Physical and Chemical Nature of the Scaling Relations between Adsorption Energies of Atoms on Metal Surfaces

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Despite their importance in physics and chemistry, the origin and extent of the scaling relations between the energetics of adsorbed species on surfaces remain elusive. We demonstrate here that scalability is not exclusive to adsorbed atoms and their hydrogenated species but rather a general phenomenon between any set of adsorbates bound similarly to the surface. On the example of the near-surface alloys of Pt, we show that scalability is a result of identical variations of adsorption energies with respect to the valence configuration of both the surface components and the adsorbates.

The discovery of linear relations between the adsorption energies of atoms and their hydrogenated species on transition metal surfaces is one of the major advances of theoretical surface science and heterogeneous catalysis in the past decade [1,2]. These relations have also been shown to hold on surfaces of oxides, nitrides, sulfides, carbidies, and functionalized graphitic materials [3–6]. Moreover, they provide the necessary atomic-scale insight to test rapidly reaction mechanisms, since they reduce the number of independent variables in microkinetic modeling, which ultimately allows determining trends in the catalytic activity of materials [4,7–9]. For the particular case of the electrochemical oxygen evolution or reduction reactions, these relations have been shown to impose a thermodynamic limitation on the performance of catalysts, which causes part of the large overpotential appearing during the operation of electrolyzers and fuel cells [4,6,10].

In spite of their fundamental importance and numerous applications, their origin is not clear and, therefore, the conditions under which they hold and the type of compounds to which they apply are not well understood. In this Letter, we take a step forward towards a deeper understanding of scaling relations that may lead to their further generalization. To this end, we have systematically studied the adsorption energies of second- and third-row atoms of groups 14–17 in the periodic table onto the near-surface alloys (NSAs) of Pt(111) and transition metals. The addition of guest atoms in the subsurface layers of a Pt host has been shown theoretically and confirmed experimentally to alter the electronic-structure properties of the Pt skin on the top layer [11–14], by this means modifying the catalytic performance of the host material.

All adsorption energies were calculated by means of density-functional theory (DFT) simulations using the VASP code [15] with the Perdew-Burke-Ernzerhof exchange-correlation functional [16]. The NSAs of Pt(111) and 3d, 4d, and 5d metals were represented by 2 × 2 supercells with a lattice constant of 3.98 Å. The Brillouin zones of all surfaces were sampled with 6 × 6 × 1 Monkhorst-Pack grids [17]. Four metal layers were used, three of which contained only Pt atoms (the top and the two bottom layers) and one formed of transition metal atoms (the subsurface layer); the adsorbate coverage on the surface was, in all cases, 1/4 ML, and the adsorption site was atop (data for bridge and hollow sites are presented in Ref. [18]). The kinetic-energy cutoff for the plane-wave basis set was 450 eV. More calculation details can be found in Ref. [18]. The DFT adsorption energies of single atoms (A) were calculated relative to the clean surfaces and the isolated atoms, according to Eqs. (1) and (2):

\[ \Delta E_A = E_{*A} - E_* - E_A. \]  

Here * denotes an active site in the surface, and *A represents the adsorbed atom A. In the following, this atom may be C, Si, N, P, O, S, F, or Cl. The scaling relation between the energetics of a given pair of species 1 and 2 is expressed in mathematical terms as [1]

\[ \Delta E_1 = \gamma \Delta E_2 + \xi. \]  

Given that \( \gamma \) and \( \xi \) are constant for a given set of adsorbates 1 and 2 for a given adsorption site on a given facet, \( \Delta E_1 \) depends explicitly only on \( \Delta E_2 \), and thus there is no direct dependence on any electronic-structure parameter in Eq. (3).

So far, scaling relations have mostly been shown to hold for adsorbed atoms and their hydrogenated species [3–6], and scalability between *O and *Cl has also been observed on (110) surfaces of rutile oxides [19]. Thus, it is of paramount importance to find out whether they exist between any other classes of adsorbed species and, if so, to determine the reason why that occurs. Figure 1 sheds light on the first question. In it, we present the scaling relations...
between the adsorption of second- and third-row atoms belonging to groups 14–17 of the periodic table on atop sites of NSAs of Pt and transition metals. In all cases the slopes are \(\sim 1\), suggesting that each pair of adsorbates binds in the same way, so that the binding energies for a given surface differ only on a constant amount of energy. Data for bridge and hollow sites are provided in Ref. [18].

