Density functional theory for modelling large molecular adsorbate-surface interactions: a mini-review and worked example

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First-principles simulation has played an ever-increasing role in the discovery and interpretation of the chemical properties of surface-adsorbate interactions. Nevertheless, key challenges remain for the computational chemist wishing to study surface chemistry: modelling the full extent of experimental conditions, managing computational cost, minimizing human effort in simulation setup, and maximizing accuracy. This article introduces new tools for streamlining surface chemistry simulation setup and reviews some of the challenges in first-principles, density functional theory (DFT) simulation of surface phenomena. Furthermore, we provide a worked example of Co tetraphenylporphyrin (CoTPP) on Au(111) in which we both analyze electronic and energetic properties with both semi-local DFT and compare to predictions made from hybrid functional and the so-called DFT+U correction. Through both review and the worked example, we aim to provide a pedagogical introduction to both the challenges and the insight that first-principles simulation can provide in surface chemistry.

Keywords: density functional theory, Hubbard U, surface science, super cell generation, transition metals, porphyrins

1. Introduction

Simulation has become increasingly central in studies ranging from catalysis[1] to materials science.[2] In surface science in particular, such work can provide critical insight into short-lived intermediates and reactive species as well as the relationship between electronic and energetic properties. Nevertheless, numerous challenges remain for computational chemists studying surface chemistry, including but not limited to:

1. **Knowing and taking into account full experimental conditions**. Although useful experiments are carried out under ultra-high vacuum on pristine surfaces to obtain precise measurements of surface-adsorbate interactions[3], most practical systems relevant to surface chemistry are much more complex. Under reaction conditions, transient disorder and dynamics likely predominates at a solid-liquid interface, and defects and reconstructions may form[4] at the surface even under gas-phase conditions. Without knowing the precise species present in an experiment, the

computational chemist must guess at which reactive species to model.

2.   Managing computational cost. Even when all species are known from experiment, higher levels of disorder mandate larger unit cells that may be outside of the scope of accessible simulations, which is currently a few hundred atoms or thousands of valence electrons for traditional codes. Furthermore, dynamic sampling by first-principles simulation is limited to a few ps for large systems, meaning that most modern calculations must still focus on inferring properties from static slab calculations in vacuum.   Recent advances that help to enlarge the scope of systems that can be studied with first-principles include density-oriented methods[5], reduced, linear-scaling methods[6, 7, 8, 9, 10, 11, 12, 13], advances in stream-processing hardware coupled to algorithmic developments[14, 15, 16], and multi-level approaches.[17, 18, 19, 20] Nevertheless, the computational chemist must evaluate some trade-offs to balance computational accuracy and efficiency.

3.   Streamlining simulation efforts. In order to study surface chemistry phenomena, the computational chemist must be able to straightforwardly generate complex unit cells and coordinates for the systems of interest. Although often these procedures are carried out by hand using tools such as Vesta[21], the supercell builder function in the Avogadro[22] molecular visualizer, or providing information about crystal symmetry within a simulation code such as CRYSTAL[23], high-throughput screening has motivated the development of streamlined repositories, especially for bulk materials.[24, 25, 26] Commandline slab generation may be carried out within the atomic simulation environment (ASE) python code[27], but complex and precise adsorbate alignment on surfaces has still typically required hand building or custom single-use scripts. In Sec. 3, we will discuss a recent extension of the molSimplify code[28] intended to streamline this process further.

4.   Maximizing and evaluating model accuracy. Simulation of any system beyond a handful of atoms requires some approximation to the full quantum-mechanical problem. The large, extended systems relevant to surface chemistry further limit the scope of accessible methods and corresponding approximations. At the same time, the desire to model precise bond rearrangement events and electronic properties mandates that we maximize accuracy wherever possible. Despite well-known shortcomings[29, 30], semi-local Kohn-Sham density functional theory (DFT) [31, 32, 33, 34] has remained the method of choice for studying the large systems relevant to surface chemistry. A growing area of interest is to apply statistical efforts that enable quantification of prediction uncertainty to energetic predictions in catalytic cycles through analysis of functional sensitivity[35, 36, 37, 38, 39, 40] or intrinsic Bayesian statistics in new semi-local functional development.[41] We will now consider in detail both the limitations of practical DFT for surface chemistry as well as some remedies.

