Linear scaling relations have led to an understanding of trends in catalytic activity and selectivity of many reactions in heterogeneous and electro-catalysis. Yet, linear scaling between the chemisorption energies of any two small molecule adsorbates is not guaranteed. A prominent example is the lack of scaling between the chemisorption energies of carbon and oxygen on transition metal surfaces. In this work, we show that this lack of scaling originates from different re-normalised adsorbate valence energies of lower-lying oxygen versus higher-lying carbon. We develop a model for chemisorption of small molecule adsorbates within the $d$-band model by combining a modified form of the Newns-Anderson hybridisation energy with an effective orthogonalization term. We develop a general descriptor to $a$ priori determine if two adsorbates are likely to scale with each other.

I. INTRODUCTION

Understanding the formation of a bond between a metallic surface and an adsorbate is critical to the field of heterogeneous catalysis.\textsuperscript{1–6} In principle, the bond (free) energies of all intermediates and transition states of a process fully determines the rate, but in most cases the number of such bond energies is so large that it becomes very difficult to single out why a given catalyst surface is the optimal catalyst for the reaction studied.\textsuperscript{7} Scaling relations have provided a method to define a few bond energies as descriptors of the catalytic rate.\textsuperscript{7–10} It has been found quite generally that, for a given surface structure, the bond energies of intermediates and transition states scale linearly with a few bond energies, and once these relations have been found, the full kinetics can be described as a function of the descriptors. These scaling relations result in the “volcano” relationships between rates/selectivities and descriptors that are used extensively in heterogeneous catalysis. It provides a theoretical basis for the heuristic Sabatier principle,\textsuperscript{11} which suggests that the optimal catalyst is one with an optimal bond energies for relevant intermediate(s). The scaling relations show which intermediate(s) are relevant and the optimal value(s) for the binding energy of these intermediate(s).

Linear or piece-wise linear scaling relationships are observed when two adsorbates bind to the metal through the same atom such as C*, CH*, CH$_2$* and CH$_3$*,\textsuperscript{12,13} where * denotes the surface. However, it is not always observed when the binding atom is different, such as in the case of C* and O*.\textsuperscript{7} There is currently no $a$ priori measure to suggest if the chemisorption energies of two arbitrary adsorbates scale with one another.

In this work, we develop a model which allows for an $a$ priori estimation of whether the chemisorption energies of two adsorbates scale with each other. We use the Hammer-Nørskov model, which suggests that the trends in adsorption energies of transition metals are related to the bonding between the adsorbate valence states and metal $d$-bands.\textsuperscript{5} The hybridisation energy is described using a modified form of the Newns-Anderson model,\textsuperscript{14} combined with an effective expression for the orthogonalisation energy. The model demonstrates that the root cause of lack of scaling between two adsorbed species lies in differences of their re-normalised adsorbate valence energies. For instance, O–p states are considerably lower in energy than C–p states. Through this analysis, we identify the conditions under which carbon and oxygen do scale with each other.

II. CHEMISORPTION ENERGIES OF CARBON AND OXYGEN DO NOT SCALE

In this section, we discuss the lack of linear scaling relations between the chemisorption energies of C* and O*. We use DFT calculations to obtain these chemisorption energies (see Section VI for computational details). In general, for any adsorbate $A$, the chemisorption energy $\Delta E_A$ is defined as,

$$\Delta E_A = E_{A^*} - E_s - E_A$$

where $A^*$ represents $A$ adsorbed on the surface, $s$ is the free surface and $A$ is the adsorbate in vacuum. Figure 1a shows the chemisorption energies of O* plotted against that of C*. It is evident that there is a significant amount of scatter and no linear scaling relations are observed.

Despite the lack of linear scaling, there is, broadly, an increasing trend for both C* and O* energies in Figure 1a. Metals that bind C* strongly (for example, Fe) also bind O* strongly and those that bind C* weakly (Au, Ag) also bind O* weakly. However, due to the noticeable amount of scatter, this general “rule” does not always hold. Consider the example of platinum: For a constant $\Delta E_C$, $\Delta E_O$ is about 2 eV weaker than what linear scaling would predict. This weaker than expected binding affects the catalytic activity of Pt, where it is considered weak.

