Bayesian Learning of Chemisorption for Bridging Complexities of Electronic Descritors

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Article

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Bayesian Learning of Chemisorption for Bridging Complexities of Electronic Descriptors

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Abstract

Building upon the d-band reactivity theory in surface chemistry and catalysis, we develop a Bayesian learning approach to probing chemisorption processes at atomically tailored metal sites. With representative species, e.g., *O and *OH, the Bayesian model trained with ab initio adsorption properties of transition metals predicts site reactivity at a diverse range of intermetallics and near-surface alloys while naturally providing uncertainty quantification from posterior sampling. More importantly, this conceptual framework sheds light on the orbitalwise nature of chemical bonding at adsorption sites with d-states characteristics ranging from bulk-like semi-elliptic bands to free-atom-like discrete energy levels, bridging complexities of electronic descriptors for the prediction of novel catalytic materials.

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Adsorption of molecules or their fragments at transition-metal surfaces is a fundamental process for many technological applications, such as chemical sensing, molecular self-assembly, and heterogeneous catalysis. Because of the convoluted interplay between electron transfer and orbital coupling, chemical bonding can be formidably complex. Recent decades have brought major advances in spectroscopic tools [1, 2] which reveal orbitalwise information of chemisorbed systems and concurrently in predicting chemical reactivity at sites of interest via electronic factors, e.g., number of valence $d$-electrons [3], density of $d$-states at the Fermi level [4], $d$-band center [5], and $d$-band upper edge [6, 7]. Compared with a full quantum-mechanics treatment of many-body systems, the simplicity of physics-inspired descriptors comes at a cost of limited generalization, particularly for high-throughput materials screening in which variations of site composition and configuration are sufficiently large to invalidate the perturbation approximation. Incorporation of multi-fidelity site features into reactivity models with machine learning (ML) algorithms has shown early promise for the prediction of adsorption energies with an accuracy comparable to the typical error ($\sim0.1 \text{–} 0.2 \text{ eV}$) of density functional theory (DFT) calculations [8–12]. However, the approach is largely black-box in nature, prohibiting its physical interpretation. Developing a theory-based, generalizable model of chemisorption that bridges complexities of electronic descriptors and predicts the binding affinity of active sites to key reaction intermediates with uncertainty quantification represents one of the biggest challenges in fundamental catalysis.

Here we present a Bayesian inference approach to probing chemisorption processes at metal sites by learning from ab initio datasets. The model is built upon the basic framework of the $d$-band reactivity theory [5] while employing a Newns-Anderson-type Hamiltonian [13, 14] to capture essential physics of adsorbate-substrate interactions. Such types of simplified Hamiltonians were originally used for describing magnetic properties of impurities in a bulk metallic host [13] and later extended with success by Newns and Grimley to chemisorption at surfaces [14, 15]. A basis set of orbitals consisting of the adsorbate and substrate states was used for solving the hybridization problem within a self-consistent Hartree-Fock scheme [14]. Despite a remarkable success in advancing the basic understanding of adsorption phenomena at surfaces, particularly for $d$-block metals [6], its application in materials design remains limited due to the lack of accurate model parameters and meaningful error estimates. Bayesian inference produces the posterior probability distribution of model parameters under the influence of observations and prior knowledge [16]. With representative species, e.g., $^*$O and $^*$OH, we demonstrate the predictive performance and physical interpretability of the Bayesian models for chemical bonding at a diverse range of in-
termetallics and near-surface alloys, bridging complexities of electronic descriptors in search of novel catalytic materials.

Figure 1. Illustration of chemical bonding at transition-metal surfaces within the \( d \)-band reactivity theory. An adsorbate \( A \) with a valence electron at a discrete energy level \( \epsilon_0^A \) first interacts with the free-electron-like \( sp \)-states of the substrate \( M \), forming a broadened resonance at \( \tilde{\epsilon}_a \) accompanied with electron transfer. Conceptually, it further overlaps and hybridizes with the narrowly distributed \( d \)-states, which leads to a splitting into bonding and anti-bonding states. The work function \( \phi \) and Fermi level \( \epsilon_F \) of \( M \) are marked.

