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Unifying Theory of Electronic Descriptors of Metal Surfaces upon Perturbation

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We present a unifying theory for predicting electronic descriptors (e.g., the d -band center ϵ_d) of transition and noble metal surfaces by interpretable deep learning. Distinct from black-box machine learning models, fundamental insights into underlying physical processes can be obtained without sacrificing prediction accuracy. In addition to the charge transfer, strain, and ligand effects in the conventional wisdom, we identified orbital resonance in d -electron hopping as a crucial factor that modulates the shape of the d -states distribution, thereby shifting ϵ_d of a d -metal site upon perturbation. Our findings reveal the promise of machine learning in advancing domain knowledge, paving the way toward theory-guided, data-driven design of materials beyond brute-force screening.

Prediction of the electronic structure of atoms, molecules, and condensed matters is the foundation of quantum chemical simulations, underpinning our basic understanding of diverse properties of materials^{1–3}. From the Schrödinger equation⁴ for many-body systems of electrons and nuclei to the one-electron Kohn-Sham formulation^{5,6}, computational science has been a mainstream paradigm in providing a delicate description of electronic states for a collection or periodic array of atoms, crucial for materials design toward practical applications, such as catalyzing chemical and energy transformations⁷. However, the self-consistent field methods beyond the bottom rung on Jacob’s ladder⁸ of density-functional approximations with increasingly complex ingredients of the electron density or Kohn-Sham orbitals become computationally intractable in exploration of an infinite chemical space. In recent years, machine learning (ML) has gained prominence as a valuable tool for predicting electronic descriptors of materials⁹ (e.g., moment characteristics of electronic density of states^{10–12}, band gap¹³, and charge carrier mobility¹⁴), attributed to its ability to discern intricate patterns in high-dimensional data. Nevertheless, modern ML algorithms, particularly deep learning¹⁵ with pre-engineered or self-derived features, tend to learn highly nonlinear correlations rather than causal relationships, and thus extracting knowledge from data remains a challenging task^{16–22}.

To realize highly efficient, accurate, and most importantly, interpretable prediction of the materials’ property of interest, an emerging approach is to hybridize learning algorithms with domain science. This strategy has proven to be promising for predicting interatomic forces in atomistic modeling of materials²³, partial charges of atoms in molecules²⁴, viscosity of disordered matter²⁵, and chemical reactivity of solid surfaces^{22,26–28}. As a key concept in heterogeneous catalysis with d -metal active sites, the energy distribution of the site-resolved density of d -states ρ_d is known to govern their interactions with surface species, including reaction intermediates and transition states²⁹. According to the Hammer-Nørskov d -band theory³⁰, the binding energy of an adsorbate chemisorbed at d -metal surfaces linearly correlates with the d -band center ϵ_d of site atoms (the first moment of the locally projected density of d -states relative to the Fermi level ϵ_F). This electronic descriptor has been widely used for understanding reactivity trends of d -block metals, bimetallics,

and metal compounds to a certain extent^{31,32}. Within this context, several key factors come into play that govern variations in ϵ_d of a d -metal site upon perturbation, including lattice strain manifested by interatomic distances and metal ligand dictated by the spatial extent of the d -orbitals r_d of neighboring atoms^{33–36}. Both of these factors exert an influence on orbital overlap, thereby affecting the d -band dispersion. Additionally, any charge transfer, or the lack thereof, can change or put a constraint on the d -band filling f_d , with direct implications on ϵ_d . Due to the convoluted interactions involved, it is difficult to decouple different effects and extract actionable insights into electronic descriptors of active sites. An in-depth understanding of governing factors is needed for rational design of catalytic materials with specific reactivity properties^{37–40}.

In this Letter, we present a unifying theory, enabled by interpretable deep learning, for predicting electronic descriptors of d -block metal sites at a broad range of metal surfaces with varying composition, structure, facet/termination, and external strain. In addition to the charge transfer, strain, and ligand effects in the conventional wisdom, a resonance effect in d -electron hopping on the d -band shape (e.g., skewness, kurtosis), and thus ϵ_d , has been identified. The physical insights gained here can be directly translated into design strategies of catalytic materials with fine-tuned electronic descriptors.