1.1. Errors in Practical DFT

Although DFT is in principle exact, several key approximations made in practical DFT are known to limit accuracy (the reader is encouraged to review the details of DFT theory and practice outlined in Refs. [34] and [42]). Namely, in Kohn-Sham DFT, Coulomb repulsion of each electron is computed with the total density, giving rise to self-interaction error (SIE). The exchange-correlation (xc) functional in DFT must then correct SIE, take into account quantum-mechanical exchange, and model correlation, i.e., that the probability distribution of one electron is affected by the probability distribution of another electron. In practice, well-known xc approximations such as the local density approximation (LDA) and the generalized-gradient approximation (GGA) contain terms that depend locally on the density and its gradient, only reproducing short-range exchange and correlation. Furthermore, these xc approximations do not reproduce exact exchange or eliminate SIE.

Unlike DFT, the Hartree-Fock (HF) theory explicitly accounts for exact quantum-mechanical exchange and Coulomb repulsion but in the context of a single Slater determinant wavefunction that excludes any treatment of correlation. This behavior of HF theory has motivated the development and application of both global and range-separated hybrid functionals that incorporate an admixture of HF exchange with improved accuracy over pure LDAs or GGAs (for a thorough review of hybrid functionals, see Ref. [43]). However, application of hybrid functionals to periodic systems in surface chemistry applications is computationally costly due to the high expense of computing non-local exchange. Furthermore, metallic behavior cannot be preserved with HF theory, and therefore some properties of metallic solids are better described by the simplest LDA approximation.

Despite their ability to describe metallic behavior, the LDA and GGA xc approximations are plagued by both one- and many-electron SIE[29, 30, 44, 45, 46], where the latter corresponds to SIE still present in many one-electron SIE-free functionals.[29] These self-interaction errors give rise to well-known problems in dissociation energies[44, 47, 48, 49, 50], barrier heights[51], band gaps[52, 53], electron affinities[54, 55, 56], and other manifestations of delocalization error.[57, 58, 59] Many-electron SIE and delocalization error are typically illustrated by relating approximate xc behavior to the exact energy functional, which should be piecewise linear[60, 61] with respect to fractional addition or removal of charge (q):

$$E(q) = (1-q)E(N) + qE(N+1) \qquad (1)$$

as evaluated between the N- and $N+1$-electron systems. This behavior can only be reproduced by a derivative discontinuity[62, 63, 64, 65] in the xc functional, but the forms of common (e.g., LDA or GGA) xc approximations lack this discontinuity.

Instead, semi-local DFT functionals produce a deviation from linearity in E(q)

with convex behavior[29, 66] (Figure 1) [Figure 1 near here]. For molecular systems, tuning strategies[67, 68, 69, 70, 71, 72, 73, 74, 75, 76] have been developed within range-separated hybrid functionals to reproduce piecewise linearity and improve predictions.[71, 77] However, the observed curvature shows marked size-dependence[78, 79, 80, 81], apparently vanishing for large systems. The reason absolute curvatures diminish may be interpreted as follows: the error in each integer endpoint is already substantial for a large system, with the N or $N+1$ electrons in the system heavily delocalized, and addition of a fractional electron does not alter this behavior substantially. Thus, while curvature corrections work well for molecules, they are less widely applied for solids, where the computational cost of HF exchange also makes this approach challenging. Alternatively, orbital-dependent self-interaction corrections have also been pursued for some time[82, 83, 84, 85, 86, 87], but they often lack rotational invariance, introduce other complications that prevent easy application to either molecules or solids such as complex wavefunctions, and are generally designed to eliminate one-electron SIE but may not suitably address many-electron SIE.[88]