\textsuperscript{a)}Electronic mail: jkno@dtu.dk
FIG. 1. a) Scatter plot of DFT chemisorption energies of O, $\Delta E_O$, and C, $\Delta E_C$; the colour refers to the row in the periodic table, $3d$ metals are red, $4d$ metals are blue and $5d$ metals are green. Note that there is no scaling between the adsorbates ($R^2 = 0.56$); scaling of b) $\Delta E_O$ and c) $\Delta E_C$ with the $d$-band centre. The adsorbate is always placed at the most stable site, which is at hollow for all transition metals.

binding for oxygen based reactions\textsuperscript{15,16} but has a lot of interesting carbon chemistry.\textsuperscript{8,13,17–24} Furthermore, the noble metals (Au, Ag and Cu) appear to tail-off, having significantly weaker O* and C* chemisorption energies.

Figure 1(b,c) shows the chemisorption energies of O* and C* plotted against the $d$-band centre, a commonly used descriptor in heterogeneous catalysis.\textsuperscript{5} The tailing-off behaviour of the chemisorption energies at large negative $\epsilon_d$ values is similar to that seen in Figure 1a.

Scatter in Figure 1a is markedly reduced when each row of transition metals are plotted separately as shown in Figure 1(d-f). Mid-row transition metals for each series display linear behaviour (Fe, Co, Ni for $3d$; Ru, Rh, Pd for $4d$ and Os, Ir, Pt for $5d$), with the final elements of each row (Cu, Ag, Au) falling off a linear fit.

These observations raise two fundamental questions for understanding scaling relations:

1. Why do the noble metals (Cu, Ag and Au) deviate from the linear scaling relationships constructed along a given row of transition metals (such as in Figure 1d-f)?

2. What is the source of the scatter in scaling relations across rows of the periodic table (such as in Figure 1a, deviation in red, blue and green points)?

In the following, we present a model of chemisorption, which is able to explain these observations.

III. MODEL OF CHEMISORPTION

In this section, we develop a model for the chemisorption of mono-atomic adsorbates that includes hybridisation and orthogonalisation contributions. Following the Hammer-Nørskov $d$-band model,\textsuperscript{5} we split the total chemisorption energy into the aforementioned components as,

$$E_{chem} = E_{hyb} + E_{ortho} + \text{constant} \quad (1)$$

The hybridisation component of the energy, $E_{hyb}$, is incorporated through the Newns-Anderson model

$$E_{hyb} = \frac{2}{\pi} \int_{-\infty}^{\epsilon_f=0} \arctan \left( \frac{\Delta_d + \Delta_0}{\epsilon - \epsilon_a - \Lambda} \right) d\epsilon - 2\epsilon_a \quad (2)$$

where $\Delta_d$ represents a continuous, $\epsilon-$dependent coupling element, $V_{ak}$, between the metal $d$-density of states and the adsorbate state. In line with Ref\textsuperscript{14}, it is taken to be a semi-ellipse centered around $\epsilon_d$ with a width $w_d$. $\Delta_0$
is a constant contribution applied to approximate the broadening of the adsorbate states into resonances upon interaction with sp-states of the metal, Λ is the Hilbert transform\(^{14}\) of \(\Delta_d + \Delta_0\) and \(\epsilon_a\) is the renormalised energy level of the adsorbate, after interaction with the sp states of the metal (see SI Section II for further details) and \(\epsilon_f\) is the Fermi level (set to 0). The factor of 2 in both terms represents degeneracy of the spin up and down states considered in the model. The adsorbate projected density of states is given by,

\[
\rho_{aa}(\epsilon) = \pi^{-1} \frac{\Delta_d + \Delta_0}{[\epsilon - \epsilon_a - \Lambda]^2 + (\Delta_d + \Delta_0)^2}
\]

where the \(\epsilon\) dependence of \(\Delta\) and \(\Lambda\) has been omitted for clarity. The occupancy of the adsorbate state is given simply by \(n_a = \int_{-\infty}^{\epsilon_f} \rho_{aa}(\epsilon) d\epsilon\).

