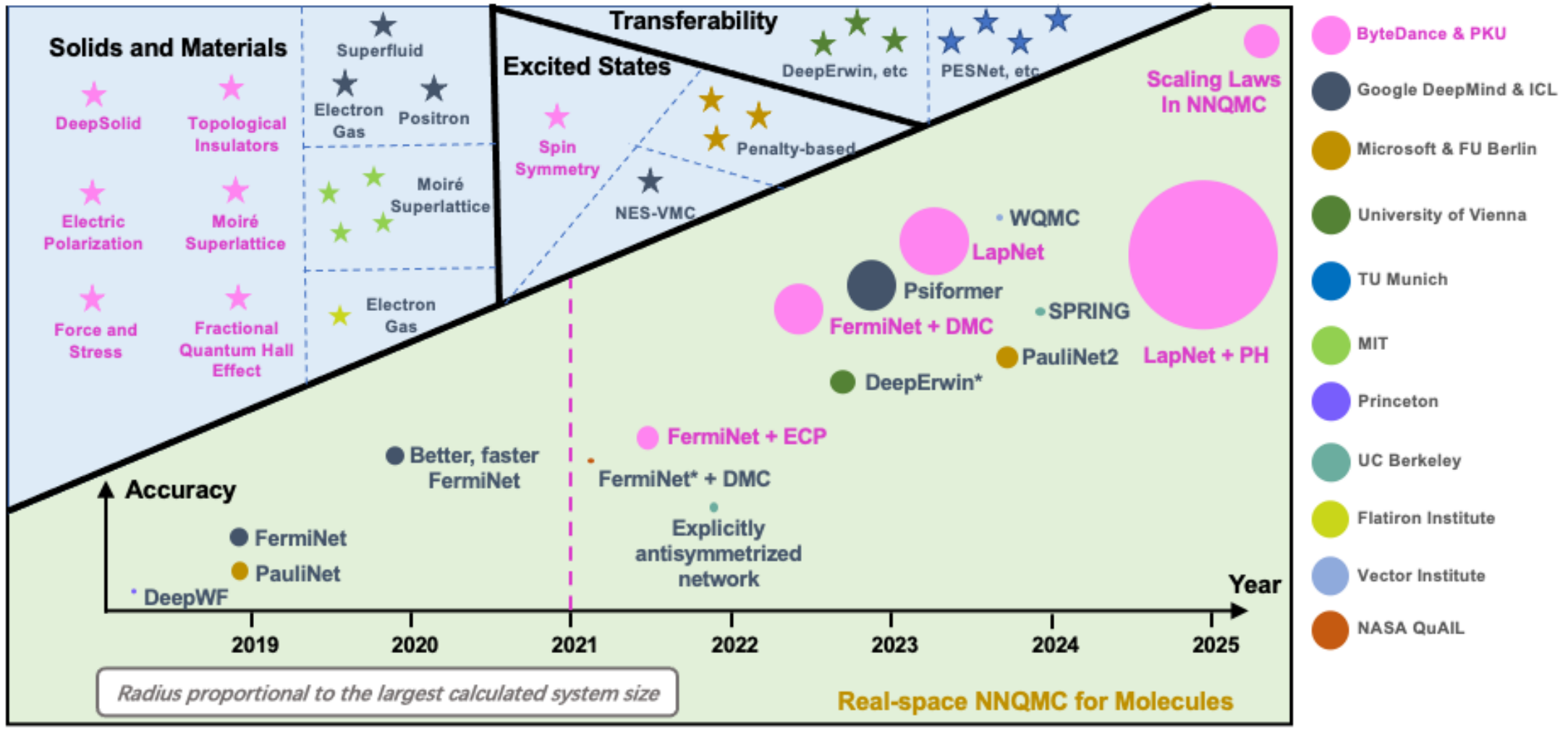
Reinforcement Learning, no external data, energy is the natural loss!

神经网络波函数



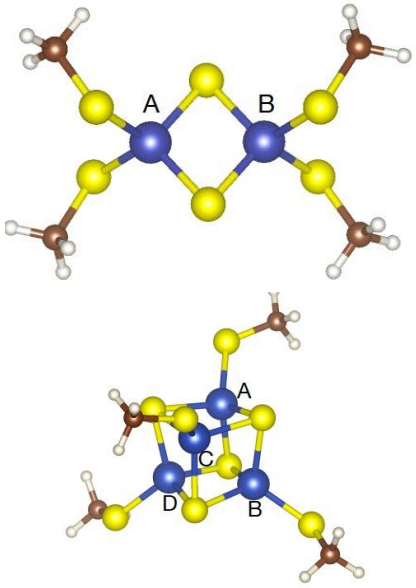
Qian et al. *WIREs Comput Mol Sci* **15**, e70015 (2025)

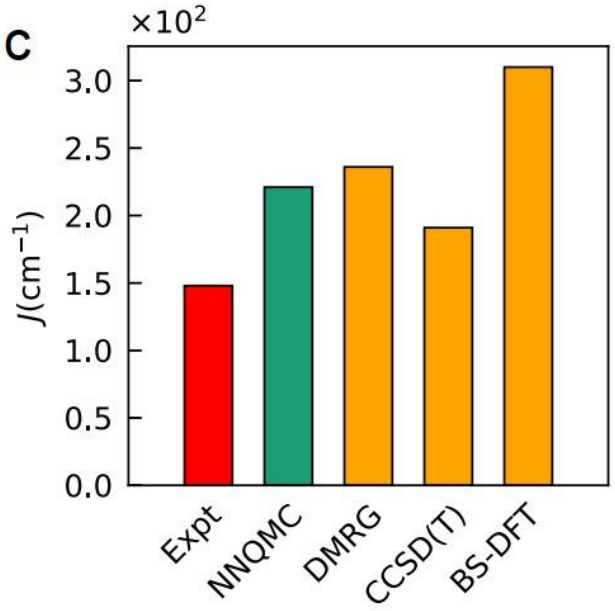
神经网络波函数


Solids and Materials
DeepSolid
Topological Insulators
Electric Polarization
Moiré Superlattice
Force and Stress
Fractional Quantum Hall Effect
Superfluid
Electron Gas
Positron
Moiré Superlattice
Electron Gas
Transferability
Excited States
Spin Symmetry
NES-VMC
Penalty-based
DeepErwin, etc
PESNet, etc
Scaling Laws In NNQMC
WQMC
LapNet
Psiformer
FermiNet + DMC
SPRING
PauliNet2
LapNet + PH
DeepErwin*
FermiNet + ECP
Better, faster FermiNet
FermiNet* + DMC
Explicitly antisymmetrized network
Accuracy
FermiNet
PauliNet
DeepWF
Year
2019
2020
2021
2022
2023
2024
2025
Radius proportional to the largest calculated system size
Real-space NNQMC for Molecules
ByteDance & PKU
Google DeepMind & ICL
Microsoft & FU Berlin
University of Vienna
TU Munich
MIT
Princeton
UC Berkeley
Flatiron Institute
Vector Institute
NASA QuAIL

深度学习波函数方法的应用（分子）

Benchmark energy and magnetic coupling of iron-sulfur clusters

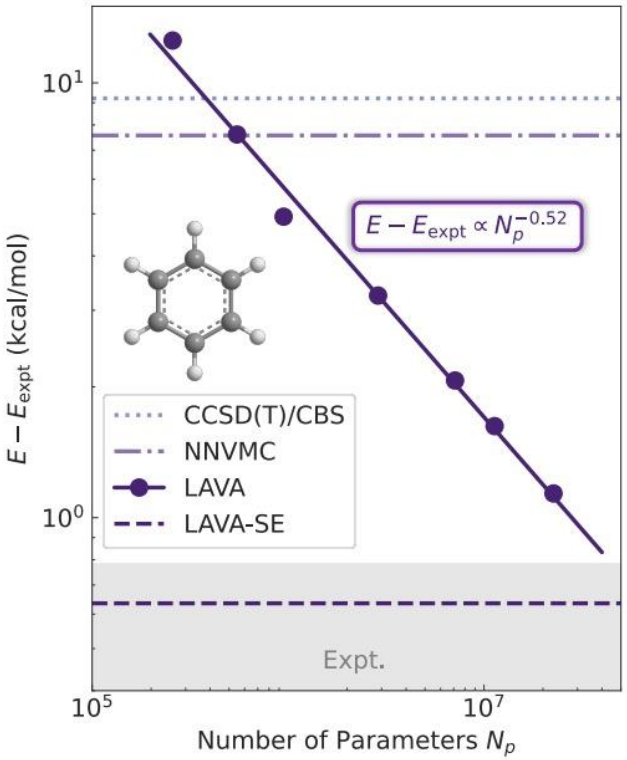




268 electrons (with local Pseudopotential)

Fu et al. arXiv:2505.19909

Approaching neural scaling laws with new optimizer

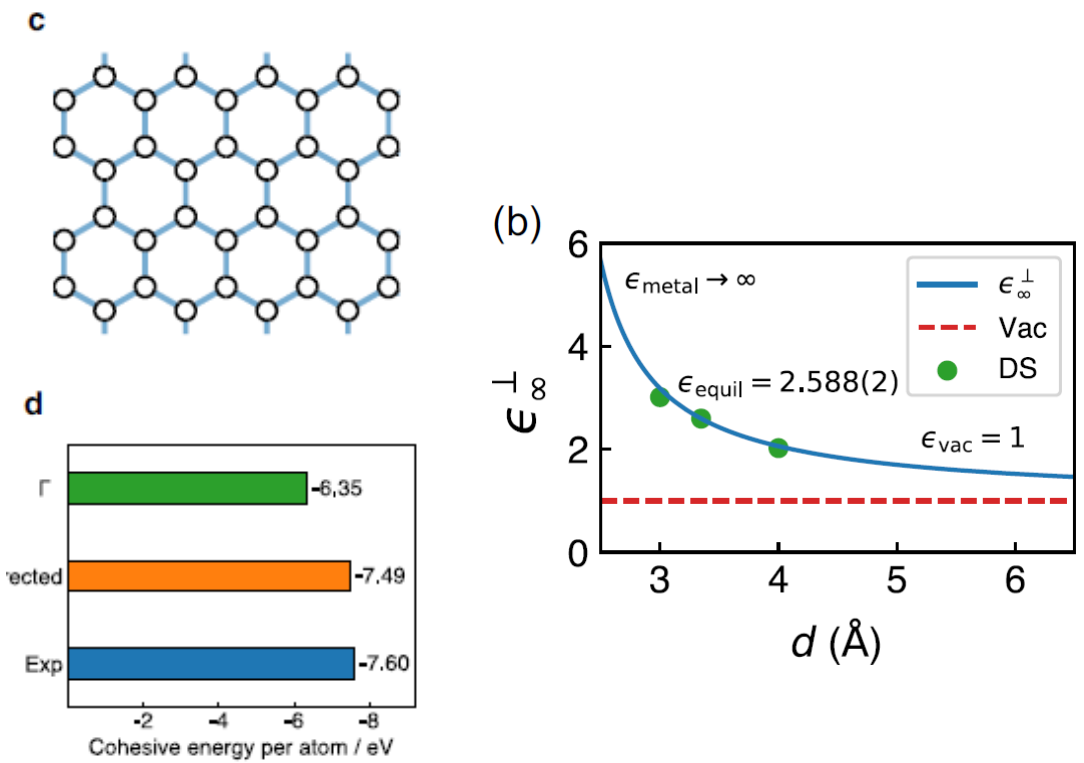


KJ/mol accuracy

Jiang and Wen et al. arXiv:2508.02570

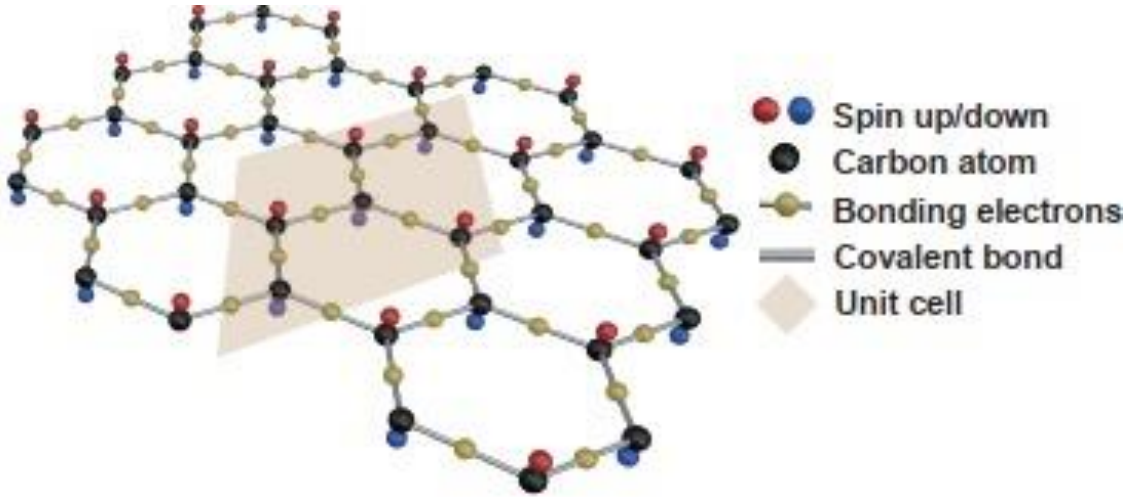
深度学习波函数方法的应用（固体材料）

Benchmark cohesive energy and electric polarization



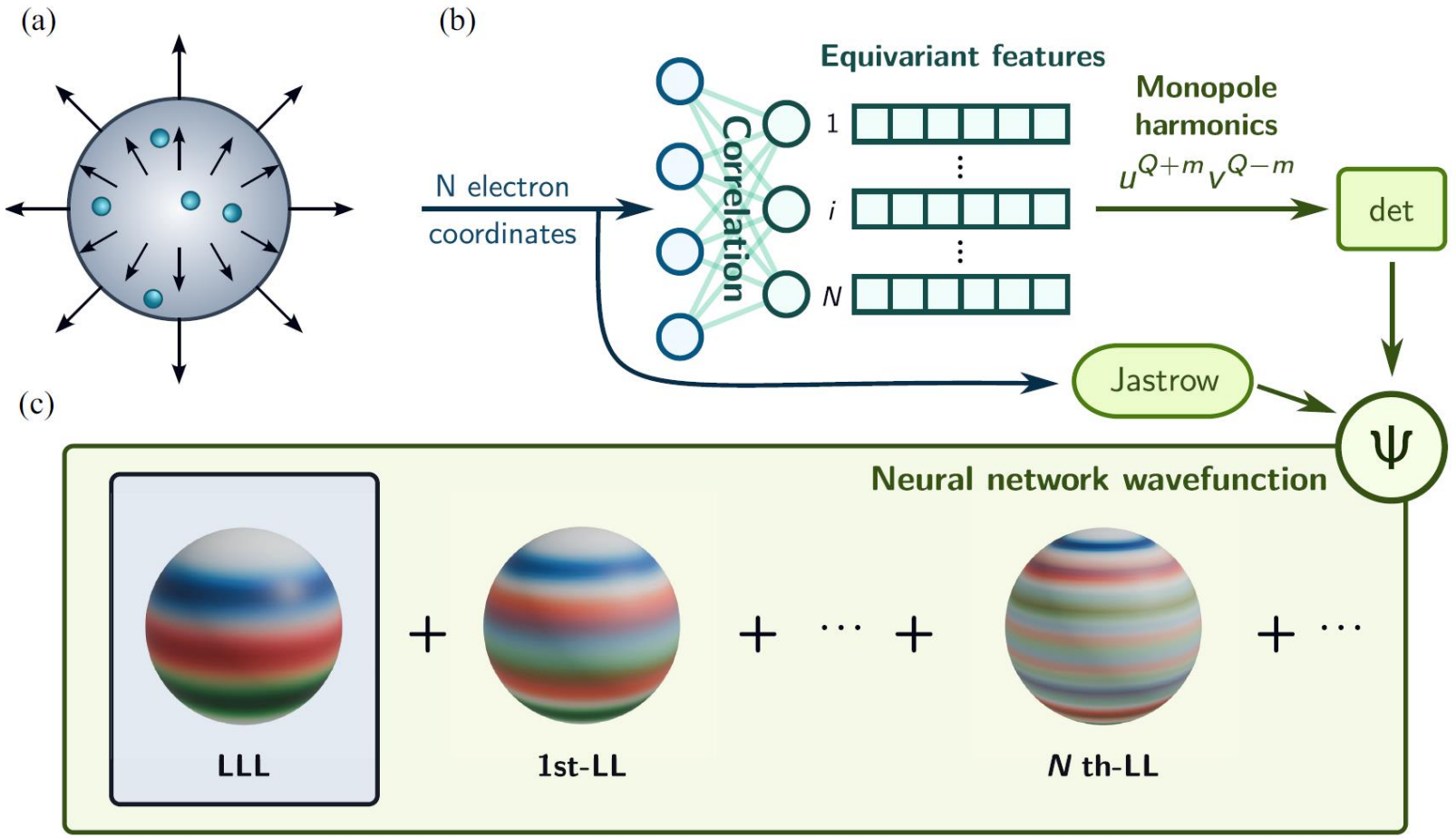
Li, Li, JC, ***Nat. Commun.*** 13, 7895 (2022)
Li, Qian, JC, ***Phys. Rev. Lett.*** *132, 176401* (2024)

Valence bond structure of graphene: a particle view of many-body electronic structure with neural network wavefunction.



