The amount of under-potential-deposited (UPD) H(ads), if it forms on Cu(111), is small compared to what forms on Pt(111). According to experimental literature, current density on polycrystalline copper increases slowly in the over-potential-deposited (OPD) potential range beginning at 0 V and rises rapidly at several hundred mV negative potential. Using a comprehensive density functional theory for the electrochemical interface, including Fermi level shifts, in this article we attribute this behavior to calculated weak H adsorption which requires the potential to be reduced to \(-0.0\) V(SHE) in order for H(ads) deposition to commence. A literature estimate, based on exchange current densities, of the activation energy for H2 evolution at 0 V is \(-0.32\) eV. As the coverage increases with increasingly negative potentials, we calculate the H adsorption energy decreases at a rate \(0.27\) eV/V for Cu(111), and this will decrease the effective activation energy. We propose that the observed rapid increase in current density at approximately \(-0.4\) V corresponds to \(-0.5\) ML coverage by H(ads) and reflects the decreasing activation energy at more negative potentials. We also relate our calculated findings to the literature for electrolese copper deposition and to literature for palladium-doped copper as a heterogeneous hydrogenation catalyst.

In this article we used quantum theory to explore hydrogen evolution from Cu(111) electrode surfaces. Hydrogen atoms bond weakly to copper surfaces and for significant hydrogen evolution to take place, an overpotential relative to the 0.0 V standard reversible potential must be applied. The first step is deposition of H(ads). In acidic electrolyte the reaction is

\[
H^+ (aq) + e^- \rightarrow H_{ad} (U) \tag{1}
\]

and in alkaline electrolyte

\[
H_2O (l) + e^- \rightarrow H_{ad} (U) + OH^- (aq) \tag{2}
\]

There are additional ways in which hydrogen can be introduced to copper surfaces as H(ads). In alkaline electrolyte hydrogen is evolved from copper surfaces when aldheyde groups are oxidized without potential control in alkaline electrolyte, that is at the potentials of zero charge (PZC), during electrolese copper deposition.\(^1\) In this case the goal is depositing copper atoms on selected substrates and H\(_2\) formed from combination of H(ads) on copper,\(^4\) is a secondary product. Hydrogen can also be introduced to copper surfaces as H(ads) by spillover of H bonded to Pd atoms on the copper surface.\(^5\) In this case H\(_2\) dissociation is activated by the Pd ad-atom and the weakly held spillover H(ads) performs hydrogenation of organic molecules.

To reduce water to hydrogen in alkaline electrolytes over copper electrodes requires high overpotentials of around 0.2 V.\(^6,7\) This contrasts with the small overpotential over platinum. Exchange current densities for hydrogen evolution in alkaline electrolyte for several transition metals, including copper, have been correlated to theoretically calculated H\(_2\)(g) chemisorption energies in a volcano plot.\(^8\) In the plot Pt is near the peak on the left hand side and Pd, Fe, Ni, Co, and W were also on the left (too strongly adsorbed) and Cu, Au, and Ag were on the right hand side (too weakly adsorbed). In Ref. 9 overpotentials for measured current densities of 1.0 mA/cm\(^2\) correlated well with the exchange current densities in the volcano plot. The development of understanding and applications of volcano plots continues with an extension to facets on nanoparticles.\(^10\) The multitude of variables that affect the exchange current densities used in volcano plots continue to be explored.\(^11\) In this article we address the overpotential of hydrogen evolution on the Cu(111) electrode. To do this, we employ theoretically calculated Gibbs energies, which are equal to the internal energies plus \(p\Delta V\) and \(T\Delta S\) contributions.

The ability to calculate reversible potentials for forming H(ads) as functions of coverage was demonstrated recently for forming under potential deposited (UPD) H(ads) on Pt(111).\(^12\) In that study very close agreement with cyclic voltamograms from the literature was found. The same computational approach was used in this study of over potential deposited (OPD) H(ads) on Cu(111).

