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Establishing and Understanding Adsorption−Energy Scaling Relations with Negative Slopes

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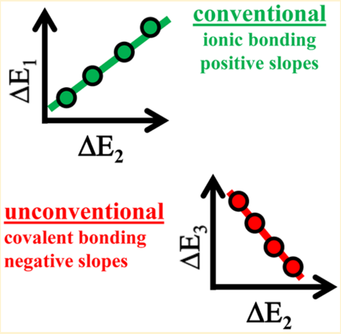
Supporting Information

ABSTRACT: Adsorption−energy scaling relations are widely used for the design of catalytic materials. To date, only linear scaling relations are known in which the slopes are positive. Considering the adsorption energies of F, O, N, C, and B on transition metals, we show here that scaling relations with negative slopes also exist between certain adsorbates. The origin of such unconventional scaling relations is analyzed in terms of common descriptors such as d-band center, work function, number of outer electrons, electronic charge on the adsorbates, integrated crystal orbital overlap populations, and crystal orbital Hamilton populations. Conventional scaling relations are formed between adsorbates such as F, O, N, and C, which create ionic-like bonds with surfaces. Conversely, anomalous scaling relations are established between those and covalently bound adsorbates such as B. This widens the theory of adsorption−energy scaling relations and opens new avenues in physical chemistry and catalysis, for instance, in direct borohydride fuel cells.



It is widely accepted that the adsorption properties of transition-metal surfaces are determined by their geometric and electronic structures.[1] Such extended agreement came after numerous works reporting correlations between structural parameters, adsorption energies, and catalytic activities.[2−9] Those "structure−energy" relations are complemented by a variety of "energy−energy" relations, such as Brønsted−Evans−Polanyi relations,[10−12] bulk−surface relations,[13] and adsorption−energy scaling relations,[4,14−18] which have enormously facilitated the in silico design of new materials because of their simplicity.[1,16] The adsorption energies of species 2 scale with those of species 1 as follows

$$\Delta E_1 = m\Delta E_2 + b \quad (1)$$

where b is a constant that depends on surface coordination.[15] So far, m has always been found to be positive, as in some approaches it is estimated as the ratio between the lack of bonds of species 1 and 2 to reach the octet[4,15] or as the ratio of the bond orders in other approaches.[16,17,19]

Analyzing the density functional theory (DFT) adsorption energies of F, O, N, C, and B on the close-packed surfaces of 4d and 5d transition metals, we will show here for the first time that negative slopes are possible in scaling relations. This intriguing phenomenon is related to significant differences in the metal−adsorbate bonds made by species 1 and 2 in eq 1.

For completeness, we will analyze conventional and unconventional scaling relations altogether. Figure 1 shows the scaling relations between the most stable adsorption energies of N and the other adsorbates under study on the closest-packed surfaces of 4d and 5d metals. While the scaling between F, O, C, and N is normal ($m > 0$), B and N exhibit an atypical negative slope (see Table S14 and Figure S9 in the Supporting Information (SI)). Hence Figure 1 raises an important question: How can one rationalize negative slopes in adsorption−energy scaling relations?

To address this question, we resort to a mathematical formulation of scaling relations used before to understand the nature of their slope and offset,[4,15] noting that other authors have considered alternative bond-order formulations.[16,17,19] Within this approach, ΔE_1 and ΔE_2 are a function of a set of surface or adsorbate electronic-structure parameters, denoted $\{\omega_i\}$

$$\Delta E_1 = F(\{\omega_i\}) + \alpha_1 \quad (2)$$

$$\Delta E_2 = G(\{\omega_i\}) + \alpha_2 \quad (3)$$

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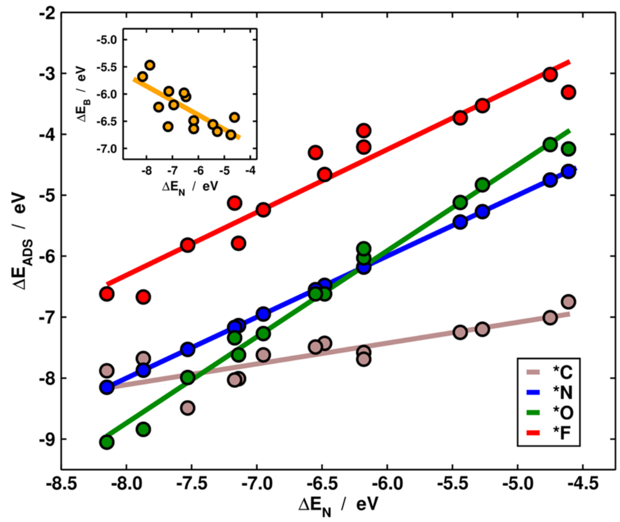