Building upon the rectangular d -band approximation^{36,41}, we developed an analytical model relating the d -band center ϵ_d of a d -metal site with physically transparent factors, i.e., d -band filling f_d and width W_d (see details of the derivation in Supplemental Material⁴²), as shown in Eq. 1,

$$\epsilon_d = W_d \left[\frac{\epsilon_d^\infty}{W_d^\infty} - (f_d - f_d^\infty) \right], \quad (1)$$

where ∞ represents the reference system chosen as an atom in the bulk metal of face-centered cubic (fcc) phase, W_d is the full width of a rectangular band, and f_d is the fractional d -band filling (0–1). Both ϵ_d and ϵ_d^∞ are relative to ϵ_F . For a hypothetical 2D square lattice of atoms with a single atomic orbital and equal separation d , a rectangular density of states emerges from the free electron approximation (Fig. 1a)⁴². Utilizing the tight-binding approximation, the distinctive features of the critical points can be captured, manifested as Van Hove singularities (Fig. 1b), see the derivation in Supplemental Material⁴².

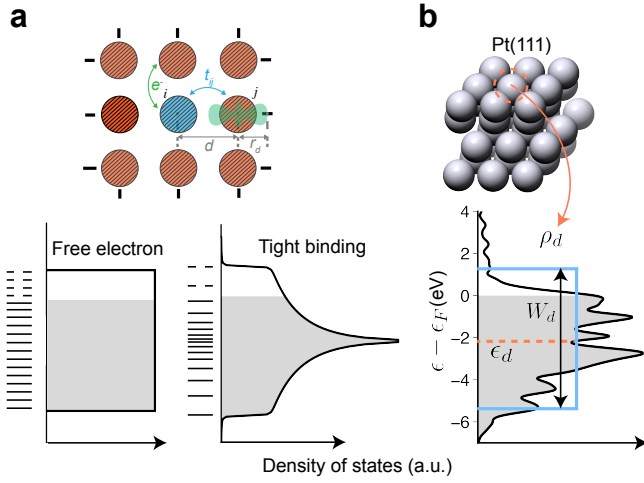


Figure 1. (a) For a hypothetical 2D array of metal atoms with a single valence orbital separated by the distance d , there is the formation of a set of evenly spaced states that can be represented by a uniform rectangular band within the free-electron approximation. The states below the Fermi level ϵ_F are occupied with a d -band filling f_d that can be influenced by charge transfer if any, for example due to alloying. A tight-binding treatment with the spatial extent of the d -orbital r_d and the electron hopping integral t_{ij} introduces irregularities on the band structure. (b) A self-consistent density of d -states distribution ρ_d projected onto a surface atom of Pt(111) can be well represented as a rectangle centered at ϵ_d with width W_d .

tal Material⁴² for 1D, 2D, and 3D systems. It is pertinent to note that any real-world material system, e.g. Pt(111) in Fig. 1c, characterized by a specific composition and topology, exhibits a complex band structure. This complexity can be perceived as a deviation from an idealized rectangular band. In this model, there are two terms that contribute to ϵ_d of a d -metal site. The first term describes the site behavior under a constant f_d , i.e., without d -charge transfer. Since ϵ_d^∞ is below the Fermi level for d -metals with $f_d > 0.5$, the ϵ_d of a site atom is negatively correlated with its W_d ^{36,43}, i.e., the center moves down (up) in energy as the band widens (narrows). The second term represents a rigid-band scenario with the electron inflow (outflow) of the d -orbitals, which shifts the d -band down (up), accordingly⁴⁴.