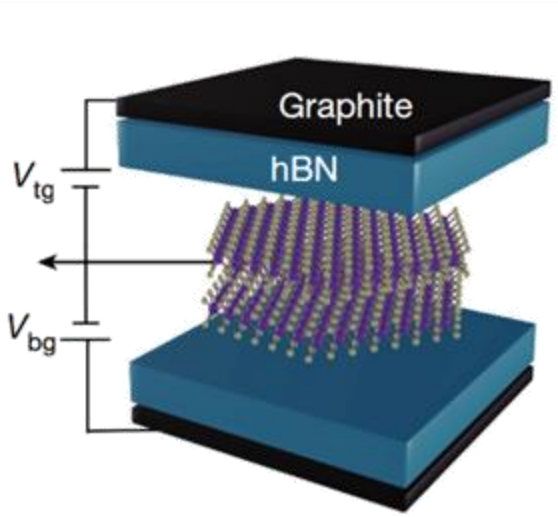
Wang, Fu, Li, Ren, JC, arXiv 2508.13751 (2025)

深度学习波函数方法的应用（量子霍尔效应）

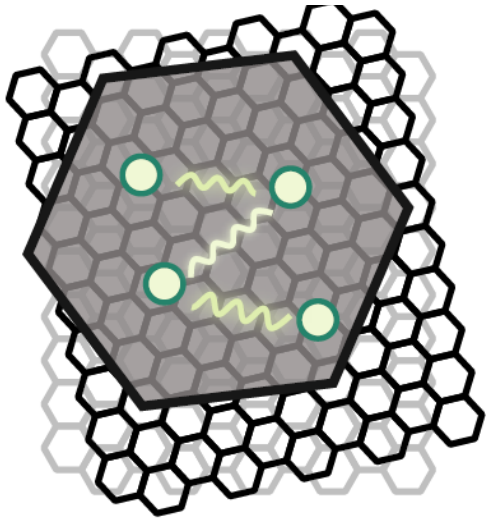


Qian,..., JC, PRL 134 176503 (2025)

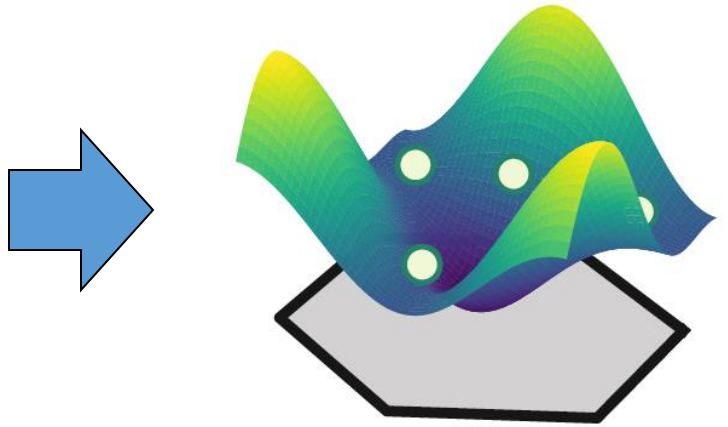
深度学习波函数方法的应用（关联拓扑态）



moiré lattice device



Electrons in moiré materials



Electrons in moiré potential

$$\hat{H} = \sum_i \left[-\frac{\Delta_i}{2m^*} + V_M(\mathbf{r}_i) \right] + \frac{1}{2} \sum_{i \neq j} \frac{1}{\epsilon |\mathbf{r}_i - \mathbf{r}_j|} ,$$

$$V_M(\mathbf{r}) = -2V \sum_{i=1}^{3} \cos(\mathbf{b}_i \cdot \mathbf{r} + \phi) .$$

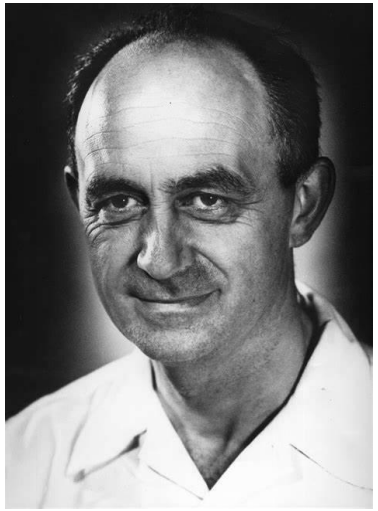
内容提纲

1. AI for 第一性原理计算
   A. 深度学习波函数方法
   B. 深度学习密度泛函
2. AI for 分子动力学模拟
   A. 机器学习力场
   B. 降维与聚类
3. AI for 构效关系探索

密度泛函

Thomas Fermi model, 1927

Llewellyn Thomas



Enrico Fermi

体系能量是电子密度的泛函

$$E_{TF}[n(r)] = \frac{3}{10}(3\pi^2)^{2/3}\int n^{5/3}(r)\,dr - Z\int \frac{n(r)}{r}\,dr + \frac{1}{2}\iint \frac{n(r_1)n(r_2)}{r_{12}}\,dr_1 dr_2$$

密度泛函理论

Walter Kohn

Pierre Hohenberg

Lu Jeu Sham

Hohenberg Kohn Theorems, 1964

1. 薛定谔方程解的基态能量是电子密度的唯一泛函；

$$E = E[\rho(r)]$$

2. 最小化能量泛函的电子密度是薛定谔方程的解对应的真实的电子密度；

$$\rho_{true}(r) = \arg\min E[\rho(r)]$$

Kohn Sham equation, 1965

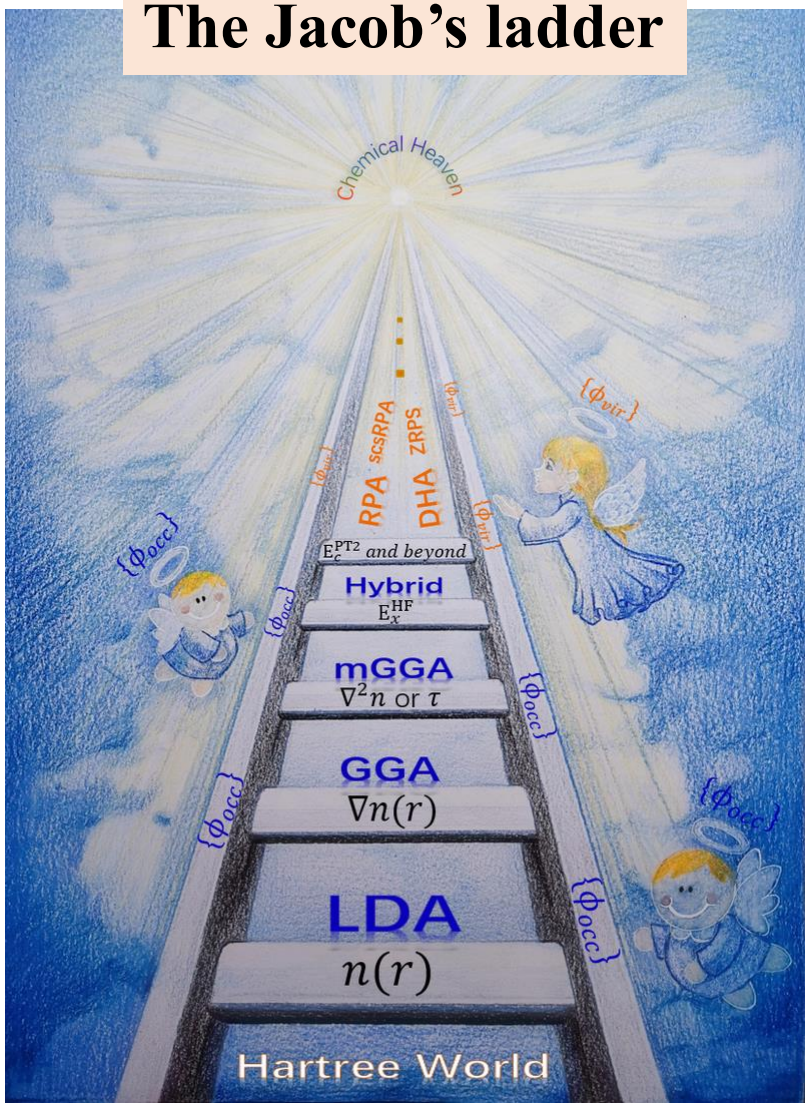
$$\left\{-\frac{\hbar^2}{2m}\nabla^2 + V_{ext} + V_H + V_{xc}\right\}\psi_i(r) = \varepsilon_i\psi_i(r)$$

$\psi_i(r)$: Kohn-Sham orbital
ε_i : orbital energy

V_{xc} : exchange correlation potential

深度学习密度泛函（交换关联泛函）

The Jacob's ladder



WIREs Computational Molecular Science 2020, 11 (1)

如何得到严格的交换关联泛函？

$$E_{xc}[\rho(r), \psi_i(r), \ldots] \qquad V_{xc} = \frac{\delta E_{XC}}{\delta n(r)}$$

理论设计

- 考虑理论的约束
- 特定情况下满足的解析形式
- 特殊体系的严格解

数据拟合

- 实际体系的更精确的计算结果

（监督式）机器学习：交换关联泛函的拟合

深度学习密度泛函（交换关联泛函）

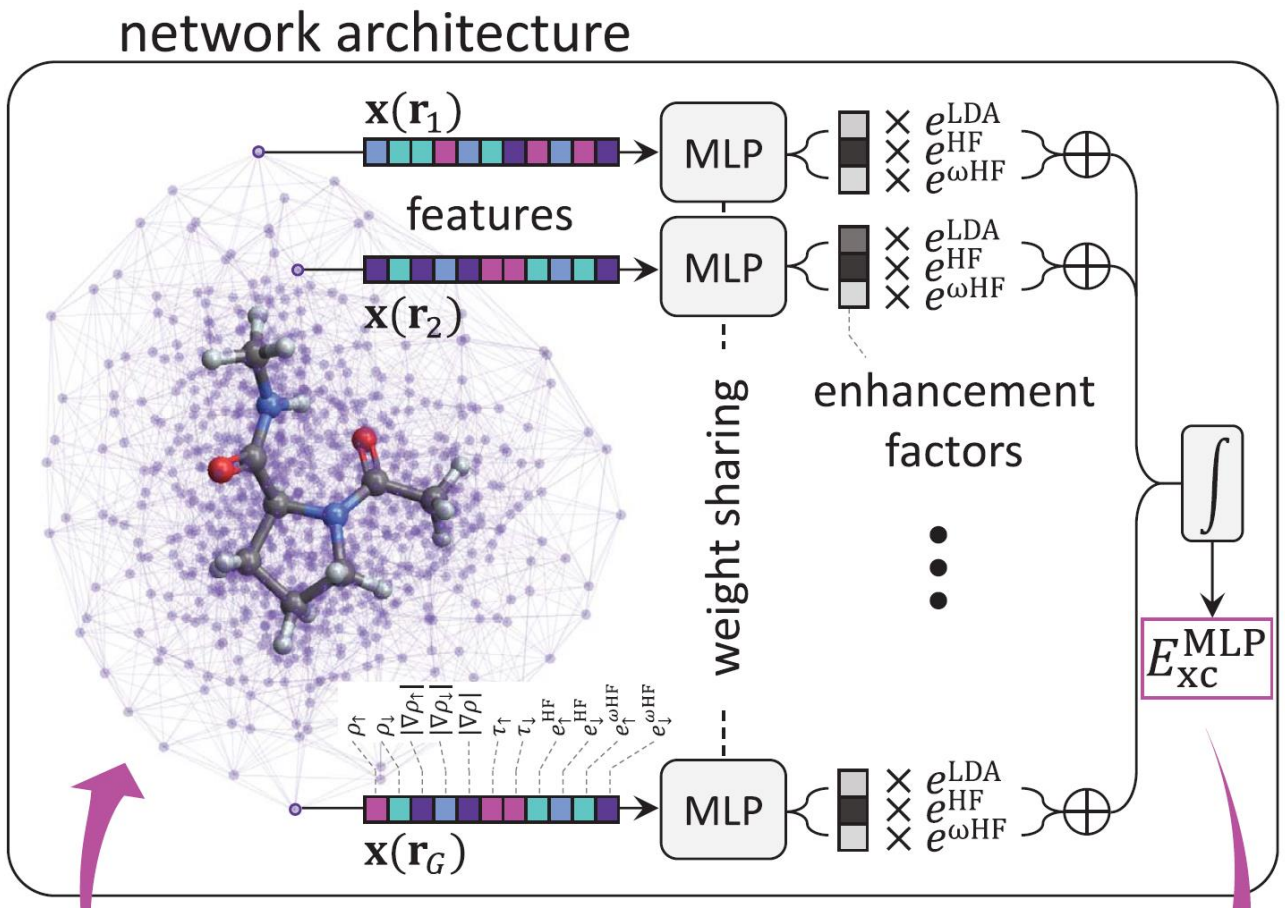
MLP: multilayer perceptron

Hybrid functional

$$E_{\mathrm{xc}}^{\mathrm{DM21}} = E_{\mathrm{xc}}^{\mathrm{MLP}} + E_{\mathrm{D3(BJ)}}.$$

$$E_{\mathrm{xc}}^{\mathrm{MLP}}[\rho] = \int \mathbf{f}_\theta(\mathbf{x}(\mathbf{r})) \cdot \begin{bmatrix} e_{\mathrm{x}}^{\mathrm{LDA}}(\mathbf{r}) \\ e^{\mathrm{HF}}(\mathbf{r}) \\ e^{\omega\mathrm{HF}}(\mathbf{r}) \end{bmatrix} \mathrm{d}^3\mathbf{r}.$$