Within surface chemistry, delocalization error and SIE may be interpreted as follows: energetics of adsorbates and surfaces will be sensitive to the relative degree of delocalization permitted in a coordination geometry. For instance, the electrons of an isolated atom or molecule brought into contact with a surface will have increased opportunity for delocalization, whereas the large N-electron surface will be relatively unchanged (Figure 2) [Figure 2 near here]. Thus, more strongly coordinating geometries will be stabilized over weakly interacting ones, and binding energies will be overestimated. Only in the unlikely case that coordination and delocalization are roughly equivalent across an entire reaction coordinate will SIE not impact relative energetics. This delocalization error has also masked the absence of treatment of non-

local correlation in semi-local DFT by causing binding in cases where only van der Waals' interactions are present (e.g., the LDA binds the dispersion-bound Ar_2 dimer[89]). Instead, it is now recommended that non-local correlation functionals[90, 91], semi-empirical van der Waals' treatments[92], or perturbation theory approaches[93] be employed to account for this other shortcoming of semi-local DFT. Although van der Waals' interactions are critical in describing surface phenomena, particularly for physisorbed adsorbates, we focus here on the typically larger SIE and delocalization errors and refer readers to the detailed reviews of dispersion interactions in Refs. [94] and [95].

Exemplary of the challenges associated with applying practical DFT to surface chemistry is the so-called "CO on Pt(111) puzzle" first identified over 15 years ago.[96] Researchers noted that although at low coverage of CO on the Pt(111) surface, the experimental site preference was clearly one in which CO was bound to a single Pt atom (i.e., the atop position), well-converged DFT calculations instead preferred a site involving three-fold coordination with Pt (i.e., the hollow position)[96] (Figure 3) [Figure 3 near here]. This problem may be cast in terms of a SIE-driven phenomenon where higher-coordination sites are preferred to lower-coordination sites through enhanced delocalization afforded by the former (see Figure 3). Although indirect SIE-correction through hybrid functionals improves but does not completely correct site preference[97, 98, 99, 100], successful SIE-correction schemes have included applying a DFT+U-like correction directly onto the LUMO of CO to correct its placement[101] or, alternatively, applying a correction based on the singlet-triplet gap (a proxy for molecular orbital energies in isolated CO) or bond-order of the CO molecule on the two surface sites (i.e., increased delocalization in the hollow site is associated with bond order reduction).[102, 103] It was also noted[104] that surface energies and adsorption

energies in the semi-local functionals are correlated in a manner that prevents simultaneously correcting both errors needed for accurate prediction of surface phenomena. This observation has motivated the successful application of more advanced perturbation theory to reproduce site preference.[105] Alternatively, some carefully parameterized meta-GGA functionals[106], which incorporate the laplacian of the density, are able to produce correct site-ordering, although less empirical meta-GGAs are not.[107]

Although this incorrect qualitative assignment represented a disappointing failure for semi-local DFT in qualitative predictions of surface chemistry, it likely corresponds to a relatively small quantitative error ca. 0.2 eV[96] for relative energetics that is typical of errors for common exchange-correlation approximations. Nevertheless, this puzzle reflects well some of the challenges that face computational chemists who wish to study surface chemistry. Small imbalances in the opportunity for delocalization in different binding sites can give qualitatively different results, and although many-body perturbation theory may provide a viable improvement, computational cost prevents application of such methods routinely, especially for large adsorbate molecules.

1.2. The Hubbard U correction

Within extended systems for surface chemistry, one of the most widely employed methods to correct for SIE in approximate xc functionals is the so-called DFT+U approach.[108, 109, 110] Here, a Hubbard model[111] functional is added to the functional to assist in correcting electron overdelocalization for an nl subshell (e.g., $3d$ electrons) on atom I:

$$E^{\text{DFT+U}} = E^{\text{DFT}} + \frac{1}{2}\sum_{I,\sigma}\sum_{nl} U_{nl}^{I}[\text{Tr}[\mathbf{n}_{nl}^{I\sigma}(\mathbf{1}-\mathbf{n}_{nl}^{I\sigma})]] \tag{2}$$

where $\mathbf{n}_{nl}^{I\sigma}$ is an occupation matrix and σ is a spin index. The expression in eq. 2 results after making the simplifying assumption[112] that $U_{\text{eff}}=U\text{-}J$, i.e. differences in same spin and opposite spin electrons are neglected. Recent work[113] has identified that this approximation is quite suitable, especially when applying DFT+U on top of spin-polarized calculations. The occupations are calculated by projecting the molecular states, $|\psi_{k,v}\rangle$, onto a localized set of atomic states, $|\phi_m^I\rangle$, obtained during generation of the atom's pseudopotential:

$$n_{mm'}^{I\sigma} = \sum_{k,v} \langle \psi_{k,v} | \phi_{m'}^I \rangle \langle \phi_m^I | \psi_{k,v} \rangle \qquad (3)$$

where m is the m_l quantum number of each orbital in the nl subshell and k,v represent the k-point and band or orbital index of each molecular orbital.