Results

The \( d \)-band reactivity theory. Within the basic framework of the \( d \)-band reactivity theory for transition-metal surfaces, the formation of the adsorbate-metal bond conceptually takes place in two consecutive steps [5]. First, the adsorbate orbital (or orbitals) \( |a\rangle \) at \( \epsilon_0^A \) couples to the delocalized, free-electron-like \( sp \)-states of the metal substrate, leading to a Lorenzian-shaped resonance state at \( \tilde{\epsilon}_a \). Second, the adsorbate resonance state interacts with the localized, narrowly-distributed metal \( d \)-states, shifting up in energies due to the orthogonalization penalty for satisfying the Pauli principle and then splitting into bonding and anti-bonding states. The first step interaction contributes a constant \( \Delta E_0 \) albeit the largest part of chemical bonding. The variation in adsorption energies from one metal to another is determined by the metal \( d \)-states. This part of the interaction energy \( \Delta E_d \) can be further partitioned into orbital orthogonalization and hybridization contributions [17]. As a first-order approximation, the orbital hybridization energy can be evaluated by the changes of integrated one-electron energies [18]. The orbital orthogonalization cost is con-
considered simply as proportional to the product of interatomic coupling matrix and overlap matrix, $V S$, or equivalently $\alpha V_{ad}^2$, where $V_{ad}^2$ is the interatomic coupling matrix element squared when the interacting atoms are aligned along $z$-axis and $\alpha$ is the orbital overlap coefficient. The absolute value of $V_{ad}^2$ can be written as $\beta \bar{V}_{ad}^2$, in which the standard values of $\bar{V}_{ad}^2$ relative to Cu are readily available on the Solid State Table [19]. The overall adsorption energy $\Delta E$ can then be written as the sum of the energy contributions from the $sp$-states $\Delta E_0$ and the $d$-states $\Delta E_d$, with the latter of which depending on the symmetry and degeneracy of the adsorbate valence orbitals. Another important information from this framework is the evolving density of states projected onto the adsorbate orbital(s) upon adsorption, $\rho_a$. A full account of the theoretical framework is presented in the Method section.

There are a number of unknown parameters within the basic framework of the $d$-band reactivity theory as discussed above, including the energy contribution from the $sp$-band $\Delta E_{sp}^0$, adsorbate resonance energy $\tilde{\epsilon}_a$ relative to the Fermi level, $sp$-band chemisorption function $\Delta_{sp}^0$, orbital overlap coefficient $\alpha$, and orbital coupling coefficient $\beta$. By least-squares fitting of the adsorbate density of states as in Eq. 2 and the integrated one-electron energy changes to those from DFT calculations [20, 21], the Schmickler model of electron transfer has been developed to understand $H_2$ evolution/oxidation and $OH^-$ adsorption at metal-electrolyte interfaces. However, the deterministic fitting of adsorption properties from a single surface is prone to overfitting or trapping into a locally optimal region, limiting its application in catalysis.

**Bayesian learning.** We instead employ Bayesian learning to infer the vector of model parameters $\vec{\theta} = (\Delta E_{sp}^0, \tilde{\epsilon}_a, \Delta_{sp}^0, \alpha, \beta)'$ from the evidence, i.e., ab initio adsorption properties, along with prior knowledge if available [16]. In Bayes’ view, those parameters are not deterministic point values, but rather a probabilistic distribution reflecting not necessarily the random nature of physical variables but rather the uncertainty. The use of parameter distributions as opposed to computationally-derived point values has obvious advantages for uncertainty quantification. In the chemical sciences, Bayesian learning has been used for calibration and validation of thermodynamic models for the uptake of $CO_2$ in mesoporous silica-supported amines [22], designing the Bayesian error estimation functional with van der Waals correlations [23], and identifying potentially active sites and mechanisms of catalytic reactions [24], just to name a few. The Bayesian approach allows one to infer the posterior probability distribution $P(\vec{\theta}|D)$ for latent variables based on the prior $P(\vec{\theta})$ as well as the likelihood function $P(D|\vec{\theta})$ subject to the observation $D$. The
Figure 2. Bayesian parameterization. a The co-variance of the joint posterior distribution for each parameter pair and the 1D histogram of model parameters ($\Delta E_{sp}^0$, $\tilde{\epsilon}_a$, $\Delta_0^{sp}$, $\alpha$, and $\beta$) from MCMC simulations for $^*$O adsorption at the fcc-hollow site of the \{111\}-terminated transition-metal surfaces. A top view of the model structure is shown in inset. b Schematic illustration of the MCMC sampling in a multi-dimensional parameter space.
To avoid this complication, the Markov chain Monte Carlo (MCMC) method [25], whose sampling criterion only depends on the relative posterior density of the newly explored point and its preceding point, is used. To compute the transition probability of each MCMC step, we define the sum of the (negative) logarithm of the likelihood functions corresponding to projected density of states onto each adsorbate orbital and binding energies with a hyper-parameter adjusting the weight of two contributing metrics, see details in the Method section for its optimization. After a large number of MCMC samplings, burning (discard) of the first half of the trajectory and then thinning (1 out of 5 samplings) were performed before extracting converged values from the joint posterior distributions. The convergence of the MCMC sampling is checked by using parallel chains with different starting parameter sets such that the variance of interchain samplings is close or within 1.2–1.5 times to that of intrachains [25]. The complete code of Bayesian inference is available at a Github repository https://github.com/hlxin/bayeschem for public access.

