

Subsurface Control of Active-Site Distributions in Pt-Skin HEA Electrocatalysts

From single active sites to engineered active-site populations
— tuning H adsorption through the buried composition

96

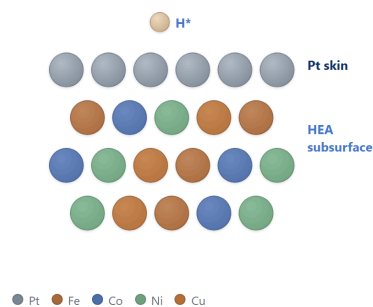
DFT H sites

3

SQS Pt-skin slabs

≈0 ΔG_{H^+} (eV)**5**

elements (HEA)

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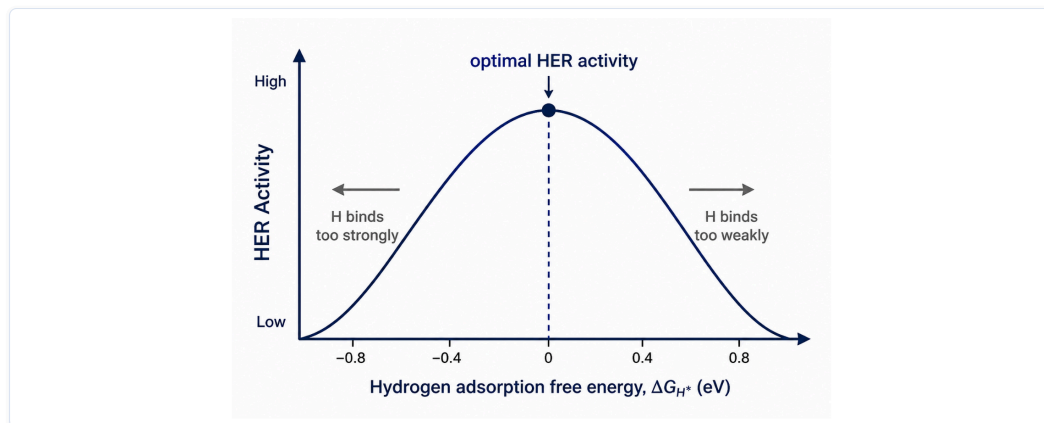
第 1 頁

封面 · Cover

今天我想說服各位一件事:在 Pt-skin 高熵合金上,催化劑設計該瞄準的,不是單一活性位點,而是一整個「活性位點族群」。我是輔仁大學化學系的廖振成。這份工作會帶大家走一條線——埋在底下的成分控制電子結構、電子結構控制吸附、吸附決定整個活性位點族群;預測,只是這套框架自然的產物。今天記得一句話就好:我們要設計的,是那群埋在底下的原子。

02 Platinum is the HER benchmark — but it is expensive

HER activity peaks when hydrogen binds at $\Delta G_{H^*} \approx 0$ — right where Pt sits. But Pt is costly and scarce, so the search for cheaper, tunable catalysts continues.



KEY MESSAGE The goal: reach Pt-like H binding ($\Delta G_{H^*} \approx 0$) with **far less Pt**.

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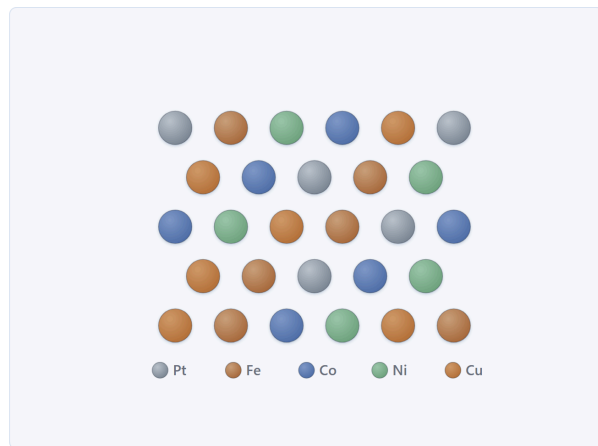
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Pt 是基準,但很貴

故事從一個很實際的矛盾開始。HER 的活性由一個量決定:吸附氫的自由能 ΔG_{H^*} ,太強太弱都不好、接近零最理想,而白金正好坐在這個最佳點上。問題是 Pt 又貴又稀有。所以真正的挑戰不是「找到好催化劑」,而是「用更少的 Pt,達到跟 Pt 一樣接近零的氫吸附」。這就是我們整個設計的起點。

03 High-entropy alloys = enormous local-environment diversity

Five-plus near-equiatomic elements, randomly mixed — so no two surface sites see the same neighbourhood



Why we care random mixing means **every surface site sees a different local environment** — one material, a continuum of distinct binding sites.

Five-plus principal elements, each near-equiatomic — a vast, **tunable composition space**.

High mixing entropy keeps it a single **disordered solid solution**.

KEY MESSAGE What makes HEAs special for catalysis is **local-environment diversity** — many distinct sites in one material.

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第 3 頁

高熵合金 = 巨大的局部環境多樣性

那替代方案是什麼?高熵合金。但今天我不打算花時間教熵——重點只有一個:高熵合金把五種以上的元素亂混在一起,於是表面上沒有兩個位點看到一樣的鄰居。它打開了一個龐大、可連續調整的成分空間。對催化來說,高熵合金真正迷人的地方,是一個材料裡就藏著無數種不同的局部環境、無數種不同的位點。

04 Pt-skin HEA: keep Pt's surface, tune the buried core

A pure-Pt outer layer over a mixed Fe-Co-Ni-Cu-Pt core — Pt-like chemistry on top, far less Pt and new tunability underneath



The Pt skin preserves Pt-like surface chemistry, while the buried high-entropy environment is used to **tune H adsorption**.

KEY MESSAGE Keep a **Pt-like surface**, let buried atoms **tune it**, and use **less Pt**.