The potential associated with this energy correction may be expressed simply in the case of a diagonal occupation matrix as:

$$V^U = \frac{U_{nl}^I}{2} \sum_{I,m} (1 - 2n_m^{I\sigma}) | \phi_m^I \rangle \langle \phi_m^I | \quad . \qquad (4)$$

Two factors thus come into play in how this potential alters the electron density of the molecule from the description obtained with the standard semi-local functional: i) if the molecular orbital does not project onto a Hubbard atom atomic orbital, then the potential will be zero and ii) the atomic component of the potential is a maximally positive ½ eV / eV of U for an empty orbital with strong atomic orbital character or -1/2 eV/eV of U for a totally filled orbital.

This effect thus both changes the hybridization of Hubbard atom levels with surrounding molecular states and creates or enlarges band gaps in cases where the highest-occupied and lowest-unoccupied molecular orbitals (HOMO and LUMO) have strong atomic character of the Hubbard atom. In the context of chemistry, bonding

molecular orbitals will generally have ½ or less pure atomic character as electrons are delocalized through hybridization to neighboring atoms. Relatively speaking, the pure DFT functional will overstabilize these orbitals, where a DFT+U correction will shift such orbitals up higher in energy (Figure 4) [Figure 4 near here]. Conversely, antibonding or nonbonding states will have stronger atomic character corresponding to nearly full atomic orbitals. The result is that occupied antibonding orbitals get stabilized, whereas unoccupied nonbonding or antibonding states will still have an $n_m^{I\sigma}$ close to zero and will thus be shifted up higher in energy (Figure 4).

In terms of the total energy shift of the DFT+U correction, low-spin, mid-row transition metal complexes generally have partially-occupied bonding states for both spin up and spin down electrons, where a high-spin configuration will have a filled spin up electron configuration that fills both bonding and antibonding states and only partially occupied spin down orbitals (Figure 5) [Figure 5 near here]. Analysis of occupation matrices for low- and high-spin cases does in fact reveal that more partially occupied atomic orbitals will cause a low-spin state to be shifted higher in energy (see eq. 2) with respect to a high-spin state (see color gradient in Figure 5), and thus DFT+U is useful for combatting well-known biases[114, 115, 116, 117] of semi-local functionals for low-spin electron configurations.

The extent of the DFT+U correction is modulated by the Hubbard U parameter, which may be calculated[118, 119] self-consistently[120] directly on the system of interest, although it is frequently used as a fitting parameter to reproduce desired chemical or physical properties. Physically, U represents the curvature of the energy or equivalently the first derivative of the eigenvalues with respect to variation in occupations of the subshell of interest at constant charge:

$$U \equiv \frac{\partial^2 E}{\partial (n_{nl}^I)^2} = \frac{\partial \varepsilon_{nl,m_l}^I}{\partial n_{nl}^I} \tag{5}$$

It has recently been emphasized[121] that this U curvature at constant electron count should not be confused with the convex curvature of the energy in semi-local functionals[29, 66] with electron removal or addition. DFT+U can in practice approximately recover correct piecewise linearity with electron removal or addition by correcting HOMO and LUMO energetics, though not necessarily at the U value represented by eq. 5. Instead, U should be adjusted until the average global curvature expression introduced by Kronik and coworkers[122] is zero:

$$\left\langle \frac{\partial^2 E}{\partial q^2} \right\rangle = \varepsilon_{N+1}^{\text{HOMO}} - \varepsilon_N^{\text{LUMO}} , \tag{6}$$

where $\varepsilon_{N+1}^{\text{HOMO}}$ is the N+1-electron HOMO eigenvalue and $\varepsilon_N^{\text{LUMO}}$ is the N-electron LUMO eigenvalue.