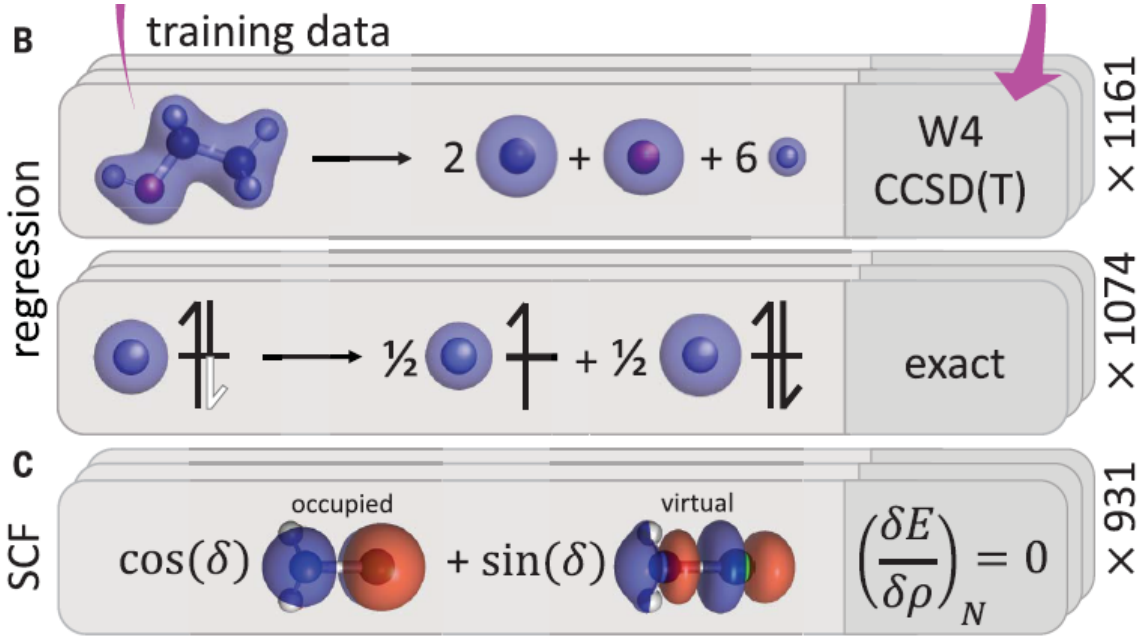
DeepMind: DM21



Kirkpatrick et al., Science 374, 1385–1389 (2021)

深度学习密度泛函（交换关联泛函）

DeepMind: DM21



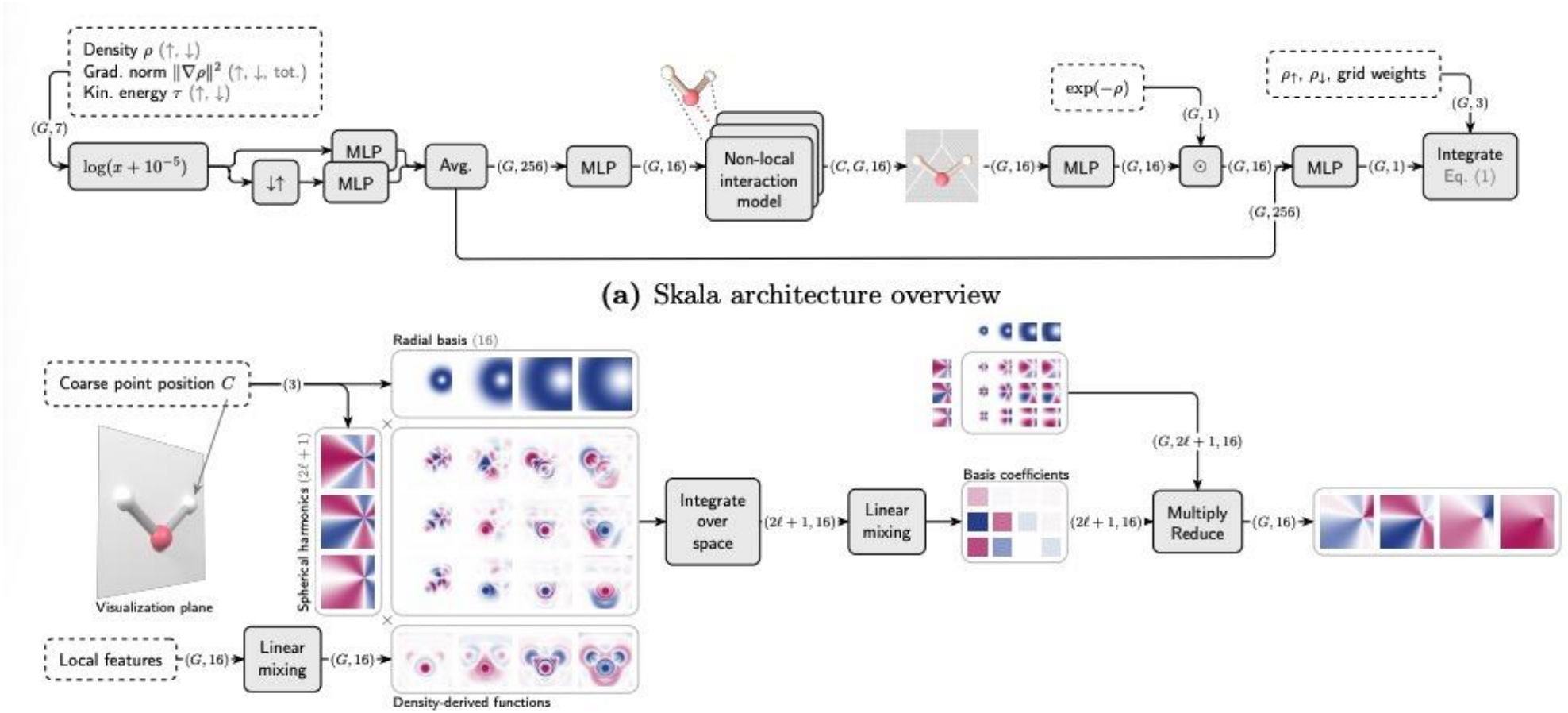
To train the functional, the sum of two objective functions was used: a regression loss for learning the exchange-correlation energy itself and a gradient regularization term that ensured that the functional derivatives can be used in self-consistent field (SCF) calculations after training.

$$\mathcal{L} = \mathbb{E}_r\left[\left(\Delta E_{\mathrm{xc},r}^{\mathrm{DM21}} - \Delta E_{\mathrm{xc},r}^{*}\right)^2\right] + \lambda \mathbb{E}_s\left[\delta E_{\mathrm{SCF},s}^2\right].$$

Kirkpatrick et al., Science 374, 1385–1389 (2021)

深度学习密度泛函（交换关联泛函）

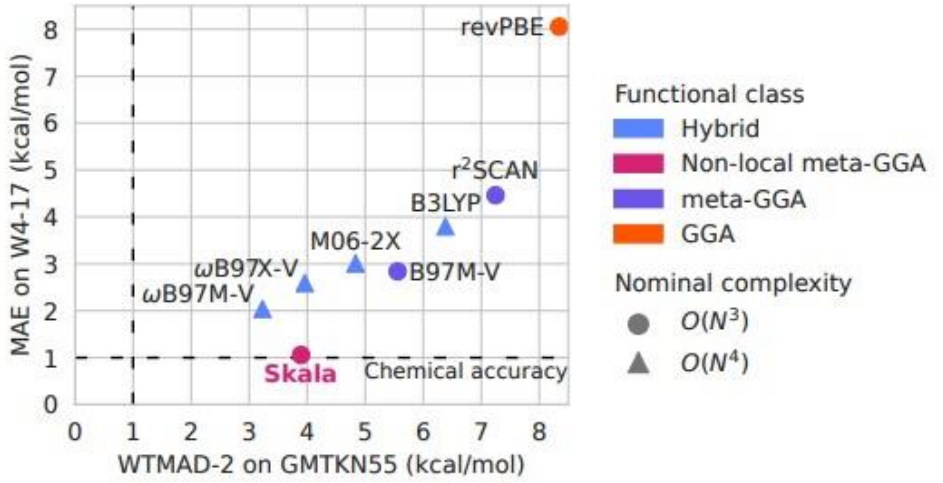
Microsoft: Skala



Luise et al., arXiv:2506.14665 (2025)

深度学习密度泛函（交换关联泛函）

Microsoft: Skala



(a)

	W4-17 (full) [MAE]	W4-17 (single ref.) [MAE]	GMTKN55 [WTMAD-2]
revPBE	8.05	7.22	8.34
r²SCAN	4.46	3.84	7.25
B97M-V	2.84	2.52	5.56
B3LYP	3.80	3.73	6.38
M06-2X	3.01	2.39	4.83
ωB97X-V	2.59	2.14	3.96
ωB97M-V	2.04	1.66	3.23
Skala	1.06	0.85	3.89

(b)

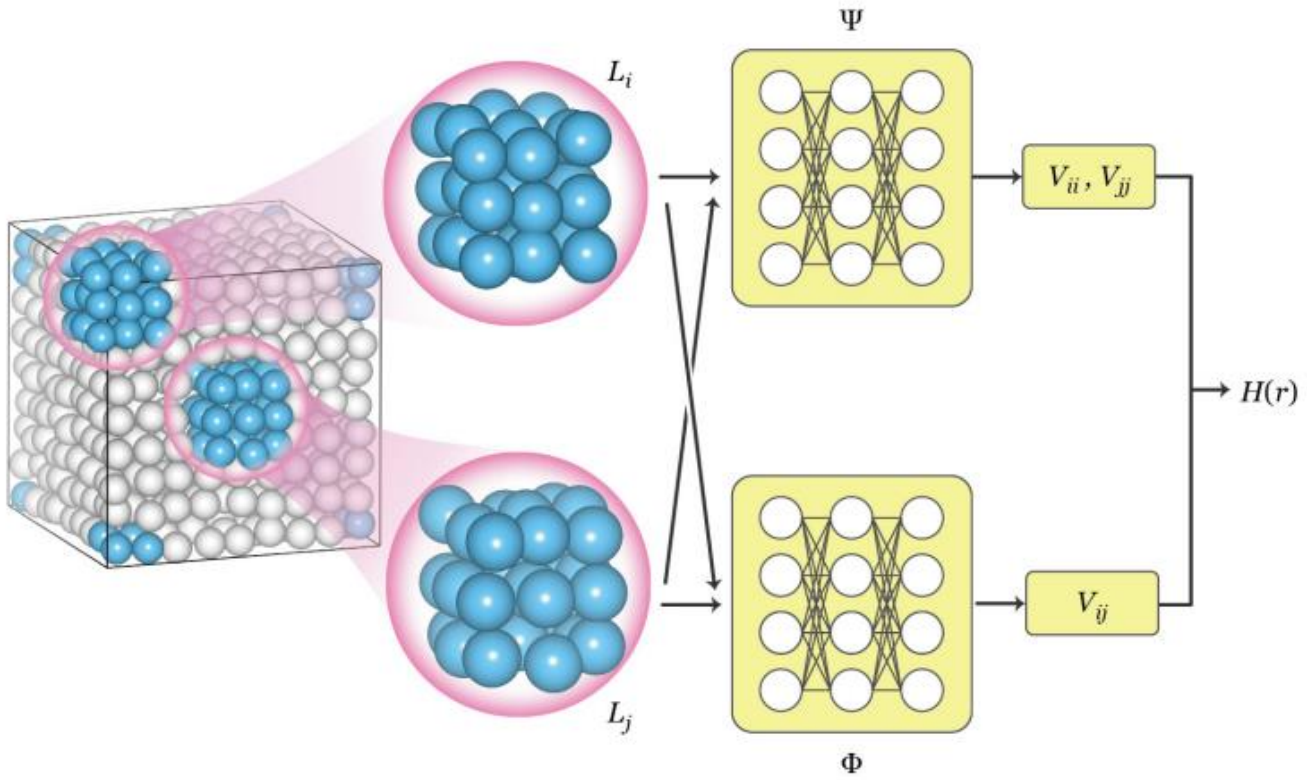
Figure 3: (a): The plot's horizontal axis shows weighted total mean absolute deviation (WTMAD-2) on the GMTKN55[14] test set for general main group thermochemistry, kinetics and non-covalent interactions. The vertical axis shows mean absolute error on the diverse atomization energies test set W4-17[66]. Skala performs similarly to the best-performing hybrid functionals, and reaches near chemical accuracy (1 kcal/mol) on W4-17. (b): Shows the precise errors (in kcal/mol) on W4-17 and GMTKN55, corresponding to the numbers in the plot. For W4-17, the table shows both the MAE on the full set (shown in the plot) as well as on the set of 183 single-reference structures with %TAE[(T)] < 10%.[72] All functionals, including Skala, were evaluated with a D3(BJ) correction, except for those with the VV10[53] correction, indicated with "-V".

Luise et al., arXiv:2506.14665 (2025)

深度学习密度泛函（哈密顿量）

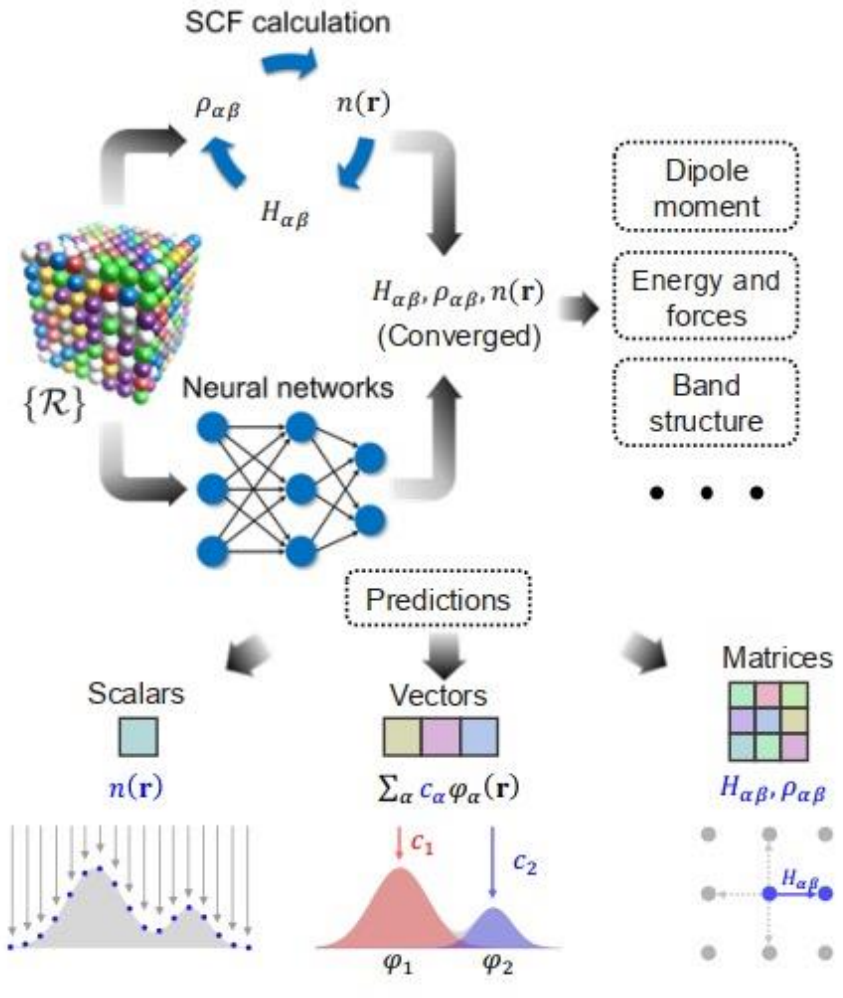
紧束缚（近似）哈密顿量

$$H(\boldsymbol{r}) = \sum_{i \neq j} V_{ij}(\boldsymbol{r}) c_i^{\dagger} c_j + \sum_{i} V_{ii}(\boldsymbol{r}) c_i^{\dagger} c_i + \text{H.c.},$$