We obtain the orthogonalisation penalty to the chemisorption energy by comparing the eigen energies from the narrow-band limit of the Newns-Anderson model with a two-level problem that includes a constant coupling term \(S\),\(^{5, 25}\)

\[
E_{\text{ortho}} = -2 (n_a + f) V_{ak} S
\]

where \(f\) is the filling of the metal states, given by

\[
f = \int_{-\infty}^{0} (\Delta_d + \Delta_0) d\epsilon \int_{0}^{\infty} (\Delta_d + \Delta_0) d\epsilon, \text{ s.t. } 0 < f < 1
\]

With the above functional form for \(E_{\text{hyb}}\) and \(E_{\text{ortho}}\), we now parametrise the sum of the two, i.e. \(E_{\text{chem}}\) (through Equation 1). We choose the O–p and C–p states to have \(\epsilon_a = -5\) eV and \(\epsilon_a = -1\) eV, respectively.\(^{26}\) The projected densities of states resulting from Equation 3 with the chosen \(\epsilon_a\) for the O* and C* also qualitatively agree with our DFT calculated projected density of states shown in Figure 2a, where the localised O* states (shown in orange) are consistently lower-lying in energy as compared to those of C* (shown in purple). Note that the adsorbate projected density of states of both O* and C* show similar features to experimental X-ray photoemission spectra, such as localised states on either side of the \(d\)-band from Ref\(^{27}\) for Cu and Ni, which further validates our approach of using a single renormalised energy for O* and C*.

As in Ref\(^{8}\), we assume that the coupling elements are proportional to those from the linear muffin tin orbital (LMTO) framework (denoted as \(V_{sd}\)),\(^{28}\) i.e. \(V_{ak}^2 = \beta V_{sd}^2\), where \(\beta\) only depends on the adsorbate species. Analogous to Ref\(^{29}\), we write \(V_{sd}\) as,

\[
V_{sd} = \eta \frac{M_a M_d}{p_a + l_a + 1}
\]

where \(\eta\) are structure factors, which do not depend on bond-length between adsorbate and metal, \(M_a\) depends on only the adsorbate states,\(^{30}\) \(M_d = (s^{2l_d+1} \Delta_1)^{\frac{1}{2}}\), where \(l_d\) and \(l_a\) are the quantum numbers of the metal \(d\)-states (\(l_d = 2\)) and adsorbate \(p\) states (\(l_a = 2\)) respectively, \(s\) is the Wigner-Seitz radii and \(\Delta_1\) is the Anderson-width (taken from bulk calculations).\(^{31}\) In this work, we set \(r = s\) to incorporate the varying bond length between the adsorbate and metal into the coupling elements (see SI Section VI for parameter fitting).

We also assume that the overlap matrix element is proportional to the coupling element, \(S = -\alpha V_{ak}\), where \(\alpha\) is another constant which is identical for all metals.

### Table I. Fitting parameters for C* and O* from a least-squares error minimisation routine

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>(\alpha) (eV(^{-1}))</th>
<th>(\beta) (eV(^{2}))</th>
<th>(\Delta_0) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C* ((\epsilon_a = -1) eV)</td>
<td>0.094</td>
<td>1.44</td>
<td>0.1</td>
</tr>
<tr>
<td>O* ((\epsilon_a = -5) eV)</td>
<td>0.062</td>
<td>4.55</td>
<td>0.1</td>
</tr>
</tbody>
</table>

The only free parameters in the model for a given adsorbate are \(\alpha\) and \(\beta\), which are independent of the metallic surface species. We obtain these parameters by fitting \(E_{\text{chem}}\) to the DFT energies in Figure 1. Table I shows the least-squares errors fitted \(\alpha\) and \(\beta\) for O* and C*. Note that \(E_{\text{chem}}\) is multiplied by 3 to account for three bonds due to the preferred adsorption site being the hollow site (see SI Section V for on top site fitting). Figure 2(b,c) shows parity plots for fitted chemisorption energies from the model vs. computed DFT energies.