For localized metal d -states, W_d is proportional to the square root of the second central moment, i.e., $W_d = \xi \sqrt{M_2^d}$, with the constant $\xi = 2\sqrt{3}$ for a rectangular band³⁶. Because of the principle of rotational invariance, M_2^d can be computed from the two-center electron-hopping paths between the valence d -orbitals of the atom of interest i and all valence orbitals ϕ of neighboring atoms j aligned along the z -axis^{2,45}, i.e., $M_{2,i}^d = \sum_{j \neq i}^{r_{ij} < r_c} \sum_{\phi} (t_{ij}^{d\phi})^2$. A cutoff radius r_c of 5.5 Å is used for its comprehensiveness in capturing pertinent orbital interactions. Within the Muffin-Tin Orbital theory², the d -electron hopping integral depends on the d -orbital sizes (ligand effect) and interatomic distances (strain effect)^{33,34} by $t_{ij}^{ds} = \eta_{ds} \hbar^2 r_{d,i}^{3/2} / m d_{ij}^{7/2}$, $t_{ij}^{dd} = \eta_{dd} \hbar^2 r_{d,i}^{3/2} r_{d,j}^{3/2} / m d_{ij}^5$, in

which the symmetry-dependent coefficients η along with the spatial extent of the d -orbital r_d of transition and noble metals are tabulated on the Solid State Table^{2,45}. Clearly, these two factors are strongly coupled with each other in determining M_2^d and thus W_d , modulating ϵ_d through Eq. 1. In some cases, one effect tends to be predominant over the other. For instance, in the epitaxial overlayer structure of bimetallic alloys, the strain from the substrate is believed to be crucial⁴⁶. However, in the epitaxial sandwich-like structure, the lattice spacing of site atoms remains unchanged, leading to the dominance of metal ligand from the subsurface layer³⁶.

With our domain knowledge, we parameterize the semi-empirical model as shown in Eq. 1, which results in $\epsilon_d = \alpha 2\sqrt{3} \sqrt{M_2^d} (\epsilon_d^\infty / W_d^\infty - \beta \Delta\chi)$, where α is a correction coefficient of $2\sqrt{3} \sqrt{M_2^d}$ beyond the rectangular band approximation, $\Delta\chi$ is the difference in the Mulliken electronegativity of the site atom of interest and the geometric mean of that of its 1st nearest neighbors, and β is a linear correlation coefficient for capturing the d -charge transfer if any. We keep the bulk d -band center ϵ_d^∞ and width W_d^∞ of the reference from density-functional theory (DFT) calculations as tabulated values. In the analytical expression of M_2^d , we replace d_{ij} with ζd_{ij} , in which ζ is a bond-wise correction coefficient for electron hopping integrals. Since d_{ij} is unrelaxed interatomic distances from a graph representation of the site atoms, we anticipate that ζ contains information about the equilibrium geometry embedded in the ground truth of ϵ_d . We substitute r_d by λr_d ³⁵, in which λ is a necessary correction factor from DFT-calculated $M_2^{d,\infty}$ since r_d was originally fitted to experimental data². Among these parameters, we treat α and β as atom-specific variables that depend on the local chemical environment; ζ is a bond-wise variable for electron hopping within the cutoff radius of a site atom; and λ is considered as an element-wise quantity that is invariant with respect to site perturbation⁴². A deep learning architecture of choice with the aforementioned neural state variables α , β , and ζ , together with the global variables ξ (taking $2\sqrt{3}$) and λ , can be seamlessly integrated with the theory module to predict ϵ_d within the framework of theory-infused neural networks (TinNet)²⁷. The regression module can be built upon a graph convolutional network (GCN) or its variants, the input of which is an undirected graph, encoding the atomic information and bonding interactions of each atom with its neighbors. We include f_d , ϵ_d , and W_d in the cost function for error minimization with their DFT-calculated values as the ground truth. Since the physics beyond what is included in the semi-empirical model (Eq. 1) is embedded into machine-learned neural state variables, an in-depth understanding of governing factors for ϵ_d can be obtained from *post hoc* attribution analysis of the deep learning models once trained. It should be noted that, although similarities exist in utilizing physical equations within the learning process, as seen with physics-informed neural networks^{47,48} and symbolic regression⁴⁹⁻⁵¹, TinNet embeds domain theories in the network architectures and enables parameterization of physical models with data.