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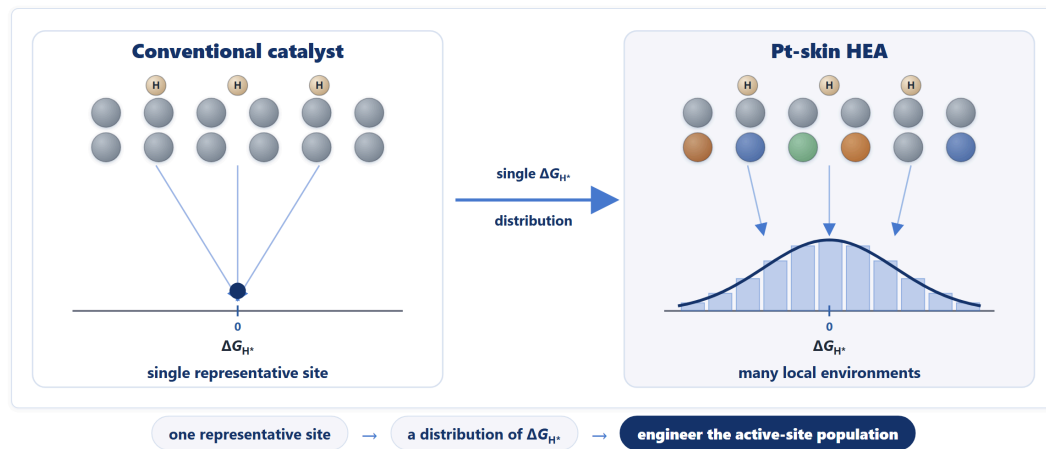
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Pt-skin:保留表面、調控內層

那怎麼同時保留 Pt 的好、又拿到高熵合金的可調性?答案是 Pt-skin。最左邊純 Pt,表面好但貴;中間一般合金,連 Pt 的表面化學都不見了;最右邊是我們的設計——最上層全是 Pt、表面化學跟 Pt 一樣,底下卻藏著 Fe-Co-Ni-Cu-Pt 的混合。一句話:把 Pt 的表面留著,讓底下的原子去調它,而且用更少的 Pt。

05 HEA catalysis is not a single-site problem

Even under a pure-Pt skin, each hollow sits above a different subsurface — so adsorption becomes a distribution



KEY MESSAGE Activity is a **distribution of sites** — so the design target is the **active-site population**, not one site.

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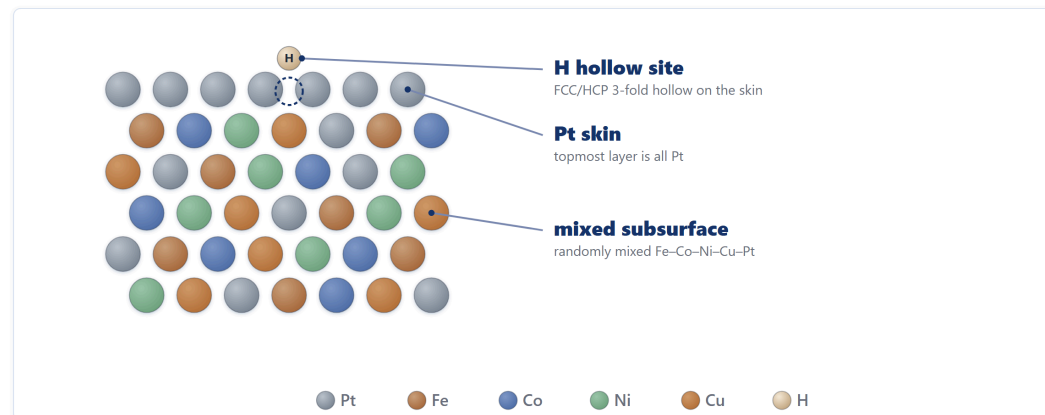
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不是單一位點,是位點族群 ★

這是今天最重要的觀念轉變,請特別記住這一頁。就算表面是一層純 Pt,因為底下是亂的,每個 hollow 位點正下方的組合都不一樣。左邊那種「一個代表性位點、一個 ΔG_{H^*} 」的想法,在高熵合金上根本不成立;右邊才是真相——同一個 Pt 表面,卻得到一整個 ΔG_{H^*} 的分布。從單一位點、到一個分布、到一個要去設計的族群:從這頁開始,請把催化想成一個活性位點族群的問題,而不是某一個位點。

06 Pt-skin: a controlled platform for the buried effect

The adsorbate always meets a Pt-rich surface; the variation comes from the composition underneath



The Pt skin fixes the surface chemistry, while the buried Fe-Co-Ni-Cu-Pt environment tunes the local H adsorption energy.

KEY MESSAGE The Pt skin isolates one clean question: how does the **buried environment tune surface Pt?**

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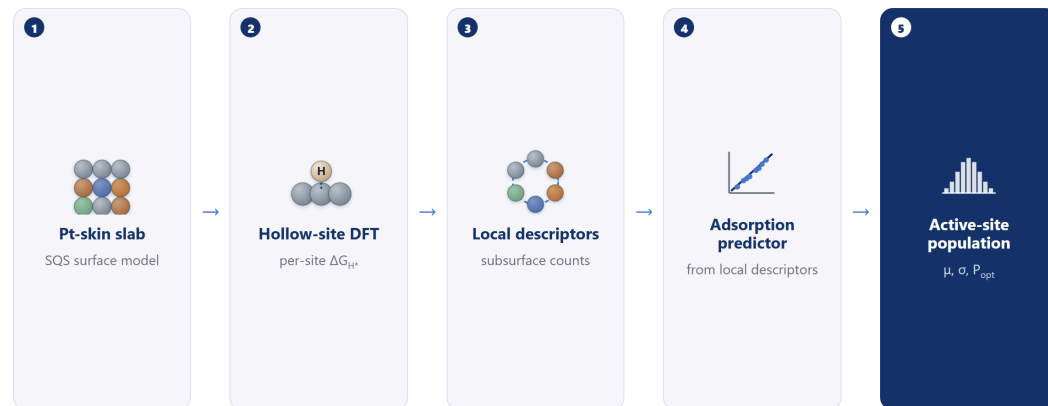
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Pt-skin 是受控平台

要研究「底下怎麼影響表面」,Pt-skin 剛好是一個乾淨的受控平台。注意:吸附的氫永遠落在 Pt 上,表面化學被釘死了,唯一在變的是底下的成分。所以這個系統幫我們把問題隔離成一個很單純的提問——在表面不變的前提下,底下的環境怎麼調表面 Pt?這正是我們能把「埋藏效應」單獨拉出來看的原因。

07 The central question of this work

Can the buried composition set — and let us predict — each site's H binding, and thus the whole active-site population?



