Orbital-Specific Modeling of CO Chemisorption

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Abstract

We demonstrate that variations in molecular chemisorption energy on different metals, different surface terminations, and different strain conditions can be accounted for by orbital-specific changes in the substrate electronic structure. Our density functional theory data set, spanning three metals, two surface terminations, and five strain states, is fit to a single model based on tight binding. A crucial aspect of the model is decomposition of the $d$-band into contributions from the five $d$ atomic orbitals. This provides a representation of the energy levels of the substrate that are directly relevant to the chemisorption bond, leading to accurate prediction of chemisorption trends.
Currently, great attention is focused on elucidating how surface modification affects surface reactivity. Recent research shows that small changes in surface electronic structure, induced by alloying or strain, can significantly change surface-catalyzed reaction rates. A quantitative understanding of how changes in surface geometry and electronic structure affect surface reactivity will enable the design of more specific and more effective catalysts. It has been shown that $\epsilon_d$, the center of the transition metal (TM) $d$-band density of states projected on the surface atoms (PDOS), is generally predictive of trends in chemisorption energies ($E_{chem}$) on TM surfaces. However, quantitative accuracy (model predictions accurate within 0.1 eV) is still elusive, and for several cases there is poor or no correlation between $\epsilon_d$ and $E_{chem}$. In this paper, using CO chemisorption as an example, we show that more rigorous examination of the surface electronic structure coupled with a simple modification of current chemisorption modeling enables us to achieve this goal.

We have compiled a database of DFT molecular top site ($E_{chem}$) and dissociative bridge site ($E_{dissoc}$) chemisorption energies and electronic structure measurements for CO on Pt, Pd, and Rh (111) and (100) surfaces. $E_{chem}$ and $E_{dissoc}$ are determined for each surface at the preferred theoretical lattice constants as well as under in-plane strains of $\pm$1% and $\pm$2%, a range easily achievable through epitaxial mismatch. Studying the response of chemisorption to strain as well as to different metals and facets deepens the study. Strain induces relatively subtle changes in $E_{chem}$ and $E_{dissoc}$ (compared to changes in metal or facet), so accurately accounting for large and small changes is a stringent test of a proposed theoretical model. Since lateral stress changes inter-planar separations, straining the systems also probes the interplay between in-plane and inter-plane perturbations to the surface geometry.

For each metal, surface, and strain state, two values for $E_{chem}$ are determined, $E_{chem}^{fix}$ and $E_{chem}^{rlx}$. The former is the energy gain when the same chemisorption geometry is fixed over the relaxed bare surface for all metals and surfaces. In the latter, full ionic relaxation is allowed in the top two metal surface layers and all C and O ionic degrees of freedom. For the dissociative systems, we only determine $E_{dissoc}^{fix}$, due to the known instability of C and O atomic adsorption at bridge sites.

We focus attention on top-site $E_{chem}$ and bridge-site $E_{dissoc}$ for clarity. The symmetries at these sites provide for zero overlap between some $d$ orbitals and the adsorbate orbitals,
making a clear distinction between orbital-specific and orbital-averaged models. Analysis of the top site also facilitates separation of the molecular chemisorption into $\sigma$ and $\pi$ contributions. However, even at low-symmetry sites, the contributions of the five $d$ orbitals to chemisorption are unequal, making our orbital-specific treatment more accurate in general.

DFT calculations are performed with a generalized-gradient approximation (GGA) exchange-correlation functional [15] and norm-conserving optimized pseudopotentials [16] with the designed nonlocal method for metals. [17, 18] Pseudopotentials were designed using the OPIUM pseudopotential package. [19] All $E_{\text{chem}}$ values have been corrected using our first-principles extrapolation procedure. [20] Metal surfaces are modeled as slabs of five layers separated by vacuum, with the $c(4 \times 2)$ surface cell for (111) surfaces and the $p(2 \times 2)$ surface cell for (100). CO top site and C and O bridge site chemisorption are modeled at coverage of $\Theta=1/4$. Calculations are done, and values of $E_{\text{chem}}$ tested to be converged within 0.02 eV, using an $8 \times 8 \times 1$ grid of Monkhorst-Pack $k$-points, reduced by symmetry where possible. [21]

The PDOS for each orbital is constructed by projecting each atomic valence pseudowavefunction (radial wavefunction multiplied by real combination of spherical harmonics) of the surface atoms onto all the Kohn-Sham orbitals. Values of $\epsilon_d$ are then calculated as the first moment of each PDOS.