Having fit \(\alpha\) and \(\beta\) to chemisorption energies from DFT, we compute the variation of \(E_{\text{chem}}\) for O* and C* with \(\epsilon_d\) for 3d, 4d and 5d series of transition metals shown in Figure 2(d,e) respectively. Note that for a fixed row, the chemisorption energy is a function of only \(\epsilon_d\), as \(V_{ak}^2\) and \(w_d\) for each row of the periodic table are functions of \(\epsilon_d\).

The model reproduces two important features present in the DFT calculated energies. First, the variation of \(E_{\text{chem}}\) for O* and C* with \(\epsilon_d\) in Figures 2(d,e) show nearly linear behaviour up to \(\epsilon_d \approx -3\) eV. At more negative \(\epsilon_d\) values, \(E_{\text{chem}}\) decreases, consistent with the DFT computed trends in Figure 1(b,c). Second, the lack of scaling between different rows of transition metals is also seen in the model chemisorption energies. Figure 2f shows \(E_{\text{chem}}\) for O* and C*, plotted against each other. Similar to the trends from DFT calculations in Figure 1(b-c), taken together the points do not scale, but they do scale when each transition metal row is plotted separately, up to the weak binding noble metals. Having developed and parameterised the model, we now use it to explain the variation of the DFT energies with \(\epsilon_d\) in Section IV.

### IV. Root Cause of Lack of Linear Scaling Lies in Differences of Re-Normalised Energies Between Adsorbates

The lack of scaling between \(E_{\text{chem}}\) of O* and C* arises from differences in how \(E_{\text{hyb}}\) and \(E_{\text{ortho}}\) of the two adsor-
bates vary with respect to $\epsilon_d$. In this section, we describe 1) why noble metals Cu, Ag and Au fall off otherwise linear scaling relationships 2) why scaling of transition metals is better performed across a fixed row. These two observations come directly from computed energies in Section II. We trace the origin of both these effects to differences in $\epsilon_a$ values of the two adsorbates.

### A. Saturation of hybridisation energies leads to fall-off of Cu, Ag and Au from linear scaling

Figure 3(a,b) shows $E_{\text{hyb}}$ of O* and C* vs. $\epsilon_d$, which has three distinct regions. At positive $\epsilon_d$ values, $E_{\text{hyb}}$ increases approximately linearly with $\epsilon_d$. At intermediate $\epsilon_d$ values ($-2.5 < \epsilon_d < 0$ eV for 4d and 5d metals and $-1.6 < \epsilon_d < 0.9$ eV for 3d metals), $E_{\text{hyb}}$ decreases with $\epsilon_d$. Finally, at large, negative $\epsilon_d$ values ($<-3.5$ eV for 4d and 5d metals and $<-1.9$ eV for 3d metals), $E_{\text{hyb}} \to 0$, i.e. it saturates completely for O*, while just starting to saturate for C*.

The difference in the variation of $E_{\text{hyb}}$ with $\epsilon_d$ at large, negative $\epsilon_d$ (< $-3.5$ eV for 4d and 5d metals and < $-1.9$ eV for 3d metals) gives rise to scatter in linear scaling relations between O* and C* along a fixed row of transition metals. For O*, the variation of $E_{\text{chem}}$ in this large, negative $\epsilon_d$ region is determined solely by $E_{\text{ortho}}$ as $E_{\text{hyb}} \to 0$. For C*, all regions of $\epsilon_d$ are jointly determined by the contributions of $E_{\text{hyb}}$ and $E_{\text{ortho}}$. This mismatch of energy contributions, $E_{\text{ortho}}$ alone for O* and $E_{\text{hyb}} + E_{\text{ortho}}$ for C*, explains why metals such as Cu, Ag and Au in the large, negative $\epsilon_d$ region fall off linear scaling relationships.