**Model development.** In Fig. 2(a), we are showing the co-variance of the joint posterior distribution for each parameter pair and the 1D histogram of model parameters ($\Delta E^0_{sp}$, $\tilde{\epsilon}_a$, $\Delta^0_{sp}$, $\alpha$, and $\beta$) from MCMC simulations for *O adsorption at the fcc-hollow site of the {111}-terminated transition-metal surfaces (Cu, Ag, Au, Ni, Pd, Pt, Co, Rh, Ir, and Ru). We assume three degenerate O$_{2p}$ orbitals as used before [26] for demonstration of the approach, while later extend it to multi-orbital models. To attain converged posterior distributions, 200k MCMC sampling steps with the Metropolis-Hastings algorithm were performed in a multi-dimensional parameter space illustrated in Fig. 2(b). In Fig. 2, the approximate contours for 68%, 95%, and 99% confidence regions are shown at the lower triangle, showing little to no correlation between most of latent-variable pairs.

With the converged Bayesian sampling, in Fig. 3(a), it shows the model-predicted adsorption energies of *O at the fcc-hollow site of transition-metal surfaces, with a mean absolute error (MAE) $\sim$0.17 eV compared to DFT calculations. The standard deviation of model prediction using the posterior distribution of model parameters ($\vec{\theta}$, $\vec{\sigma}$) is overlaid, providing for the first time uncertainty quantification of adsorption energies within the $d$-band reactivity theory. Figure 3(b) shows DFT-calculated and model-constructed projected density of states onto the O$_{2p}$ orbital using the posterior means of model parameters, taking Pt(111) as an example (see all the surfaces in Fig. S1). The chemisorption function $\Delta(\epsilon)$ and its Hilbert transform $\Lambda(\epsilon)$ along with the straight adsorbate line ($\epsilon - \tilde{\epsilon}_a$) are shown for the graphical solution of the Newns-Anderson-Grimley model [14, 15]. The intersects indicated by solid circles in Fig. 3(b) represent the O$_{2p}$-Pt$_{5d}$ bonding and
Figure 3. Model-predicted adsorption properties. a DFT-calculated *O adsorption energies (atomic O as the reference) at transition-metal surfaces vs. model prediction using the posterior distribution of model parameters ($\tilde{\theta}$, $\tilde{\sigma}$). Error bars represent the standard deviation of model prediction with 1000 random draws from converged trajectories. b Projected density of states onto the O$_{2p}$ orbital from DFT calculations (solid) and model prediction (dashed) using the posterior means of model parameters, taking Pt(111) as an example. The graphical solution to the Newns-Anderson-Grimley model is also shown, in which the adsorbate-substrate bonding and anti-bonding states are clearly captured.

anti-bonding states, with the latter above the Fermi level, suggesting a strong covalent interaction of *O at Pt(111). Given the simplicity of the model, the clearly captured electronic structure of the adsorbate-substrate system and the reactivity trend are satisfying.