The buried environment sets each site's $\Delta G_{H, i}$; the target is the resulting **active-site population** — with DFT as calibration, not a full census, kinetics, or MLP.

KEY MESSAGE The target is the **active-site population**; prediction is the route, and DFT is the calibration.

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第 7 頁

核心問題:預測族群

於是核心問題就很清楚了:底下的成分,能不能決定、進而讓我們預測每個位點的氫吸附,然後拼出整個族群?如果可以,DFT 的角色就變了——它不再是把每個位點都算一遍的普查,而是少數幾個位點的校準資料。請看這條流程的終點:不是預測器,而是「活性位點族群」。預測是路,族群才是目的。

08 Methods overview

Fe–Co–Ni–Cu–Pt Pt-skin (111): from random structure to descriptors

- 1 SQS bulk**
random alloy in a finite cell
- 2 Pt-skin slab**
4×4×6 · 96 atoms · pure-Pt top
- 3 96 hollow sites**
all FCC + HCP, 3 slabs
- 4 DFT ΔG_{H^*}**
VASP, per site
- 5 Descriptors**
local environment · d-band · surrogate prediction

DFT SETTINGS

VASP · GGA-PBE
520 eV · spin-polarized
 Γ -centered 3×3×1

FREE ENERGY

$\Delta G_{H^*} = \Delta E_{ads} + 0.24 \text{ eV}$
computational hydrogen electrode

SQS gives finite periodic slabs whose local statistics approximate a random alloy.

KEY MESSAGE A controlled **96-site hollow-site dataset** across three Pt-skin HEA surfaces.

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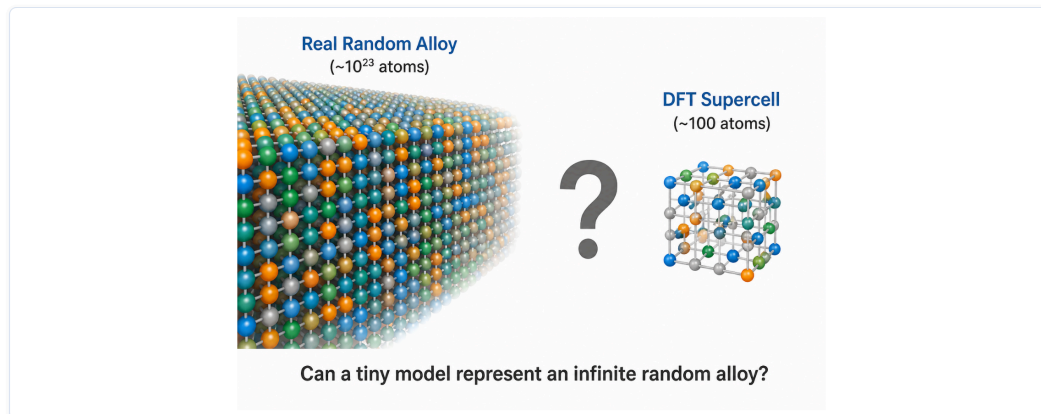
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方法總覽(精簡)

方法我講最精簡的版本。我們做 Fe–Co–Ni–Cu–Pt 的 Pt-skin (111):用 SQS 生一個統計上接近隨機的合金、切成 96 原子的 slab、頂層換純 Pt、在所有 hollow site 算 ΔG_{H^*} 、再抽局部描述符,設定是 PBE、520 eV、自旋極化。各位只要記得:這是跨三個 Pt-skin 表面、96 個 hollow site 的一份受控資料集——它是用來校準的,不是終點。

09 Can a small cell represent an infinite random alloy?

A real random alloy has $\sim 10^{23}$ atoms; DFT can treat only ~ 100 — this is the gap an SQS bridges



A real random alloy is effectively infinite, but DFT can only treat ~ 100 atoms — the SQS is the small cell built to **stand in for it**.

KEY MESSAGE An SQS lets a **~100-atom DFT cell** represent an **effectively infinite** random alloy.

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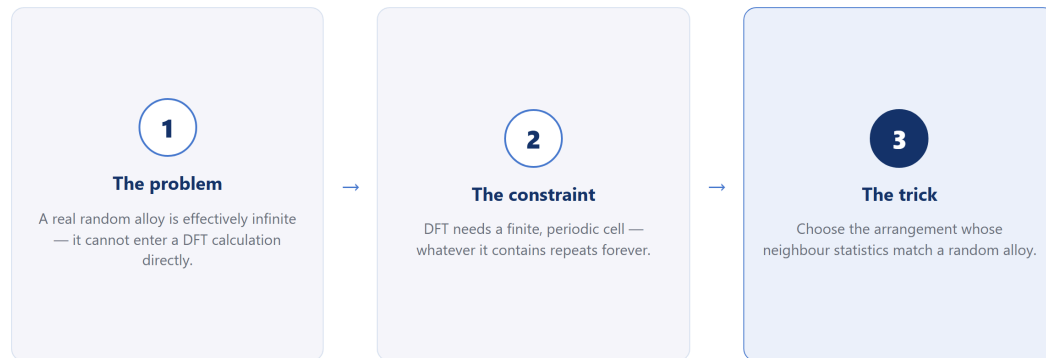
小胞能代表無限大隨機合金嗎？

這裡花一頁解釋我們為什麼需要 SQS。一個真正的隨機合金有大約 10 的 23 次方個原子, DFT 一次卻只能算大約一百個。左邊是真實的隨機合金, 右邊是我們算得動的超胞, 中間這個問號就是難點: 能不能用一個這麼小的胞, 代表一個幾乎無限大的隨機合金? SQS 就是來填這個鴻溝的。

10 What is a special quasirandom structure (SQS)?

A small periodic cell built to imitate an infinite random alloy

An SQS reproduces the local atomic statistics of a random alloy — in a cell small enough for DFT.