To quantify the $\epsilon_d$ value at which $E_{\text{hyb}}$ saturates, we compute the derivative of $E_{\text{hyb}}$ with respect to $\epsilon_d$, $E'_{\text{hyb}}$, and determine the largest $\epsilon_d$ value at which it tends to zero, which we denote as $\epsilon_s$,

$$\epsilon_s = \arg\max(\epsilon_d) \quad \text{for} \quad E'_{\text{hyb}}(\epsilon_d) \to 0 \quad E_{\text{hyb}} \to 0 \quad (6)$$

where $E'_{\text{hyb}}$ is given by,
FIG. 3. $E_{\text{hyb}}$ for a) O* b) C*; there is a clear saturation, i.e. $E_{\text{hyb}} \to 0$ in the case of O*, but only starting to saturate for C*. $E_{\text{hyb}}$ is shown as dashed lines; star denotes $\epsilon_s$, c) Scaling between $E_{\text{hyb}}$ between O* and C*; $E_{\text{ortho}}$ for d) O*, e) C*; dashed lines represent $n_a + f$ f) scaling of $E_{\text{ortho}}$ between O* and C*; g) adsorbate projected density of states for (orange) O* and (purple) C* with $\Delta$ (black); all quantities are normalised by their maximum value; $n_a$ for both adsorbates for Rh are annotated h) $\epsilon_s$, a measure of the saturation in $E_{\text{hyb}}$ in a,b for a range of adsorbate energy levels i) $E_{\text{ortho}}$ for different adsorbates $\epsilon_a = -1, -3, -5$ eV plotted against $E_{\text{ortho}}$ at $\epsilon_a = -5$ eV.

\[
\frac{dE_{\text{hyb}}}{d\epsilon_d}(\epsilon_d) = E'_{\text{hyb}}(\epsilon_d) = \frac{2}{\pi} \int_{-\infty}^{\epsilon_f=0} \frac{\Delta_d'(\epsilon - \epsilon_a - \Lambda) + \Lambda' (\Delta_d' + \Delta_0)}{\left(\epsilon - \epsilon_a - \Lambda\right)^2 + (\Delta_d' + \Delta_0)^2} d\epsilon
\]

where $\Delta_d'(\epsilon, \epsilon_d) = \partial \Delta_d / \partial \epsilon_d$ and $\Lambda'(\epsilon, \epsilon_d) = \partial \Lambda / \partial \epsilon_d$ (see SI Section III).

Figure 3(a,b), dashed lines, shows $E'_{\text{hyb}}$ for both O* and C* respectively. Consistent with the aforementioned trends in $E_{\text{hyb}}$, there are three regions of $E_{\text{hyb}}$. At positive $\epsilon_d$ values $E_{\text{hyb}}$ is negative, in line with linear increasing variation of $E_{\text{hyb}}$. At intermediate $\epsilon_d$ values, $E_{\text{hyb}}$ starts to increase, eventually vanishing at large, negative $\epsilon_d$. $\epsilon_s$ is indicated by a starred point for each row (in red, blue and green for 3d, 4d and 5d respectively). A larger, more positive value of $\epsilon_s$ indicates that saturation of $E_{\text{hyb}}$ is expected to occur at more positive values of $\epsilon_d$, as seen in O* as opposed to more negative values for C*.

$E_{\text{hyb}}$ alone cannot explain the row dependence (3d, 4d and 5d) of the scaling relations seen in Figure 1. Figure 3c shows the scaling between $E_{\text{hyb}}$ for O* and C*. For almost the entire range, there is overlap between the three rows of transition metals (with the exception of the early transition metals) implying that this quantity does not cause the row dependence of scaling seen in the computed energies of Figure 1a. To explain this row dependence, we study the other component of $E_{\text{chem}}$, i.e. $E_{\text{ortho}}$.