**Theoretical Approach**

We used a state-of-the-art density functional theory (DFT) code called Interface\(^13,14\) for all calculations. The Interface DFT calculations apply a linear combination of pseudoatomic orbitals (LCPAO)\(^15\) with norm conserving pseudopotentials (NCPP)\(^16\) as effective core potentials, a generalized gradient approximation with revised Perdew–Burke–Ernzerhof (GGA-RPBE)\(^17\) as an exchange-correlation functional, and a double zeta polarization (DZP)\(^18\) basis set. A modified Poisson-Boltzmann (MPB) theory in the code gives the energy of electrolyte polarization around solvated ions and at surfaces and a dielectric continuum statistical representation of surrounding liquid water is used.\(^18,19\) When modeling electrode surfaces we use the two-dimensional option of the Interface code and in this case the electrode potential on the standard hydrogen electrode (SHE) scale is given by the formula

\[
U (q) = [-\varphi - E_f (q)] / F \tag{3}
\]

where \(q\) is charge (e units) added to the translational unit cell, \(\varphi = 4.454\) V, the calculated thermodynamic workfunction of the standard hydrogen electrode (SHE), and \(E_f (q)\) is the Fermi energy in eV when charge \(q\) (e units) is added to the translational unit cell. The Gibbs energy of a charged surface includes an additional mass conservation term as outlined in Ref. 14 that is a function of \(E_f (q)\) and the number of electrons, anions, and cations.

For our work, three-layer Cu(111) slabs were chosen for the two-dimensional band calculations. The top two layers of the slabs were relaxed during the optimization and the bottom layer was fixed at the calculated lattice constant of 3.73 Å. The \(3 \times 6 \times 1\) k-point mesh for Monkhorst-Pack sampling\(^20\) was applied. The thermal contribution term was calculated from standard statistical thermodynamic models: for adsorbed species, it was calculated from vibration frequencies using the harmonic vibration model and the frequencies are obtained from Hessian matrix; for isolated molecules, translational, rotational, and vibration modes were included. All potentials quoted in this work are on the SHE scale.

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* Electrochemical Society Student Member.
** Electrochemical Society Member.
* Email: aba@case.edu

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What is Learned from Adsorption Energies at the Potential of Zero Charge

In order to establish the accuracy of Interface calculations compared to other methods for hydrogen adsorption studies, we calculated H-atom adsorption internal energies for four sites on Cu(111). Table I includes adsorption energies for H(ads) added the Cu surface exposed to dielectric continuum and MPB at the PZC followed by results for the vacuum interface and then literature energies for the vacuum interface using the PW91 and RPBE functionals.\(^{21}\) Whereas we used a 3-layer thick Cu slab modeled with an 18 atom translational unit cell and Ref. 21 used a 4-layer thick slab the RPBE functional results are close in value. The aqueous adsorption energies are very close to the vacuum ones. The PW91 adsorption bond strengths from the literature are 0.16 eV and 0.17 eV larger than the RPBE ones. The H atom stabilities in the fcc and hcp 3-fold sites are nearly the same for all of the computational methods. It is noted that, instead of H(g), Ref. 21 employs H\(_2\) as the reference state when calculating the strength of the surface-H bond. This makes the accuracy of the calculated surface-H bond strength dependent on the accuracy of the H\(_2\)(g) bond strength as well as the accuracy of the surface-H bond description.

We can also compare the H\(_2\) bond dissociation energies, D\(_e\), which exclude the zero-point vibrational energy, obtained using the RPBE and PBE functionals in Interface, 4.50 eV and 4.57 eV, respectively, with values from Ref. 21, which are 4.58 eV from RPBE and 4.57 eV from PW91. These all underestimate the 4.75 eV\(^{22}\) experimental value for D\(_e\) by 0.18 to 0.25 eV. Using Interface, calculated bond dissociation energies, D\(_e\), fare better at 4.31 eV and 4.38 eV for RPBE and PBE, respectively compared to the 4.48 eV experimental D\(_e\).