To reduce PDOS contributions from neighboring surface atoms, projection is performed within a sphere of radius $r_{\text{cut}}$ centered about the surface atom of interest. Standard practice is to use a constant value for $r_{\text{cut}}$ when comparing the PDOS and associated $\epsilon_d$ values of different surfaces, and $r_{\text{cut}} = 2$ a.u. is the default in some widely used DFT packages. [22, 23, 24] However, this approach leaves significant contributions from the orbitals of other atoms, making the calculated value of $\epsilon_d$ dependent on $r_{\text{cut}}$, which is undesirable.

To eliminate contamination from the orbitals of neighboring atoms, we evaluated $\epsilon_d$ at various $r_{\text{cut}}$ values. (When $r_{\text{cut}} < 0.5$ a.u., the number of FFT grid points is too small to allow spherical sampling, so data are presented for $r_{\text{cut}} \geq 0.6$ a.u.) Figure 1 shows the variation of $\epsilon_d$ with $r_{\text{cut}}$ for Pt(111) and Pt(100). It is apparent that the asymptotic behavior of $\epsilon_d$ is not reached until $r_{\text{cut}} \ll 2$ a.u. Furthermore, $\epsilon_d$ values for different surfaces, strain states and orbital angular momenta depend differently on $r_{\text{cut}}$. To obtain accurate $\epsilon_d$ values, we fit a purely quadratic function to the data and extrapolate $\epsilon_d$ to $r_{\text{cut}} = 0$. This procedure greatly reduces the contribution from the orbitals of neighboring atoms, making comparison
of $\epsilon_d$ for various systems more meaningful.

While our data confirm that $E_{\text{chem}}$ qualitatively tracks with $\epsilon_d$ for the (111) surfaces, they reveal shortcomings of using $\epsilon_d$ for modeling bonding on different facets. From Figure 2, we see that $E_{\text{chem}}$ values on different facets differ by 0.06–0.25 eV (0.15–0.85 eV for $E_{\text{dissoc}}$) even though they have the same $\epsilon_d$ and the same metal. Figure 2 and Table I show this is still true for $\epsilon_d$ with $r_{\text{cut}} \rightarrow 0$ a.u. Therefore, neither $E_{\text{chem}}^{\text{fix}}$ nor $E_{\text{dissoc}}^{\text{fix}}$ can be fit as a single function of $\epsilon_d$, when both (111) and (100) facets are considered.

By contrast, we find that facet dependence of the chemisorption energies can be fit as a single linear function of $\epsilon_{xzyz}$, the band center of the $d_{xz}$ and $d_{yz}$ orbitals. Figure 2 shows that single linear regressions of data for both facets are accurate to within 0.05 eV in all cases. This result demonstrates that focusing on the metal orbitals involved in bonding simplifies the observed chemisorption behavior and enables robust modeling.

Similarly, Table I shows that the response of $E_{\text{chem}}$ and $E_{\text{dissoc}}$ to strain is reflected in $\epsilon_{xzyz}$ but not $\epsilon_d$. The tunability of $E_{\text{chem}}$ and $E_{\text{dissoc}}$ through strain is two to ten times greater on the (111) surfaces. However, $d\epsilon_d/ds$ is identical within computational precision for the two facets of each metal, so $d\epsilon_d/ds$ is uncorrelated with $dE_{\text{chem}}/ds$ and $dE_{\text{dissoc}}/ds$. The chemisorption tunability trend is strongly reflected in $d\epsilon_{xzyz}/ds$, suggesting that the response of the $d_{xz}$ and $d_{yz}$ orbitals plays a key role in modeling top-site molecular and bridge-site dissociative adsorption of CO.