The dataset consists of 12,165 unique surface sites with a diverse range of local chemical environments in fcc surfaces. The learning curves of ML models are plotted with

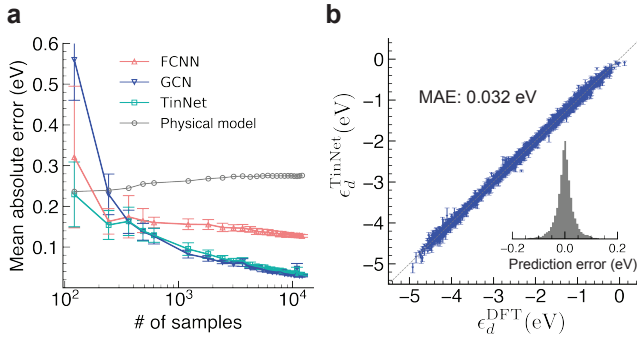


Figure 2. (a) The learning curves of FCNN, GCN, and TinNet models for the ϵ_d prediction of d -metal sites in a diverse set of d -metal catalysts. The physics-based model is also shown for comparison with data-driven deep learning models. The error bar corresponds to the standard deviation of the error estimates from nested 10-fold cross-validation. MAE represents the mean absolute error. (b) The parity plot between the DFT-calculated and TinNet-predicted ϵ_d along with the histogram of prediction errors.

the mean absolute errors (MAEs) from the nested 10-fold cross-validation as a function of the number of data samples (Fig. 2a). The details of hyperparameter optimization and model training are shown in Supplemental Material⁴². The prediction accuracy of TinNet final models (MAE: 0.032 eV) can be visualized through the parity plot (Fig. 2b). With easily accessible features of metal sites including the tight-binding d -band width W_d (i.e., $2\sqrt{3}\sqrt{M_2^d}$ from electron-hopping paths), the local electronegativity difference $\Delta\chi$, ϵ_d^∞ , and W_d^∞ , a fully-connected neural network (FCNN) model is developed showing a larger MAE (~ 0.13 eV) than TinNet models. For the purely physical model based on the rectangular band approximation (Eq. 1) and the d -charge conservation principle, the MAEs stay roughly constant (~ 0.27 eV). The prediction performance of the graph convolutional network (GCN) is also evaluated and it has a similar MAE to the TinNet models with GCN as the backend in the regression module. While advanced architectures such as SchNet⁵², GemNet⁵³, and ALIGNN⁵⁴ offer sophisticated graph representations and neural message passing, they show marginal improvements in predictive accuracy albeit with a large number of training parameters⁴². The value of the TinNet framework lies in its ability to inject scientific interpretability into learning, a merit that remains significant despite the advent of more complex network architectures.

To extract insights into the electronic structure of d -metal surfaces upon perturbation, we first carried out exploratory and *post hoc* attribution analysis for global interpretation. The distributions of machine-learned variables across all site samples are shown in Fig. 3a. The α values have a wide distribution around unity. This indicates that for a wide range of metal sites the rectangular d -band approximation is valid only for qualitative estimations while the shape correction is needed for accurate predictions. We attribute the variable pair (α, ξ) with $\xi = 2\sqrt{3}$ to a previously overlooked resonance effect, originated from the energy misalignment or off-resonance of

interacting orbitals that introduces irregularities on the band structure and influences the band shape⁵⁵. The values of $\beta\Delta\chi$ of surface sites are close to zero, which implies that the charge transfer effect induced by a local environment change is negligible, consistent with experimental measurements and the d -charge conservation principle⁵⁶. The distribution of ζ values is around 1.0 with a standard deviation of 0.04. The evidence that ζ largely captures the geometric relaxation of metal-metal bonds is shown in Supplemental Material⁴² where $\{111\}$ -terminated, strained Pd (+5.0% to -5.0%) and PdAg alloy surfaces were selected for illustration. In both series, ζd_{ij} is positively correlated with the DFT-relaxed bond lengths. Notably, the average of ζ values for a given site is inversely correlated with its bulk lattice constant, i.e., a system with a tensile (compressive) strain tends to contract (expand) once geometrically relaxed. Intuitively, the relaxation effect behaves like a “restoring force” to perturbed orbital coupling in response to the change of interatomic spacing, satisfying the bond-order conservation principle.