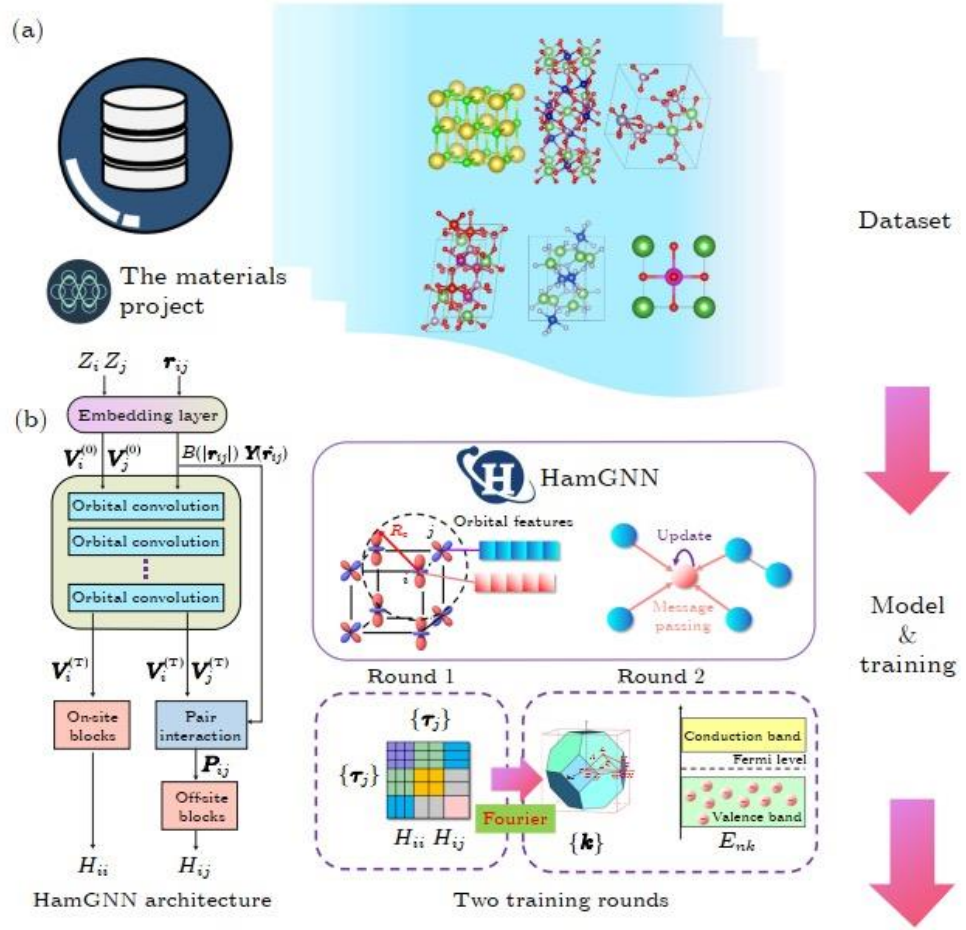


冯济等 Science Bulletin 67, 29-37 (2022)

深度学习密度泛函（哈密顿量）

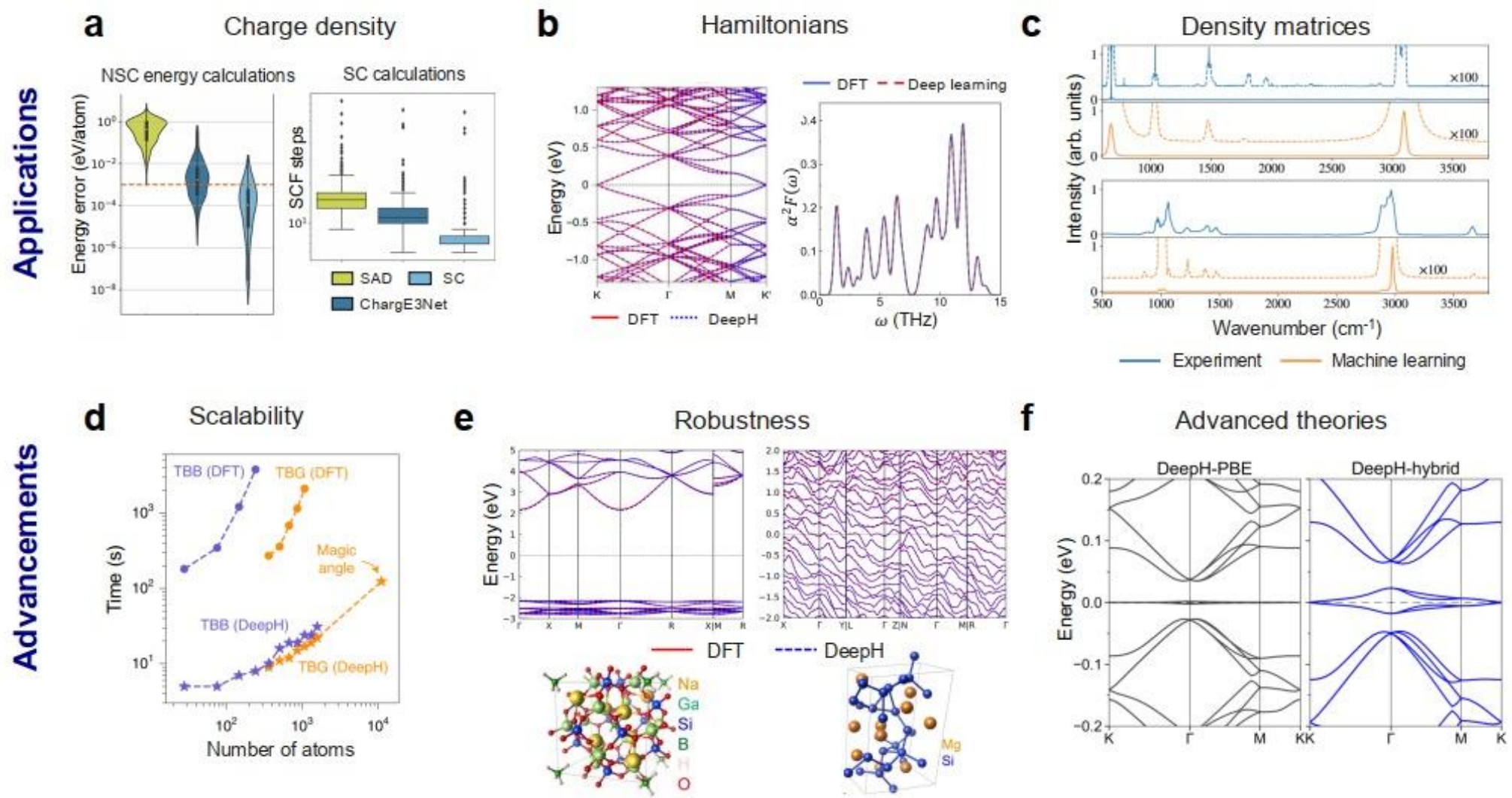


徐勇、段文晖等Nat. Comput. Sci. 2, 367–377 (2022)



向红军、龚新高等Chin. Phys. Lett. 41, 077103 (2024)

深度学习密度泛函（哈密顿量）



小结（1）：AI for 第一性原理计算

1：精度问题

- 深度学习波函数（强化学习）
- 深度学习密度泛函（交换关联泛函）（监督式学习）

2：效率问题

- 深度学习密度泛函（哈密顿量）（监督式学习）

内容提纲

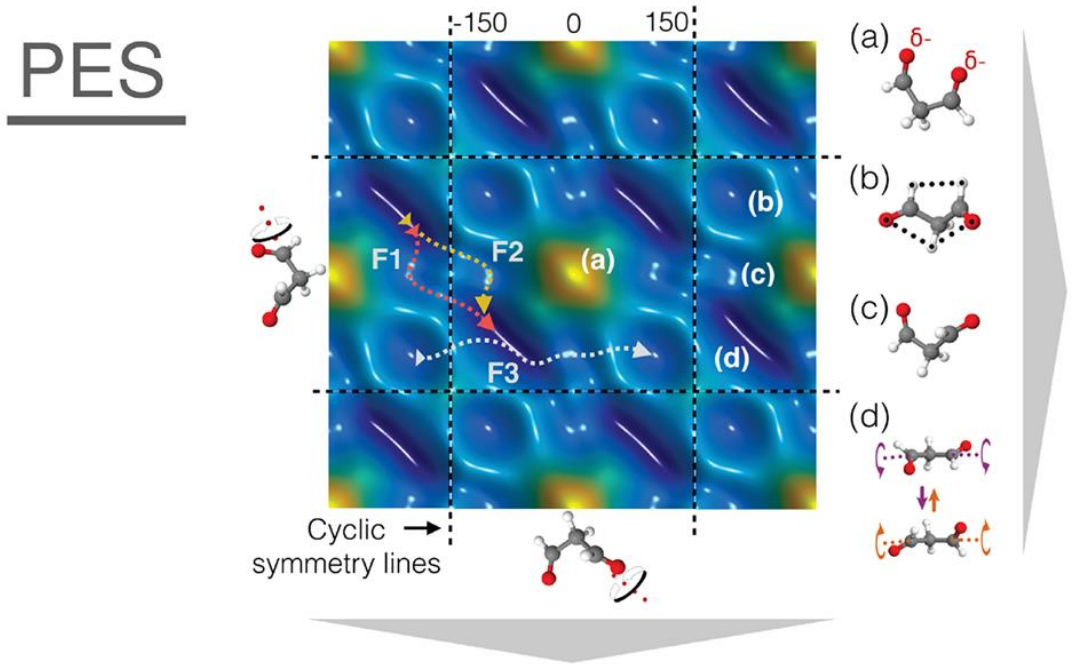
1. AI for 第一性原理计算
   A. 深度学习波函数方法
   B. 深度学习密度泛函
2. AI for 分子动力学模拟
   A. 机器学习力场
   B. 降维与聚类
3. AI for 构效关系探索

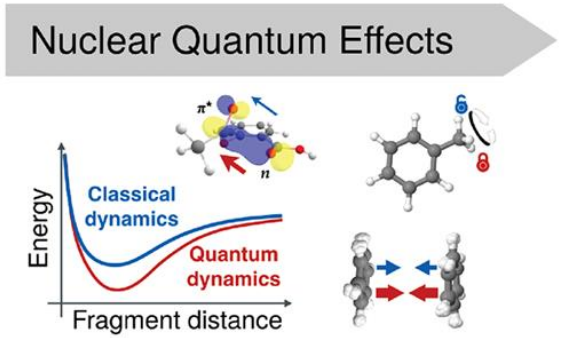
分子动力学（molecular dynamics）

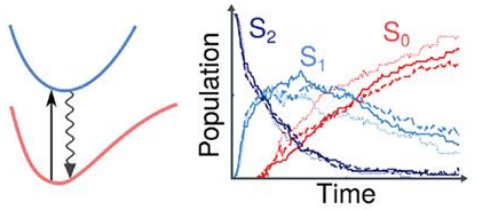
物理过程与势能面

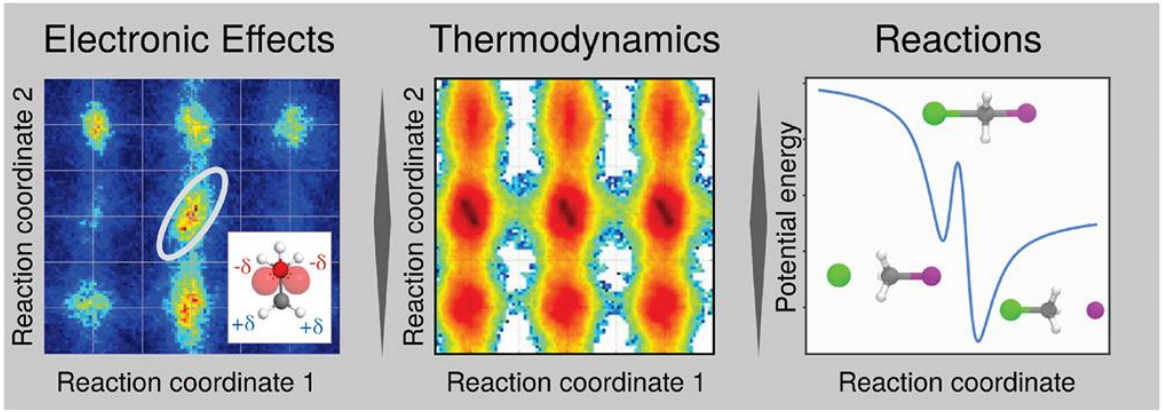
许多重要的物理现象都是关于
实际物质系统的演化过程

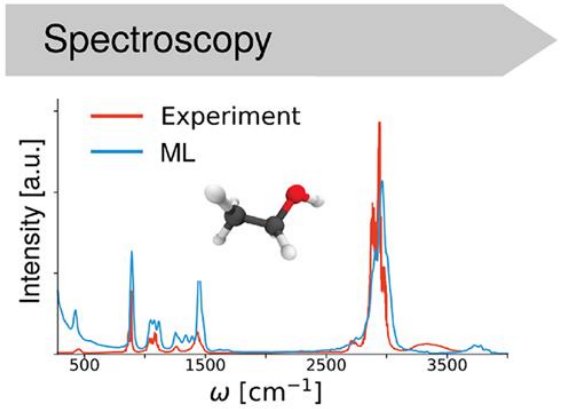
而决定演化过程的归根结底是势能面
Potential Energy Surface (PES)











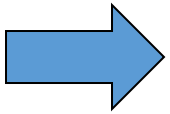
分子动力学（molecular dynamics）

哈密顿方程

$$H(p,q) = \mathrm{T(p)} + \mathrm{V(q)}$$

$$\dot{p} = -\partial_q H(p,q)$$

$$\dot{q} = \partial_p H(p,q)$$



Velocity Verlet算法

$$p_{n-\frac{1}{2}} = p_{n-1} - \frac{\tau}{2}\nabla \mathrm{V}(\mathrm{q_{n-1}})$$

$$q_n = q_{n-1} + \tau \nabla T(p_{n-\frac{1}{2}})$$

$$p_n = p_{n-\frac{1}{2}} - \frac{\tau}{2}\nabla \mathrm{V}(\mathrm{q_n})$$

V(q): 势能面是分子动力学的“动力来源”，来自粒子间相互作用

分子动力学（molecular dynamics）

- In 1955, Fermi, Pasta, Ulam and Tsingou (coding) performed the first simulation on the one dimensional chain of nonlinear oscillators at Los Alamos NL.

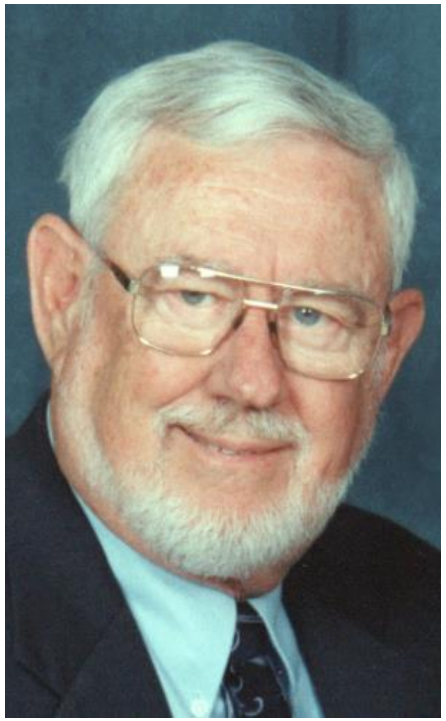
Enrico Fermi; Stanislaw Ulam; John Pasta; Mary Tsingou

分子动力学（molecular dynamics）

- In 1957, Alder and Wainwright at Lawrence Livermore NL carried out molecular dynamics simulations on a hard-sphere system to study the liquid-solid phase transition, which is considered as the first condensed phase molecular dynamics simulation.

"Fathers" of Molecular Dynamics

Berni Alder



Thomas Wainwright

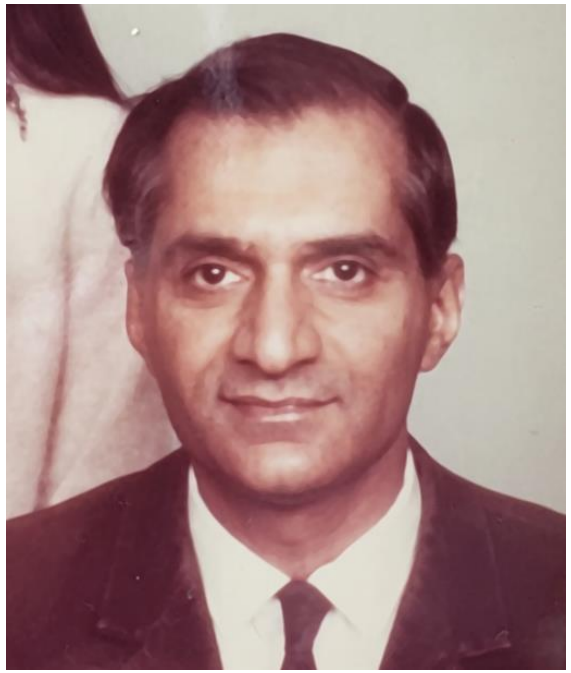
https://www.nature.com/articles/d41586-020-02858-5

分子动力学（molecular dynamics）

- In 1964, Aneesur Rahman at Argonne NL carried out molecular dynamics simulations of argon using Lennard Jones pontential, which is considered as the first example of a realistic system.

