A predictive model of molecular adsorption to metals based on \textit{ab initio} calculations

Paolo Restuccia,\textsuperscript{1,*} Ehsan A. Ahmad,\textsuperscript{1,2} and Nicholas M. Harrison\textsuperscript{1}

\textsuperscript{1}Department of Chemistry, Imperial College London, 82 Wood Lane, W12 0BZ London, UK
\textsuperscript{2}Faculty of Engineering and the Environment, University of Southampton, University Road, Southampton SO17 1BJ, UK

The description of adsorption to surfaces and interfaces is essential in many technological fields, such as catalysis, corrosion and friction. For example, an accurate prediction of the structure and properties of molecules on substrates is essential to both the design and optimisation of coatings used to protect and enhance the properties of metals. We introduce a new model for the prediction of adsorption energies of molecules to metal substrates. The model is based on easily computed, intrinsic properties of the substrate and molecules (e.g., bulk cohesive energy, work function, molecule-cluster binding and the molecular orbital energy gap). It is parameterised by combining \textit{ab initio} calculations with machine learning algorithms. The model is trained using a small set of probe molecules (e.g., H$_2$O, CO$_2$, O$_2$, N$_2$) adsorbed to a range of pure metal substrates. The model predicts the computed dissociative adsorption energy to metal surfaces with a correlation coefficient of 0.93 and a mean absolute error of 0.77 eV for the large database of molecular adsorptions stored in the Catalysis-Hub.org database. The model therefore significantly enhances current efforts to identify new molecular coatings in many research fields and thus facilitates the discovery of new environmentally friendly and inexpensive materials with specific adhesion characteristics.

INTRODUCTION

One of the most significant challenges of this century is the need for technical solutions to the increasing severe problems posed by climate change. In the last decade, our society has developed a better awareness of the necessity to embrace a more sustainable economy. In addition to radical changes in energy supply and distribution, there is a pressing need to develop technologies that can both extend the working lifetime of existing infrastructure and facilitate the development of new sustainable approaches to production and consumption. This has lead to the wide acknowledgment of the importance of controlling material surfaces and coatings \cite{1, 2}. Common phenomena, such as corrosion and friction, cause substantial economic losses every year and severely impact the environment. For example, in extending the lifetime of current infrastructure, the worldwide costs of prevention, detection and mitigation of metal corrosion alone are estimated to be 2.5 trillion US dollars per year \cite{3}. In addition, when considering the innovation of new devices, the development of micro- and nano-electromechanical systems requires new approaches for friction reduction in limited dimensions which leads to reduced efficiency and failure \cite{4}. The ability to deposit molecular and nanostructured coatings with advanced functional properties is primed to have a profound effect on such diverse technologies as wearable electronics, corrosion inhibitors and lubricant additives. One of the challenges in molecular science is therefore the need to find novel, earth-abundant, inexpensive and environmentally friendly materials that adsorb in a controlled manner to surfaces and interfaces. Historically, innovation of new materials has been a time-consuming and challenging task; it typically takes 20 to 70 years to progress from laboratory conception to widespread commercial use \cite{5}. Developments have also been mainly based on the incremental evolution of existing systems with the oft reported outcome that newly discovered solutions are based on exactly the same underlying mechanisms as their predecessors; to find something radical and innovative has usually been a matter of luck.

Extensive use is made of molecular additives for friction and corrosion reduction. A fundamental step in discovering new classes of these surfaces modifiers is a predictive understanding of the thermodynamics for both molecular and dissociative adsorption on different substrates \cite{6-11}. For this purpose, it is essential to be able to compute the binding energy (BE) of different adsorption modes with sufficient accuracy to be able to predict the molecular level adhesion of the self assembling coating. In principle this is achievable using modern atomistic simulations but in practice is problematic as the parameter space of factors that affect the BE is very large \cite{12}. There has therefore been a significant and sustained effort aimed at identifying a small number of easily computed descriptors that can accurately capture the nature of the molecule-surface interaction, and thus facilitating a simple and efficient predictive model of adsorption. In recent years the combination of high-throughput density functional theory (DFT) calculations and machine learning techniques has opened a new era of informatics-based approach to materials design, from which a number of simple models for predicting adsorption energies have emerged \cite{13-24}. These models are usually based on linear relationships using simple descriptors for both the substrate and the adsorbed molecule (e.g., the number of valence electrons, the electronegativity of the substrate \cite{14} and the ionization potential of the molecule \cite{15}). Despite their simplicity, these models have been demonstrated to be quite effective in predicting adsorption energies, especially when machine learning techniques are employed \cite{13, 15}. However, in the past

* p.restuccia@imperial.ac.uk
such models have been limited in their transferability. For instance, any given model may be limited to the ad-
sorption of molecules in one specific adsorption site (i.e., on-top or hollow). For a more extensive employment of
these predictive calculations, one would like to extend the possible range of adsorption sites to model a broader
array of realistic configurations, such as stepped edges or grain boundaries at the surface, and include a wide range
of molecular adsorbates.