There are several approaches to computing U, including a linear response approach[118, 119], direct extraction of the second derivative of the energy with respect to varied occupations, or through cluster Hartree-Fock calculations.[123, 124] Here, we review how to carry out linear-response calculations[118, 119] of U where a potential shift, α_{nl}^I, is applied to the subshell of interest:

$$V^{\text{lin}} = \sum_{I,nl} \sum_{m} \alpha_{nl}^I \left| \phi_{nl,m}^I \right\rangle \left\langle \phi_{nl,m}^I \right| , \tag{7}$$

which corresponds to a simple additional energy functional:

$$E^{\text{lin}} = \sum_{I,\sigma} \sum_{nl} \alpha_{nl}^I \text{Tr}(\mathbf{n}_{nl}^{I,\sigma}) . \tag{8}$$

The resulting reorganization in occupations is measured at different values of α, fit to a

straight line, and the slope is inverted to obtain U:

$$U_{nl}^I = \frac{d\alpha_{nl}^I}{d(n_{nl}^I)_0} - \frac{d\alpha_{nl}^I}{dn_{nl}^I} \tag{9}$$

where the 0 subscript indicates we remove any bare reorganization in the calculation that occurs due to shifted levels from the self-consistent reorganization. An example of this calculation carried out on Pt(111) surface reveals the sensitivity of computed U values to the surrounding chemistry (Figure 6) [Figure 6 near here]. Values of U are enhanced for the Pt atoms directly coordinating a bound CO, but the electronic structure is affected through alternately lower or higher values of U in surrounding atoms as well. The coordination effect on U is very short-range, however, as subsurface Pt atoms have the same value of U as is calculated on bulk Pt. A variable surface-site-specific U is likely useful[125] for careful balance of different types of surface interactions and may be best incorporated with interpolation methods that permit U to vary across a reaction coordinate.[126]

1.3. Background on Worked Example

Compared to their behavior in isolation, metalloporphyrins (MPps)[127, 128] and other macrocycles (e.g., metallophthalocyanines, MPcs)[129, 130, 131] exhibit unusual electronic and magnetic properties on heterogeneous support. These hybrid molecule-solid materials provide promise for their chemical and catalytic tunability via altering the reactive metal center, bonding environment, and metal support. Due to their biological relevance and potential for broad technological applications, surface-bound MPps have been extensively studied for applications in artificial photosynthesis, information storage, sensing, molecular electronics, and catalysis.[132, 133] Oxidation and spin states of individual tetraphenylporphyrin macrocycles (TPPs) are highly-dependent on environmental conditions[134], including small molecule adsorbates, and

the nature of the metal center.[135] Theory provides valuable insight into these interactions both through simulated STM images and through a detailed profile of the density of states around the Fermi level of macrocycles both in the gas phase and upon adsorption (see for example, Refs. [135, 136, 137, 138]). DFT simulations can provide a map of the degree of charge transfer between an adsorbed macrocycle and the surface and be used to identify the degree to which small molecule adsorbates alter the strength of charge transfer between molecules and the surface[139] (Figure 7) [Figure 7 near here]. Predictions from semi-local DFT should be interpreted with caution, however, for instance as it has been pointed out that the poor placement of occupied and virtual orbitals directly impacts its ability to simulate STM images for adsorbed CoTPP molecules on Cu and Ag.[140]

The interaction of small molecules in the gas phase, such as nitrogen monoxide (NO), carbon monoxide (CO), and molecular oxygen (O_2), with MPps and MPcs has been studied experimentally[141, 142] in an effort to control the spin states and properties of magnetic molecules by chemical switching using small reactant species.[143, 144] Scanning tunnelling microscopy (STM) had been used to identify distinct binding processes and adsorption characteristics of small molecules with MPps (M = Co, Fe) on Ag(111) and Cu(111) surfaces.[141, 145] For instance, CO binds weakly to surface-anchored Co/Fe tetraphenylporphyrin (CoTPP; FeTPP) molecules, but NO adsorption on the metal center reduces or eliminates the saddle distortion of TPPs, indicating decreased bonding between TPPs and the surface.[146] Adsorbed Mn TPPs on Au(111) have also been demonstrated to be able to carry out homolytic cleavage of O_2 both in solution[147] and vacuum[148] followed by oxygen atom adsorption onto the MnTPPs.