KEY MESSAGE An SQS is **statistically** random — not merely random-looking.

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第 10 頁 什麼是 SQS

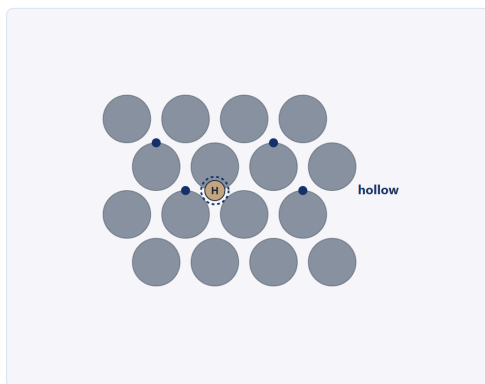
SQS 的答案很聰明:不要求胞很大,只要求它的「鄰居統計」跟隨機合金一樣。所以它的隨機是統計意義上的隨機,不是看起來亂就算數。主流程我只講到這——「我們有一個小胞,統計上等於隨機合金」;它具體怎麼被找出來,我放在最後的 backup,有興趣再看。各位只要相信:這個 96 原子的模型,統計上代表一個隨機的高熵合金。

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11 Our model: a Pt-skin (111) high-entropy slab

Top view and side view of the 4×4×6 slab — 96 atoms, six layers

TOP VIEW — PT SKIN (16 SURFACE PT)



4×4 surface cell · FCC + HCP 3-fold hollow sites (96 in total)

SIDE VIEW — 6 LAYERS



Pt skin on top · Fe–Co–Ni–Cu–Pt below (top 3 relaxed, bottom 3 fixed)

KEY MESSAGE A pure-Pt skin over the HEA subsurface — the surface looks like Pt; the **layers beneath do the tuning.**

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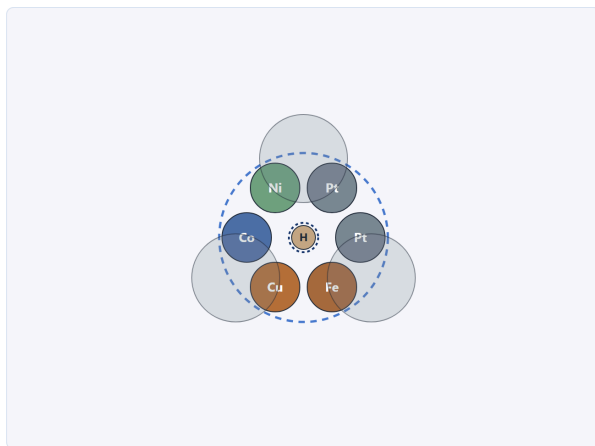
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我們的模型:Pt-skin (111) slab

這就是我們的模型。左邊俯視:表面 4×4、16 個 Pt 的 skin,氫吸在這些三配位 hollow site 上;右邊側視:六層,最上一層純 Pt,底下五層才是 Fe–Co–Ni–Cu–Pt 的混合,計算時放鬆上三層、固定下三層。一句話:表面看起來就是 Pt,真正在做調控的,是底下那幾層。

12 What we count: the 6 atoms beneath a hollow site

An x-ray view from the Pt skin into the subsurface ring



An H atom adsorbs in a **3-fold hollow site** on the Pt skin.

Make the skin transparent: directly beneath sit **6 subsurface atoms** — the local ring.

Descriptor I_s_X = counts in that ring → here Pt 2 · Fe 1 · Co 1 · Ni 1 · Cu 1.

KEY MESSAGE Each site's descriptor is the **element makeup of the 6 atoms under its hollow**.

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第 12 頁

數什麼:hollow 底下六顆原子

那我們到底數什麼?把 Pt skin 想成透明的往下看:每個 hollow 正下方剛好坐著六個 subsurface 原子,這就是它的局部環。我們最主要的描述符 I_s_X ,就是這六個原子裡各元素各有幾個。所以每個位點的身分證,就是它 hollow 底下那六顆原子的組成——非常簡單、可數。

13 The site population sits on the Sabatier optimum

ΔG_{H^*} across all 96 sites — tight and near-thermoneutral

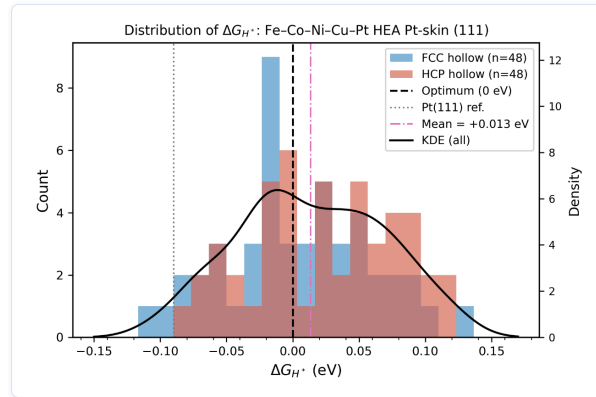


Figure 1. ΔG_{H^*} distribution over 96 FCC + HCP hollow sites (3 SQS slabs); Pt(111) reference -0.09 eV.

KEY MESSAGE The Pt-skin HEA naturally creates a **near-optimal population** of H-binding sites.