“Father” of Molecular Dynamics for real systems

The Aneesur Rahman Prize for Computational Physics is a prize that has been awarded annually by the American Physical Society since 1993. The recipient is chosen for " **outstanding achievement in computational physics research** ". The prize is named after Aneesur Rahman (d. 1987), pioneer of the molecular dynamics simulation method.



Aneesur Rahman

分子动力学（molecular dynamics）

- In 1960s and 1970s, there is a fast development and extension of molecular dynamics.
- Bruce John Berne and coworkers extended molecular dynamics simulations on diatomic liquids.
- Frank Stillinger and Aneesur Rahman performed first molecular dynamics simulations of liquid water.
- Martin Karplus and coworkers applied molecular dynamics simulations to protein for the first time.

The Nobel Prize in Chemistry 2013

© Nobel Media AB. Photo: A. Mahmoud
Martin Karplus
Prize share: 1/3

© Nobel Media AB. Photo: A. Mahmoud
Michael Levitt
Prize share: 1/3

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Arieh Warshel
Prize share: 1/3

QM/MM method: combining classical and quantum simulations

In 1970, while at Harvard, Karplus was joined by Warshel, who was a postdoctoral fellow. Karplus had already worked on computer programs that used quantum mechanics in modeling chemical reactions, whereas Warshel had extensive experience with computer modeling of molecules using classical physics. They wrote a program that modeled the atomic nuclei and some electrons of a molecule using classical physics and other electrons using quantum mechanics. Their technique was initially limited to molecules with mirror symmetry. However, Karplus was particularly interested in modeling retinal, a large complex molecule found in the eye and crucial to vision, which changes shape when exposed to light. In 1974 Karplus, Warshel, and collaborators published a paper that successfully modeled retinal's change in shape.

分子动力学（molecular dynamics）

In 1985, Car and Parrinello at SISSA started ab initio molecular dynamics.

Fathers of “ab initio” molecular dynamics （第一性原理分子动力学）

Roberto Car　　Michele Parrinello

CPMD: Car-Parrinello molecular dynamics

$$\mathcal{L}^{CP} = \frac{1}{2}\sum_I M_I \dot{\mathbf{R}}_I^2 + \sum_i \mu \int \left|\dot{\psi}_i(\mathbf{x})\right|^2 d^3x + \frac{1}{2}\sum_\alpha \eta_\alpha \dot{q}_\alpha^2$$
$$- E^{KS}\left[\rho, \{\mathbf{R}_I\}, q_\alpha\right] + \sum_{ij} \lambda_{ij}\left(\int d^3x \psi_i^*(\mathbf{x})\psi_j(\mathbf{x}) - \delta_{ij}\right)$$

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   A. 机器学习力场
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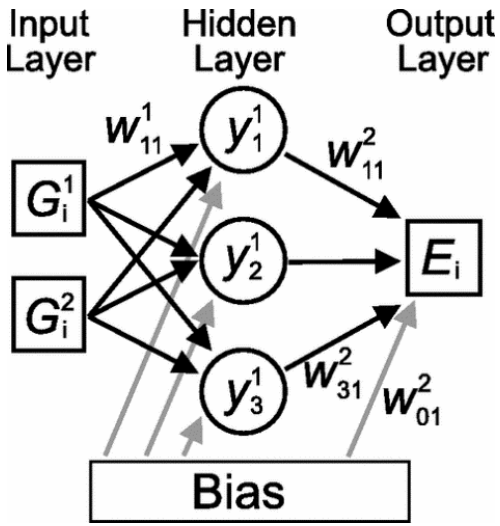
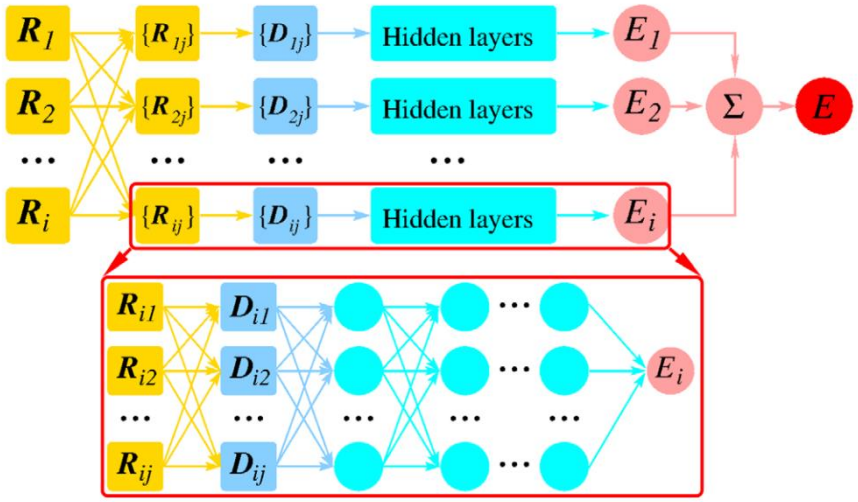
3. AI for 构效关系探索

分子动力学：机器学习力场

第一性原理	一般有DFT、QMC和WF方法，精度最高 计算代价大，限制了计算体系的规模 （几十到几百原子）
传统力场	速度最快，计算规模可以达到数万原子以上 计算精度不高，且解析形式限制了其泛用性
机器学习力场	无特设的解析形式，具有第一性原理的计算精度 速度接近于传统力场，可计算的尺度大