Here, we present a worked example of CoTPP adsorbed on Au(111), which has

been the focus of some previous study[140, 149, 150, 151, 152, 153, 154], interacting with molecular and atomic oxygen adsorbates. This system helps illustrate some of the outstanding challenges and possible solutions for the computational chemist wishing to study surface chemistry. First, in Sec. 2, we review the methods employed in this work. In Sec. 3, we introduce a simplified supercell building approach to address one of the outstanding challenges for the computational chemist in surface chemistry. In Sec. 4, we present the interplay of electronic and energetic properties obtained with van-der-Waals'-augmented, semi-local DFT on the CoTPP/Au(111) worked example, examine how predictions change with more advanced electronic structure treatment through DFT+U, and identify the extent to which DFT+U and hybrid treatments coincide. Finally, we provide our conclusions in Sec. 5.

2. Methods

Plane-wave, density-functional theory (DFT) calculations were carried out using the open source Quantum-ESPRESSO package.[155] The orthorhombic simulation cell consisted of one Co-TPP molecule and three layers of Au(111) surface for a total of 167 atoms and 1223 valence electrons. This slab of Au(111) was selected both due to computational cost considerations and previous observations of expedient convergence of molecular properties with slab representations[135], although for smaller adsorbates five or more layers would be preferred to reproduce bulk properties in the center of the slab. For the electronic structure calculations, the Perdew-Burke-Ernzerhof[156] (PBE) generalized gradient approximation (GGA) was augmented with a semi-empirical van der Waals correction (DFT-D2)[92] that recovers correct treatment of dispersion interactions not directly included in semi-local DFT functionals. A wavefunction cutoff of 25 Ry and charge density cutoff of 250 Ry was previously validated[135] in conjunction with ultrasoft pseudopotentials. We note that Au was described with semi-core $3d$ states in the valence. In order to aid convergence and description of the metallic

states of Au, an electronic temperature (smearing) of 0.01 Ry was applied, and all atoms were given an initial guess of 0.05 starting magnetization in these spin-polarized calculations.

Structural minimizations of Co-TPP were carried out in which the Au slab was constrained to its bulk, experimental lattice parameter of 4.08 Å. Although in surface catalysis, it is common practice to optimize the lattice parameter in order to avoid stabilizing species due to strain, that procedure is avoided in this work for a number of reasons. First, our interest in Co-TPPs is derived from unpublished experimental observations of self-assembled monolayers of Co-TPPs on a surface, necessitating use of an experimental lattice parameter in order to match the experimental Co-TPP ordering. Second, because the focus of this work is primarily O adsorption onto the Co-TPP itself, it is far less sensitive to lattice parameter derived strain effects on binding energy than if we were investigating the direct adsorption of O onto Cu(111).

The Co-TPP molecule was oriented at a 39.5° angle with respect to the [$1\bar{1}0$] direction on the fcc (111) plane in order to approximate the 14.0 ± 0.5 Å separation between metal centers observed for self-assembled TPP layers without metal centers in experiments.[157] The final unit cell upon rotation was slightly orthorhombic at 15.0 Å x 14.4 Å in the Co-TPP plane (Figure 8) [Figure 8 near here]. The saddle shape of CoTPP (16° angle of the pyrrole hydrogen atoms off the Co-porphine base plane, Figure 9) and partial rotation of the phenyl rings (e.g. 40° C-C-C-C dihedral between the phenyl ring and porphine base, Figure 9) were obtained by geometry optimizing an initially flat structure [Figure 9 near here]. This saddling in the optimized structure is consistent with previous observations[158] on metal surfaces. Additional vacuum between slabs was provided for a total 22.5-Å cell length in the z-direction. The minimum energy structure for Co-TPP on Au(111) was then used as a starting point for

minimizations with adsorbed molecular oxygen or atomic oxygen present. Initial minimizations with oxygen species consisted of 12 single O atom and 12 molecular O_2 binding configurations (see Figure 10) [Figure 10 near here]. Eight additional double O atom configurations were also considered, corresponding to different adsorption sites on opposite sides of the Co center. All optimized geometries are provided in the Supplementary Material.

Select DFT+U calculations[108] were carried out with U (= 2, 4, or 6 eV) applied to the $3d$ states of Co in spin-restricted doublet or quartet calculations on the full system (CoTPP/Au) as well as the isolated molecule (CoTPP) frozen to its surface optimized geometry. A linear response U[108] was calculated on each of these structures as well in both spin states. Löwdin populations were used for charge transfer analysis through comparing charges of isolated and combined molecule-slab geometries as well as for quantifying spin and partial charge on select atoms.