Figure 1 shows that the adsorption energies of C* and Si*, N* and P*, O* and S*, and F* and Cl* scale linearly and that the slope is in each case \(\sim 1\), reflecting the fact that an identical coupling to the surface leads to a scaling relation between a given pair of adsorbates. For scaling relations between single atoms and their hydrogenated species [1], the slope was defined as

\[
x = \frac{\Delta E_{1, \text{TOP}}}{x_{\text{max}} - x},
\]

where \(x\) is the number of hydrogen atoms bonding to the considered adsorbed species and \(x_{\text{max}}\) is the maximum number of hydrogen atoms that can bond to the atom. However, the evidence provided in Fig. 1 confirms that scalability is possible for adsorbates that bind similarly to surfaces, regardless of the presence or absence of bonds to hydrogen atoms. Therefore, we propose that the slope of the scaling relations can be more generally defined as the ratio between the number of bonds that species 1 lacks to reach its valence number and the number of bonds that species 2 lacks to reach its valence number. Since this concept is more general, it covers, of course, the particular case of atoms and their hydrogenated species. Now, the reason for the existence of generalized scaling relations must stem from the correlation between adsorption energies and surface electronic-structure parameters, which is the basis of the surface-science approach to understanding heterogeneous processes at surfaces [2, 11, 20–22]. Thus, if the adsorption energies of species 1 and 2 depend upon a set of electronic-structure parameters, denoted as \(\{\omega_i\}\), with \(i = 1, 2, 3, \ldots\), and the variations are described by functions \(f\) and \(g\), so that \(\Delta E_1 = f(\{\omega_i\}) + \alpha_0\) and \(\Delta E_2 = g(\{\omega_i\}) + \beta_0\), the existence of a scaling relation in the way shown in Eq. (3) strictly requires that Eq. (4) be fulfilled:

\[
f(\{\omega_i\}) = \gamma g(\{\omega_i\}).
\]

Equation (4) is essentially a reformulation of Eq. (3) which provides additional physicochemical insight, since it directly links electronic structure and energetic scalability. One of the consequences of Eq. (4) is that scaling relations hold for any set of adsorbates that satisfy its condition, as shown above in Fig. 1. Besides, if species 1 and 2 fulfill the condition in Eq. (4), we find that the offset in Eq. (3) depends on the slope \(\gamma\) in the following way:

\[
\xi = \alpha_0 - \gamma \beta_0.
\]
Since Pt has 10 valence electrons, C and Si have both 4 valence electrons, N and P have 5, O and S have 6, and F and Cl have 7, we find that the minimum in adsorption energy among the NSAs is located in each case at a different guest metal, being the minimum at 10 for C* and Si* (corresponding to Ni, Pd, and Pt), 9 for N* and P* (corresponding to Co, Rh, and Ir), 8 for O* and S* (corresponding to Fe, Ru, and Os), and 7 for F* and Cl* (corresponding to Mn, Tc, and Re). This constant number of electrons can be understood in terms of the 8- and 18-electron rules for the adsorbate and the surface components, respectively. These rules are well-known concepts in inorganic chemistry [23–25]. The idea underlying these rules is that when the electron cloud surrounding an atom resembles that of a noble gas, the stability is optimized [23–25].

Lewis diagrams for all minima in Fig. 2 are provided in Fig. 3.

Figures 2 and 3 suggest that the adsorption energies appear to be straightforward functions of both the number of valence electrons of the components of the surface and that of the adsorbate. Moreover, the addition of both numbers is a fixed constant, which enables predictions in other systems like NSAs of Au and transition metals or pure metals. Therefore, these three parameters are key electronic-structure parameters of the set \( \{f, g\} \) that governs the variations of the functions \( f \) and \( g \) in Eq. (4). Moreover, the fact that in each panel of Fig. 2 the vertical separation between the curves is constant implies that the energetic difference between the adsorbed states, \( E_{ads1} - E_{ads2} \), i.e., the energetic difference between the adsorbed states, is also approximately constant and has an average value of 0.76 eV. This means that the ways each pair of adsorbates in Fig. 2 couple to the surface are identical, and hence the difference in adsorption energies comes from the difference in orbital energies and sizes of species 1 and 2 (from 2p to 3p). In Ref. [18], we also provide data for the adsorption of B and Al which agree with the trends shown here.

Finally, we address the problem of nonscalability between adsorbed species. Having established the rules shown above, it is possible to rectify the nonscalability in a simple way: If, for instance, one assumes that \( f \) and \( g \) are third-order functions of the total number of valence
In principle, Eq. (6) could be expressed in terms of energies and those estimated by means of Eq. (6) is only the agreement between DFT-calculated adsorption energies of N* and O*. Based on Fig. 2, they correspond to elements to the left and to the right of the same group of the periodic table for their scaling to be smooth.

