Why platinum excels at hydrogen evolution

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Platinum is a nearly perfect catalyst for the hydrogen evolution reaction, and its high activity has conventionally been explained by its close-to-thermoneutral hydrogen binding energy ($\Delta G \approx 0$). However, many candidate non-precious metal catalysts bind hydrogen with similar strengths, but exhibit orders-of-magnitude lower activity for this reaction. In this study, we employ newly-developed electronic structure methods that allow fully potential-dependent reaction barriers to be calculated, in order to develop a complete working picture of hydrogen evolution on platinum. Through the resulting ab initio microkinetic models, we assess the mechanistic origins of Pt’s high activity. Surprisingly, we find that the hydrogen atoms with $\Delta G \approx 0$ are kinetically inert, and instead it is the weaker-bound hydrogens (which bind on top of Pt atoms, rather than in hollow sites) that are kinetically active. These on-top hydrogens have particularly low barriers for surface combination of $H$ to $H_2$, explaining the high reaction rates, and the exponential variations in coverages can uniquely explain Pt’s strong kinetic response to the applied potential. This explains the unique reactivity of Pt that is missed by conventional Sabatier analyses, and suggests true design criteria for non-precious alternatives.

Recent climate reports call for carbon emissions to be rapidly phased out in order to limit global warming’s most severe impacts, calling for 50% reductions by $\sim$2030 and (net) zero emissions by $\sim$2050.\(^1\) While many scalable carbon-free electricity generation sources exist, the path to carbon-neutral fuels and chemicals is less obvious. We argue that these technologies must be rapidly developed for the efficient conversion of electricity into fuels. The most readily deployable approach is to make $H_2$ (from $H_2O$) with renewable electricity, then use the $H_2$ in existing chemical processes—such as Haber–Bosch for ammonia synthesis, Fischer–Tropsch (preceded by reverse water-gas shift) for fuel synthesis, hydrotreating for biomass upgrading, or direct use in fuel-cell vehicles.

Functionally, platinum is a nearly perfect catalyst for the hydrogen evolution reaction (HER). In acidic media, platinum begins evolving $H_2$ (from $H_2O$) with renewable electricity, then use the $H_2$ in existing chemical processes—such as Haber–Bosch for ammonia synthesis, Fischer–Tropsch (preceded by reverse water-gas shift) for fuel synthesis, hydrotreating for biomass upgrading, or direct use in fuel-cell vehicles.

Conventionally, Pt’s activity has been explained by its hydrogen binding energy,\(^6,7\) which has been calculated to be almost perfectly thermoneutral at the equilibrium potential,\(^8,9\) maximizing the activity towards HER in accordance with the Sabatier principle.\(^10\) Despite extraordinary efforts to synthesize earth-abundant, inexpensive and stable catalysts based on this principle, alternate electrocatalysts with close-to-thermoneutral differential hydrogen binding energy exhibit HER activities that are orders of magnitude lower than on platinum.\(^11–20\) Thus, hydrogen binding energy alone cannot explain the superior HER activity of platinum catalysts.

Hydrogen evolution is a two-electron reaction commonly considered in two elementary steps:

\[
\begin{align*}
* + (H^+ + e^-) & \xrightarrow{\text{Volmer}} H* \\
H* + (H^+ + e^-) & \xrightarrow{\text{Heyrovsky}} H_2 + * \\
2H* & \xrightarrow{\text{Tafel}} H_2 + 2* 
\end{align*}
\]

where $*$ is a catalytic site and $H*$ is a surface-bound hydrogen. The Volmer reaction places atomic hydrogen on the catalyst surface via proton discharge from the electrolyte, coupled with electron transfer from the electrode. $H_2$ is liberated by either the Heyrovsky or Tafel step, as shown above. The Volmer and Heyrovsky steps include the explicit transfer of an electron, suggesting that their elementary rate constants will have a strong potential dependence; the Tafel step is non-electrochemical and its rate constant can be expected to have negligible potential dependence, save for field effects. Since $H*$ appears in each elementary step, it is perhaps not surprising that the hydrogen binding strength has traditionally been employed as a first descriptor of reactivity.