To demonstrate the approach for general adsorbates with multiple valence orbitals that possibly contribute to bonding, we have explicitly treated O$_{2p}$ states with the doubly degenerate $p_{xy}$ orbitals and the single $p_z$ orbital in Bayesian learning. We infer model parameters ($\tilde{\epsilon}_a$, $\Delta^0_{sp}$, and $\beta$) corresponding to each non-equivalent adsorbate orbital together with an orbital-independent $\alpha$ [27] and a global parameter $\Delta E^0_{sp}$. The posterior parameter distributions are shown in Fig. S2. From the posterior means of model parameters, we can see that the orbital coupling coefficient $\beta$ of $p_{xy}$ (1.67 eV$^{-1}$) is smaller than that of $p_z$ (1.77 eV$^{-1}$), consistent with the symmetry analysis that the $p_{xy}$ orbitals that are parallel to a surface form $\pi$-bonds with the $d$-states, while the $p_z$ orbital can interact through a stronger $\sigma$ bond. A weaker coupling manifests itself in a narrower orbital splitting of $\pi/\pi^*$ than that of $\sigma/\sigma^*$, which has been previously observed using the angle-resolved photoemission spectroscopy on Cu and Ni [28]. In Fig. S3 and S4, it shows that the model-constructed projected density of states onto symmetry-resolved orbitals closely resemble the DFT-calculated
distributions and the predicted values of *O adsorption energies have a MAE $\sim 0.17$ eV, suggesting the robustness and generalizability of the approach.

To test prediction capability of the Bayesian model for unseen systems, we took the *OH species as a case study because of its fundamental importance in understanding the nature of chemical bonding [29] and practical interests as a key reactivity descriptor in metal-catalyzed electrochemical O$_2$ reduction [30], CO$_2$ reduction [31], H$_2$ oxidation in alkaline electrolytes [32], etc. Three frontier molecular orbitals, i.e., 3$\sigma$, 1$\pi$, and 4$\sigma^*$, are assumed to be involved in chemical bonding [29]. Symmetry-resolved, molecular orbital density of states of states projected onto OH along with adsorption energies are used as the DFT ground truth $Y$ in Eq. 6. With the Bayesian model developed here (see Fig. S5-7 for posterior parameter distributions, model-predicted adsorption energies and projected density of states on training samples), we predict *OH binding energies at a diverse range of intermetallics and near-surface alloys. Specifically, we included A$_3$B, A$'$@A$_{ML}$, A-B@A$_{ML}$, A$_3$B@A$_{ML}$, A@A$_3$B, and A@AB$_3$, where A (A$'$) represents 10 fcc/hcp metals used in the model development and B covers $d$-metals across the periodic table (see ref [33] for structural details and tabulated data). The A sites of above-mentioned surfaces exhibit diverse characteristics of the metal $d$-states ranging from bulk-like semi-elliptic bands to free-atom-like discrete energy levels [34], as illustrated in Fig. 4(a) using Pt and Ag$_3$Pt as examples. Similar to previous observations of single-atom alloys with coinage metal hosts [34, 35], a reactive guest metal often exhibits peaky signatures within the $d$-band due to the energy misalignment of coupling $d$-$d$ orbitals [7]. A direct consequence of such diverse electronic properties of adsorption sites is that no single electronic descriptor can capture the local chemical reactivity accurately. Encouragingly, the Bayesian model, parameterized using 10 pristine transition-metal data, predicts *OH adsorption energies on 512 alloy surfaces with a MAE 0.16 eV, see Fig. 4(b), similar to data-driven ML models [8–11] and outperforming the state-of-the-art electronic descriptors, e.g., the $d$-band center $\epsilon_d$ (MAE: 0.20 eV) and upper edge $\epsilon_u$ (MAE: 0.23 eV).

**Orbitalwise interpretation of chemical bonding.** More importantly, the Bayesian framework with built-in physics allows us to quantitatively interrogate the underlying mechanism of chemical bonding that is difficult to obtain from purely data-driven regression models. Taking *OH adsorption at the M (10 fcc/hcp metals) site of \{111\}-terminated Ag$_3$M intermetallics as examples, Fig. 4(c) shows the partition of *OH adsorption energies resulting from the 2$^{nd}$ step interaction ($\Delta E_d$) into orbital orthogonalization and hybridization. As we can see, for 3$d$, 4$d$, and 5$d$ series...
Figure 4. Model test and interpretation. a The $d$-states of a transition-metal site exhibit diverse characteristics ranging from bulk-like semi-elliptic bands to free-atom-like discrete energy levels (Pt and Ag$_3$Pt as examples). b DFT-calculated vs. model-predicted adsorption energies of *OH at the atop site of {$111$}-terminated intermetallics and near-surface alloys. c Partition of *OH adsorption energies at the M site of Ag$_3$M into orbital hybridization and orthogonalization of $3\sigma$, $1\pi$, and $4\sigma^*$ orbitals with the metal $d$-states.