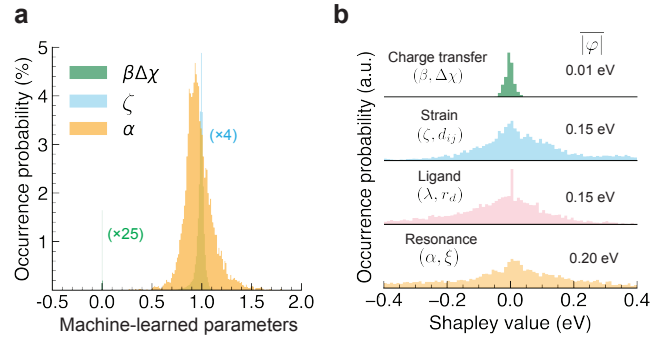


Figure 3. (a) The histograms of machine-learned values ($\beta\Delta\chi$, ζ , α) from 10-fold cross-validated final models. (b) The histograms of the Shapley values φ of physical variable pairs for contributing to the ϵ_d shift of metal sites relative to pure metals of the same site type, e.g., $\{111\}$. The mean of the absolute Shapley values $|\varphi|$ for each effect is shown to characterize their overall importance.

To quantitatively decouple the contributions from different effects on ϵ_d , SHAP (SHapley Additive exPlanations)⁵⁷ analysis was performed with the pure metal surfaces of fcc phase as the base reference. Machine-learned neural state variables and their special pairs, i.e., $(\beta, \Delta\chi)$, (ζ, d_{ij}) , (λ, r_d) , and (α, ξ) , were a set of players in cooperative game theory. Thanks to the additive characteristics of Shapley values, individual gains from a variable pair can be joint together. The distributions of their Shapley values are plotted in Fig. 3. Across the whole dataset, the charge transfer effect contributed by $(\beta, \Delta\chi)$ plays almost no role in tuning ϵ_d with a mean absolute Shapley value of 0.01 eV, reaffirming the d -charge conservation principle in electronic structure of d -metals. The strain (ζ, d_{ij}) and ligand (λ, r_d) effects have a similar value of 0.15 eV, consistent with the traditional wisdom. Importantly, the newly proposed resonance effect from (α, ξ) contributes the most to the ϵ_d shift with a mean of absolute Shapley value changes ~ 0.20 eV.

To further understand the physical origin of the ϵ_d shift of

a d -metal site upon perturbation, e.g., alloying, we have performed a subgroup analysis of catalytically relevant $\text{Pt}_{\text{ML}}/\text{M}$ alloy surfaces with a Pt monolayer on $\{111\}$ -terminated M substrates^{38,39}. The Shapley values of each variable pair relative to Pt(111) are plotted in Supplemental Material⁴², showing a clear dominance of the strain effect on this series of model structures. It can also be seen that the Shapley values of ζ and d_{ij} generally change oppositely, which is resonant with the aforementioned trend of the geometric relaxation as a secondary effect in strain perturbation. To unravel the underlying factors governing different contributions, we correlate the Shapley values from each variable pair with physically transparent factors. Since the origin of charge transfer, strain, and ligand effects is known, it is not surprising that there are linear correlations between their Shapley values with the electronegativity χ , the bulk lattice constant a , and d -orbital radius r_d of the substrate M, respectively, as shown in Fig. 4. Noteworthy, we found that there is a strong correlation of the resonance effect with ϵ_d^∞ of the substrate M relative to ϵ_F . According to the moment theorem⁵⁸, the shape of a d -band, characterized by high-order moments, e.g., skewness, kurtosis, is closely related to the site energy change ($\epsilon_i - \epsilon_j$) that appears as part of the multi-site hopping integrals. It is important to note that such energy off-resonance does not affect the M_2^d of the d -band (see proof in Supplemental Material from both solid-state physics and chemistry perspectives⁴²). Among the $\text{Pt}_{\text{ML}}/\text{M}(111)$ surface alloys with $5d$ metals as the substrate, the one with Re has the highest skewness (+0.48) defined as the normalized 3^{rd} central moment of the d -band, $M_3^d/(M_2^d)^{3/2}$. The formation of unoccupied states skewed toward high energies due to a misalignment of interacting d -