Figure 1. Normal scaling relations between the adsorption energies (ΔE_{ADS}) of N and 2p atoms. Inset: anomalous scaling relationship between ΔE_B and ΔE_N (see also Figure S9). The equations of the linear fits appear in Table S14.

where F and G are differentiable functions. Because α_1 and α_2 depend on surface coordination,[5,6,15] they are constant here, as we only consider adsorption on closest-packed surfaces.

Finding the parameters that belong in the set $\{\omega_i\}$ is important to determine whether scalability is possible between two adsorbates.[4,15] Thus, as part of $\{\omega_i\}$ we consider here some well-known descriptors: d-band center (ε_d), work function (Φ), excess Bader charge on the adsorbates,[20] number of "outer electrons" (N_M, equivalent in metals to the number of valence electrons[3]), crystal orbital overlap population (*coop*), and crystal orbital Hamilton population (cohp) integrated to the Fermi level (Figures S5−S7).[21,22] Figure 2 shows that those descriptors are all linear functions of N_M, that is, $\{\omega_i\} = H(N_M)$. Plausible arguments justify the relationships in this Figure, as discussed in detail in Section S5. Note in passing that the descriptors in Figure 2 require self-consistent calculations to be estimated, but N_M gives the highest predictive accuracy (Table S12).

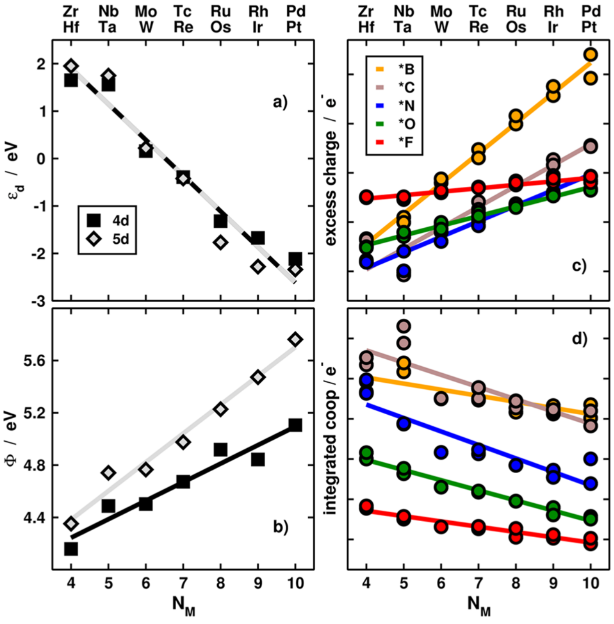

Figure 2. Relationships between various descriptors and the metal's number of outer electrons (N_M). (a) Surface d-band center (ε_d); (b) work function (Φ); (c) excess Bader charge on the adsorbates; and (d) integrated crystal orbital overlap population (*coop*) upon 2p atom adsorption.

The adsorption energies (ΔE_{ADS}) of 2p atoms appear in Figure 3 as a function of N_M (see also Tables S5 and S13).

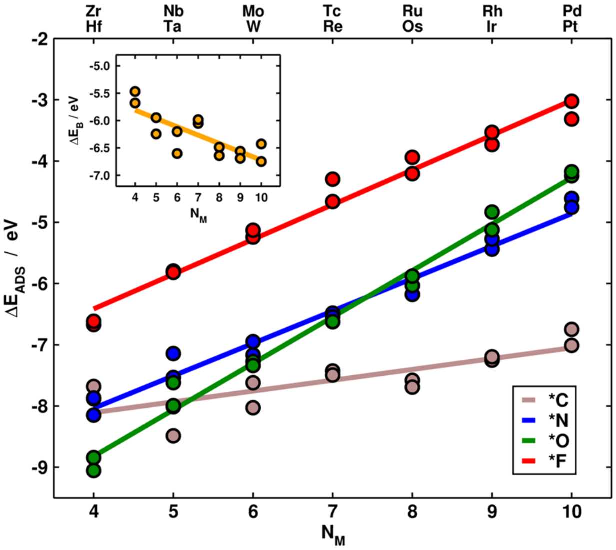

Figure 3. Adsorption energies of 2p atoms as a function of the number of outer electrons of transition metals. Inset: Data for B. Reported ΔE_{ADS} are those of the most stable adsorption sites; see Tables S5 and S13.