of the guest metal M, the orthogonalization and hybridization contributions decrease in magnitude from left to right across the periodic table, while the hybridization dominates the reactivity trends. The changes in $\Delta E_{\text{hyb}}^d$ can be understood from the Newns-Anderson-Grimley model, with the position and occupancy of adsorbate-substrate anti-bonding states tracking with the $d$-band center or upper edge. The orthogonalization energy is proportional to $f$ and $V_{\text{ad}}^2$ (see Eq. 4), which are offsetting each other to a certain extent ($V_{\text{ad}}^2$ decreases while $f$ increases across 3$d$, 4$d$, and 5$d$ series), leading to a less dominant role than the hybridization. The orbitalwise contributions from $3\sigma$, $1\pi$, and $4\sigma^*$ shown in Fig. 4(c) with different fill patterns suggest that the main contribution of *OH adsorption at $d$-metal surfaces is from the $1\pi$ orbital. This is supported by projected molecular orbital density of states in Fig. S7, which shows that $3\sigma$ and $4\sigma^*$ are forming resonance
states after their interactions with the \( sp \)-states of the metal site without noticeable splitting due
to \( d \)-states. Thus, they do not contribute to the observed trend of *OH adsorption. The Bayesian-
optimized orbital coupling coefficients of \( 3\sigma \) and \( 4\sigma^* \) are rather small (.12 and .001 as shown in
Fig. S5, respectively), supporting unfavorable orbital overlaps with the \( d \)-states. This rationalizes
the observation that *OH prefers the nearly-parallel adsorption geometry on most of the \( d \)-metals
to maximize the interaction of the \( 1\pi \) orbital with metal \( d \)-states, while *OH on Na(111) adsorbs
more strongly in a up-straight orientation because of a lack of such directional interactions. This
orbitalwise insight of chemical bonding could provide guidance in tailoring orbital-specific char-
acteristics of the metal \( d \)-band for desired catalytic properties through site engineering.

**Conclusions**

To conclude, we present the first Bayesian model of chemisorption by learning from *ab initio*
adsorption properties. The model leverages the well-established \( d \)-band reactivity theory and a
Newns-Anderson-type Hamiltonian for capturing essential physics of chemisorption processes.
We demonstrated that the Bayesian models of descriptor species, e.g., *O and *OH, optimized
with pristine transition-metal data predicts adsorption energies at a diverse range of atomically-
tailored metal sites with a MAE \(~0.1–0.2\) eV while providing uncertainty quantification. In-
corporation of physics-based models into data-driven ML algorithms, e.g., deep learning, might
hold the promise toward developing highly accurate while interpretable reactivity models. Fur-
thermore, this conceptual framework can be broadly applied to unravel orbital-specific factors
governing adsorbate-substrate interactions, paving the path toward design strategies to go beyond
adsorption-energy scaling limitations in catalysis.

**Methods**

**DFT calculations** Spin-polarized DFT calculations were performed through Quantum ESPRESSO [36]
with ultrasoft pseudopotentials. The exchange-correlation was approximated within the generalized gra-
dient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) [37]. \{111\}-terminated metal surfaces
were modelled using \((2 \times 2)\) supercells with 4 layers and a vacuum of 15 Å between two images. The bot-
tom two layers were fixed while the top two layers and adsorbates were allowed to relax until a force criteria
of .1 eV/Å. A plane wave energy cutoff of 500 eV was used. A Monkhorst-Pack mesh of \( 6 \times 6 \times 1 \) was used
to sample the Brillouin zone, while for molecules and radicals only the Gamma point was used. Gas phase
species of O and OH were used as the reference for adsorption energies of *O and *OH, respectively. The
projected atomic and molecular density of states were obtained by projecting the eigenvectors of the full
system at a denser $k$-point sampling ($12 \times 12 \times 1$) with a energy spacing 0.01 eV onto the ones of the part, as determined by gas-phase calculations. Further details and tabulated data can be found in ref [9].