In the current work we present a new predictive linear model that uses appropriate physical descriptors to pre-
dict the adsorption of a wide range of molecules to multiple substrates in a variety of surface adsorption sites.
The model is based on a combination of systematic DFT calculations and machine learning. The model reported
here accurately predicts the different dissociative adsorption energies of a range of probe molecules over simple
homogeneous metallic substrates. Despite its simplicity, the model can accurately predict the BE of molecules in
different configuration sites and it is devised in a form that facilitates its extension to more complicated struc-
tures (e.g., oxides, carbonates or defective surfaces). The model is sufficiently accurate to guide the discovery and
optimisation of molecular adsorbates in order to improve the functionality of corrosion inhibitors and lubricant ad-
ditives and is likely to find application in fields such as catalysis, molecular electronics and biomedicine [25–27],
where the adsorption of molecules and molecular films underpins many important processes.

RESULTS AND DISCUSSION

The general definition for the computed BE to a sur-
face may be written as:

\[
BE = E_{\text{tot}} - (E_{\text{sub}} + E_{\text{mol}}) \tag{1} 
\]

where \(E_{\text{tot}}\) is the computed total energy for a system
composed of a molecule adsorbed on a substrate and \(E_{\text{sub}}\)
\((E_{\text{mol}})\) is the energy for the isolated substrate (molecule).
With this definition, a negative (positive) BE indicates
that the dissociation process is favourable (unfavorable).

The total BE can be analysed in terms of many contribu-
tions that may be related to properties of the molecule and
the surface [28–30]. Defining a comprehensive model
for the BE is challenging. A recent approach proposed
by Dean et al. [15] succeeded in predicting the BE of
probe molecules to metal nano-particles. This model is
based on the idea that BE can be adequately represented
by stability descriptors for the adsorbate, the adsorption
site, the substrate and a simply computed estimate of the
interaction between the molecule and the surface. These
assumptions led to the following linear equation for the
BE:

\[
BE = a + b \times CE_{\text{local}} + c \times \text{IPEA} + d \times \text{MADs} \tag{2} 
\]

where \(CE_{\text{local}}\) is the term to describe the local cohesive
energy of the adsorption site, IPEA is the negative av-
erage between the ionization potential and the electronic
affinity of the molecule, and the MADs is the gas phase
BE between the adsorbate and one atom of the metal sub-
strate, which is obtained through \textit{ab initio} calculations,
and represents the descriptor for the adsorbate-metal in-
teraction. Although this model proved to be effective in
the prediction of BE, with correlation coefficient \(R^2\) of
around 0.94 and a mean absolute error (MAE) of around
0.1 eV, there are some limitations in the employed ap-
proach: i) the adsorbates were always in an on-top site
configuration, limiting the possibility to predict the BE
in other adsorption sites such as hollow or bridge, and ii)
the model has been trained only on noble metals nano-
particles and slab surfaces, such as Ag, Au and Cu, nar-
rowing the range of possible substrates over which the
prediction is effective.

In order to overcome these limitations, we present here
a model using suitable descriptors for the adsorption of
molecules over flat substrates. In particular, we propose
the following equation for the prediction of BE:

\[
BE = a + b \times CE_{\text{B}} + c \times \left( W_{\text{F}} - \frac{E_{\text{gap}}}{2} \right) + d \times \text{MBE} \tag{3} 
\]

where \(CE_{\text{B}}\) is the cohesive bulk energy for the substrate
atomic species, \(E_{\text{gap}}\) is the optical band gap of the ad-
sorbed molecule, \(W_{\text{F}}\) is the work function of the sub-
strate, \(MBE\) is the Molecule-Bulk Energy, which resembles
the MADs of Eq. 2 and it is computed using \textit{ab initio}
theory; \(a, b, c\) and \(d\) are the linear coefficients for
the regression. \(CE_{\text{B}}\) provides a general estimate of the
strength of the interaction between the substrate atoms
and the MBE provides a simply computed estimate of the
substrate-molecule interaction. The third term contains
the difference between the surface work function and the
middle of the optical gap of the adsorbed molecule which
in frontier molecular orbital theory controls the charge
transfer and hybridisation contributions to the surface
binding [31–33]. The MBE term is computed as:

\[
\text{MBE} = \sum_{i=1}^{n_{\text{frag}}} E_{\text{complex},i} - E_{\text{B,M},i} - \mu_{\text{G,mol},i} \tag{4} 
\]

where \(n_{\text{frag}}\) is the number of molecular fragments con-
sidered in the dissociative adsorption process, \(E_{\text{complex}}\)
is the total energy of a molecular functional group adsorbed
on a single atom of the metal substrate, \(E_{\text{B,M}}\) is the bulk
energy of a single atom of the substrate atomic species
and \(\mu_{\text{G,mol}}\) is the chemical potential of the molecular
fragment generalised from the fragment energy to allow
for the adsorption environment. This quantity provides
an easily computed and flexible estimate of the strength
of adhesion between the adsorbate and the substrate. In
contrast to the MADs term proposed by Dean et al., where all the functional groups are computed as isolated components, in the proposed MBE term we refer all energies to a consistent reference enabling the use of pre-computed data in a transferable predictive model. Another advantage of this approach is choosing the proper reference for the chemical potential in the calculation of MBE. In the current work, we chose to refer $\mu_{G,\text{mol}}$ to the isolated gas phase molecule for the sake of simplicity. However, it is possible to reference the chemical potential to different environments including solvated species, as shown in recent electrochemical studies [34–36].

![FIG. 1: Ball and stick representation of the models used](image)

In the current work, ordinary least squares (OLS) linear regressions were used to determine the coefficients in Eq. 3 from a training set of ab initio energies using the statsmodels library [37] provided in Python 3 [38]. For the OLS regression, we adopted a training set of statsmodels 10 regressions were used to determine the coefficients for the OLS regression, we adopted a training set of statsmodels the efficiency and accuracy of the proposed model. The OLS regression does not provide a good fit to the data, with a perfect set of predictions and the mean absolute error (MAE) is almost 2 eV. The parity plot in Figure 2 shows the correlation coefficient, MAE is the mean absolute error.

(a) First approach for MBE, as shown in Fig. 1a. $R^2 = 0.21$, MAE = 1.97 eV.

(b) Second approach for MBE, as shown in Fig. 1b. $R^2 = 0.83$, MAE = 0.89 eV.

(c) Third approach for MBE, as shown in Fig. 1c. $R^2 = 0.94$, MAE = 0.52 eV.

### Table I: Regression coefficients, i.e., Coefficient Estimate, Standard Error (SE) and P-value, for the different approaches employed for MBE calculation in the case of a) single metal atom, b) a small metal cluster and c) a large metal cluster. Cases are trained using the dataset provided in the Supplementary Information. $R^2$ is the correlation coefficient, MAE is the mean absolute error.

| Coefficient | Estimate | SE    | P-value |
|-------------|----------|-------|---------|
| a           | 2.2460   | 1.6048| 0.167   |
| b           | -0.7268  | 0.3114| 0.023   |
| c           | 0.8900   | 0.2721| 0.002   |
| d           | -0.0886  | 0.0970| 0.365   |

| Coefficient | Estimate | SE    | P-value |
|-------------|----------|-------|---------|
| a           | 1.5812   | 0.7064| 0.029   |
| b           | -0.2925  | 0.1461| 0.050   |
| c           | 0.1793   | 0.1122| 0.116   |
| d           | 1.0163   | 0.0691| 3 $\cdot 10^{-21}$ |

| Coefficient | Estimate | SE    | P-value |
|-------------|----------|-------|---------|
| a           | 0.7426   | 0.4208| 0.083   |
| b           | -0.1735  | 0.0874| 0.052   |
| c           | 0.8900   | 0.2721| 0.002   |
| d           | 0.9927   | 0.0370| 3 $\cdot 10^{-34}$ |

### Analysing Contributions to the MBE

An appropriate calculation of the MBE is essential for the efficiency and accuracy of the proposed model. The simplest level of approximation used here is that proposed by Dean et al. in which the MBE is computed as Eq. 4, i.e., the binding energy is the energy difference in the gas phase of a specific fragment obtained during the dissociative process and one metal atom of the substrate [15]. An example of this possible configuration to calculate MBE is shown in Fig. 1a for the case of Cl adsorbed to a Cu atom. The regression statistics are shown in Table Ia, while Figure 2 shows the parity plot of the model training against the DFT computed adsorption energies for the predicted BE.