While F, O, N, and C bind more weakly as N_M increases, in line with previous observations,[3−6] the opposite is true for B (Figure 3, inset). Therefore, the trends in ΔE_{ADS} depend not only on the nature of the metals, as traditionally accepted, but also on the adsorbates. This is important because most descriptors do not incorporate adsorbate features, as descriptor-based analyses aim at predicting ΔE_{ADS} using the properties of clean surfaces only.[1]

Because N_M scales with ε_d, Φ, Bader excess charge, and integrated *coop*/*cohp*, all descriptors capture the adsorption−energy trends similarly (Figures S1−S4, Tables S6−S11). Note, however, that B is always atypical, as the slopes of its correlations have opposite signs compared with the others. In summary, Figures 1 and 2 show that numerous descriptors and adsorption energies depend linearly on N_M (see also Section S2), so eqs 2 and 3 are simplified as follows

$$\Delta E_1 = f(N_M) + \lambda_1 \tag{4}$$

$$\Delta E_2 = g(N_M) + \lambda_2 \tag{5}$$

Where f, g are differentiable functions and λ_1, λ_2 are constants. The scaling relation in eq 1 is fulfilled if f and g are proportional: $f(N_M) = m\, g(N_M)$,[4,15] as exemplified in Figure 2. If both f' and g' are definite positive or negative (where $f' = \partial f/\partial N_M$, $g' = \partial g/\partial N_M$), then $m > 0$, which corresponds to conventional scaling relations (e.g., ΔE_N vs ΔE_C, ΔE_O, ΔE_F).[1−9,14−16,23−26] Conversely, if f' is definite positive and g' is definite negative or vice versa, $m < 0$, as for ΔE_B versus ΔE_N.

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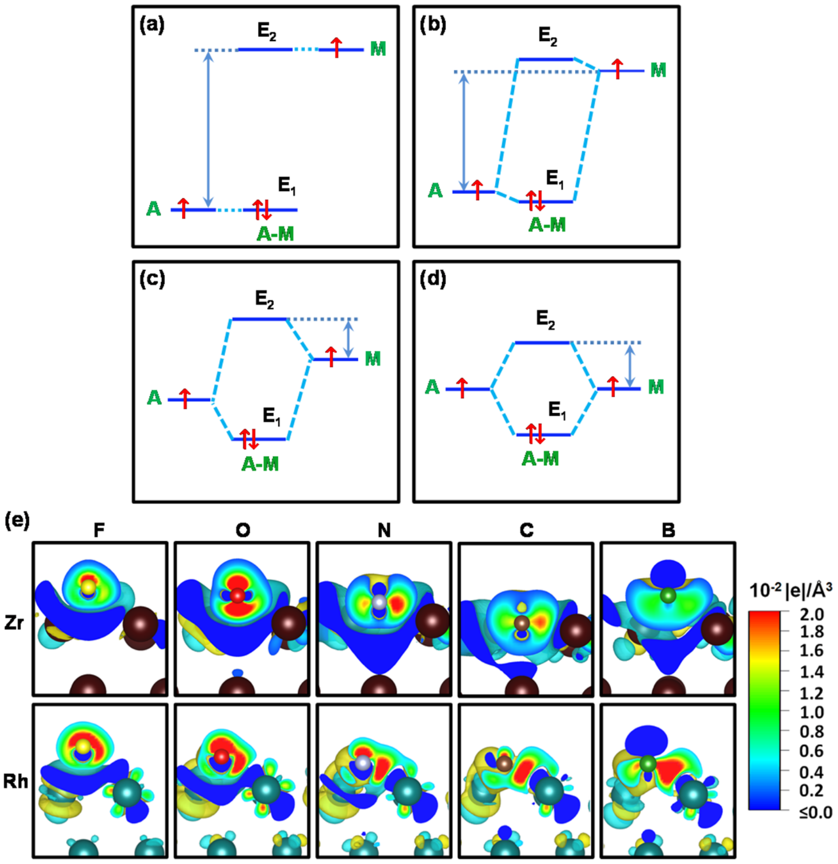

Figure 4. Interactions between adsorbate A and metal M based on Hoffmann's model.[27] The energy-level difference between A and M decreases progressively from (a) to (d). F and O bonding correspond to (b), B bonding to (c), and N and C are in between. (e) Differential charge density map for adsorption of 2p atoms on Zr(0001) and Rh(111). Yellow, red, gray, brown, light-green, dark-green and maroon spheres represent F, O, N, C, B, Rh, and Zr, respectively. Blue and yellow-red isosurfaces indicate charge depletion and accumulation. The 2D profile is a cut along a Rh/Zr−adsorbate bond.