levels between Pt and Re downshifts the distribution in order to keep a constant f_d , revealing the underlying origin of the resonance effect of electronic descriptors in d -metal catalysis.

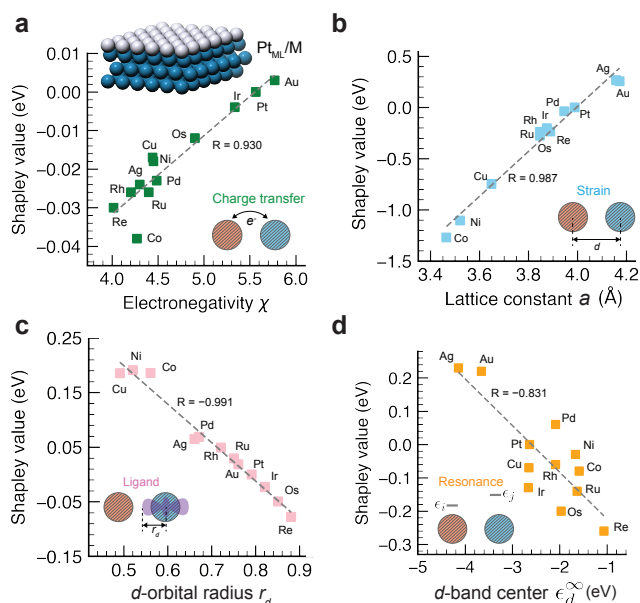


Figure 4. Subgroup interpretation of the $\text{Pt}_{\text{ML}}/\text{M}(111)$ overlayer alloys. The correlation between the Shapley value of each variable pair in contributing to the ϵ_d shift and the underlying governing factor for charge transfer (a), strain (b), ligand (c), and resonance (d). Schematics are shown for illustrating each physical effect.

In summary, by integrating domain knowledge into graph neural networks we develop a unifying theory for predicting electronic descriptors, particularly the d -band center ϵ_d , of transition and noble metal surfaces upon perturbation. Compared with purely data-driven ML models, theory-infused deep learning attains a similar prediction accuracy while being intrinsically interpretable. With *post hoc* attribution analysis, we provide in-depth interpretation of contributing effects to the ϵ_d of a d -metal site in a broad range of catalytically relevant systems. Most importantly, we identified a resonance effect as a previously overlooked mechanism modulating the ϵ_d shift in addition to the charge transfer, strain, and ligand effects. The framework provides a holistic way of equipping data-driven deep learning with scientific interpretability, particularly for advancing theoretical knowledge in electronic structure of d -metal sites and opening up a new avenue toward theory-guided, data-driven design of solid materials for catalysis applications.

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All source data along with Jupyter notebooks for data preprocessing, model development, and *post hoc* analysis are available from the GitHub repository: https://github.com/hlxin/tinnet_dos.

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H.X. and Y.H. conceived the idea and designed the computational approach. Y.H. and S.H.W. conducted DFT calculations and machine learning model development. Y.H. performed the detailed model interpretation. M.K. designed the TinNet web interface. All authors contributed to the writing and editing of this manuscript.

The authors declare no competing interests.