**TABLE I:** $E_{\text{chem}}^{\text{fix}}$, $E_{\text{chem}}^{\text{rlx}}$, $E_{\text{dissoc}}^{\text{fix}}$, $\epsilon_d$, and $\epsilon_{xzyz}$ in eV for the (111) and (100) surfaces of Pt, Rh, and Pd. The slope of each quantity with respect to in-plane strain, ($d/ds$), is also reported, in units of meV/%strain. ($\epsilon_d$ and $\epsilon_{xzyz}$ use $r_{\text{cut}} \rightarrow 0$ a.u.)

|        | $E_{\text{chem}}^{\text{fix}}$ | $dE_{\text{chem}}^{\text{fix}}/ds$ | $E_{\text{chem}}^{\text{rlx}}$ | $dE_{\text{chem}}^{\text{rlx}}/ds$ | $E_{\text{dissoc}}^{\text{fix}}$ | $dE_{\text{dissoc}}^{\text{fix}}/ds$ | $\epsilon_d$ | $d\epsilon_d/ds$ | $\epsilon_{xzyz}$ | $d\epsilon_{xzyz}/ds$ |
|--------|-------------------------------|-------------------------------------|-------------------------------|-------------------------------------|-------------------------------|-------------------------------------|--------------|------------------|-----------------|---------------------|
| Pt(111) | -1.49                         | -36                                | 1.99                          | -158                                | 1.77                          | 20                                  | -1.74        | 18               | 0.15            | 29                  |
| Pt(100) | -1.69                         | -3                                 | 1.03                          | -65                                 | -1.76                         | 20                                  | -1.63        | 7                | 0.15            | 26                  |
| Rh(111) | -1.56                         | -27                                | 1.03                          | -65                                 | -1.68                         | 24                                  | -1.35        | 25               | 0.11            | 24                  |
| Rh(100) | -1.65                         | -18                                | 1.03                          | -65                                 | -1.68                         | 24                                  | -1.28        | 14               | 0.15            | 20                  |
| Pd(111) | -1.23                         | -25                                | 1.03                          | -65                                 | -1.58                         | 29                                  | -1.50        | 26               | 0.15            | 19                  |
| Pd(100) | -1.32                         | -5                                 | 1.03                          | -65                                 | -1.58                         | 29                                  | -1.50        | 9                | 0.15            | 19                 |

To explain the observed trends in $E_{\text{chem}}$ as the metal identity, facet, and strain state
are varied, we reconsider the model for CO chemisorption. A second-order perturbative picture of chemisorption involving interacting molecular and metal orbitals is simple and intuitive, and has been known for some time. Hammer, Morikawa, and Nørskov (HNM) achieved significant success modeling molecular interactions with solid surfaces with a single perturbative term involving $\epsilon_d$, the $d$-band center. Guided by the trends presented above, we cast an orbital-specific analysis (OS) in the HNM model form, modeling top-site chemisorption as a perturbative interaction between molecular orbitals and the $d$-band PDOS of each spatial orbital:

$$E_{\text{chem}}^{\text{OS}} = E_{sp} - 4 \left\{ \frac{fV_\pi^2}{\epsilon_{2\pi^*} - \epsilon_{xzyz}} + fS_\pi V_\pi \right\}$$

$$-2 \left\{ \frac{(1 - f)V_\sigma^2}{\epsilon_d - \epsilon_{5\sigma}} + (1 + f)S_\sigma V_\sigma \right\}$$

(1)

where $f$ is the idealized filling of the metal $d$ bands, $V$ and $S$ are perturbation matrix elements and overlap integrals, respectively, labeled by symmetry, $\epsilon_{2\pi^*}$ and $\epsilon_{5\sigma}$ are the CO molecular orbital energies, $\epsilon_{xzyz}$, the band center of the $d_{xz}$ and $d_{yz}$ orbitals and $\epsilon_d$ is the band center of the $d_{z^2}$ orbitals. As in the original HNM model, $\alpha$ and $\beta$ are introduced as fitting parameters common to all metals, and $V_\pi^2 \approx \beta V_{sd}^2$ and $S_\pi \approx -\alpha V_\pi$. From our analysis of DFT orbitals, we find that $S_\sigma/S_\pi$ to be sensitive in the limit of desired accuracy to both metal identity and adsorption geometry. Our overlap analysis gives $S_\sigma/S_\pi$ is 1.182, 1.156, and 1.200 for Pt, Rh, and Pd, respectively. $E_{sp}$ is found to be -0.15 eV from DFT calculations on Al surfaces and assumed to be independent of metal identity, facet, or strain. For the (111) and (100) surfaces, we find that $f$ for each of the decomposed $d$-bands is well approximated by the idealized filling of the metal $d$-bands, $f = (\nu - 1)/10$, where $\nu$ is the valence of the metal atom.