Moreover, the mean absolute error (MAE) between the DFT-calculated adsorption energies and those estimated by means of Eq. (6) is only 0.07 eV. In principle, Eq. (6) could be expressed in terms of any kind of functions, not only cubic polynomials. This correction to nonscalability between two adsorbed species could be used to reduce the number of parameters in bi- or tridimensional volcano plots (see, for instance, Ref. [7]) and, furthermore, to make these plots based on the number of valence electrons of both the surface and the reaction intermediates adsorbed on the surface. It is noteworthy that the simple electron-counting analysis shown here has also proved successful in capturing the energetic trends in such diverse systems as functionalized graphitic materials and oxides, illustrating the role of periodicity in the properties of materials [6,26,27]. Nevertheless, it is worth noting that one of the reasons why we observe smooth trends in the plots of binding energies vs valence electrons is due to configurational correlations, since all surfaces with and without adsorbates are geometrically similar [28]. Moreover, we do not exclude that some other parameters such as band moments, characteristic d radii, Pauli repulsion, or matrix elements may be part of the set of key parameters that determine the variations of adsorption properties throughout the d series [11,29]. More information on this respect can be found in Ref. [18], where we present projected densities of states, d-band centers and fillings, and relevant geometric data for the NSAs with 3d metals. In conclusion, we have shown here the existence of generalized scaling relations that apply to any species that bind similarly to surfaces. We found that the underlying physics and chemistry behind scaling relations are closely related to the overall electronic stability of the systems, and a simple solution to rectify nonscalability was proposed and tested with remarkable outcomes.

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Supplementary Information for:

Physicochemical Nature of the Scaling Relations between Adsorption Energies of Atoms on Metal Surfaces

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1) Full Calculation Details: all adsorption energies were calculated by means of DFT simulations using the Vienna Ab-initio Simulation Package (VASP)[1] with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [2]. The NSAs of Pt(111) and 3d, 4d, and 5d metals were represented by 2x2 supercells with a lattice constant of 3.98 Å. Four metal layers were used, three of which contained only Pt atoms (the top and the two bottom layers) and one formed of transition metal atoms (the subsurface layer); the adsorbate coverage on the surface was, in all cases, ¼ ML and the adsorption site was atop. The vertical separation between successive slabs was in all cases more than 16 Å and dipole corrections were applied. The search for optimal geometries was performed using a cut-off for the plane-wave basis set of 450 eV. The Brillouin zones of all surfaces were sampled with $6 \times 6 \times 1$ Monkhorst-Pack grids [3]. The Fermi level was smeared by the Methfessel-Paxton approach [4] with a Gaussian width of 0.2 eV, and all energies were extrapolated to $T = 0$ K. During structure optimization, the two topmost layers were allowed to relax in all directions, adsorbates were only allowed in the z-direction, and the 2 bottom layers were fixed at the optimized bulk positions. The relaxations of the atoms were carried out with the quasi-Newton minimization scheme, until the maximum force on any atom was below 0.05 eV Å$^{-1}$. Ionic cores were described by Projector Augmented Wave (PAW) potentials [5].

2) Data for Bridge and Hollow Sites: we have calculated the adsorption energies of C*, Si*, N*, P*, O*, S*, F*, and Cl* on bridge sites and on their most stable hollow sites (please see Table S.1). Figure S.1 shows the results for bridge sites, while Figure S.2 shows the results for the most stable hollow sites.
Figure S.1. Scaling relations for adsorbates on bridge sites for Al vs. B (yellow), Si vs. C (black), P vs. N (red), S vs. O (green), and Cl vs. F (blue). The least-squares fits to the sets of points are provided to the right together with the correlation coefficient.

Figure S.2. Scaling relations for adsorbates on hollow sites for Al vs. B (yellow), Si vs. C (black), P vs. N (red), S vs. O (green), and Cl vs. F (blue). The least-squares fits to the sets of points are provided to the right together with the correlation coefficient.
The results in Figures S.1 and S.2 lead to the conclusion that scaling relations also exist for atoms adsorbed on bridge and hollow sites. However, the slopes for $P^*$ vs. $N^*$ and $O^*$ vs. $S^*$ noticeably deviate from the ideal slope of 1. Considering all the calculated slopes on top, bridge, and hollow sites, for the 2p (B to F) and 3p (Al to Cl) elements we obtain an average slope of 1.07 with a standard deviation of 0.20, which is within the accuracy of DFT at its standard level.