However, it is known that underpotential deposition of hydrogen ($H_{UPD}$) also occurs on Pt electrodes.\(^21–26\) Experimentally, this is observed in cyclic voltammograms as a capacitive event at potentials on the positive side of the equilibrium potential ($>0$ V$\text{RHE}$), before $H_2$ evolution takes off ($<0$ V$\text{RHE}$). The generally accepted microscopic view of this phenomenon based on electronic structure calculations is adsorption of H into the metallic fcc-hollow sites,\(^27–29\) creating an almost complete monolayer around the equilibrium potential of HER, before the surface begins to evolve $H_2$. These strongly-bound $H_{UPD}$ have a binding energy near $\Delta G = 0$, and are conventionally used in “volcano” plots explaining Pt’s activity.\(^8,9\) After the hollow sites fill, the next available sites are those on top of Pt; these overpotential-deposited H’s ($H_{OPD}$) have a much weaker binding free energy, similar to that of Au or Ag,\(^29\) which are relatively poor catalysts for this reaction. Thus, there is apparent contradiction...
and uncertainty about the roles of these two types of bound hydrogen.\textsuperscript{22,29,30}

Clearly, to describe Pt’s activity at a more sophisticated level requires knowledge of potential-dependent reaction barriers. However, electronic structure calculations of reaction barriers with explicit consideration of applied potential are scarce. This stems from the limitations associated with conventional density functional theory (DFT),\textsuperscript{31,32} which only allows for straightforward accounting of potential dependence of thermodynamically stable intermediates (i.e., via the computational hydrogen electrode model, CHE\textsuperscript{33}). Although means to calculate barriers within conventional DFT have been explored for HER,\textsuperscript{28} they suffer from little control over potential and coverages and from the need to extrapolate to constant-workfunction behavior, making the methods computationally expensive and the interpretation of results challenging.

The advent of grand-canonical electronic structure schemes has allowed for explicit control of applied potential in atomistic studies of electrocatalytic systems by varying the number of electrons, allowing the workfunction to be tuned relative to some reference potential.\textsuperscript{34–42} In particular, the solvated jellium (SJ) method\textsuperscript{43} accomplishes potential control for periodic systems by employing a counter charge in a solvated jellium slab, which localizes the excess charge on the reactive side of the electrode surface. In this work, we use this SJ method to directly calculate elementary step energetics of the hydrogen evolution reaction on Pt(111) as functions of the applied potential. Moreover, we relate these microscopic quantities to macroscopic behavior via microkinetic models and calculate Tafel slopes for all possible HER mechanisms.

**Potential Dependence of Barriers.**—Minimum energy pathways were calculated with the SJ method at a range of fixed voltages, shown in Figure 1; the key figures relevant to the discussion are shown here, while additional scenarios are found in the supporting information. We find that the barrier for the Volmer step is relatively low, but a strong function of potential. Since approximately a monolayer of H\textsubscript{UPD} is expected to be present at the onset of hydrogen evolution, Figure 1 shows the barrier for adsorbing an on-top H while all hollow sites are saturated. Barriers were also low for proton discharge to the same (on-top) site on pristine Pt(111), i.e., Pt(111) with vacant fcc-hollow sites.\textsuperscript{41} For proton discharge into the fcc-hollow sites, we observe that the reaction proceeds via an on-top site, followed by diffusion into the fcc-hollow site. This is shown in the supporting information. As shown in Figure 1, the reaction energy of this step changes linearly with applied potential, while the reaction barrier decreases quadratically with increasing overpotentials.

The Heyrovsky reaction—the electrochemical H\textsubscript{2} liberation step—is also a strong function of potential, and Figure 1 shows that it is a much more difficult process than the Volmer step. This figure shows the barrier involving an on-top (H\textsubscript{OPD}) atom; when we calculate the Heyrovsky reaction starting from a hollow (H\textsubscript{UPD}) atom, we find the atom first diffuses to an on-top site before reacting, resulting in a higher barrier in net. Compared to the Tafel reaction barriers, we see it is higher at most reasonable potentials, although a microkinetic model will shed greater insight into the relative pathways.