分子动力学：机器学习力场





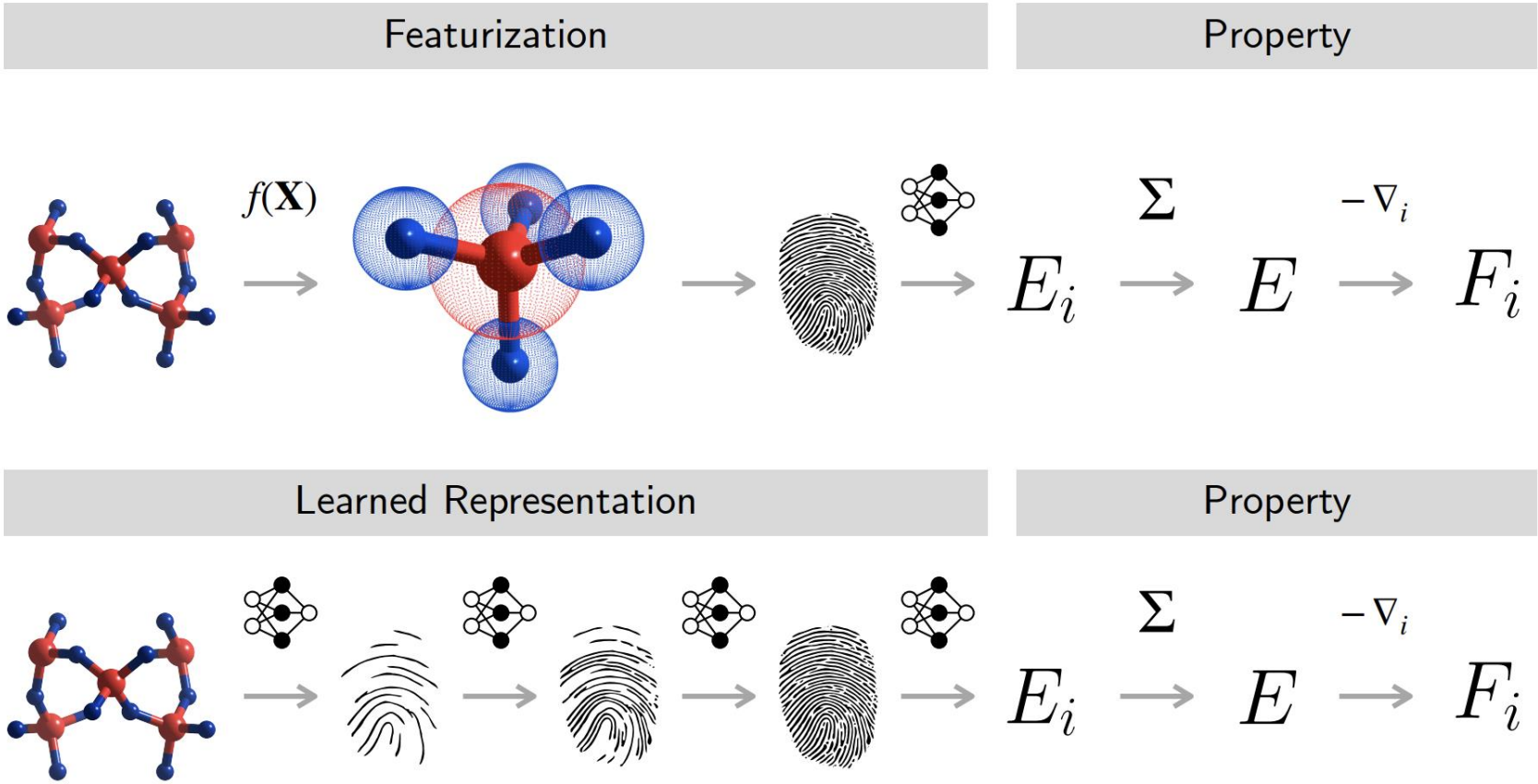
自BPNN开始，传统深度学习模型的架构包含如下特征：

- 总能量被分解为“局域环境能量”E_i之和，用神经网络表示E_i
- 原子坐标通过描述符G_i^μ（即特征）进入神经网络

Behler Parrinello Neural Network　　DeepMD-kit

分子动力学：机器学习力场

对分子信息的卷积操作：图神经网络GNN

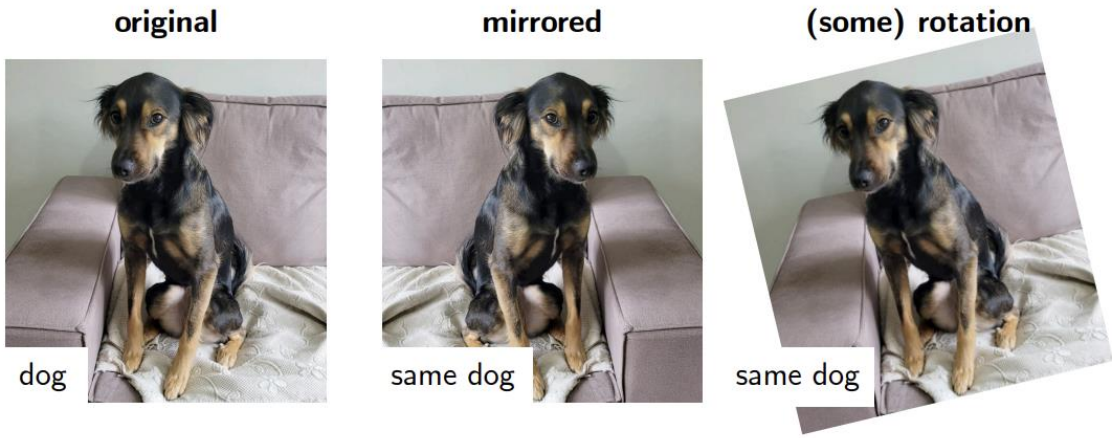


利用图卷积（graph convolution）进行特征提取后，
我们可以构建一个端到端的神经网络力场模型，无需特征工程。

分子动力学：机器学习力场

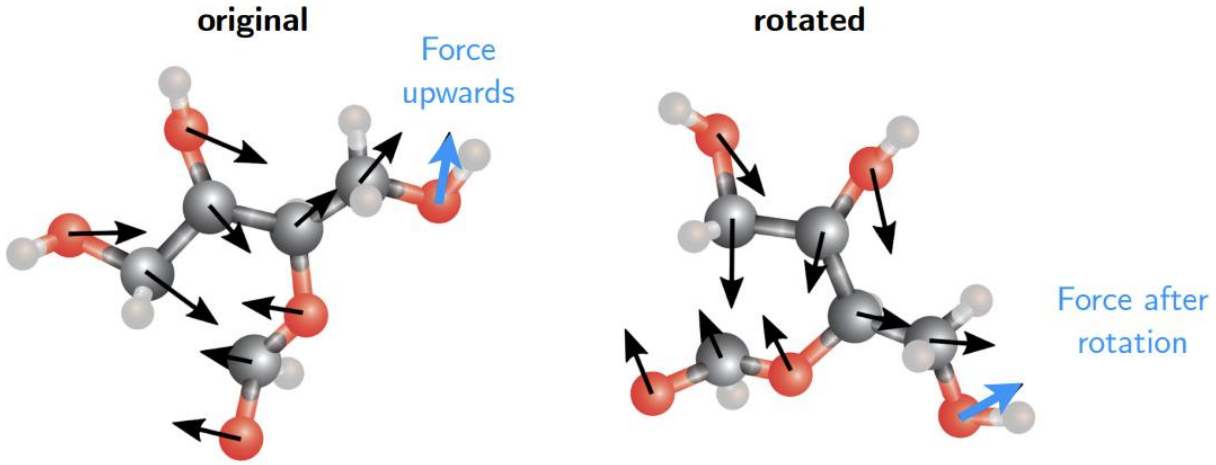
等变神经网络

Invariance



Equivariance

$$D_Y[g]f(x) = f(D_X[g]x) \quad \forall g \in G, \forall x \in X$$

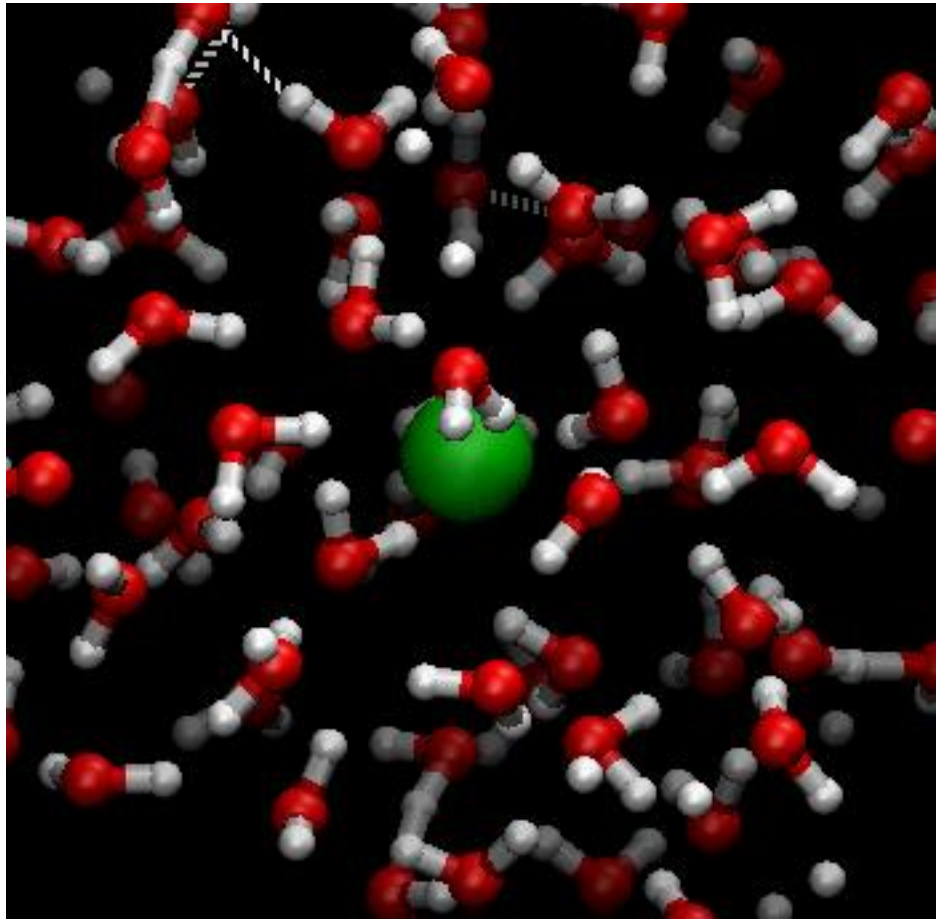


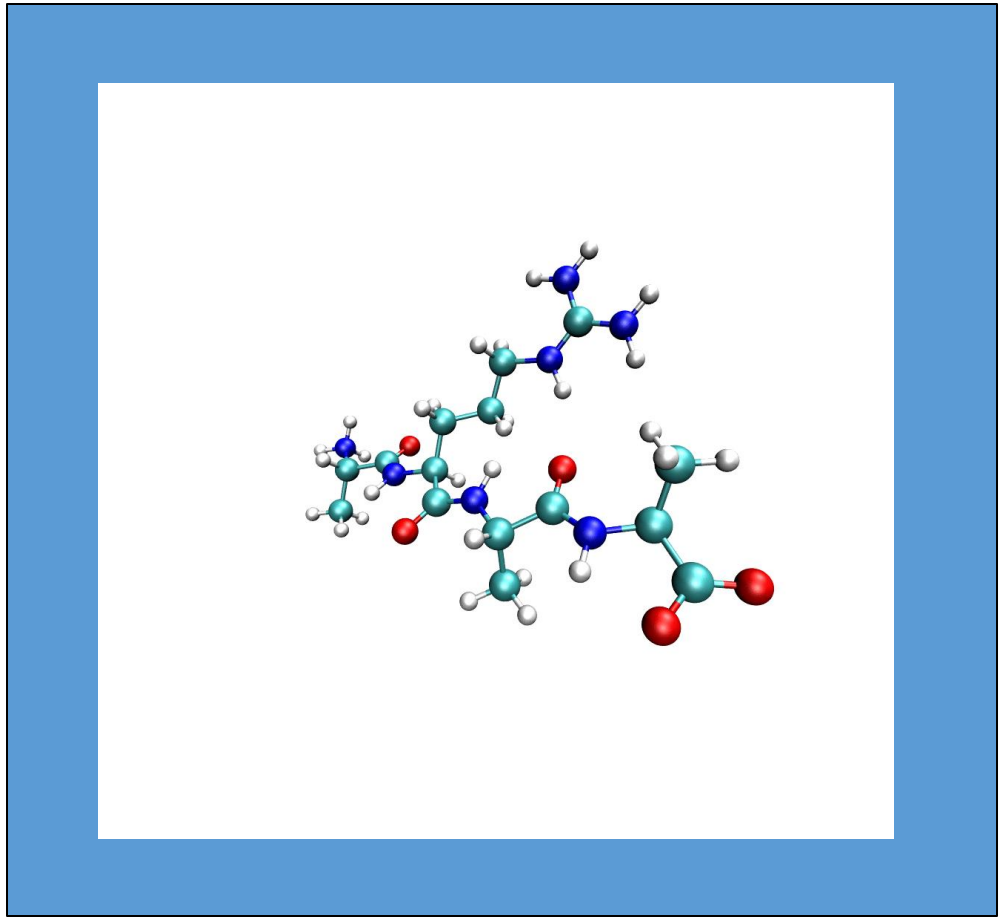
等变(equivariant)与不变(invariant)相对，指当对系统施加一个变换时，其中的某些特征会随着一个同样的变换而变换。

内容提纲

1. AI for 第一性原理计算
   A. 深度学习波函数方法
   B. 深度学习密度泛函
2. AI for 分子动力学模拟
   A. 机器学习力场
   B. 降维与聚类
3. AI for 构效关系探索

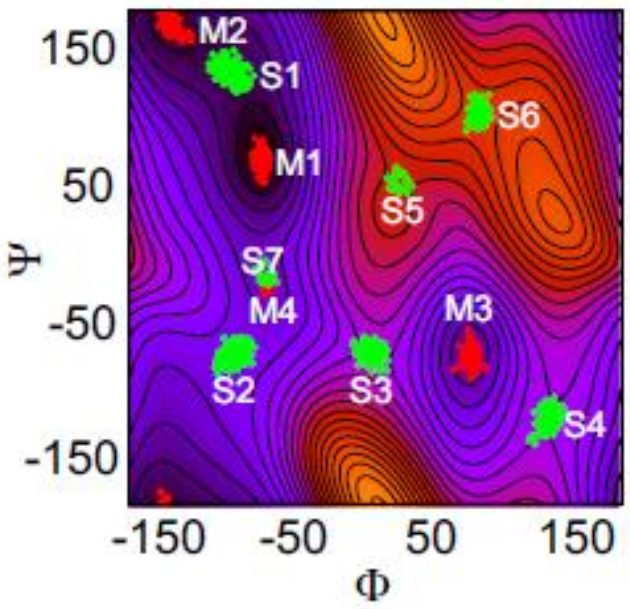
轨迹分析



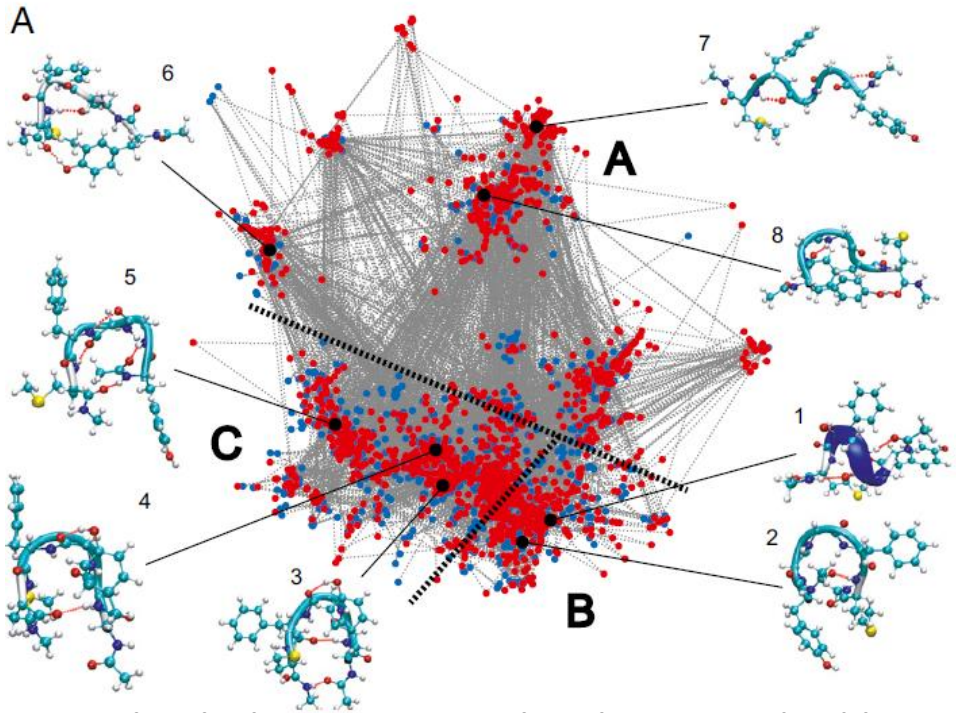


分析复杂结构

Example: Locating landmarks on high-dimensional free energy surfaces



FES as a function of the dihedral angles Φ and Ψ



Met-enkephalin in vacuum has been studied by START with the 10 Ramachandran dihedral angles as CVs.

Chen et al. PNAS 112, 3235 (2015)

加速采样

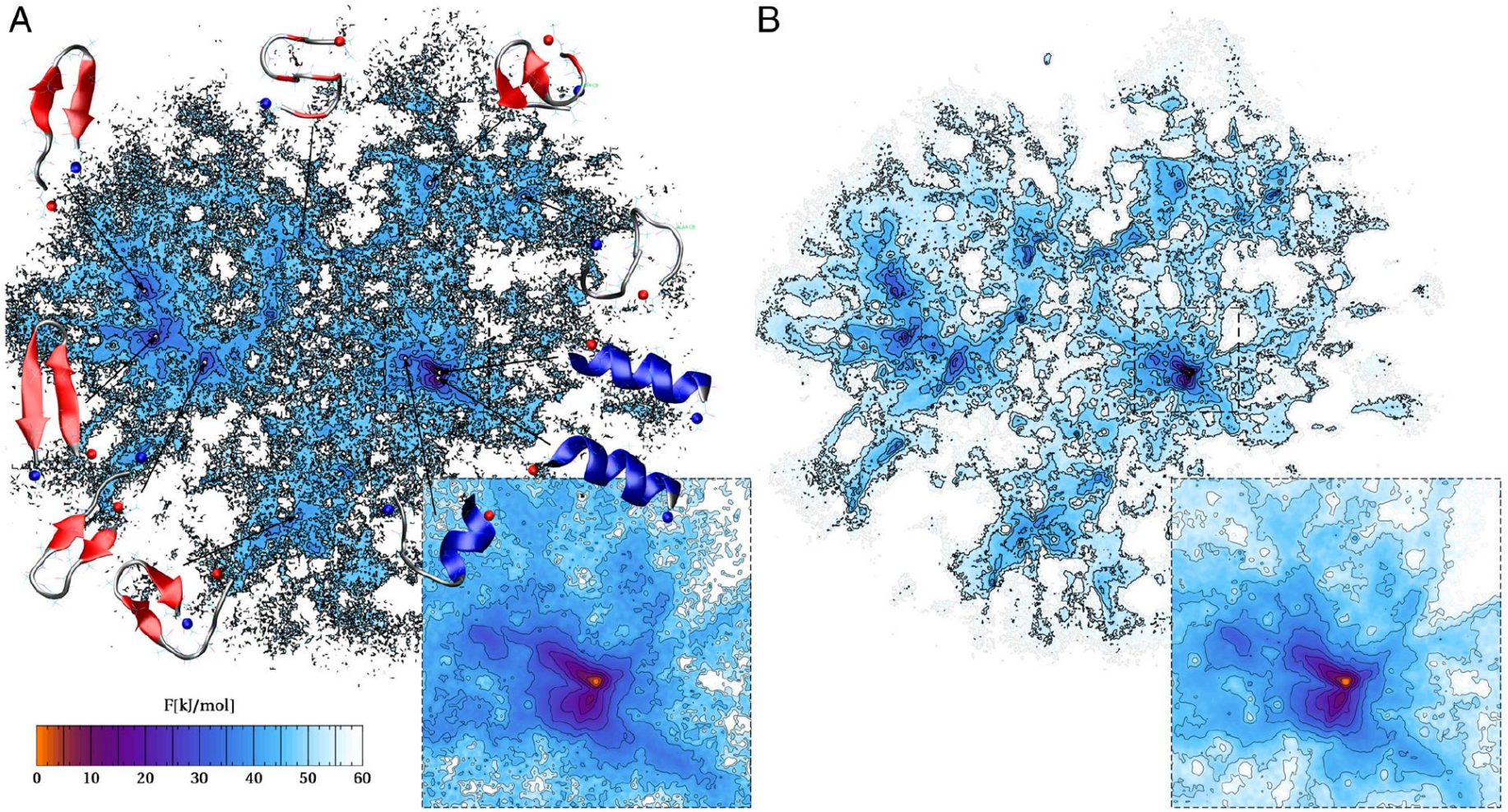


Fig. 4. The free-energy landscape for ala12 in implicit solvent calculated from parallel tempering (*A*) and field-overlap metadynamics (*B*) simulations. Here the free energy is shown as a function of the sketch-map coordinates and is seen to be very rough. In contrast to Fig. 3 each of the highlighted structures lies in a separate basin in the free-energy surface. In these structures the red and blue balls indicate the positions of the N and C termini, respectively.

降维与聚类

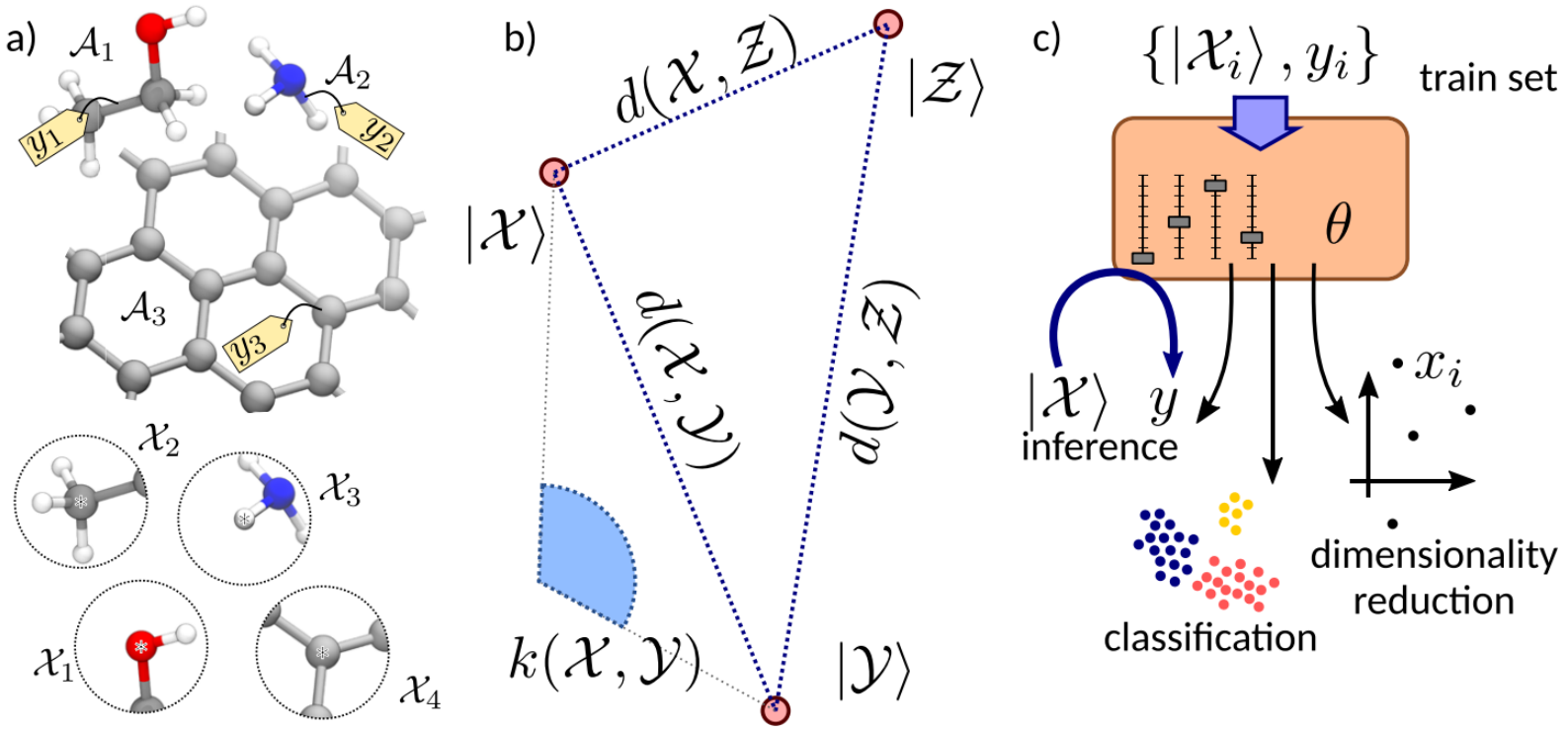
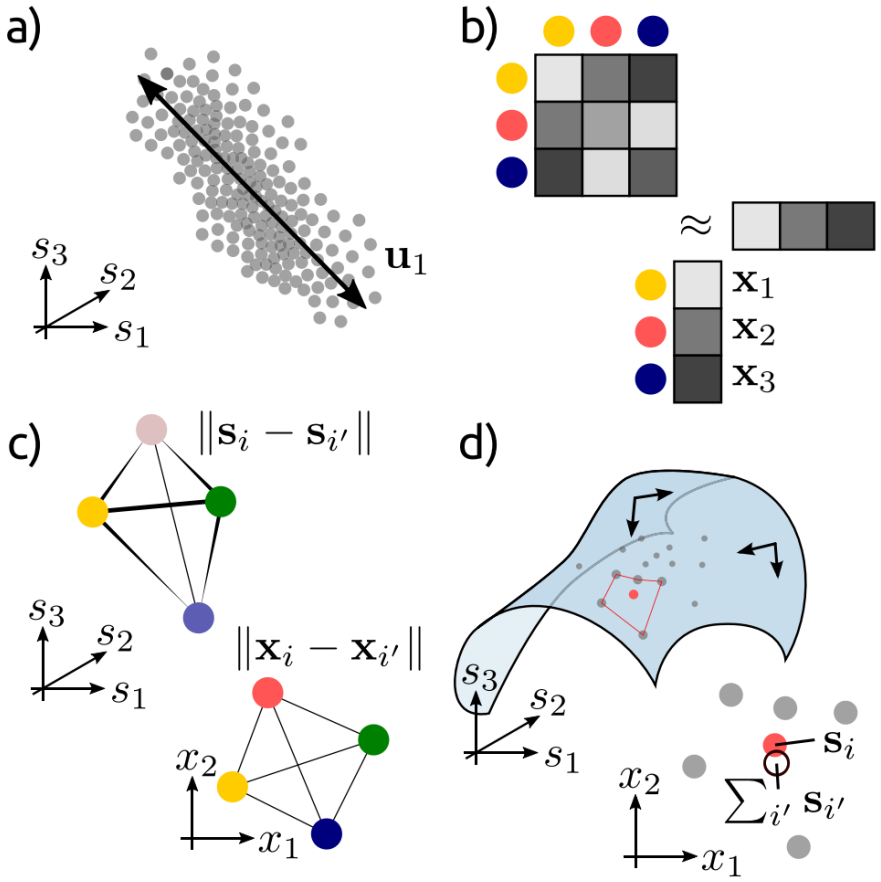


FIG. 1. A schematic representation of the main ingredients of atomistic machine learning. (a) Structures $\mathcal{A}$ or local environments $\mathcal{X}$ are the inputs of the model, possibly with labels y associated with them. (b) The inputs are associated with a mathematical representation, in terms of vectors of features $|\mathcal{X}\rangle$, a measure of similarity d, or a kernel k. (c) The machine-learning model, controlled by a series of hyperparameters θ, is trained based on a set of inputs. It can be then used for a number of machine-learning tasks.