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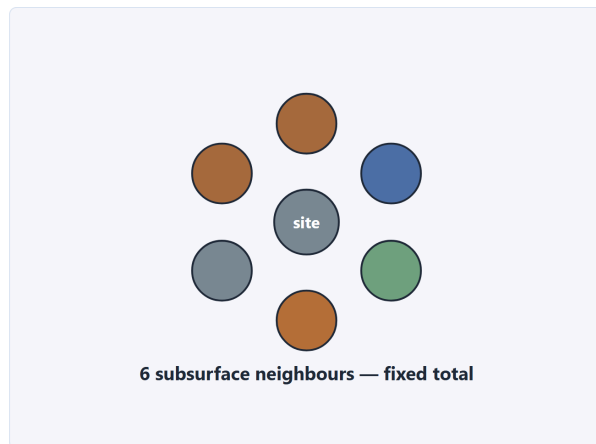
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位點族群落在 Sabatier 最佳點(92%)

先看結果,這也是今天第一個漂亮的數字:96 個位點裡,有 92% 的 ΔG_{H^*} 絕對值「已經」落在 0.10 eV 以內。平均 +0.013 eV、幾乎熱中性,標準差只有 0.055 eV、非常窄;對照純 Pt(111) 是 -0.09 eV。換句話說,這個 Pt-skin 高熵合金,自己就長出了一整個接近最佳的位點族群。

14 A trap hides in the simplest analysis

RECOVERING THE TRUE CHEMISTRY · the subsurface counts are not independent — they add to a fixed total



Add one Fe and you must **remove** another element. The five counts are **compositionally coupled**.

Caution A raw correlation for one element absorbs everyone else's effect — **correlation, not cause**.

The fix is **partial correlation**: hold the other counts fixed, then ask what each element does.

KEY MESSAGE In a constrained alloy, naïve correlation can point at the **wrong element**.

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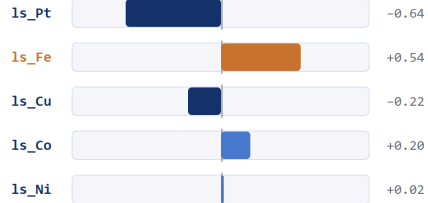
還原真化學(1):counts 耦合

接下來三頁,我不是要教統計,而是要把真正的化學還原出來。第一步先看一個陷阱:底下六個原子,五種元素的數量並不是獨立的——它們加起來永遠是六;我多放一個 Fe,就一定得拿掉別的。所以直接對單一元素做相關,會把別人的效果一起算進去,那是相關、不是因果。要看到真化學,得先把這個耦合移掉。

15 The apparent ranking is misleading

RECOVERING THE TRUE CHEMISTRY · raw Pearson correlation of each subsurface count with ΔG_{H^+} (n = 96)

APPARENT RANKING (RAW R VS ΔG_{H^+})



1s_Pt is genuinely the strongest signal ($r = -0.64$, $p < 10^{-12}$).

Trap Fe looks important (+0.54) — but this is mostly Pt's complement: "few Pt here," not "Fe acting."

Cu and Co look weak here — only a method that removes the coupling can tell.

Bars left of centre = strengthen H binding · right = weaken. Fe is flagged.

KEY MESSAGE At face value Fe rivals Pt — a classic **collinearity artifact**.

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還原真化學(2):原始排序會誤導

看這張原始相關就知道為什麼危險。表面上 1s_Pt 是 -0.64 最強,可是 1s_Fe 居然有 +0.54,好像 Fe 也很關鍵;但這是假象——Fe 多通常只是因為這裡 Pt 少,它吃到的 是 Pt 的補集,不是 Fe 自己在作用。如果停在這張圖,我們 會指錯元素。

16 The corrected hierarchy follows chemistry

RECOVERING THE TRUE CHEMISTRY · remove the coupling → a stable, electronegativity-ordered hierarchy

CONTROLLING FOR THE OTHER COUNTS UNMASKS THE TRUE RANKING



Fe collapses from apparent hero to weakest; **Cu rises** to second. The order tracks **electronegativity (χ)**, not arithmetic.

More-electronegative subsurface neighbours pull charge from surface Pt → weaker H binding.

KEY MESSAGE A stable, **electronegativity-ordered** descriptor hierarchy: Pt > Cu > Ni ≈ Co > Fe.

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還原真化學(3):真正的階層

把耦合移掉、做 partial correlation,真正的階層就現形了:Pt > Cu > Ni ≈ Co > Fe。剛剛看似關鍵的 Fe 掉到最弱,Cu 升到第二;而且這順序不是算術巧合,它跟電負度一致——底下鄰居電負度越高,越把表面 Pt 的電子拉走、Pt-H 越弱。請各位記得的,不是 partial correlation 這個方法,而是這個由電負度決定的、真正的描述符階層。

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17 Subsurface Pt is the dominant handle

More Pt beneath the skin → weaker H binding, ΔG_{H^*} rising through zero

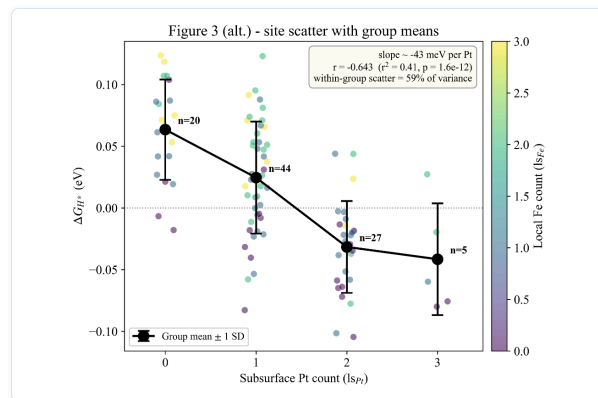


Figure 3. ΔG_{H^*} vs subsurface Pt count; points coloured by local Fe count, black = group mean ± 1 SD. Trend $r = -0.64$ (≈ -43 meV per subsurface Pt).

KEY MESSAGE One countable quantity — **subsurface Pt** — predicts which way H binding moves.