If the H\(_2\) dissociation energy in Ref. 21 were increased by 0.18 eV to match the experiment, the literature values in Table I would become 0.09 eV less negative. This illustrates the effect of uncertain accuracy in the D\(_e\) calculations for H\(_2\)(g).

A second test of numerical accuracy of Interface and other methods is the calculated diatomic CuH bond strength. Using the RPBE functional, we calculated for D\(_e\) (D\(_0\)) 2.57 eV (2.46 eV). The PBE functional, which is similar to the PW91 functional, gives the values 2.69 eV (2.57 eV). The larger values for PBE were also seen in the adsorption bond strengths in Cu(111) shown in Table I. For diatomic CuH, the literature presents many theoretical results for D\(_e\) ranging from 2.52 eV to 2.79 eV in one study,\(^{23}\) and from 2.58 eV to 2.79 eV in another.\(^{24}\) For comparison, we calculated the D\(_e\) value using the Gaussian 09 code\(^{25}\) in the B3LYP hybrid density functional option with LANL2DZ for Cu and 6–31++G** for H and obtained 2.72 eV. Experimental estimates of D\(_e\), which include zero-point vibrational energies, cover a range of values and the average of a series of thermodynamic studies yielded 2.63 ± 0.06 eV.\(^{26}\) Using the harmonic constant \(\omega_0 = 1941.26 \text{ cm}^{-1}\) from Refs. 21,27 the corresponding D\(_e\) value is 2.75 ± 0.06 eV, in agreement with the Gaussian calculations.

### Table I. Calculated II adsorption energies without compensation for zero-point energies, at the aqueous and vacuum interfaces for the vacuum interface using the Interface code and literature values for the vacuum interface.

| Adsorption site | Interface (RPBE) a | literature (vacuum)b,c |
|----------------|--------------------|------------------------|
| 1-fold | −1.69 | −1.66 |
| 2-fold | −2.08 | −2.08 |
| 3-fold, fcc | −2.19 | −2.20 |
| 3-fold, hcp | −2.20 | −2.21 |

\( ^a \)H\(_2\)(g) + Cu(111) \( \rightarrow \) 1/6 ML H(ads).  
\( ^b \)1/4 ML H(ads).  
\( ^c \)Energy for 1/3 H\(_2\)(g) + Cu(111) \( \rightarrow \) H(ads).

### Table II. Calculated energies (eV) for dissociative adsorption of H\(_2\)(g) on Cu(111) based on 1/6 ML H(ads) coverage.

| Interface | RPBE | PW91 |
|-----------|------|------|
| \( \Delta \)E | 0.11 | 0.09 |
| \( \Delta \)G(0 K) | −0.03 | −0.05 |
| \( \Delta \)G(T) | 0.42\(^b\) (0.25\(^b\)) | 0.40\(^b\) (0.23\(^b\)) |

\( ^a \)T = 298 K.  
\( ^b \)Corrected value based calculated reaction energy reactions for the reaction in Eq. 4.  
\( ^c \)T = 420 K.

Our goal was to calculate the coverage of H(ads) as a function of the potential applied to the Cu(111) electrode. This was done in two ways. First, we calculated \( U_{\text{cell}} \) for adding H atoms to the surface, increasing the coverage in increments of 1/6 ML, beginning at zero coverage and ending at 1 ML coverage. For 0 ML, 1/6 ML, 1/3ML, 1/2 ML, 2/3 ML, 5/6 ML and 1 ML, an 18 Cu-atom translational unit cell was used. Two surface patterns were calculated when coverage, but the RPBE and PBE results are 0.18 eV and 0.06 eV less, respectively, than experiment.