J. Chem. Phys. 150, 150901 (2019)

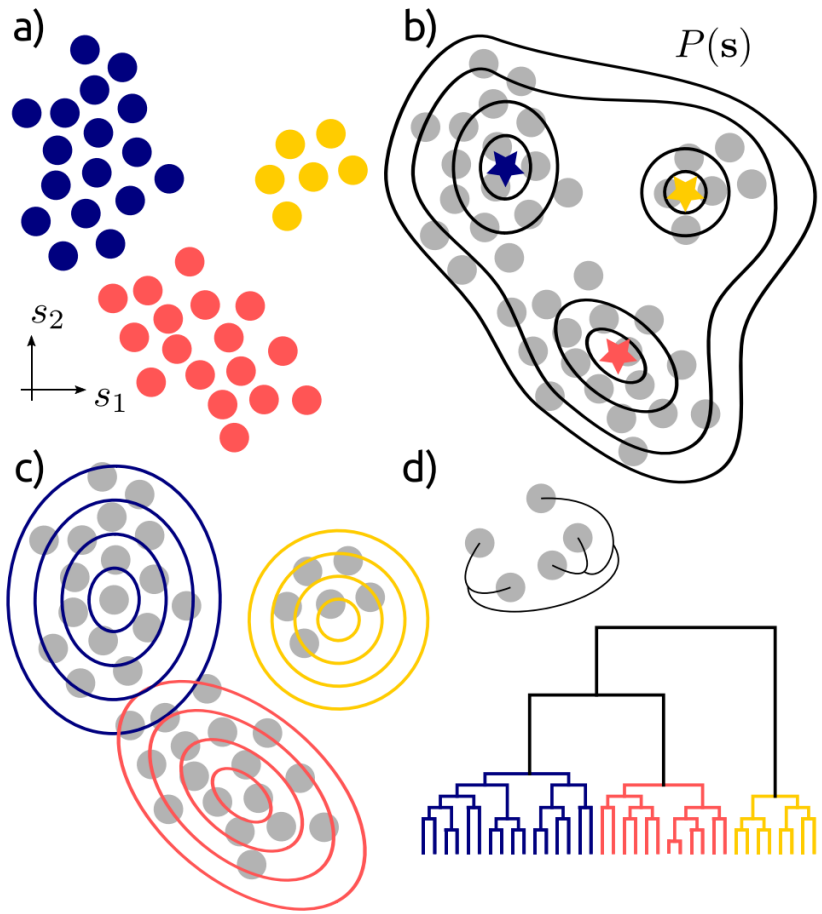
降维算法



Dimensionality reduction

FIG. 4. A summary of the main strategies underlying dimensionality reduction techniques. (a) Several methods (starting from PCA) attempt to identify the low-dimensional subspace that captures the largest fraction of the input data variance. (b) This is equivalent to finding the best $\mathcal{L}^2$-norm approximation of the Gram matrix and generalizes to kernel methods. (c) Multidimensional scaling and related approaches attempt to reproduce the similarity between high-dimensional data points in low dimension. (d) Embedding methods explicitly try to preserve local relations between points, under the assumption that they lie on a (locally) low-dimensional manifold.

聚类算法



Clustering

Clustering algorithms aim to recognize groups of input points that are related to each other and different from other groups of inputs. For instance, clusters could represent different classes of molecules, or configurations of a given system that are separated by a sparsely populated, or seldom accessed region

FIG. 3. A summary of clustering techniques. (a) A set of points in a finite-dimensional feature space are clustered together in a way that reflects some underlying common characteristic. (b) Density-based clustering identifies maxima in the probability distribution of inputs in feature space. (c) Distribution-based clustering determines a model of the data distribution as a combination of cluster probabilities. (d) (Hierarchical) linkage clustering determines work by accretion of clusters starting on inputs that are closest together in input space.

小结（2）：AI for 分子动力学模拟

1：精度问题	机器学习力场 材料的建模问题 监督式学习
2：效率问题	降维与聚类 序参量和增强采样 非监督式学习

内容提纲

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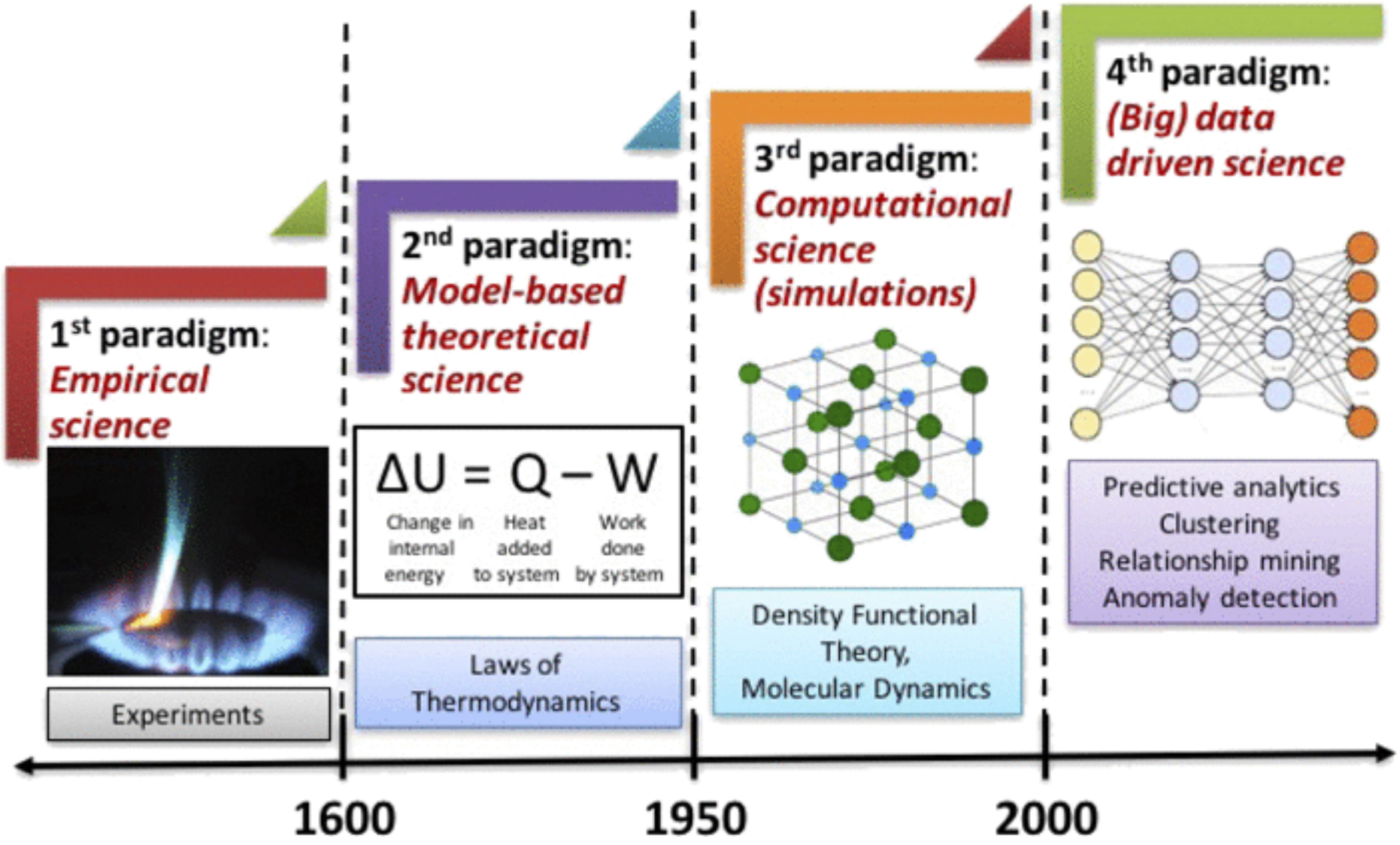
2. AI for 分子动力学模拟
   A. 机器学习力场
   B. 降维与聚类
3. AI for 构效关系探索

物态调控与材料研发

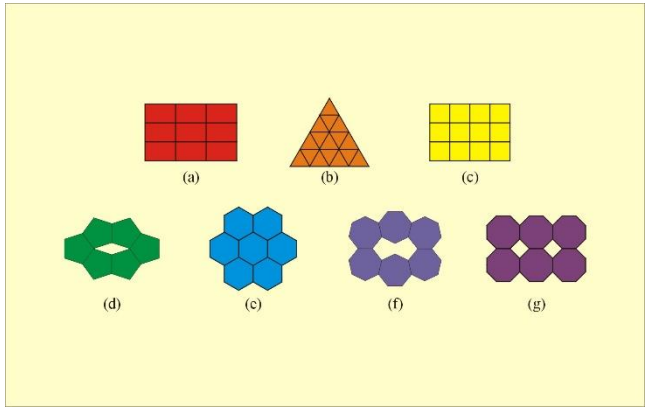

1st paradigm:
Empirical science
Experiments
2nd paradigm:
Model-based theoretical science
ΔU = Q – W
Change in internal energy
Heat added to system
Work done by system
Laws of Thermodynamics
3rd paradigm:
Computational science (simulations)
Density Functional Theory, Molecular Dynamics
4th paradigm:
(Big) data driven science
Predictive analytics
Clustering
Relationship mining
Anomaly detection
1600
1950
2000