The corresponding conventional orbital-averaged (OA) model form is given by:

$$E_{\text{chem}}^{\text{OA}} = E_{sp} - 4 \left\{ \frac{fV_\pi^2}{\epsilon_{2\pi^*} - \epsilon_d} + fS_\pi V_\pi \right\}$$

$$-2 \left\{ \frac{(1 - f)V_\sigma^2}{\epsilon_d - \epsilon_{5\sigma}} + (1 + f)S_\sigma V_\sigma \right\}$$

(2)

We fit the data for both fix and rlx chemisorption systems to the Equation 1 and Equation 2. Figure 3 shows the correlation between DFT and model values for the more realistic rlx chemisorption systems. We calculate the root-mean-square error (RMSE) as
an evaluation of the model, considering the (111) and (100) data separately and combined. When Equation 2 is used to fit the data, the RMSE is 0.051 and 0.100 eV for the (111) and (100) surfaces respectively, and 0.079 eV overall. When Equation 1 is used to fit the data, the RMSE is 0.052 and 0.051 eV for the (111) and (100) surfaces respectively, and 0.052 eV overall. This shows that the more sophisticated model form of Equation 1 is required to achieve the same level of accuracy for these two surfaces.

We now address why different levels of model sophistication are needed to achieve the same accuracy in predicted $E_{\text{chem}}$ on the (111) and (100) surfaces. First, we consider the salient electronic structure differences between the (111) and (100) surface facets. The $dd$ metal bonding can be decomposed by symmetry into $\sigma$, $\pi$, and $\delta$ contributions. \[28\] The square lattice of the (100) surface allows for strong $dd\sigma$ overlap between neighboring $d_{x^2-y^2}$ orbitals. Our DFT data show that $\epsilon_{x^2-y^2}$ is significantly lower on (100) surfaces than on (111), as shown for Pt in Figure 1. Since (100) surface atoms have eight nearest neighbors while the (111) atoms have nine, the other $d$ orbitals are less stable on (100) surfaces to varying extents, with $\epsilon_{xz}$ and $\epsilon_{yz}$ significantly higher on (100) than (111). Averaging all the $d$ orbitals causes the rise in bonding-relevant $\epsilon_{xz}$ and $\epsilon_{yz}$ to be masked by the drop in bonding-irrelevant $\epsilon_{x^2-y^2}$, so that even though $\epsilon_{xzyz}$ closely tracks the increase in $E_{\text{chem}}$ on the (100) surface relative to the (111) surface, the averaged $\epsilon_d$ does not.

When tensile strain is applied to a TM surface, the weakened in-plane bonding destabilizes the $d$ orbitals. $\epsilon_d$ shifts upward, leading to stronger $E_{\text{chem}}$. \[7\] This basic prediction was confirmed in the DFT study of Mavrikakis et al. \[9\] However, different $d$ orbitals shift by different amounts, based on their orientations relative to the surface.

In addition, the inter-planar spacing between the top two metal layers ($r_{12}$) responds to the strain, and this further affects substrate electronic structure, again in an orbital-specific way. Tensile lateral strain usually decreases $r_{12}$, while compression increases $r_{12}$. The bonding-relevant $d_{xz}$ and $d_{yz}$ orbitals of the top layer have the strongest interaction with the second layer atoms, so the relaxation of $r_{12}$ significantly reduces the effect of lateral strain for these orbitals. This is why $d\epsilon_{xzyz}/ds$ is less than $d\epsilon_d/ds$ for all surfaces studied (Table I).

The effect of $r_{12}$ relaxation on strain tunability is also strongly facet-dependent. On the more open (100) surface, relaxations of $r_{12}$ are larger, making $d\epsilon_{xzyz}$ smaller for each (100) facet studied than for the corresponding (111) facet. This explains why the tunability of
$E_{\text{chem}}$ (fix and rlx) and $E_{\text{dissoc}}^{\text{fix}}$ are much lower on (100) surfaces than on (111) surfaces.

Our demonstration that a single orbital-specific chemisorption model can be applied to different facets, strains, and metals, has implications for the modeling and design of more realistic catalyst surfaces. DFT studies have found that reactions on late TMs are more likely to proceed on defects such as steps and kinks. The model presented suggests that one should examine how different nearest-neighbor and inter-planar separations affect the orbital-specific electronic structure, and predict chemisorption properties accordingly.