After mathematically outlining the existence of scaling relations with negative slopes, it is important to determine what distinguishes B chemically from the other adsorbates. To do so, we first resort to the qualitative explanations of molecular-orbital theory.[27] The interaction between adsorbate A and metal M can be classified in the four categories in Figure 4a−d. If the orbital energy levels of A and M (for M, the energy level represents relevant d and s states around the Fermi level) are largely different (Figure 4a), then the interaction is ionic. As the energy-level difference between A and M decreases (Figure 4b), covalent interactions are strengthened. However, the bonding is still mainly ionic, corresponding to the interaction between transition metals and electronegative atoms (e.g., F, O). The differential charge density maps (Figure 4e) show considerable charge withdrawal from Zr or Rh by F and O, indicative of mostly ionic bonds. When the energy-level difference decreases (Figure 4c), the orbital mix is larger, leading to stronger covalent interactions. This is the case of bonds between transition metals and less electronegative atoms (e.g., B). Figure 4e shows that considerable charge builds up between Zr or Rh and B, meaning that their bonds are largely covalent. For N and C, both ionic and covalent bonding contribute significantly. Finally, for A and M at the same energy level, the orbital mixture is maximal and the bonding is purely covalent (Figure 4d). The trends in Pauling's ionicity[28] for Zr or Rh bonds with 2p atoms in Figure S8 agree with the analysis in Figure 4.

Furthermore, Figure 4 suggests that dissimilar orbital overlaps lead to ionic and covalent bonds that cause different scaling relations (Figure 1). Thus orbital overlap is essential to quantitatively distinguish between B, C, N, O, and F bonds with surfaces. Figure 5 shows the integrated *coop* values versus the adsorbates' number of outer electrons (N_A). A nearly linear correlation is observed between integrated *coop* and N_A for F, O, N, and C. However, B deviates significantly, as shown by Δ*coop*. Interestingly, Δ*coop* is inversely proportional to N_M so that late transition metals set off less than the early ones (Figure 5, inset), justifying the negative slope in Figure 1. An analogous explanation is obtained from integrated cohp in Section S5. Hence simultaneously using adsorbate and metal descriptors (N_A, N_M), we conclude that B-metal bonds are qualitatively and quantitatively different from the other adsorbate−metal bonds studied.

In conclusion, classifying metal−adsorbate bonds into ionic and covalent helps rationalize conventional and unconventional adsorption-energy scaling relations. Conventional relations are observed between highly electronegative adsorbates such as F, O, N, and C. The covalence of B-metal bonds introduces negative slopes in its scaling relations with those adsorbates. These results and others[7] widen the state of the art in scaling relations and open new avenues, for instance, in the design of better catalysts for direct borohydride fuel cells.[29]

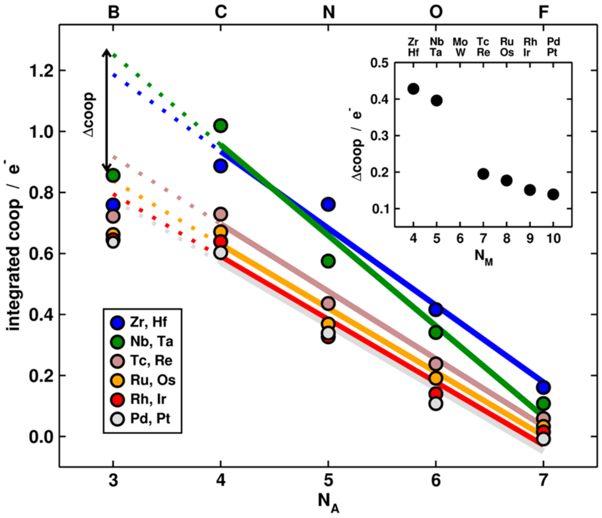

Figure 5. Relationship between integrated *coop* and the adsorbate's number of outer electrons (N_A). Inset: Δ*coop* (deviations in *coop* from the linear trends for B) as a function of the metals' number of outer electrons (N_M).