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subsurface Pt 是主導旋鈕

在這個階層裡,最主導的單一旋鈕,就是 subsurface Pt 的數量。橫軸是底下 Pt 個數、縱軸 ΔG_{H^*} , 相關 -0.64 、大約每多一個 Pt 變化 -43 meV; 底下 Pt 從 0 到 3, 把位點一路帶過零點。但注意黑色的群組平均——趨勢雖明確, 組內散布還是很大、佔了近六成的變異, 這再次提醒我們它是一個族群。一句話: 光是底下有幾個 Pt, 就能預測氫吸附往哪走。

18 The electronics confirm the mechanism

A site-projected d-band-center effect, measured atom by atom

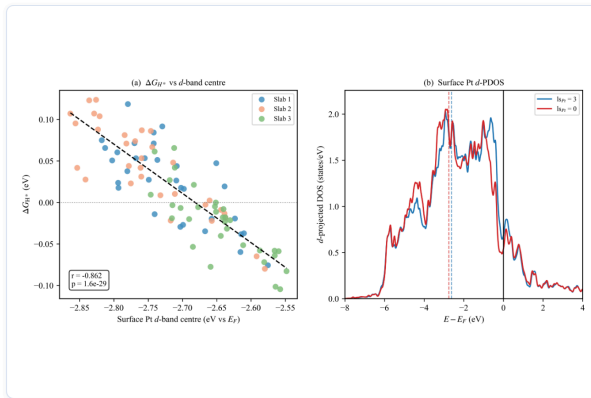


Figure 6. (a) ΔG_{H^*} vs surface-Pt d-band center ($r = -0.86$). (b) d-projected DOS for high vs low subsurface Pt.

KEY MESSAGE The descriptor is not a fit — it is the **d-band center** doing the work.

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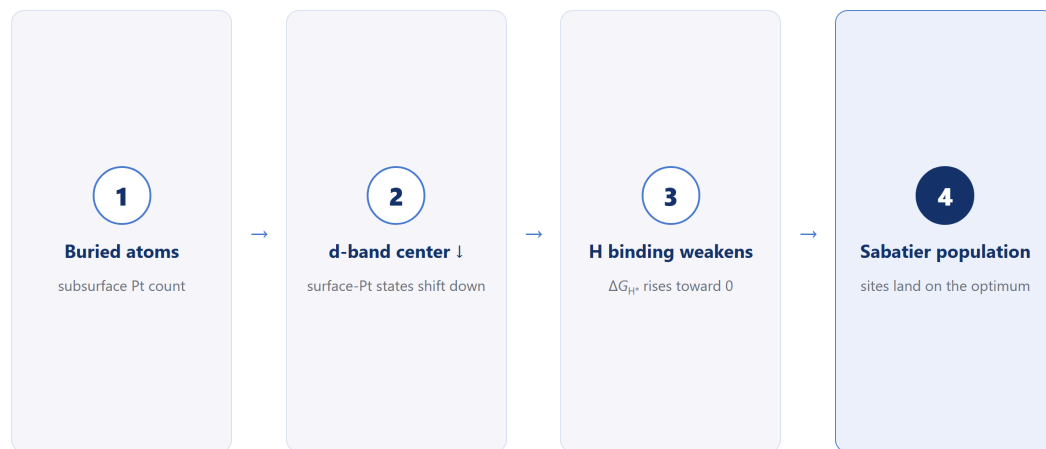
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電子結構印證機制(d-band)

那背後的物理是什麼?是 d-band center。我們一顆一顆抽表面 Pt 的 d-band center,跟 ΔG_{H^*} 的相關高達 -0.86 ;右邊 PDOS 也看得到,底下 Pt 多的時候,表面 Pt 的 d 態整個下移。所以這不是硬湊的擬合,真正在背後做功的,是 d-band center——這是整套框架的物理核心。

19 The mechanism in one line

A closed causal chain, each link independently measured



KEY MESSAGE Composition, electronics, and energetics tell **one consistent story**.

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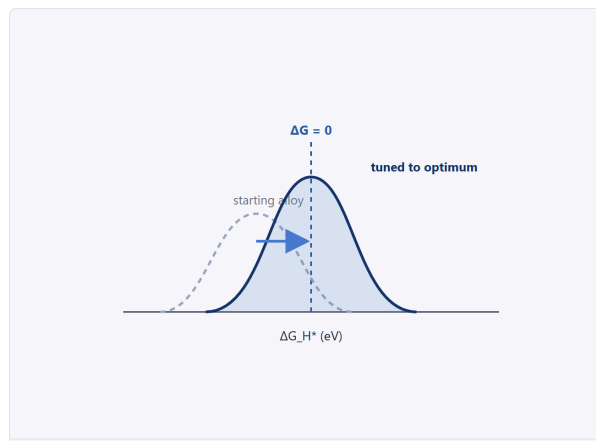
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一行講完機制

把整條因果鏈串成一句: 底下 Pt 上升、表面 Pt 的 d-band center 下移、Pt-H 變弱、 ΔG_{H^*} 往零靠近, 最後所有位點落在最佳點附近、形成族群。而且每一個環節我們都獨立量到了。成分、電子、能量, 講的是同一個一致的故事——這也是我整場最喜歡的一頁。

20 The conceptual advance: engineer the active-site population

Shift the whole ΔG_{H^*} distribution — its centre and spread — with the buried composition, not one site at a time



Tune the subsurface Pt / Cu / Ni / Co / Fe balance to slide the whole population toward $\Delta G_{H^*} = 0$.

Buried composition → electronic structure → adsorption → active-site population.

We stop optimizing one site and start **engineering the population**; the d-band center is the transferable bridge.

KEY MESSAGE Move from optimizing a single active site to **engineering the active-site population** — buried composition is the handle.