B. Row dependence of scaling stems from orthogonalisation energies

Figure 3(d,e) solid lines, show $E_{\text{ortho}}$ as a function of $\epsilon_d$ and dashed lines show the sum of $n_a$ and $f$, which are multiplicative factors to $E_{\text{ortho}}$ (Equation 4). At positive $\epsilon_d$ values, $E_{\text{ortho}}$ increases with $\epsilon_d$ due to the increase in $V^2_{sd}$, $n_a$ and $f$. For mid-to-late transition metals, $E_{\text{ortho}}$ decreases with $\epsilon_d$ due to a decrease in $V^2_{sd}$, though $n_a + f$ still tend upwards.

Differences in the behaviour of $n_a + f$ with $\epsilon_d$ between $-3 < \epsilon_d < 0$ for O* and C* cause row-dependence of $E_{\text{ortho}}$ and hence $E_{\text{chem}}$. Figure 3f shows the scaling be-
between $E_{\text{ortho}}$ of O* and C*; noticeable deviations are seen in linear scaling of $E_{\text{ortho}}$, but also in overlap between the rows of transition metals. Furthermore, differing behaviour of $n_{\text{a}} + f$ with $\epsilon_d$ is a consequence of different $\rho_{\text{ad}}(\epsilon)$ (determined from Equation 3) for different adsorbates, i.e. different $\epsilon_a$. As an example, Figure 3g shows $\rho_{\text{ad}}(\epsilon)$ for C* (purple) and O* (orange) on Rh, a mid-row transition metal. Since $\epsilon_a$ for C* is more positive than O*, the adsorbate projected density of states broadens and splits differently, resulting in different $n_{\text{a}}$ and hence row-dependent scaling behaviour.

C. Generalising findings to determine scaling relations

We now generalise our findings beyond C* vs O* scaling by proposing a descriptor to determine the $\epsilon_d$ value up to which scaling is expected for a fixed row, i.e. regions where the chemisorption energies are dictated by both hybridisation and repulsive interactions.

In general, if two adsorbates have similar $\epsilon_a$, they are likely to scale. Figure 3h shows $\epsilon_a$ for a range of re-normalised energy levels $\epsilon_a$. Since each $\epsilon_a$ value corresponds to a specific $\epsilon_a$ value for each row of transition metals, it suffices to say that two adsorbates with similar $\epsilon_a$ are likely to scale. This condition is satisfied for scaling relations between adsorbates binding to the metal with the same atom, such as C* vs. CH$_x$* ($x = 1, 2, 3$), COOH* vs CO* and OOH* vs OH*. It does not hold for adsorbates with very different $\epsilon_a$ and corresponding $\epsilon_a$, such as C* and O*.

We note in passing that the value of $\epsilon_a$ is dependent on how scaling is constructed. We expect different $\epsilon_a$ and scaling behaviour when a scaling line is constructed using just a single metal with varied facets ($V_{\text{ad}}$ is a constant for a fixed metal, rather than $= f(\epsilon_d)$, see SI Section IV for further discussion). Since scaling lines are, in general, constructed across metals, we emphasize this type of scaling in this work.

Finally, Figure 3i shows the effect that different $\epsilon_a$ have on the row-dependent scaling behaviour. By plotting $E_{\text{ortho}}$ against $E_{\text{ortho}}$ at $\epsilon_a = -5$ eV (for O*), we determine for which range of $\epsilon_a$ row dependent scaling is to be expected. For $\epsilon_a = -3$ eV, $E_{\text{ortho}}$ for 3d, 4d and 5d elements show less mismatch than for the case of $\epsilon_a = -1$ eV. Overall, adsorbates with similar $\epsilon_a$ values are likely to not show row-dependence in their scaling behaviour. The range of allowable $\epsilon_a$ values depends on the variation of $E_{\text{ortho}}$ across and along rows of the periodic table.

D. Fitting scaling lines in practice

Our analysis of C* and O* scaling in this section produces two main insights for the use of scaling lines in constructing activity volcanoes.

1. When constructing scaling lines for elements of the same row, metals with large, negative $\epsilon_d$ values, such as noble metals may be left out. The reason is that they are likely to fall off linear scaling lines, as their energies are largely governed by orthogonalisation and not hybridisation. A more rigorous analysis may include using $\epsilon_a$ to gauge which metals linear scaling should be fit to.