Single point energies were also obtained with the graphical-processing-unit accelerated code TeraChem[16, 159] using the B3LYP[160, 161, 162] hybrid exchange-correlation functional. These energies were computed for isolated doublet and quartet CoTPPs both bare and with oxygen adsorbed and held frozen in the GGA-optimized CoTPP/Au geometry. For efficiency, these hybrid calculations were carried out with the composite LACVP* basis set, which is a combination of the Los Alamos double-zeta effective core potential on Co and the 6-31G* basis set on all other atoms.

3. Slab Generation Approach

One key challenge associated with studying surface science phenomena from first principles is simply in the generation of the initial coordinates. Part of this challenge may be in whether there is available experimental data to guide orientations of self-assembled monolayers on the surface or to inform coverages and preferred

surface sites. The remaining challenge is in user-friendly generation of adsorbate geometries on slab surfaces, which may be presently carried out with VESTA[21], ASE[27], or a combination of imported crystal coordinates from a source such as the Crystallography Open Database[163] with the supercell builder feature in Avogadro.[22] Nevertheless, orientation of complex adsorbates onto slab models often requires user-built scripts or hands-on manipulation.

For this purpose, we now introduce a supercell builder extension to the recently developed[28] molSimplify python toolkit that automates the generation of transition metal-containing and supramolecular complexes. The supercell builder extension automates generation of coordinates for periodic systems such as the CoTPP with and without oxygen adsorbates on Au(111) studied in this work (see Figs. 1-3) through i) slab generation and ii) surface placement tools. For slab generation, the code flexibly repeats unit cells, which are specified by the user as 3D coordinates in .xyz, .mol, or .cif[164] file formats along with the necessary set of cell axis lengths (A, B, C) and angles between the cell axes (α, β, γ) or, alternatively, cell vectors (**a**, **b** and **c**). We leverage OpenBabel conversion tools[165] to support the .cif format due to its wide availability in open source and commercial databases such as Crystallography Open Database[163] and Cambridge Structural Database[166], respectively. Similar to other software packages that contain slab-generation tools[21, 22, 27], our slab builder tool duplicates the atoms in the input unit cell to reach a target number of units or closest integer repeats to produce the volume specified by the user (example shown in Figure 11) [Figure 11 near here]. For instance, the target size of our Au(111) surface is x=15 Å, y=15 Å, z=5 Å. In order to study adsorption on a specific crystal face, the user should specify a set of Miller indices, (*h, j, k*), which define a family of planes parallel to the plane intersecting the lattice axes, (***a,b,c***) at $\frac{\|\mathbf{a}\|}{h}$, $\frac{\|\mathbf{b}\|}{j}$, and, $\frac{\|\mathbf{c}\|}{k}$, respectively.

The code then calculates a new set of basis vectors for the unit cell, performs the duplication, and rotates the coordinates to align the Miller index normal vector along the z-direction before constructing a repeating supercell. The procedures for obtaining the final crystal facet, which follow closely to the implementation in the ASE code[27, 167], are provided in more detail in the Supplementary Material Text S1 and Figures S1-S2.

In addition to the features present in other slab generation tools[21, 22, 27], molSimplify incorporates a suite of geometry functions for aligning ligands, which may be leveraged and extended for the generation of precise surface-adsorbate configurations. Once inorganic or organic complexes are generated with the standard molSimplify code[28] using internal or external ligand libraries, users can place both these generated structures on slabs (e.g., CoTPP placed on Au(111) in this work) along with additional molecules at surface sites on the adsorbed molecule (e.g., O placed on CoTPP in this work). This easily scripted interface enables automated computational studies of surface chemistry and catalysis, e.g., by varying surface coverage and adsorbate spacing for adsorbate interaction studies or for comparing the energetics of adsorbate binding modes on differing surface sites.