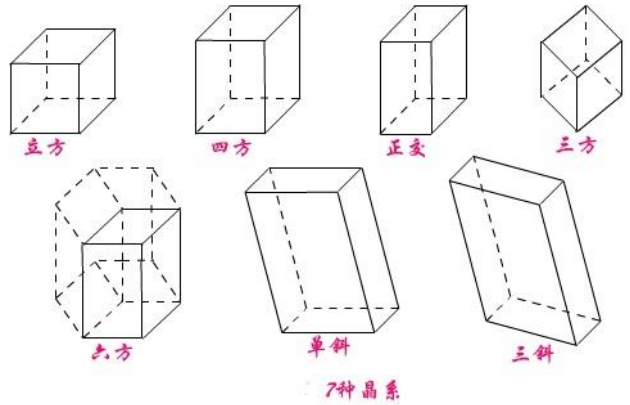
构效关系

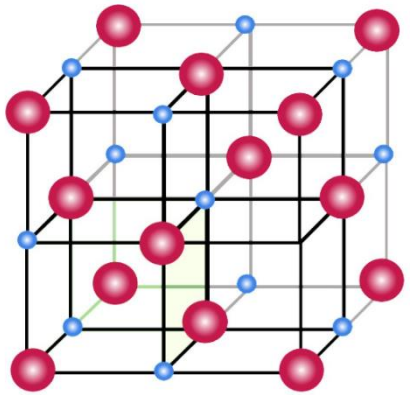
构效关系研究的旧范式

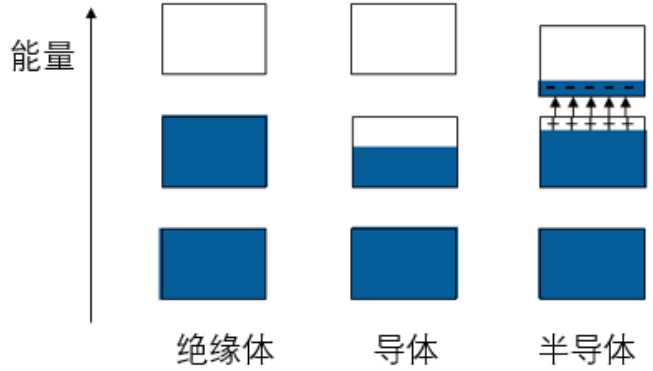
固体物理：周期性、晶格、原子结构、原子间相互作用、声子、能带、原子磁矩

关键词：简化与近似





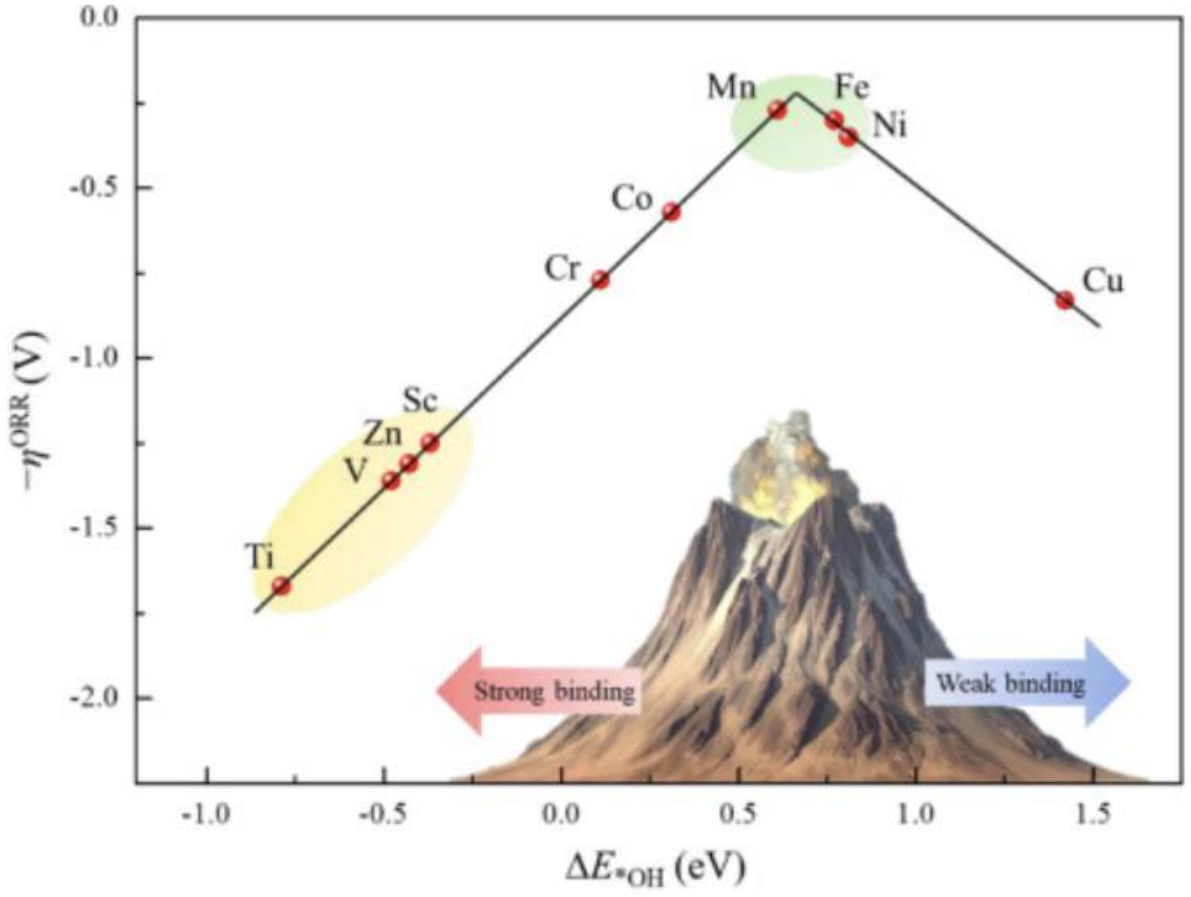




描述符：中间量

理解和建立“描述符”和“物性”之间的因果关系

构效关系



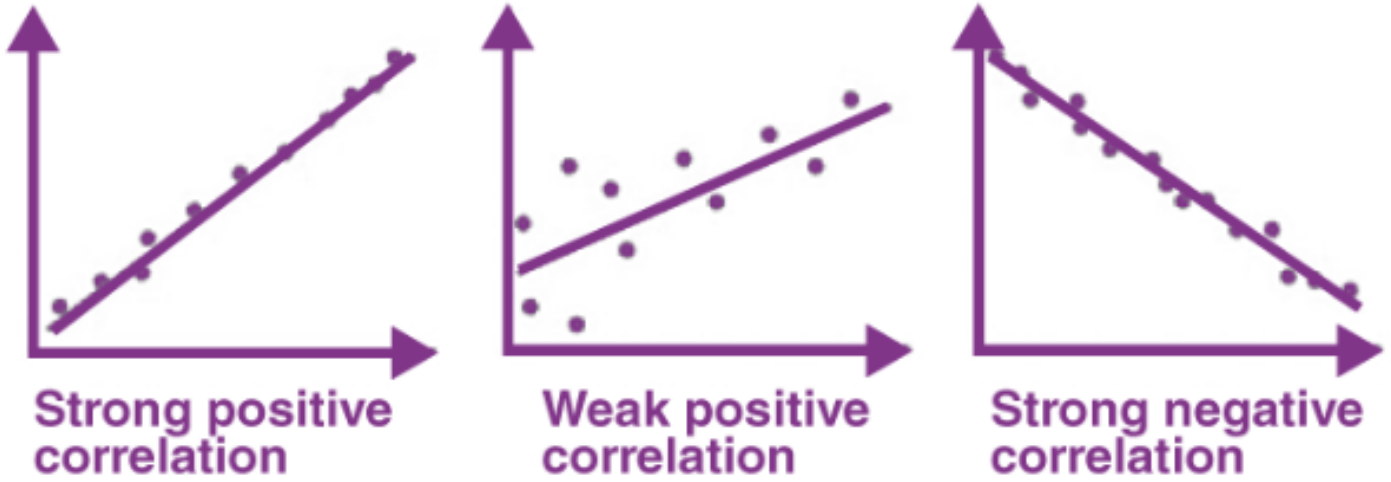
“化学活性”与“吸附能力”之间的“火山图”关系
因果关系：电子d带中心理论

构效关系

大数据和人工智能主导的新研究范式

寻找“规则”和“基因”

重“关联性”，轻“因果关系”



构效关系探索：数值回归

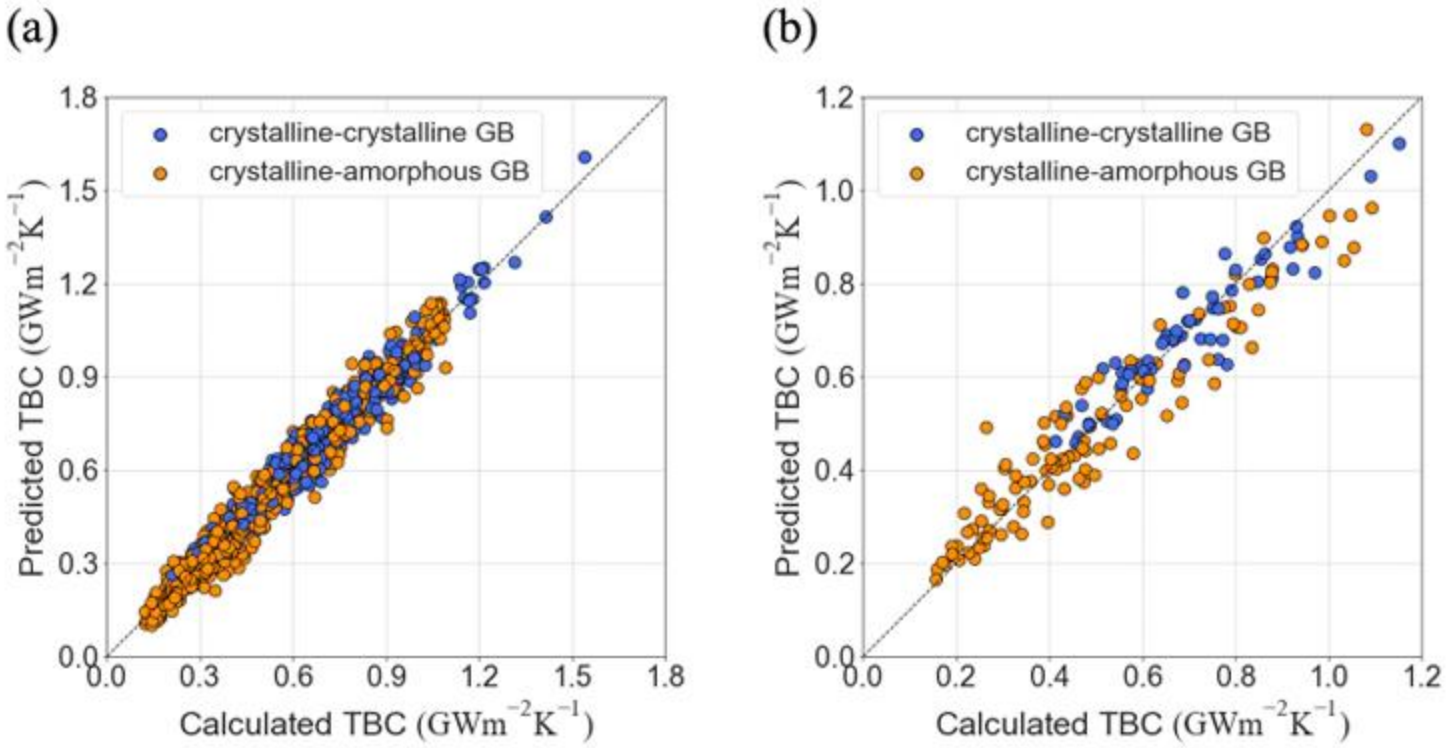


Table 1. Six-fold cross-validation results for thermal boundary conductance prediction of all training structures, ordered by root mean squared error (RMSE).

Model	RMSE (GWm^{-2}K^{-1})	MAPE
Ensemble	0.064	9.9%
ExtraTrees	0.078	11.3%
KNN	0.081	12.4%
GradientBoosting	0.087	15.6%
CatBoost	0.091	14.4%
AdaBoost	0.094	17.5%
XGBoost	0.098	19.8%
RandomForest	0.100	18.6%
HistGB	0.107	19.3%
LightGBM	0.108	23.0%
Linear regression	0.187	28.8%

Mean absolute percentage error (MAPE) was calculated for interpretation purpose. The ensemble model was constructed by averaging individual predictions from the five best models.

界面热导的机器学习预测模型

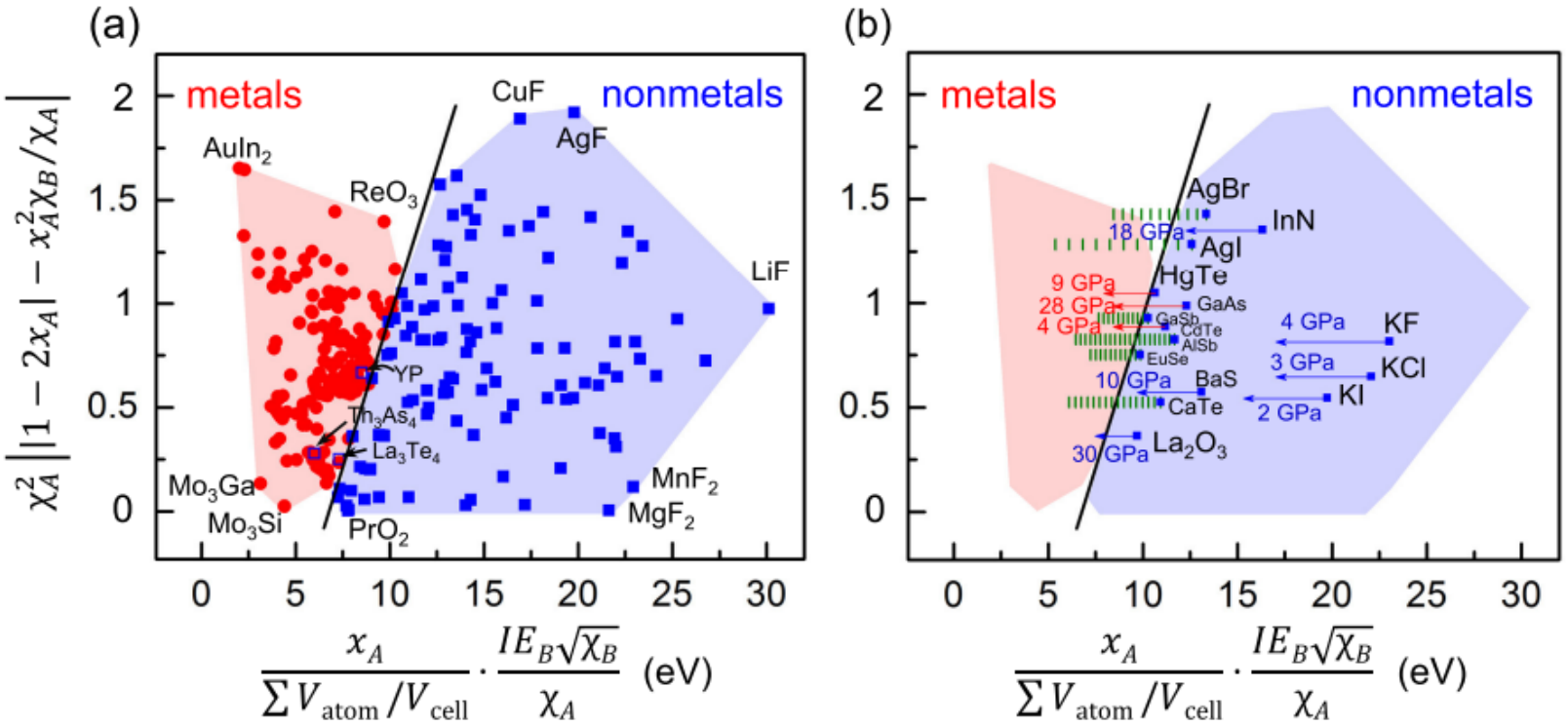
npj Computational Materials (2022) 8:219

构效关系探索：符号回归

$$\underset{c\in\mathbb{R}^M}{\operatorname{argmin}}\|\boldsymbol{P}-\boldsymbol{D}\boldsymbol{c}\|_2^2+\lambda\|\boldsymbol{c}\|_1,$$

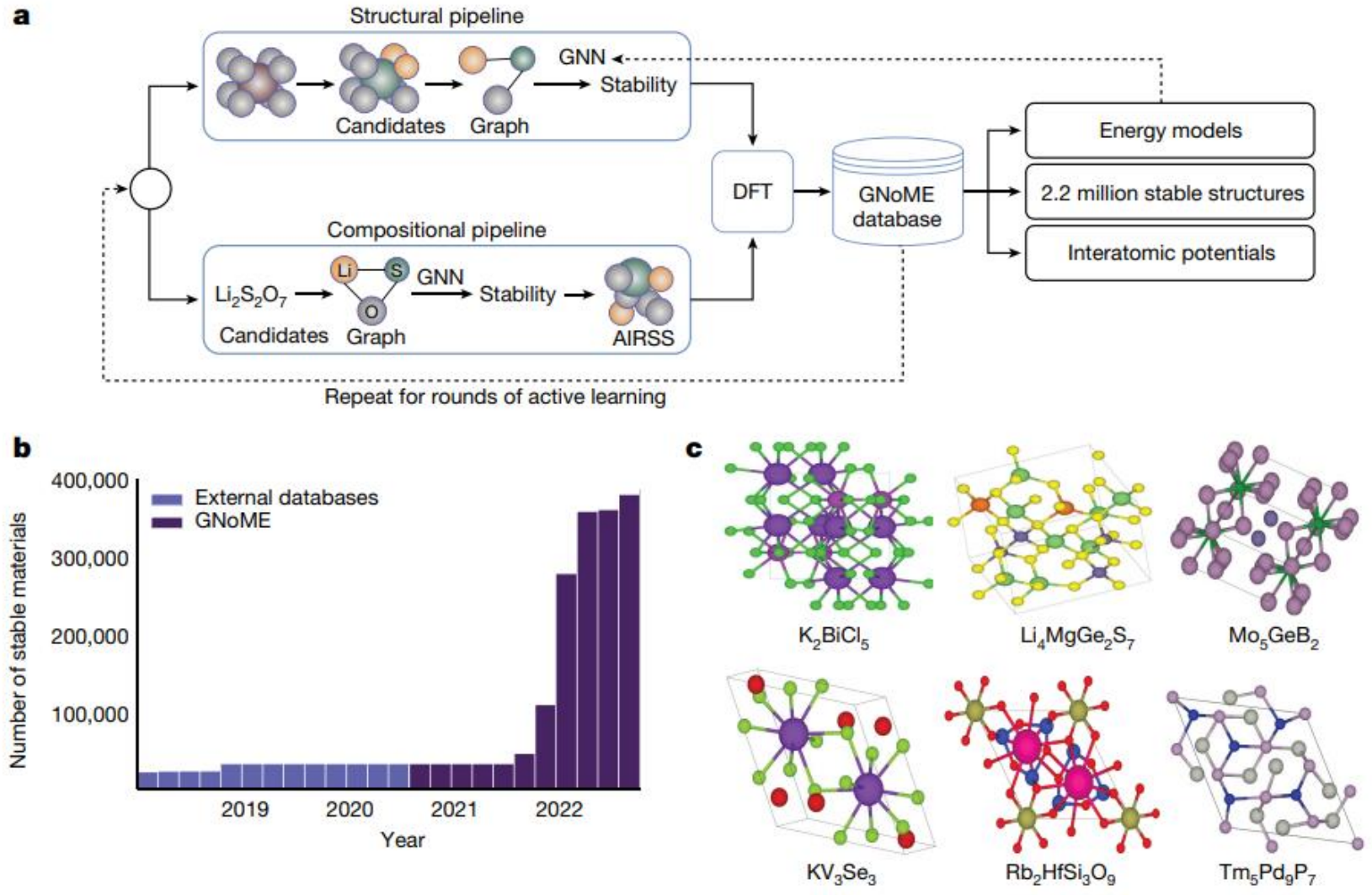
P: 物性特征
D: 描述符矩阵，是单个描述符d的组合
c: 模型参数

$$\hat{\boldsymbol{H}}^{(\mathrm{m})}\equiv\left\{I,+,-,\times,/,\exp,\log,|-|,\sqrt{},^{-1},^{2},^{3}\right\}[\phi_1,\phi_2],$$



Phys. Rev. Lett. 114, 105503 (2015); Phys. Rev. Mater. 2, 083802 (2018)

反向结构设计：生成模型



Nature 624, 80–85 (2023)

小结（3）：AI for 构效关系

1：精度问题	数值回归 符号回归 监督式学习
2：效率问题	生成模型 监督式学习+强化学习

总结与展望

解决旧问题！

发现新问题！