This approximation provides a rather poor prediction of the BE: the correlation coefficient $R^2$ is around 0.21 (an $R^2$ of 0 corresponds to no correlation and of 1.0 to a perfect set of predictions) and the mean absolute error (MAE) is almost 2 eV. The parity plot in Figure 2 confirms that the linear regression does not provide a good description of the BE. Although Dean et al. have shown convincingly that this approach reproduces the energy of adsorption to metallic nanoparticles in an on-top configuration of several radical groups (namely, CH$_3$, CO and OH), it evidently fails to do so when the molecules are adsorbed on a wide range of substrates.

A possible explanation for this discrepancy is that the...
FIG. 2: Parity plot for the training of the model against the DFT BE calculations with the MBE approach proposed in Eq. 4 and the system shown in Fig. 1a. The black solid line represents the parity between the computed DFT BE and the predicted value.

variations of the interactions in the hollow and bridge adsorption sites considered here are not captured by binding to a single metal atom. This suggests that a somewhat larger cluster is required to take into account the different adsorption site configurations in the calculation of MBE such as that represented in Figure 1b. Here the Cl is adsorbed to a four atom cluster based on the hollow site presented by the Cu(111). This is the smallest cluster, for this specific substrate, which retains the symmetry of the surface adsorption site. We conveniently create these clusters that resemble the surface adsorption sites for all the considered substrates in our training set and the geometries employed for these calculations are provided as Supplementary Information. With the use of this cluster approach, we change the definition of MBE as follows:

$$\text{MBE} = \sum_{i=1}^{n_{frag}} E_{\text{complex},i} - E_{\text{cluster},i} - \mu_{G,\text{mol},i}$$ \hspace{1cm} (5)

where all the terms of Eq. 5 are the same as Eq. 4, apart from $E_{\text{cluster},i}$ which is the energy of the cluster modelling the substrate. This approach leads to a significant improvement in the BE prediction, as shown in both Table 1b and Figure 3. There is a significant improvement in both the correlation coefficient (around 0.83) and the MAE (around 0.9 eV).

Extending this approach, one can compute the MBE from adsorption to the 10 atom cluster displayed in Figure 1c for the case Cl adsorbed to a hollow site on Cu. This cluster also maintains the adsorption site symmetry. From Figure 4 it is evident that the model based on this MBE provides a satisfactory description of the adsorption energetics with a correlation coefficient of 0.94, and a more significant reduction of the MAE to 0.5 eV.

In addition, all of the fitted parameters have a P-value equal or smaller than 0.05, which is the threshold to obtain a confidence level of 95% in the predictions of the model. Even if this threshold should not be seen as a sharp edge for statistical significance [41], the obtained values for both the P-value and the standard errors provide a rigorous test for the effectiveness of our model.

The model proposed here is therefore able to predict BE with a fidelity comparable to the current state of the art but for a variety of adsorption geometries and adsorbates. The MAE for the training set is somewhat higher that of the model reported by Dean et al. of around 0.1 eV but it is computed for a training dataset with a much larger range of BE (from -10 to +3 eV), so the associated relative error is comparable.

|                  | Model MBE | MBE |
|------------------|-----------|-----|
| $R^2$            | 0.94      | 0.93|
| MAE (eV)         | 0.52      | 0.56|
| RMSE (eV)        | 0.69      | 0.79|

Before proceeding with the model validation analysis,
it is interesting to note the importance of MBE in calculating the BE since its OLS regression coefficient $d$ is the one with the smallest relative error and P-value. To understand how relevant this term is in calculating the predicted BE, we compare two different types of dataset training. The first is the one we discussed in the previous paragraph and is shown in Figure 4. The second is based on a simple OLS regression of the MBE values of the considered reaction paths against the computed DFT BE. The results are shown in Figure 5 and Table II. It is apparent that qualitatively the first training approach (blue dots) provides similar results to the one based solely on MBE (red squares), highlighting the greater importance of the MBE term in the definition of the model. A deeper analysis involving the regression coefficients, such as $R^2$, MAE and the root mean square error (RMSE), shows us a clearer picture. Although $R^2$ is similar in both scenarios (0.94 vs 0.93), we notice an increase in both MAE and RMSE when considering in training only MBE by 8% and 14%, respectively. Therefore, even if the MBE is an essential part of the definition of this new model, it is important to consider all the physical terms we have identified in the definition of Eq. 3, in order to minimize the average error in the BE.