Functionally, the barriers of the Volmer and Heyrovsky steps exhibit similar, non-linear behavior with respect to potential. As a simple model of this behavior, we can consider the initial and final states to lie in quadratic potential energy wells, and the reaction barrier to be described by the point of intersection, (functionally) similar to Marcus theory.\textsuperscript{45,46} This form captures the basic physics expected:\textsuperscript{47} as the elementary reaction energy becomes strongly exothermic (\(\Delta E < 0\)), we expect the reaction to smoothly approach an activationless state (\(E^\dagger \to 0\)); similarly, when the elementary reaction becomes highly endothermic (\(\Delta E \gg 0\)), we expect no additional barrier beyond the energy change of the reaction (\(E^\dagger \to \Delta E\)). This simple parabolic picture leads to the relation:

\[
E^\dagger = \begin{cases} 0 & \Delta E < -4b \\ \frac{(\Delta E + 4b)^2}{16b} & -4b \leq \Delta E \leq 4b \\ \Delta E > 4b & \end{cases}
\]

Here, we choose to formulate this with the parameter \(b\), which can simply be interpreted as the barrier when the elementary step is thermoneutral (\(\Delta E = 0\)); that is, the intrinsic barrier. The two potential-dependent steps are plotted in this form in Figure 2, where we can see this one-parameter model captures the data well. The limiting behavior is evident for the Volmer reaction; the reaction approaches the activationless and barrierless regions for highly negative and positive potentials, respectively. The difference in the reactions is quite apparent by the difference in the calculated intrinsic barriers: \(b\) is only 0.13 eV for depositing the first proton on Pt (Volmer), but is 0.77 eV to liberate H\textsubscript{2} electrochemically (Heyrovsky). We assert that this one-parameter model is superior to both the two-parameter Brunsted-Evans-Polanyi (BEP) relations\textsuperscript{48–50} and linear transition-state scaling relations\textsuperscript{51–53} that are in common use for catalytic reactions, as the parabolic scaling smoothly captures the limiting forms and appropriate curvatures, making it ideal for use in microkinetic models.

The Tafel step—non-electrochemical H\textsubscript{2} liberation—is not electrochemical in nature, and its barrier as calculated in the SJ method shows this: its energetics are essentially independent of the applied potential (Figure 1). The barriers show no potential dependence, and the slight potential dependence of the reaction energy is a consequence of a small change in surface dipole (due to reorientation of the water bilayer when H\textsubscript{2} is incorporated); this energetic spread is negligible compared to the Volmer and Heyrovsky reactions. A much stronger effect is the originating sites of the H atoms involved: the combination of two top (H\textsubscript{OPD}) hydrogens is much eas-
The insets represent the initial, transition and final states at the equilibrium potential. All reaction barriers were calculated with the SJ method at constant potential, using the climbing-image nudged elastic band (CI-NEB)\textsuperscript{43,44} to find the minimum-energy path through the grand-canonical potential energy surface.

We also calculated this for two hollow-adsorbed atoms, and found an even higher barrier, nearly 1 eV, as shown in the supporting information. A comparison of the Tafel barriers with the Heyrovsky reaction shows the top–top Tafel to be much lower, whereas the top–hollow may be more comparable.

**Fixed-Potential Free Energy Diagrams.**—Free energy diagrams for the Volmer–Heyrovsky and Volmer–Tafel mechanisms are shown in Figures 3–5, where we also distinguish between top–hollow (H\textsubscript{UPD} + H\textsubscript{OPD}) and top–top (H\textsubscript{OPD}+H\textsubscript{OPD}) Tafel mechanisms. All values are tabulated in the supporting information. In all mechanisms, the initial state for the Volmer reaction includes a solvated proton in the electrochemical double layer. While this represents the initial state in our computational setup, it is in fact a pseudo-initial state with partial charge transfer. This fractional charge transfer has been investigated by Chen and coworkers,\textsuperscript{54} who found that the partial charge transfer is not a consequence of self-interaction in DFT,\textsuperscript{55–59} but rather due to hybridization of the metal electrode and the protonated water bilayer when the additional proton is located close to the interface. In our calculations, this phenomenon is evident from both Bader charge analysis\textsuperscript{60} and the grand-canonical description itself, where the latter indicates that only fractional numbers of electrons need to be injected into the system in order to keep potential constant throughout the reaction (see supporting information). Hence, a complete free energy diagram must account for the proton shuttling from the true initial state—a proton solvated deep in the bulk of the electrolyte—into the metal-solvent interface. We account for this by relating the chemical potential of the proton-electron pair to that of gaseous hydrogen via CHE,\textsuperscript{33,61}

\[
\mu (\text{H}^+) + \mu (\text{e}^-) = \frac{1}{2} \mu (\text{H}_2(g)) - neU.
\]  