3) Geometric Data: as mentioned in the manuscript, a step further in complexity would be to include in our model the electrostatic effects that the adsorbates and the elements in the subsurface induce in the Pt skin, such as Pauli repulsion and covalent attraction. In this respect, the works of Hongliang Xin and Suljo Linic [6] are rather illustrative. They found exceptions to the d-band model of Hammer and Norskov [7] due to the dominant repulsion between nearly-filled d-bands and adsorbate states of almost filled valence shells for NSAs of Pd and Pt with late-transition metals (from groups 6 to 10 of the periodic table). We expanded their work to cover the whole series of transition metals (groups 3 to 12) and present in the following two figures a geometric-electronic analysis of the two effects present in the Pt skin, i.e. the attraction/repulsion between the skin and the adsorbates, and the attraction/repulsion between the skin and the subsurface layer, respectively.

Figure S.3. Average Metal-adsorbate distances for NSAs of Pt and transition metals for 2p and 3p elements adsorbed on atop position. The error bars limit the maximum and minimum distances found through the d-series.
According to Figure S.3, 2p (C and N) and 3p (Si and P) elements with half-filled valence shells bind closer to the surface than those with almost empty (B and Al) or almost filled (F and Cl) valence shells.

The geometric-electronic picture is completed by Figure S.4, in which we observe a similar effect: elements with half-filled d-bands (groups 6 to 9) tend to have shorter interlayer distances than those with nearly empty (groups 3 and 4) or nearly filled d-bands (groups 11 and 12).

Based on Figures S.3 and S.4, we conclude that the Pt skin has dominant attractive interactions with half-occupied electronic shells and dominant repulsive interactions with densely or poorly occupied electronic shells. It is noteworthy that in both cases the number of valence electrons again correlates well with the variables in question, and that the variations are neither linear nor monotonic. We remark at this point that the appearance of electrostatic attractions/repulsions comes as a result of the presence of different atoms in the Pt lattice and therefore the variations in the physicochemical properties of this material should, in principle, be well captured by simple descriptors belonging to these different atoms, which is what we observe with the adsorption energies and the total valence electrons.

Figure S.4. Interlayer distances for NSAs of Pt and 3d (black), 4d (blue), and 5d (red) metals versus the number of valence electrons of the element in the subsurface layer. The interlayer distance is taken as the average vertical distance between the 1st and the 2nd layers of the NSAs.
4) **Densities of States**: following previous results by Kitchin et al [8] and Xin and Linic [6] we used four layers in our calculations. However, we calculated the density of states for the NSA of Pt and Ti with four and seven layers projected onto the Pt skin to ensure convergence on the number of layers needed for obtaining accurate results. The results are presented below in Figure S.5.

![Projected density of states onto the Pt skin in a NSA of Pt and Ti. The energies are referred to the Fermi level. The results for four layers (blue) and seven layers (red) are provided for comparison.](image)

**Figure S.5.** Projected density of states onto the Pt skin in a NSA of Pt and Ti. The energies are referred to the Fermi level. The results for four layers (blue) and seven layers (red) are provided for comparison.

The d-band centers are located at -2.77 and -2.84 eV for the systems with four and seven layers, respectively. Moreover, the adsorption energies of C* on atop positions for the systems with 4 and 7 layers are -3.20 eV and -3.16 eV, respectively. Based on these evidences, we conclude that four layers are sufficient for an accurate description of these systems. We have included this figure in the supplementary material.

Furthermore, in Figure S.6 we provide a plot that shows the variations in the d-band for the NSAs of Pt and 3d metals with respect to pure Pt. We remark at this point that a qualitatively similar plot can be found in the seminal works by Kitchin et al [8] on NSAs of Pt for a smaller range of elements (only from Ti to Ni), using a different code (Dacapo), different exchange-correlation functional (RPBE) and different pseudopotentials (Ultrasoft pseudopotentials).
Figure S.6. Densities of states projected on the Pt atoms in the top layer of NSAs with 3d elements in the subsurface layer. The d-band centers are shown in each panel as vertical lines and the number of d-electrons per Pt atom is provided to the right of the plot. The dashed line corresponds to the Fermi level.