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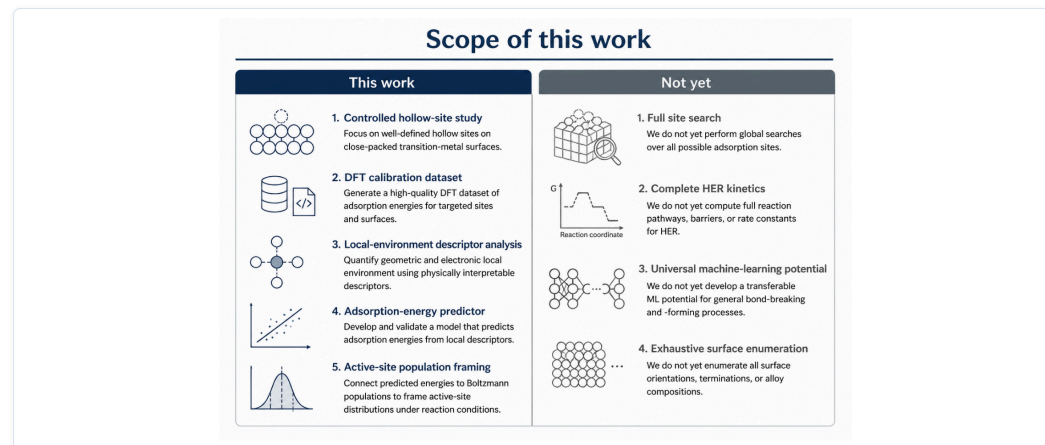
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觀念進展:設計位點族群 ★

如果整場只記一頁,我希望能是這一頁——這是這份工作真正的觀念進展。既然底下成分透過 d-band 控制吸附,那設計的對象,就應該是整個 ΔG_{H^*} 分布,它的中心和寬度,而不是某一個位點。請把這條鏈記起來:埋藏成分 → 電子結構 → 吸附 → 活性位點族群。我們不再優化一個位點,我們開始設計整個族群,而底下的成分,就是那個旋鈕。

21 Scope: what this work is — and is not

A controlled hollow-site calibration study and predictor framework — not a full search, kinetics, or MLP



KEY MESSAGE A descriptor-based local adsorption-energy predictor — the seed for active-site population estimation.

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第 21 頁

範圍:是什麼、不是什麼

在給各位看「預測」之前,先誠實地畫好界線。這份工作是:一個受控的、hollow-site、局部環境的吸附能框架;它不是:完整的 MLP、不是完整的 HER 動力學、不是把所有位點窮舉的搜尋,跨成分的轉移也還沒驗證。接下來我講的每一句,都在這條界線之內。

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22 Because the physics is simple, the population is predictable

A few local descriptors capture the d-band physics — so adsorption can be predicted, not enumerated

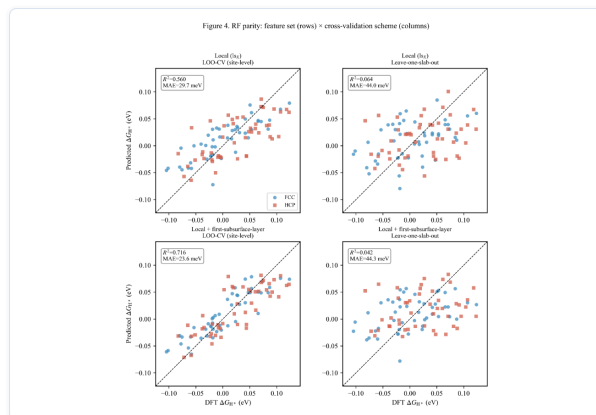


Figure 4. Predicted vs DFT ΔG_H^* from local descriptors (leave-one-out cross-validation).

KEY MESSAGE The mechanism is simple enough that **local descriptors predict adsorption** — ML is the evidence, not the point.

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第 22 頁

物理簡單,所以族群可預測

正因為背後的物理這麼簡單,吸附才變得可以預測。少數幾個局部描述符就抓住了 d-band 的物理,所以我們不需要把每個位點都算過。我試了很多種模型,它們都收斂到差不多 30 meV 的誤差——重點不是用了幾種演算法,而是:不管用哪一種,誤差都一樣小,代表是物理描述符在說話,不是某個演算法的功勞。機器學習在這裡是證據,不是主角。

23 DFT becomes calibration — from sites to populations

A handful of DFT sites calibrates the descriptors; the descriptors estimate the whole population

- 1 **Local composition + coordinates**
each hollow site's environment
- 2 **Local descriptors**
subsurface counts · geometry · d-band
- 3 **Descriptor model**
DFT-calibrated on 96 sites
- 4 **Predicted ΔG_{H^+}**
for uncalculated sites
- 5 **Active-site population**
 μ, σ, P_{opt}

DFT learns the rule — it does not enumerate every site.

A controlled **local-environment model** — calibrated, not yet a full MLP.

Goal rapid estimation of **active-site populations** across HEA composition space.

KEY MESSAGE The 96 DFT sites are **calibration for estimating active-site populations** across composition space.

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第 23 頁

DFT 變成校準

所以 DFT 的角色,正式從「普查」變成「校準」。流程是:每個 hollow 的局部成分跟座標、抽描述符、用少數 DFT 位點校準、再去估計沒算過的位點,最後拼出整個族群的 μ 、 σ 、最佳位點比例。我再強調一次界線:目前它是一個受控的局部環境模型,還不是完整 MLP。這 96 個 DFT 位點,是用來校準、估計族群的資料,不是終點。

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24 Where this goes next

Validated within these compositions; the frontier is population engineering across composition space

VALIDATED NOW

- Within the studied Pt-skin hollow-site dataset; the **d-band** descriptor transfers across the three compositions

NEXT

- Cross-composition **population engineering** — binary → quinary
- Carry the subsurface handle to **OER / ORR / CO₂RR**
- Toward **descriptor-guided, autonomous catalyst discovery**

KEY MESSAGE From within-composition evidence toward **descriptor-guided population engineering** across composition space.

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第 24 頁 下一步

那接下來呢?目前確定的:在我們研究的這幾個成分、hollow-site 範圍內成立,而且只有 d-band 這個描述符看起來能跨成分轉移。下一步:把這套族群工程推到跨成分——從二元一路到五元;把 subsurface 這個旋鈕帶到 OER、ORR、CO₂RR;最終走向描述符引導的、自動化的催化劑探索。

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25 Three things to take home

Subsurface control of active-site distributions in Pt-skin HEA

1 HEA catalysis is a population problem

96 Pt-skin sites form a near-optimal population ($\mu = +0.013$ eV; 92% within ± 0.10 eV) — **engineer the distribution**, not one site.