(3)

where the proton–electron pair and hydrogen gas are in equilibrium at the equilibrium potential, and any deviation from the standard reduction potential is dealt with in post-processing. Hence, the stable intermediates—as well as the overall reaction—are subject to the thermodynamic constraints imposed by the well-known CHE model; we have indicated the CHE states with wide bars in the figures.

All three mechanisms begin with an identical step: proton shuttling from the bulk into the metal–solvent interface followed by a Volmer step to form an H\textsubscript{OPD} species. The initial proton shuttling step is endergonic in free energy. We interpret this as a consequence of the decreased entropy of the solvated proton in the confined electrochemical double layer relative to its bulk solvated counterpart; the entropic reduction (\(\Delta (TS)\)) was -0.3 to -0.4 eV at room temperature for all studied diffusion steps.

In the Volmer–Heyrovsky mechanism, the following step is the electrochemical \(\text{H}_2\) liberation (Heyrovsky)
step, which occurs in a similar fashion, but with a much higher intrinsic barrier. The Volmer–Tafel mechanisms involve a Tafel (associative H₂ desorption) step, which has no potential dependence, and a second proton deposition step, either to an on-top or a hollow site.

**Microkinetic Models.**—We extend the atomistic results above to macroscopic observables via microkinetic models; the implementation details are included in the supporting information. Figure 6 shows the potential-dependent current densities, Tafel slopes and coverages of the three studied mechanisms. The names in the figure refer to the rate-limiting step; all three mechanisms also contain Volmer (proton deposition) steps, which will become important in the subsequent discussion. The Heyrovsky path has the lowest current over the reported range of potentials and appears to be of little importance except possibly at large overpotentials, discussed later. The Tafel mechanism—limited by H⁺ combination—is the dominant pathway, which is considered for two cases. The top–top mechanism dominates over the broadest range of potentials, although at potentials near the equilibrium potential the top–hollow Tafel may be significant.

Of particular importance in mechanistic studies of electrocatalytic systems are Tafel slopes \( (dU/d\log_{10} j) \), which reveal the relationship between driving force (potential) and reaction rate (current).\(^{62–64}\) We offer an intuitive picture of Tafel slopes for this study. While the full microkinetic model presented in Figure 6 includes all barriers, let’s instead assume that the hydrogen-liberating step has a rate equation of

\[
r = k_t \cdot a_1 \cdot a_2
\]

where \( \{a_i\} \) indicate thermodynamic activities of the reactants. As shown in the supporting information, this rate-limiting step can be expressed as

\[
r \propto \exp\left\{-(\Delta G_\text{‡} + \Delta G_1 + \Delta G_2)/k_B T\right\} \equiv \Delta G_\text{net}
\]

where \( \Delta G_\text{‡} \) is the reaction barrier and \( \{\Delta G_i\} \) are from equilibrated reactant activities when \( a_i < 1 \). (When \( a_i \approx 1 \), the associated \( \Delta G_i \) drops out of \( \Delta G_\text{net} \).) Since \( j \propto r \), the Tafel slope is \( dU/d\log r = -k_B T \ln 10 \cdot dU/d(\Delta G_\text{net}) = dU/d(\Delta G_\text{net}) \cdot 59 \text{ mV/dec} \) (at 298 K).

That is, the Tafel slope can be directly inferred from the potential dependence of \( \Delta G_\text{net} \).