Using the experimental values for the D\(_e\) (D\(_0\)) for H\(_2\) and CuH in the reaction

\[
\text{H}_2 + 2\text{Cu} \rightarrow 2\text{CuH}
\]

the energy changes \( \Delta \_\_ \) were −0.75 eV (−0.78 eV), and using RPBE density functional results from Interface, the energy differences were −0.64 eV (−0.61 eV). In both cases \( \Delta \_\_ \) and \( \Delta \_\_ \) are within 0.03 eV from one another, demonstrating a near cancellation of zero-point energy contributions, and the Interface results are, respectively, 0.11 eV and 0.17 eV less negative than experiment. Using Interface to calculate these properties with the PBE functional gave for \( \Delta \_\_ \) and \( \Delta \_\_ \), −0.81 eV (−0.76 eV), which are, respectively, 0.06 eV more negative and 0.02 eV less negative than experiment.

Similar relative results are expected for dissociative adsorption of H\(_2\) on Cu(111) in 3-fold sites in Ref. 5. There, forming two H adsorption bonds from H\(_2\) gave the reaction energy with PW91 that was 0.34 eV more stable than when RPBE was used (Table II). The PW91 results were the basis of energy analyses of H(ads) on Cu(111) formed by H\(_2\) dissociation over Pd ad-atoms and their spilling over onto the copper surface.\(^7\)

### Gibbs adsorption energy of H\(_2\)(g) on Cu(111) at 0 K and 298 K.

References 5–7 used H\(_2\)(g) for the reference state for the H adsorption energies on Cu(111). Table II shows adsorption energies calculated using this reference state. Included are Interface RPBE results and RPBE and PW91/PBE results from Ref. 5 without zero-point energies. The properties displayed are \( \Delta \)E, \( \Delta \)G(0 K), and \( \Delta \)G at temperatures greater than 0K, \( \Delta \)G(T). From the values of \( \Delta \)G in this table it is concluded that at 0 K 2H(ads) are more stable than H\(_2\)(g) and as the temperature is raised to around room temperature H\(_2\)(g) becomes the stable phase of hydrogen. In what follows we are primarily concerned with the Gibbs energy of adsorption at 298 K. Applying the 0.17 eV overestimate of the RPBE reaction energy from Eq. 4 to the aqueous 298 K result of 0.42 eV in Table II gives a value of 0.25 eV. This corrected value should be close to the true value at 298 K for the dissociative desorption Gibbs energy for H\(_2\)(g) on Cu(111) in aqueous electrolyte at the PZC.

Electrochemical Deposition of H(ads) on Cu(111) and H\(_2\) Evolution

Our goal was to calculate the coverage of H(ads) as a function of the potential applied to the Cu(111) electrode. This was done in two ways. First, we calculated \( U_{\text{cell}} \) for adding H atoms to the surface, increasing the coverage in increments of 1/6 ML, beginning at zero coverage and ending at 1 ML coverage. For 0 ML, 1/6 ML, 1/3ML, 1/2 ML, 2/3 ML, 5/6 ML and 1 ML, an 18 Cu-atom translational unit cell was used. Two surface patterns were calculated when coverage,
θ, was 1/6 ML, 1/3 ML, 1/2 ML, and 2/3 ML, and Figure 1 shows the more stable ones.

To determine reversible potentials reversible as a function of coverage we write Eq. 1 as

$$\text{H}_{\text{ads}}(\theta) + \text{H}^+ (\text{aq}) + e^- (U) \rightleftharpoons \text{H}_{\text{ads}}(\theta + 1/6 \text{ML})$$ [5]

The Gibbs energies of the left hand and right hand sides of this equation are calculated for a series of potentials by changing the added charge in increments of 0.1 e and graphed, as in the example of Figure 2. Second order curves are fitted to the two data sets and their potential of crossing is the predicted reversible potential for depositing 1/6 ML additional H(ads). Then the coverage at midway points, $\theta + 1/12$ ML, is plotted as a function of potential as shown in Figure 3. The Langmuir configurational entropy-based energy, $-7k_b \ln([1-\theta]/\theta)$ was added to give the final predicted coverage vs. potential curve in Figure 4. Deposition is predicted to begin at about 0.0 V, suggesting UPD deposition will not take place on Cu(111).