METHODS

All adsorption energies (ΔE_{ADS}) were calculated using VASP[30] with PBE.[31] (2 × 2) 5-layer (111), (0001), and (110) slabs for fcc, hcp, and bcc transition metals were used, separated by 15 Å of vacuum. The two bottommost layers were fixed at the bulk distances, and the three topmost layers and the adsorbates were fully relaxed. The Brillouin zones were sampled with 5 × 5 × 1 Monkhorst–Pack grids.[32] The plane-wave cutoff was 400 eV. ΔE_{ADS} was calculated using the most stable adsorption configurations (Table S13) relative to the clean surfaces (E_*) and the isolated atoms (E_A)

$$\Delta E_A = E_{A^*} - E_* - E_A \qquad (6)$$

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.6b02430.

> (1) DFT/experimental Φ and lattice constants of transition metals, experimental first ionization energies for metals and adsorbates. (2) ΔE_{ADS} versus various descriptors. (3) Data and correlations. (4) Adsorption sites. (5) More about Figures 2 and 4, integrated cohp. (6) Additional scaling relations. (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Norskov, J. K.; Bligaard, T.; Rossmeisl, J.; Christensen, C. H. Towards the Computational Design of Solid Catalysts. *Nat. Chem.* **2009**, *1*, 37–46.

(2) Hammer, B.; Nørskov, J. K. Theoretical Surface Science and Catalysis - Calculations and Concepts. *Adv. Catal.* **2000**, *45*, 71–129.

(3) Calle-Vallejo, F.; Inoglu, N. G.; Su, H. Y.; Martinez, J. I.; Man, I. C.; Koper, M. T. M.; Kitchin, J. R.; Rossmeisl, J. Number of Outer Electrons as Descriptor for Adsorption Processes on Transition Metals and Their Oxides. *Chem. Sci.* **2013**, *4*, 1245–1249.

(4) Calle-Vallejo, F.; Martinez, J. I.; García-Lastra, J. M.; Rossmeisl, J.; Koper, M. T. M. Physical and Chemical Nature of the Scaling Relations between Adsorption Energies of Atoms on Metal Surfaces. *Phys. Rev. Lett.* **2012**, *108*, 116103.

(5) Calle-Vallejo, F.; Martinez, J. I.; García-Lastra; Sautet, P.; Loffreda, D. Fast Prediction of Adsorption Properties for Platinum Nanocatalysts with Generalized Coordination Numbers. *Angew. Chem., Int. Ed.* **2014**, *53*, 8316–8319.

(6) Calle-Vallejo, F.; Sautet, P.; Loffreda, D. Understanding Adsorption-Induced Effects on Platinum Nanoparticles: An Energy-Decomposition Analysis. *J. Phys. Chem. Lett.* **2014**, *5*, 3120–3124.

(7) Michaelides, A.; Hu, P. Insight into Microscopic Reaction Pathways in Heterogeneous Catalysis. *J. Am. Chem. Soc.* **2000**, *122*, 9866–9867.

(8) Huang, B.; Xiao, L.; Lu, J.; Zhuang, L. Spatially Resolved Quantification of the Surface Reactivity of Solid Catalysts. *Angew. Chem., Int. Ed.* **2016**, *55*, 6239–6243.

(9) Huang, B.; Zhuang, L.; Xiao, L.; Lu, J. Bond-energy Decoupling: Principle and Application to Heterogeneous Catalysis. *Chem. Sci.* **2013**, *4*, 606–611.

(10) Michaelides, A.; Liu, Z. P.; Zhang, C. J.; Alavi, A.; King, D. A.; Hu, P. Identification of General Linear Relationships between Activation Energies and Enthalpy Changes for Dissociation Reactions at Surfaces. *J. Am. Chem. Soc.* **2003**, *125*, 3704–3705.

(11) Zeinalipour-Yazdi, C. D.; van Santen, R. A. Kinetic Rates and Linear Free Energy Relationships for Water Dissociation on Transition and Noble Metal Dimers. *J. Phys. Chem. A* **2009**, *113*, 6971–6978.

(12) Wang, S. G.; Temel, B.; Shen, J.; Jones, G.; Grabow, L. C.; Studt, F.; Bligaard, T.; Abild-Pedersen, F.; Christensen, C. H.; Nørskov, J. K. Universal Brønsted-Evans-Polanyi Relations for C–C, C–O, C–N, N–O, N–N, and O–O Dissociation Reactions. *Catal. Lett.* **2011**, *141*, 370–373.