Incorporating the effects of strain and $r_{12}$ relaxation on the relevant PDOS centers greatly improved chemisorption modeling. We therefore suggest that if further couplings between PDOS centers and adsorbate structure can be parameterized, the resulting model could offer even greater accuracy and broader applicability.

In conclusion, we use the energy levels of the substrate $d$-band projected onto the substrate atomic orbitals and their overlap with the CO bonding molecular orbitals, in a second-order perturbation theory-type model for chemisorption. The resulting model is able to account for changes in $E_{\text{chem}}$ on different surface facets under different conditions of strain. We have also shown that trends in the dissociative chemisorption of CO at bridge site are governed by the same orbital-specific factors. The results shown here should be generally valid for other molecular and atomic adsorption on higher index surfaces and for perturbations other than strain.

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[30] Taking the top site as an example, $S_{\pi,i} \neq 0$ for $d_{xz}$ and $d_{yz}$ only, and $S_{\sigma,i} \neq 0$ for $d_{z^2}$. HMN values of $\epsilon_{2\pi} = 2.5$ eV and $\epsilon_{5\sigma} = 7$ eV are used. Moderate changes to these values re-scales the dependence of $E_{\text{chem}}$ on $\epsilon_d$ without significantly changing any presented results.

[31] For the fix data, the best fit to Equation 1 is achieved when $\alpha = 0.0619$ eV and $\beta = 1.052$ eV$^2$, and the best fit to Equation 2 is achieved when $\alpha = 0.0578$ eV and $\beta = 0.938$ eV$^2$. For the rlx data, the best fit to Equation 1 is achieved when $\alpha = 0.0619$ eV and $\beta = 1.050$ eV$^2$, and the best fit to Equation 2 is achieved when $\alpha = 0.0604$ eV and $\beta = 1.048$ eV$^2$. 

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FIG. 1: (a) Variation in $\epsilon_d$ as a function of projection sphere cutoff radius $r_{\text{cut}}$ for Pt(111). $\epsilon_{x^2-y^2}$, $\epsilon_{xz}$, $\epsilon_{y^2}$, and $\epsilon_{xy}$ PDOS centers are shown by circles, squares, diamonds, up-triangles, and down-triangles, respectively. (b) Same as (a) for Pt(100).

The graphs demonstrate the importance of extrapolating $r_{\text{cut}} \to 0$ a.u.: for Pt(111) the asymptotic $d$-band centers are more nearly equal than their large-$r_{\text{cut}}$ estimates; for Pt(100) they are more dissimilar.
FIG. 2: Plots of $E_{\text{chem}}^\text{fix}$ and $E_{\text{dissoc}}^\text{fix}$ vs. $\epsilon_d$ and $\epsilon_{xzyz}$ for Pt (circle), Rh (square), and Pd (diamond) (111) surfaces (open) and (100) surfaces (filled). Data for five lateral strain states (0%, ±1%, and ±2%) are shown. Linear regressions are shown for each metal. (a) $E_{\text{chem}}^\text{fix}$ vs. $\epsilon_d$, $r_{\text{cut}}=2$ a.u. (b) $E_{\text{dissoc}}^\text{fix}$ vs. $\epsilon_d$, $r_{\text{cut}}=2$ a.u. (c) $E_{\text{chem}}^\text{fix}$ vs. $\epsilon_{xzyz}$, $r_{\text{cut}} \to 0$ a.u. (d) $E_{\text{dissoc}}^\text{fix}$ vs. $\epsilon_d$ and $\epsilon_{xzyz}$, $r_{\text{cut}} \to 0$ a.u.
FIG. 3: Correlation plots of modeled $E_{chem}$ and $E_{chem,DFT}$. Pt (circle), Rh (square), and Pd (diamond) (111) surfaces (open) and (100) surfaces (filled). Data for five lateral strain states (0%, ±1%, and ±2%) are shown. (a) $E_{chem}^{OA}$ (Equation 2) vs. $E_{rlx}^{chem,DFT}$. (b) $E_{chem}^{OS}$ (Equation 1) vs. $E_{rlx}^{chem,DFT}$.

The plots show that orbital-specific modeling (Equation 1) is required to achieve the same quality of correlation for both (111) and (100) facets.