After the training, the following step is to validate the model for use in predicting new dissociation paths for larger molecules. To do so, we compared its predictions to reaction energies computed and tabulated in previous work.
current model is less reliable in describing the dissociative adsorption in this weak bonding region. Another possible explanation for this behaviour can also be found in the different exchange and correlation functional employed in our study: as explained in the Method section, we used the generalized gradient approximation (GGA) for the MBE calculation, whereas the data retrieved from Catalysis-Hub.org were all computed within the BEEF-vdW approximation, which has specific corrections to take into account the dispersion interactions. The absence of the latter in our model can explain the differences arising from the weakly bonded systems.

Apart from these outliers, the prediction of tabulated values is remarkably accurate. As for the original fit to the training set, the intercept of the model has a significant associated error and P-value. It is therefore interesting to test the performance of the model when this parameter is neglected, this data is displayed in Figure 6b. It is notable that i) without \( a \) there is only a slight offset in the predicted BE which does not affect the general behaviour of the parity plot, with \( R^2 \), MAE and RMSE essentially unchanged, and ii) the estimated error bars for each energy are substantially reduced. This latter observation is explained by the fact that half of the error in the predicted BE is due to the uncertainty of \( a \), which is the coefficient with the highest relative error and P-value.

The discussion above demonstrates that the current model provides a low cost prediction of the BE to homogeneous metal substrates. It is interesting to speculate on the extension of the model to a more general framework for predicting adsorption to a wider range of substrates. A natural extension would be to design a simple MBE cluster calculation for the oxide and carbonate substrates, which are essential in many technological applications and for which there is currently a lack of predictive models regarding molecular adsorption.

CONCLUSION

In summary, we report a new model of molecule-surface binding based on the combination of \textit{ab initio} calculations with machine learning algorithms, such as ordinary least squares regression. This model provides an estimate of the adsorption of small molecules to metal substrates given a set of easily computed descriptors. The model distinguishes different reaction sites and between molecular and dissociative adsorption accurately, especially for larger adsorption energies (values greater than \( \pm 1 \) eV). Compared with an independent and well established database of computed adsorption energies, the predicted values suggest that the model is transferable in that it can provide equally accurate BE predictions for a variety of functional groups and surfaces from outside the training set. The model is constructed so that its extension to different substrates (e.g., oxides and carbonates) and technically relevant functional groups is straightforward. We expect the model to find widespread use in a variety of applications. For example, the innovation of new coatings for friction and corrosion reduction and the development of novel anti-pathogen coatings to reduce disease transmission via surfaces.
METHOD

BE calculation in slab configuration

For the adsorption energies of the training set (i.e., the slab systems) and the calculation of the MBE terms, Spin-polarized DFT calculations were performed using the projector-augmented wave method (PAW) as implemented in the plane-wave code QUANTUM ESPRESSO (QE) [43]. We used the PAW pseudopotentials [44] from the PSLibrary 1.0.0 [45] within the generalised gradient approximation (GGA) of Perdew, Burke and Enzerhoff (PBE) [46] for the exchange-correlation energy. The electronic wave functions are expanded as a linear combination of plane waves up to a kinetic energy of 95 Ry, which we find is sufficient to converge the total energies to 0.003 eV Å⁻¹ and 10⁻² eV. The Monkhorst-Pack grid [47] is used for sampling the Brillouin Zone, but different k-mesh for each structure under study were considered. In particular, we selected the optimal k-point grid for each slab geometry, whereas all the calculations involving clusters had a sampling at Gamma point due to the large cell dimensions. To improve the convergence, the Marzari-Vanderbilt cold smearing [48] method is used for the sampling of the Fermi surface, with a width of 0.27 eV in order to obtain accurate forces. The convergence criteria of forces and energy are 0.003 eV Å⁻¹ and 10⁻² eV.

Band gap calculation for molecule in gas phase

For the calculation of the molecular band gap (i.e., the energy difference between the HOMO and LUMO), we performed DFT calculations using the CRYSTAL17 computational suite [49, 50], in which the crystalline orbitals are expanded as a linear combination of a local basis set composed by atom-centered Gaussian orbitals with s, p, or d symmetry. For all the elements employed in the molecular calculations (namely, H, C, N, O, F, S, Cl, we used the 6-31G** basis sets [51–57]. The approximation of the exchange and correlation functional is based on the Becke, 3-parameter, Lee-Yang-Parr (B3LYP) hybrid functional incorporating 20% Hartree-Fock exchange [58–60]. The Coulomb and exchange terms are summed directly and truncated using overlap criteria with thresholds of 10⁻¹⁰, 10⁻¹⁰, 10⁻¹⁶, 10⁻²⁰, 10⁻³⁰ as described elsewhere [50, 61].

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