2 Subsurface composition controls H adsorption through the d-band

An electronegativity-ordered hierarchy (Pt > Cu > Ni \approx Co > Fe); subsurface Pt lowers the surface-Pt d-band center.

3 Toward descriptor-guided catalyst design

Because the physics is simple, the population can be predicted and engineered from local descriptors — a practical route to catalyst discovery (≈ 30 meV error).

KEY MESSAGE HEA site heterogeneity is, at heart, a **subsurface problem** — and a solvable one.

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第 25 頁 帶走的三件事

如果今天帶三件事走:第一,高熵合金的催化是一個族群問題——要設計的是分布,不是單一位點。第二,底下的成分透過 d-band 控制吸附,給出一個電負度排序的階層 Pt > Cu > Ni \approx Co > Fe。第三,正因為物理簡單,族群可以從局部描述符被預測、被設計,通向描述符引導的催化劑設計。

Design the buried atoms — not only the active sites

Buried composition → electronic structure → adsorption → the active-site population: the design framework for Pt-skin HEA catalysts.

AT A GLANCE

System	Fe-Co-Ni-Cu-Pt Pt-skin (111)
Data	96 DFT sites · 3 SQS slabs
Centre	$\Delta G_{H^+} = +0.013$ eV · 92% optimal
Driver	subsurface Pt → d-band ($r = -0.86$)
Predictable	≈30 meV from local descriptors

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With students Peggy P. M. J. and Yu-Huan Huang (黃宇桓)

第 26 頁

結語:設計埋藏的原子

總結成一句話,也是我今天最想留給各位的:設計那群埋在底下的原子,而不只是表面的活性位點。埋藏成分 → 電子結構 → 吸附 → 活性位點族群,這就是 Pt-skin 高熵合金的設計框架。謝謝大家,也歡迎指教;這份工作感謝 NSTC 的支持與我的學生們。

Backup — how the SQS is constructed

Supporting detail for Q&A: choosing the arrangement, and the Monte-Carlo annealing that finds it.

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第 27 頁

Backup · SQS 怎麼建

以下是 backup, 留給 Q&A。如果有人問 SQS 到底怎麼被找出來, 我們可以翻到這裡: 怎麼挑排列、以及用蒙地卡羅退火怎麼找到它。

28 Choosing an SQS: match the neighbours

Same composition, different arrangement — pick the one closest to random



clustered

mismatch: **high**



partly ordered

medium



random-like

low ✓ SQS

Count each atom's neighbours: the fractions should match the bulk composition.

Minimise the mismatch — the Warren-Cowley parameter $\alpha \rightarrow 0$ — over the nearest shells.

Next the following two slides show how that arrangement is actually **found**.

KEY MESSAGE The SQS is chosen by **neighbour statistics**, not by eye.

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第 28 頁

怎麼挑 SQS(backup)

挑 SQS 的關鍵是看鄰居。同樣成分有很多排法:團簇的跟隨機差很遠,部分有序的好一點,鄰居統計最接近隨機的那個才是 SQS。我們用 Warren-Cowley 參數量化落差、讓它趨近零。重點:SQS 是用鄰居統計挑的,不是用眼睛看的。

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29 Finding an SQS is an optimization

Swap two atoms, re-score the neighbour statistics, keep what gets closer to random



Each swap proposes a candidate structure; the **correlation mismatch (error)** falls as the arrangement approaches a random alloy.

KEY MESSAGE An SQS is found by **minimising the mismatch** between its neighbour statistics and a true random alloy.

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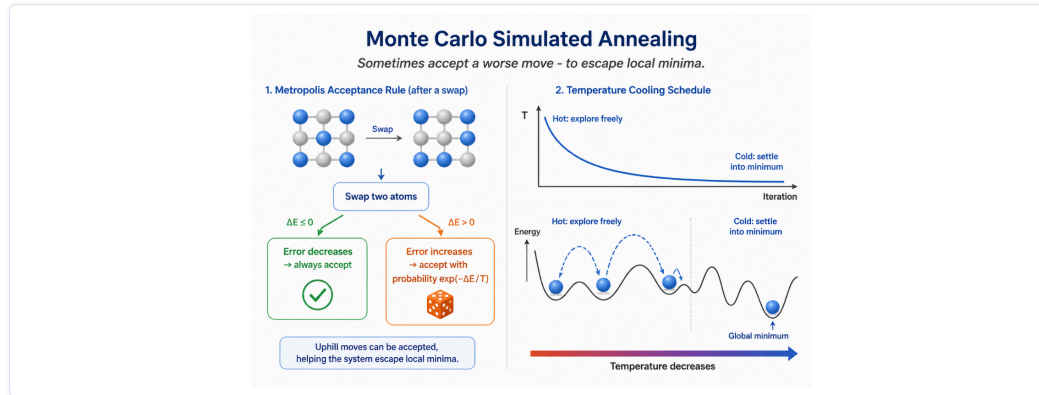
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找 SQS 是最佳化(backup)

而「挑」本身就是一個最佳化。隨機交換兩個原子、重算鄰居統計的誤差,變好就保留——你看誤差從 0.62、0.31 一路降到 0.12。找 SQS,就是最小化我的結構跟真隨機合金之間的統計落差。

30 Monte Carlo annealing finds the global best

Always accept improving swaps; accept worsening ones with probability $\exp(-\Delta E/T)$, cooling slowly



Simulated annealing accepts occasional **uphill moves** and lowers the "temperature" gradually, so the search escapes local minima and converges to the smallest statistical error.

KEY MESSAGE Annealing reaches the SQS with the **lowest correlation mismatch** — not just a nearby local minimum.

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第 30 頁

蒙地卡羅退火(backup)

但只接受變好的交換會卡在 local minimum。所以我們用蒙地卡羅退火:變好一定接受,變差也以 $\exp(-\Delta E/T)$ 的機率接受,溫度再慢慢降;這樣才能找到統計誤差全域最低的結構,而不是停在附近的小坑。這就是我們產生 SQS 的方式。