(13) Calle-Vallejo, F.; Díaz-Morales, O. A.; Kolb, M. J.; Koper, M. T. M. Why Is Bulk Thermochemistry a Good Descriptor for the Electrocatalytic Activity of Transition Metal Oxides? *ACS Catal.* **2015**, *5*, 869–873.

(14) Abild-Pedersen, F.; Greeley, J.; Studt, F.; Rossmeisl, J.; Munter, T. R.; Moses, P. G.; Skúlason, E.; Bligaard, T.; Nørskov, J. K. Scaling Properties of Adsorption Energies for Hydrogen-Containing Molecules on Transition-Metal Surfaces. *Phys. Rev. Lett.* **2007**, *99*, 016105.

(15) Calle-Vallejo, F.; Loffreda, D.; Koper, M. T. M.; Sautet, P. Introducing Structural Sensitivity into Adsorption-energy Scaling Relations by Means of Coordination Numbers. *Nat. Chem.* **2015**, *7*, 403–410.

(16) Montemore, M. M.; Medlin, J. W. Scaling Relations between Adsorption Energies for Computational Screening and Design of Catalysts. *Catal. Sci. Technol.* **2014**, *4*, 3748–3761.

(17) Abild-Pedersen, F. Computational Catalyst Screening: Scaling, Bond-order and Catalysis. *Catal. Today* **2016**, *272*, 6–13.

(18) van Santen, R. A.; Tranca, I. How Molecular Is the Chemisorptive Bond? *Phys. Chem. Chem. Phys.* **2016**, *18*, 20868−20894.

(19) Jones, G.; Studt, F.; Abild-Pedersen, F.; Norskov, J. K.; Bligaard, T. Scaling Relationships for Adsorption Energies of C-2 Hydrocarbons on Transition Metal Surfaces. *Chem. Eng. Sci.* **2011**, *66*, 6318−6323.

(20) Tang, W.; Sanville, E.; Henkelman, G. A Grid-based Bader Analysis Algorithm Without Lattice Bias. *J. Phys.: Condens. Matter* **2009**, *21*, 084204.

(21) Tachibana, M.; Yoshizawa, K.; Ogawa, A.; Fujimoto, H.; Hoffmann, R. Sulfur-gold Orbital Interactions Which Determine the Structure of Alkanethiolate/Au(111) Self-assembled Monolayer Systems. *J. Phys. Chem. B* **2002**, *106*, 12727−12736.

(22) Eichler, A.; Kresse, G.; Hafner, J. Ab-initio calculations of the 6D Potential Energy Surfaces for the Dissociative Adsorption of H-2 on the (100) Surfaces of Rh, Pd and Ag. *Surf. Sci.* **1998**, *397*, 116−136.

(23) Calle-Vallejo, F.; Krabbe, A.; Garcia-Lastra, J. M. How covalence breaks adsorption-energy scaling relations and solvation restores them. *Chem. Sci.* **2016**, DOI: 10.1039/C6SC02123A.

(24) Peterson, A. A.; Nørskov, J. K. Activity Descriptors for CO2 Electroreduction to Methane on Transition-Metal Catalysts. *J. Phys. Chem. Lett.* **2012**, *3*, 251−258.

(25) Stephens, I. E. L.; Bondarenko, A. S.; Gronbjerg, U.; Rossmeisl, J.; Chorkendorff, I. Understanding the Electrocatalysis of Oxygen Reduction on Platinum and Its Alloys. *Energy Environ. Sci.* **2012**, *5*, 6744−6762.

(26) Koper, M. T. M. Thermodynamic Theory of Multi-electron Transfer Reactions: Implications for Electrocatalysis. *J. Electroanal. Chem.* **2011**, *660*, 254−260.

(27) Hoffmann, R. A Chemical and Theoretical Way to Look at Bonding on Surfaces. *Rev. Mod. Phys.* **1988**, *60*, 601−628.

(28) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1960.

(29) Ma, J.; Choudhury, N. A.; Sahai, Y. A Comprehensive Review of Direct Borohydride Fuel Cells. *Renewable Sustainable Energy Rev.* **2010**, *14*, 183−199.

(30) Kresse, G.; Furthmuller, J. Efficient Iterative Schemes for Ab Initio Total-energy Calculations Using a Plane-wave Basis Set. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1996**, *54*, 11169−11186.

(31) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865−3868.

(32) Monkhorst, H. J.; Pack, J. D. Special Points for Brillouin-zone Integrations. *Phys. Rev. B* **1976**, *13*, 5188−5192.