The second computational approach depends on H(g) adsorption Gibbs energies at the PZC. Figure 5 shows a trend to becoming progressively weaker as the coverage increases from 0 ML to 1 ML. The data points are scattered from the line fit but they represent the coverages employed in the first method. The reversible potentials, $\Delta G_{\text{ads}}$, were calculated from the Gibbs energies of adsorption using the relation

$$U_{\text{rev}} = \left( -1.98 \text{ eV} - \Delta G_{\text{ads}} \right) / F$$ [6]

where 1.98 eV is the calculated standard Gibbs formation energy of H(g) from H$_2$(g) and F is the Faraday constant. Equation 6 comes from adding the equation $\text{H}^+ (\text{aq}) + e^- \rightleftharpoons \frac{1}{2} \text{H}_2 (U^0 = 0 \text{ V})$ and

$$U_{\text{ads}} = 0.26555 \phi - 1.83583$$


**Figure 6.** Coverage of OPD H(ads) vs. potential of Cu(111) electrode using the data in Figure 5 in Eq. 5.

\[ \Delta G^o = 0.00 \text{ eV} \] to the equation \( \frac{1}{2} H_2 \rightarrow H(g) \) (\( \Delta G^o = 1.98 \text{ eV} \)) and the result to the equation H(g) + surface \( \rightarrow \) H(ads) (\( \Delta G_{ads} \)). Using Eq. 6 is computationally much less intensive than the first method. Figures 3 and 6 illustrate that onset potentials by both methods are about \(-0.1 \text{ V} \) by both methods when the Langmuir terms are not included and in Figures 4 and 7 both are about 0.0 V when they are. Recognizing that the H adsorption energies are underestimated by about 0.1 eV when the RPBE functional is used, we can consider the consequences of moving the curves to the curves of the right \( 0.1 \text{ V} \). This would correspond to a narrow region of UPD H(ads) beginning at a potential a bit higher than 0.1 V.

If \( H_2(g) \) is the stable phase at room temperature, as suggested previously, we might expect small amounts of \( H_2 \) evolution around 0.0 V when the coverage of H(ads) is sparse. Since the adsorption energies at 3-fold hollow and 2-fold bridging sites differ by only \( 0.1 \text{ eV} \) in the coverage this barrier to forming \( H_2 \) causes its slow evolution. How-ever, as Figure 5 shows, the H adsorption bond strength decreases at a rate of 0.27 times the increase in coverage, which begins at 0 ML and ends at 1 ML. It is to be expected, therefore, that as the coverage increases, the effective activation energy will decrease and the reaction rate will increase. Then, as Eqs. 2, 3, 5, and 6 show, OPD H(ads) coverage increases rapidly as the potential decreases. This is associated with and helps explain the sharp rise in current density that begins at \( -300 \text{ mV} \) overpotential on polycrystalline Cu electrode surfaces at 20°C.8

During electrolel Cu deposition H(ads) is a side product and \( H_2(g) \) is observed at potentials well above the standard reversible for its evolution.3,4 As the above discussion shows in this article, UPD H(ads) is not stable on Cu(111) and as a concentration builds up recombination to form \( H_2(g) \) should be facile. The removal of H(ads) may also be necessary for electrolel Cu deposition to proceed.

**Conclusions**

According to our findings in this article, theory that has made good predictions for UPD H(ads) formation on Pt(111) also makes good predictions for OPD H(ads) formation on Cu(111). Two procedures, one employing potential dependence of reactant and product Gibbs energies for going from one coverage to another to determine \( \eta_{rev(0)} \) and a computationally much simpler procedure which employs Gibbs energy changes at the PZC for going from one coverage to another yield remarkably similar results. This is because the adsorption Gibbs energies of hydrogen atoms are weakly dependent on the Cu(111) electrode potential. Our findings provide explanation for (i) the PZC phenomenon of spillover H(ads) on copper being active for hydrogenation chemistry, (ii) the evolution at the PZC of \( H_2(g) \) from copper during electrolel copper deposition with aldehyde reductants, and (iii) a qualitative understanding of the dependence of the evolution rate of \( H_2(g) \) from OPD H(ads) on the copper electrode potential.

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