The $d$-band reactivity theory To revisit the $d$-band theory of chemisorption along with new developments, let’s consider a metal substrate $M$ in which electrons occupy a set of continuous states with one-electron wavefunctions $|k\rangle$ and eigenenergies $\epsilon_k$, and an isolated adsorbate species $A$ with a valence electron described by an atomic wavefunction $|a\rangle$ at $\epsilon_0^a$, see Fig. 1. When the adsorbate is brought close to the substrate, the two sets of states will overlap and hybridize with each other. The strength of such interactions is determined by the coupling integral $V_{ak} = \langle a|\hat{H}|k\rangle$, where $\hat{H}$ is the system Hamiltonian. Within the Newns-Anderson-Grimley model of chemisorption [13–15], $\hat{H}$ is defined as,

$$\hat{H} = \sum_\sigma \left\{ \epsilon_{a\sigma} n_{a\sigma} + \sum_k \epsilon_k n_{k\sigma} + \sum_k (V_{ak} c_{k\sigma}^\dagger c_{a\sigma} + H.c.) \right\},$$

(1)

where $\sigma$ denotes the electron spin, $n$ is the orbital occupancy operator, and $c^\dagger$ and $c$ represent the creation and annihilation operator, respectively. The first two terms in Eq. 1 are the one-electron energies from the adsorbate and the substrate when they are infinitely separated in space. The last term captures the coupling, or intuitively electron hopping, between the adsorbate orbital $|a\rangle$ and a continuum of substrate states $|k\rangle$. If the one-electron states of the whole system can be described as a linear combination of the unperturbed adsorbate and substrate states, the one-electron Schrödinger equation can be solved using the Green’s function approach [14]. In Fig. 1, we illustrate the chemisorption process of a simple adsorbate onto a $d$-block metal site characterized by delocalized $sp$-states and localized $d$-states [17]. The interaction of the adsorbate state at $\epsilon_0^a$ with the structureless $sp$-states, typically accompanied with electron transfer from/to the Fermi sea, results in a broadened resonance (or so-called renormalized adsorbate state) at a perturbed energy level $\tilde{\epsilon}_a$. Conceptually viewing chemical bonding as consecutive steps in Fig. 1, the renormalized adsorbate state then couples with the narrowly distributed $d$-states, shifting up in energies due to orbital orthogonalization that increases the kinetic energy of electrons and splitting into bonding and anti-bonding states. One important information from this framework is the evolving density of states projected onto the adsorbate orbital $|a\rangle$ upon adsorption

$$\rho_a(\epsilon) = \frac{1}{\pi} \frac{\Delta(\epsilon)}{[\epsilon - (\epsilon_a + \Lambda(\epsilon))]^2 + \Delta(\epsilon)^2},$$

(2)

in which spin is neglected for simplicity. The effective adsorbate energy level, denoted by $\epsilon_a$, is determined by the image potential of a charged particle in front of conducting surfaces and the Coulomb repulsion between electrons in the same orbital [14]. The chemisorption function $\Delta(\epsilon)$ includes contributions from
the \textit{sp}-states and the \textit{d}-states

\[
\Delta(\epsilon) = \pi \sum_k V_{ak}^2 \delta(\epsilon - \epsilon_k) = \Delta_{sp} + \Delta_d.
\]  

(3)

To simplify the matter, only the 2\textsuperscript{nd} step interaction, i.e., the coupling of the renormalized adsorbate state with the substrate \textit{d}-states, is explicitly considered in Eq. 2. As a new development in our approach, we include an energy-independent constant $\Delta_{0sp}$ along with $\Delta_d$ as the chemisorption function $\Delta(\epsilon)$. The inclusion of $\Delta_{0sp}$ provides a lifetime broadening of the adsorbate state, serving as a mathematical trick to avoid burdensome sampling of the resonance, i.e., the Lorentzian distribution $\tilde{\rho}_a$ from the 1\textsuperscript{st} step interaction in Fig. 1. Accordingly, $\epsilon_a$ will be replaced by the renormalized adsorbate state at $\tilde{\epsilon}_a$. Attributed to the narrowness of a typical metal \textit{d}-band, $\Delta_d$ can be simplified as the projected density of \textit{d}-states onto the metal site $\rho_d(\epsilon)$ modulated by an effective coupling integral squared $V_{ad}^2$, i.e., $\Delta_d \simeq \pi V_{ad}^2 \rho_d(\epsilon)$. $\Lambda(\epsilon)$ is the Hilbert transform of $\Delta(\epsilon)$. In this framework, the interaction energy between the adsorbate and the substrate can be partitioned into two contributions, i.e., $\Delta E_{sp}$ and $\Delta E_d$. $\Delta E_{sp}$ is the energy change due to the interaction of the unperturbed adsorbate orbital(s) with the delocalized \textit{sp}-states, while $\Delta E_d$ is the energy contribution from further interactions with the localized \textit{d}-states of the substrate. Since all \textit{d}-block metals have a similar, free-electron-like \textit{sp}-band, $\Delta E_{sp}$ can be approximated as a surface-independent constant $\Delta E_{0sp}$ albeit the largest contribution to bonding [17]. To calculate $\Delta E_d$, we include both the attractive orbital hybridization $\Delta E_{d}^{hyb}$ and repulsive orbital orthogonalization $\Delta E_{d}^{orth}$ [27, 38]:

\[
\Delta E_{d}^{hyb} = \frac{2}{\pi} \int_{-\infty}^{\epsilon_F} \tan^{-1} \left( \frac{\Delta(\epsilon)}{\epsilon - \tilde{\epsilon}_a - \Lambda(\epsilon)} \right) d\epsilon - 2 \int_{-\infty}^{\epsilon_F} \epsilon \tilde{\rho}_a d\epsilon
\]

\[
\Delta E_{d}^{orth} = 2(\langle \tilde{n}_a \rangle + f) S_{ad}|V_{ad}|.
\]

(4)

The constant 2 considers spin degeneracy of the orbital, $\langle \tilde{n}_a \rangle$ is the occupancy of the renormalized adsorbate state by integrating the Lorentzian distribution $\tilde{\rho}_a$ up to the Fermi level $\epsilon_F$ (taken as 0), and $f$ is the idealized \textit{d}-band filling of the metal atom. The $\tan^{-1}$ is defined to lie between $-\pi$ to 0 since $\Delta_{0sp}$ is a non-zero constant across the energy scale [-15, 15] eV. Thus there is no need to explicitly include localized states even if present below or above the \textit{d}-band. As a good approximation, the overlap integral $S_{ad}$ is linearly proportional to the coupling integral for a given adsorbate, i.e., $S_{ad} \approx \alpha |V_{ad}|$, in which $\alpha$ is termed the orbital overlap coefficient. Similarly, the effective coupling integral squared $V_{ad}^2$ can be written as $\beta \bar{V}_{ad}^2$, where $\beta$ denotes the orbital coupling coefficient and $\bar{V}_{ad}^2$ characterizes the interorbital coupling strength when the bonding atoms are aligned along the \textit{z}-axis at a given distance [39]. Its values of \textit{d}-block metals relative to that of Cu are readily available on the Solid State Table [19].
Bayesian learning

Due to the computationally intensive nature of the MCMC algorithm, there is a need for a more efficient implementation of the Newns-Anderson-Grimley model than what is obtained by Python and standard libraries like SciPy and NumPy. We make extensive use of Cython, a C++ extension to the standard Python, to speed up the performance (10−1000 times) of some CPU-intensive functions in the model, e.g., Hilbert transform. To perform MCMC sampling, we use PyMC, a flexible and extensible Python package which includes a wide selection of built-in statistical distributions and sampling algorithms [40], e.g., Metropolis-Hastings. A “burn-in” of the first half of the samplings and then thinning (1 out of 5 samplings) was performed to ensure that subsequent ones are representative of the posterior distribution. Convergence of our MCMC-based sampling was verified using parallel chains [25]. The MCMC sampling results can be directly visualized using corner, an open-source Python module. We took Normal for floating-point variables unrestricted in sign, LogNormal for non-negative parameters, and Uniform for others.

$\Delta E_{sp}^0$ and $\tilde{\epsilon}_a$ can be estimated from DFT calculations of the adsorbate on a simple metal, e.g., sodium (Na) at the face-centered cubic (fcc) phase. Specifically, for $^{*}\text{O}$, we used $\Delta E_{sp}^0 \sim N(-5,0,1), \tilde{\epsilon}_a \sim N(-5,1), \Delta E_{sp}^0 \sim LN(1,0.25), \beta \sim LN(2,1),$ and $\alpha \sim U(0,1)$. For $^{*}\text{OH}$, we used $\Delta E_{sp}^0 \sim N(-3,0,1), \tilde{\epsilon}^{3\sigma}_a \sim N(-6,1), \tilde{\epsilon}_1 \sim N(-2,1),$ and $\tilde{\epsilon}^{4\sigma}_a \sim N(4,1)$. We assume that the predicted adsorption properties from Eqs. 2 and 4 are subject to independent normal errors. Specifically, for the property $Y$ and the surface $i$ we have