Consider first if the Tafel step \( (\text{H}^+ + \text{H}^+) \) is rate-limiting: \( \Delta G_\text{‡} \) is not a function of \( U \), so the only potential dependence comes from \( q_{12} \), both of which are coverages. When coverages are low \( (\theta < 1) \), \( \Delta G_\text{net} = \Delta G_1 + \Delta G_2 \approx 2\theta U \), and \( dU/d(\Delta G_\text{net}) = 1/2 \), giving a Tafel slope of 30 mV/dec. This matches both the top–top and top–hollow behavior in Figure 6 when coverages are low. However, when a coverage approaches unity, its activity in equation (4) becomes a constant and a factor of
\( \Delta G \) drops out of \( \Delta G_{\text{net}} \), giving a slope of 59 meV/dec, as seen in the top–hollow mechanism after the hollow sites saturate. By identical logic, when both coverages approach unity, the rate becomes insensitive to voltage and the Tafel slope \( \rightarrow \infty \); we see this at large negative potentials for both top–top and top–hollow. This behavior a priori outrules the hollow–hollow mechanism, as has been proposed by earlier theoretical studies, since the UPD coverage approaches unity at 0 V SHE in both the presented results and experimental studies.  

In summary, the rate changes rapidly when coverages change rapidly, which can only occur when coverages are very low; that is, orders-of-magnitude below 1, suggesting that only two weakly-bound H\(^+\)s can be responsible for a Tafel slope of 30 mV/dec.  

For the Heyrovsky mechanism, the reaction barrier is a function of \( U \) as we calculated in Figures 1–2; by linearizing eq. (2) (about zero driving force) we directly estimate \( \Delta G^f = \Delta G^f_0 + \beta eU \), with \( \beta = 0.5 \). \( a_1 \) is the activity of a dissolved proton, which is constant at fixed pH, so \( \Delta G_1 \) is absent from \( \Delta G_{\text{net}} \). \( a_2 \) is again hydrogen coverage. Therefore, when \( \theta \ll 1 \), \( \Delta G_{\text{net}} = 1.5 eU \) and the Tafel slope is 39 mV/dec, matching that seen in the microkinetic model. When \( \theta = 1 \), \( \Delta G_{\text{net}} = 0.5 eU \) and the Tafel slope is 118 mV/dec, matching that seen microkinetically when sites saturate.  

Based on this simple analysis, we can conclude that the only way to achieve a Tafel slope of \(~30\) mV/dec is in the limit when both activities correspond to coverages that are changing exponentially. In our analysis, this can only be caused by the weak-binding hydrogens (top–top), and the UPD hydrogen must be a kinetic spectator over most HER potentials.  

While the Tafel slopes are in excellent agreement with experimental results, the current densities are not. This is to be expected, for a number of reasons. First, in the absence of an internal reference potential, we use an approximate value of 4.4 V for the absolute standard hydrogen electrode potential; current responds exponentially to potential. Second, it can be challenging to accurately assign the activity reference state from limited-size atomistic calculations, affecting pre-factors in transition-state theory. Finally, DFT itself has limited accuracy, and deviations of 0.1–0.2 eV are to be expected. However, we note that a slight cathodic shift of the reference potential by \( \sim 150 \) mV leads to experimentally observed exchange current densities in combination with a Tafel slope of 30 mV dec\(^{-1}\). Interestingly, at nearly the same potentials the top-top Tafel mechanism becomes the dominating mechanism and supersedes the top-hollow mechanism, which exhibits higher currents at more anodic potentials.  

**Why Pt excels.**—Although many further refinements can be made to such a model, we now have enough information to understand why platinum so uniquely excels at the hydrogen evolution reaction. The prevailing view of Pt’s high reactivity is that the hydrogen binding (free) energy is near zero. Simultaneously, much speculation has persisted on the role of the UPD hydrogen atoms: are they kinetically active or merely spectators? However, our analysis makes clear that there must be two exponentially varying coverages as driving forces in order to see such high current response to potential (30 mV/dec): this can only occur with hydrogen that bind significantly weaker than \( \Delta G = 0 \); that is, the UPD hydrogens must be active. This is in agreement with experimental conclusions reached by He and colleagues. The UPD hydrogens are then kinetically inactive—but do promote the kinetic response by allowing for the weaker on-top hydrogens to become kinetically accessible. The weakly-bound hydrogens have both exponentially-varying coverage and a low barrier for the non-electrochemical Tafel step.  