2. Linear scaling is likely to be much improved when all metals belong to the same row of transition metals. The suitability of using multiple rows can be judged based on the $E_{\text{ortho}}$ scaling between the two adsorbates.

Note that, in practice, there could be several other reasons for lack of scaling between two adsorbates. Relaxation of the surface and site dependence of the adsorbate might cause scatter on simple transition metal surfaces. For that reason one should always consider scaling for a fixed surface structure. However, the adsorbates and surfaces we describe in this work are transition metals with the simplest of mono-atomic adsorbates, with chemisorption energies in the dilute coverage limit. The fact that these simple systems do not scale in an obvious manner shows the complexity associated with surface chemical bond formation. Care must be taken while fitting linear scaling relations for transition metals for more complex reactions and intermediates.

V. CONCLUSION

In this work, we develop a model to understand why chemisorption energies of O* and C* do not follow a linear scaling relation. Following the $d$-band model of chemisorption, our model combines a modified version of the Newns-Anderson hybridisation energy with effective terms for the orthogonalisation repulsion. We show that lack of linear scaling along a row of the periodic table is a consequence of the saturation of the hybridisation energy of O* for metals with lower lying $d$-band centres, while the hybridisation energy for C* shows little to no saturation at relevant ranges of $\epsilon_d$. We suggest a measure, $\epsilon_s$, for the highest $\epsilon_d$ value at which saturation is expected. We quantify the row-dependence of scaling by determining the variation of the orthogonalisation energy with the $d$-band centre and show that adsorbates with similar $\epsilon_a$ are likely across rows. Finally, we show that linear scaling relations can be recovered in the case of C* and O* by considering metals of the same row of the transition metal series, bar noble metals.

VI. COMPUTATIONAL METHODS

Density functional theory calculations were carried out using Quantum ESPRESSO. Core electrons were treated using pseudopotentials from the SSSP Precision
pseudopotential database.\textsuperscript{34} Valence electrons were described using plane-waves with kinetic energy and density cutoffs of at least 80 Ry and 600 Ry respectively. In cases where the recommended cutoffs are greater than these values, the larger of the two is used. Gaussian smearing of width 0.0075 Ry (\approx 0.1\text{ eV}) was used for all calculations. A k-point mesh of (4, 4, 1) was used for all surface calculations. The PBE\textsuperscript{35} functional was used to describe exchange and correlation effects. Calculations were considered converged if the maximum force on each atom was less than $10^{-4}$ Ry Bohr$^{-1}$ and the energy difference between successive SCF cycles is less than $2 \cdot 10^{-5}$ Ry. All calculations were performed \textit{without} spin polarisation. Structures were prepared using the Atomic Simulation Environment.\textsuperscript{36} The adsorbate was initially placed at symmetrically inequivalent sites at the start of the relaxation. It is found that adsorbates at the hollow site for all metals have the lowest energy. Provenance of each calculation in this work was stored using AiiDA\textsuperscript{37} and performed using the AiiDA quantumespresso plugin.

The Newns-Anderson expressions were implemented using trigonometric functions from the Python \texttt{numpy}\textsuperscript{38} library. Multi-precision C-library \texttt{arb}\textsuperscript{39} was used to integrate the projected density of states using the \texttt{acb\_calc\_integrate} function. Decimal precision of 50 was used throughout this work. Least-squares error fitting were performed using the Python \texttt{scipy}\textsuperscript{40} library.

**DATA AVAILABILITY**

Python code used to generate all figure in this manuscript are available at \url{https://github.com/sudarshanv01/newns-anderson}. The Newns-Anderson equations and those used in the text for the chemisorption energies and their derivatives are implemented in Python and can be accessed through the following package: \url{https://github.com/sudarshanv01/CatChemi AiiDA archive files will be made available publicly prior to publication.}

**ACKNOWLEDGMENTS**

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