Looking at Figure S.9 we note that neither the d-band center nor the d-band filling change monotonically throughout the 3d series. This means that for NSAs with elements from Sc to Zn the d-band center does not strictly increase or strictly decrease but it has a minimum at Pt-V and a maximum at Pt-Cu. To facilitate the analysis, we provide in Figure S.7 the variations of both variables with respect to the total number of valence electrons of the elements present in the bare surfaces. It is noteworthy in Figure S.7 that in both panels the minima is located at Pt-V, which has 15 valence electrons in total. This is not surprising because the bare surfaces do not have enough electrons to fulfill the 18-electron rule for each component. Instead, if we consider a
simple electron-counting picture as in Fig. 3 in the manuscript, we conclude that with 15 electrons in total the Pt skin can fill its s and d-bands and V can fill only half of its d-band, which maximizes its stability. In conclusion, there is also a search for maximum stability in the bare surfaces, but the lack of available electrons makes the trends resemble those of the Friedel model of cohesive energies for transition metals, in which the maximal stability is found at half-filled d-bands [9].

**Figure S.7.** Characteristics of d-band of the Pt skin in NSAs of Pt and 3d metals plotted as a function of the total number of valence electrons of the surface: (top) d-band center, and (bottom) d-band filling. The metal in the second layer of the alloy is provided in the alternative x axis in the top panel.

An important fact to remark here, based on Figure S.7, is that the d-band center seems not to be a good descriptor for the trends on adsorption energies over this class of materials since it has a minimum point at 15 electrons (Pt-V for the 3d elements or group 5 in the periodic table in general) whereas the adsorption energies have minima at 24 (groups 7 to 11 when elements from
groups 13 to 17 are adsorbed). This mismatch gives rise to trends similar to those in Figure 4 in the manuscript. In fact, Xin and Linic [6] have reported before some clear exceptions to the d-band model within the NSAs. This highlights the importance of using a monotonic descriptor in order to observe well-defined and smooth trends. To give an example of this, we draw our attention to Figure S.8 in which the oxygen binding energy on atop position is plotted versus the average energies of the d-bands of Pt NSAs with 3d elements in the subsurface layer. We note in this Figure that the trends from Pt-Sc to Pt-V and from Pt-Mn to Pt-Cu are against the d-band model since for these subsets of points as the average energy of the d-band becomes less negative, the binding energies get more positive, while the d-band predicts increased binding strength as the d-band center moves towards the Fermi level.

![Figure S.8](image)

**Figure S.8.** Adsorption energies of oxygen on atop sites as a function of the d-band center of the Pt skin in NSAs with 3d elements in the subsurface layer.

5) **Data for B and Al:** in Figure S.9 we present the results for the adsorption of Al and B on NSAs of Pt and transition metals on top sites, as well as their scaling relationships (data for bridge and hollow can be found in Figures S.1 and S.2). From Figure S.9 we conclude that the analysis shown in the main text also applies to these two elements. The gas-phase references for B and Al are the isolated atoms, as they are for the rest of the adsorbates in the manuscript.
Furthermore, we present in Figure S.10 the Lewis diagrams for the hypothetical systems A-Pt-M that are most stable along the transition metal series when B is adsorbed. Due to the fulfillment of the 18-electron rule by the surface components and the octet rule by the adsorbate, the minimal adsorption energies are located at a total number of valence electrons of 24, which corresponds in this case to NSAs of Pt and group 11 (Cu, Ag, Au) elements.
6) **Most Stable Adsorption Sites and Scalability**: in Table S.1 we provide the most stable adsorption sites for each adsorbate on the Near-Surface Alloys of Pt and transition metals.

From the information in Table S.1 we conclude that most adsorbates have a preferred adsorption site which is maintained throughout the 3d, 4d and 5d series with some exceptions, normally observed for late transition metals. Taking C as an example, its preferred adsorption site is the hcp hollow and the exceptions are Pt-Zn, Pt-Pd, Pt-Cd, Pt-Pt, Pt-Au, and Pt-Hg, all of them composed of late transition metals, in which it prefers to adsorb on fcc hollow sites.

Moreover, in order to show that scalability exists between species adsorbed on different sites, we present below a figure for the scaling relationship between F and Cl on their most stable adsorption sites, which are atop and a combination of fcc hollow and bridge sites, respectively (See Table S.1).

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**Figure S.10.** Lewis diagram for the hypothetical system B-Pt-M corresponding to the minima in Figure S.9. When the system adsorbate-plus-NSA is in the minima, the adsorbate follows the octet rule and Pt and M follow the 18-electron rule, thus maximizing the stability of the system. Red lines are used to indicate shared pairs of electrons, while •• represent lone pairs and arrows represent dative bonds.
Table S.1. Preferred adsorption sites for several adsorbates on NSAs of Pt and 3d, 4d, and 5d metals.

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<th>N</th>
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<th>Si</th>
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Figure R.1. Top: trends in adsorption energies of Cl* and F* on their most stable adsorption sites. Note that both minima are found at 24 electrons. Bottom: scaling relationship between Cl* and F*.

REFERENCES