$$Y_i = \hat{Y}_i(\vec{\theta}) + \sigma \epsilon_i, \ i = 1, 2, \ldots, n$$  \hspace{1cm} (5)

where $\epsilon_i$ is an independent and standard normal random variable and $\sigma$ is the standard deviation, allowing for a mismatch between the model prediction $\hat{Y}_i(\vec{\theta})$ and the DFT ground truth $Y_i$. In this approach, we define the likelihood function of the property $Y$ from $n$ observations [41]

$$P(Y|\vec{\theta}, \sigma) \propto \sigma^{-n} \exp \left[ -\frac{1}{2\sigma^2} \sum_{i=1}^{n} \left\{ Y_i - \hat{Y}_i(\vec{\theta}) \right\}^2 \right],$$  \hspace{1cm} (6)

where the sum runs over $n$ training samples for the property $Y$, which is either the projected density of states onto an adsorbate orbital or adsorption energies. For adsorption energies, $Y_i$ and $\hat{Y}_i$ are scalar values with no ambiguity. For projected density of states, it is a vector of paired values, i.e., the one-electron energy of a state and its probability density, thus deserving a clarification. The mean squared residuals of model prediction from Eq. 2 for the surface $i$ is used as $\{Y_i - \hat{Y}_i(\vec{\theta})\}^2$ in Eq. 6. To compute the transition probability of each MCMC step, we define the sum of the (negative) logarithm of the likelihood functions corresponding to projected density of states onto each adsorbate orbital and binding energies with a hyper-parameter $\lambda$ adjusting the weight of two contributing metrics, i.e., $-\sum \ln(P_{\text{ps}}) - \lambda \ln(P_{\Delta E})$. To optimize this parameter, we varied it on a grid of 1, 10, 100, and 1000, and found that 100 is the optimal value to
obtain the best performance in adsorption energy prediction. The complete code of Bayesian inference is available at a Github repository https://github.com/hlxin/bayeschem for public access.


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Illustration of chemical bonding at transition-metal surfaces within the d-band reactivity theory. An adsorbate A with a valence electron at a discrete energy level $\tilde{\epsilon}_a$ first interacts with the free-electronlike sp-states of the substrate M, forming a broadened resonance at $\sim \tilde{\epsilon}_a$ accompanied with electron transfer. Conceptually, it further overlaps and hybridizes with the narrowly distributed d-states, which leads to a splitting into bonding and anti-bonding states. The work function $\phi$ and Fermi level $\epsilon_F$ of M are marked.
Figure 2

Bayesian parameterization. a The co-variance of the joint posterior distribution for each parameter pair and the 1D histogram of model parameters ($\Delta E_{0sp}$, $\Delta 0_{sp}$, $a$, $a$, and $b$) from MCMC simulations for *O adsorption at the fcc-hollow site of the {111}-terminated transition-metal surfaces. A top view of the model structure is shown in inset. b Schematic illustration of the MCMC sampling in a multi-dimensional parameter space.
Figure 3

Model-predicted adsorption properties. a DFT-calculated *O adsorption energies (atomic O as the reference) at transition-metal surfaces vs. model prediction using the posterior distribution of model parameters ($\theta; \sigma$). Error bars represent the standard deviation of model prediction with 1000 random draws from converged trajectories. b Projected density of states onto the O2p orbital from DFT calculations (solid) and model prediction (dashed) using the posterior means of model parameters, taking Pt(111) as an example. The graphical solution to the Newns-Anderson-Grimley model is also shown, in which the adsorbate-substrate bonding and anti-bonding states are clearly captured.
Figure 4

Model test and interpretation. a The d-states of a transition-metal site exhibit diverse characteristics ranging from bulk-like semi-elliptic bands to free-atom-like discrete energy levels (Pt and Ag3Pt as examples). b DFT-calculated vs. model-predicted adsorption energies of *OH at the atop site of {111}-terminated intermetallics and near-surface alloys. c Partition of *OH adsorption energies at the M site of Ag3M into orbital hybridization and orthogonalization of $3\sigma$, $1\pi$, and $4\sigma^*$ orbitals with the metal d-states.

Supplementary Files

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- supp.pdf