This leads to the obvious question: if the role of Pt’s UPD hydrogen is to allow weaker hydrogen binding, why wouldn’t more noble metals, such as gold, be highly active as well? On such a noble system, we’d expect to have exponentially-varying coverages, and transition-state scaling suggests that we would also have a lower Tafel barrier. However, the intuition from transition-state scaling is wrong: the Tafel barrier on Au is significantly higher: about 0.6 eV. \(^{52}\) This is not a deviation from scaling behavior, but is because the Tafel reaction proceeds from two hollow sites on Au, rather than two top sites on Pt. (We expect that Au may therefore follow the Heyrovsky route, but this will require future microkinetic analyses on Au to confirm.) Thus, the role of the UPD hydrogens in Pt—which are experimentally observed as a capacitative event just before the onset of

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**FIG. 6:** Microkinetic models for the three mechanisms in Figures 3–5.
HER—is to both weaken the hydrogen bonding strength and allow for the Tafel reaction to proceed through a more facile, top–top, mechanism. Thus, we can understand why Pt is so uniquely reactive: more noble metals are forced into a hollow–hollow mechanism that carries an energetic penalty, while more reactive metals that can employ the top–top mechanism will also have higher Tafel barriers (via scaling) and further would bind hydrogen too strongly to have exponentially variable coverages, giving sluggish current responses. We hope that these insights can lead to the atomic-scale design of alternative catalysts with activities that rival Pt.

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METHODS

We use the Solvated Jellium (SJ) method to incorporate potential into \textit{ab initio} electronic structure calculations. This method, which has been published elsewhere,\cite{solvent} allows for the addition/subtraction of electrons (or fractions thereof) to/from the unit cell in order to keep the electrode potential constant. The SJ method is implemented in the GPAW\cite{gpa1,gpa2} electronic structure code and allows for systematic and selective charging of the metal-solvent interface. The dipole-induced electric field is screened with implicit and explicit water, where the implicit solvent module is a grid-based model developed by Held and Walter.\cite{held} The explicit water is modeled as a hexagonal, icelike structure with an H-down geometry (\textit{i.e.} every other water molecule has a hydrogen atom pointing towards the surface). This interfacial water geometry has been shown to be the most stable geometry for protonated, that is, acidic water bilayers, at the potentials of interest for HER.\cite{solvent,her1,her2,her3} The reaction pathways are all performed at constant potential, and the relevant energy comparison is therefore the grand potential energy

\[ E = E_{\text{DFT}} + N_e \Phi_e, \]  

where \( E_{\text{DFT}} \) is the constant-charge (canonical) energy. The post-processing correction term includes the electrode work function, \( \Phi_e \), and the number of added/subtracted electrons. In the complete free energy reaction diagrams presented in the main article, free energy contributions are included via normal mode analysis in the harmonic limit at 298 K:\cite{harmonic}

\[ \Delta \Omega = \Delta E + \Delta ZPE + \int_0^T C_p \, dT - T \Delta S, \]  

where \( \Delta E \) is the grand canonical energy (eq. 5) extrapolated to 0 K, and subsequent terms come from normal mode analyses. We observe one imaginary frequency at the transition state for each elementary reaction. This imaginary frequency represents an M-H or O-H stretch—the intuitive saddle point geometries for these reactions.

The Pt(111) electrode is modeled as a 3x2x3 slab, where the bottom layer is fixed at the optimized lattice constant (3.97 Å). The systems are sampled on a 4x6x1 k-point mesh. The unit cell is 30 Å in the \( z \)-direction and periodic in \( xy \), and a dipole-correction\cite{coulomb} is included in the \( z \)-direction. All calculations are performed at the generalized gradient approximation (GGA) level with the Perdew-Burke-Ernzerhof (PBE)\cite{pbe} exchange-correlation functional. The reaction barriers are calculated using the climbing-image nudged elastic band (CI-NEB)\cite{ci-neb} approach, and all systems were relaxed until the forces acting on each unconstrained atom were below 0.05 eV/Å and 0.03 eV/Å for kinetic barriers and stable endstates, respectively. A schematic of a typical unit cell is shown in the supporting information.