Using the surface placement tool, any object (e.g., molecule or cluster) that the original molSimplify generates can be placed on a periodic slab. For instance, the CoTPP molecule may be generated in molSimplify by specifying a Co center and a tpp ligand. For the placement procedure, the user must specify distance of the object to the surface in one of three ways: i) physisorption: the sum of van der Waals radii between aligning species is used, ii) chemisorption: the sum of covalent radii between aligning species is used, or iii) a user-specified custom distance. The placement tool supports several alignment modes: i) centered: adsorbed object center of mass (COM) is placed

above the surface center; ii) staggered: adsorbed object COM is placed above midpoint between surface sites closest to the center of symmetry of the surface; and iii) align-by-atom: user specifies type and number of surface atoms (e.g., O in TiO_2), and a list of atom types or indices for the adsorbed object. Here, the align-by-atom procedure with chemisorption distance (2.7 Å) was used to align the Co atom to an Au(111) surface site, which only requires specifying the Co, Au atom types. Atom indices may be obtained from the graphical visualization tool in molSimplify[28] or directly from the xyz coordinate file. The code places the object at target sites by iteratively minimizing the sum-of-squared error (SSE) between the target aligning atom distance, dt_i, and actual distance, d_i, over all i object atoms being aligned:

$$\varepsilon = \sum_i (d_i - dt_i)^2 \ . \tag{10}$$

For single-atom alignments, the object atom is placed directly above the target surface site, and the object is rotated 360° around the alignment axis to maximize slab-object distances and inter-object distances if an object was previously placed. This approach is also designed to minimize periodic-image effects and help the user identify the most computationally-efficient supercell.

For two or more aligning object atoms, the object is rotated around the axis between the aligning object COM and target surface atoms COM to minimize the SSE in target distances while incrementally lowering the object from 15% above final target height. Each step is only accepted if the SSE decreases, otherwise the incremental approach to the surface is halved, and the process terminates after three sequential step failures. The code also supports force field optimization (e.g., with MMFF94[168] by default) to relax the geometry of the non-aligning atoms as the object is lowered towards the surface. Additional special cases for rotation and alignment are outlined in the Supplementary Material Text S2. Following this initial placement, the code will

optionally align an axis in the molecule at a user-specified angle to a line on the surface (e.g., 40° for N-Co-N off the $\begin{bmatrix} 1\,\overline{1}0 \end{bmatrix}$ surface in Au(111) here, which is achieved by providing the indices of the TPP N atoms, target angle, and surface vector).

The code supports multiple adsorbate placement as indicated by the user specifying a number of objects or a desired coverage fraction. Once a single adsorbate is placed on a surface site, that site is removed from the free site list, and the process is repeated (see flowchart in Figure 12) [Figure 12 near here]. Each subsequent attachment site is chosen as the one that maximizes the minimum inter-adsorbate spacing, taking unit cell periodicity into account. Additional molecules (e.g., O on CoTPP here as in Fig. 3) can be added by repeated use of the placement tool in a 'layer-by-layer' approach where the first attached molecule (e.g., CoTPP on Au(111)) becomes part of the new cell surface. This sequential strategy maximizes placement flexibility while allowing for easy syntax and scripting (see flowchart in Figure 12). In this work, single or multiple O atoms or O_2 molecules are adsorbed by specifying the target indices in the now-adsorbed CoTPP on Au(111) in a second run of the placement tool. Thus, supercell generation tools are making it increasingly straightforward to investigate surface-adsorbate and multi-layer adsorbate interactions critical to understanding surface science phenomena.

4. Results and Discussion

4.1. Binding Energetics

Although we have highlighted some potential challenges for semi-local DFT in predicting relative energetics of adsorbates, it remains the method of choice for its combination of efficiency and reasonable accuracy. Additionally, although semi-local DFT energetics may be erroneous, geometric properties are often still quite good. Thus, we first evaluate DFT energetic and structural properties and then later (4.4) evaluate the sensitivity of these approximations to exchange-correlation functional choice. We

first performed DFT structural minimizations of CoTPP on Au(111) (Figure 1). Starting from our generated structure with a flat porphine base and rotated phenyl rings, the structure relaxed to a saddle geometry (Figure 9), consistent with previous observations.[158] In each case, we added atomic and molecular oxygen to specific sites at initial guesses corresponding to chemisorption distances (see Figure 10) on the optimized CoTPP/Au(111) with the molSimplify periodic extension.

For all 12 sites considered, O_2 weakly physisorbs with binding energies of 0.15 eV or less and long distances to the porphyrin in non-specific orientations. The only exception to this observation is slightly stronger binding observed for site **1**, which corresponds to cobalt center of the CoTPP. Here, the binding energy with respect to isolated CoTPP/Au(111) and triplet O_2 molecule is 0.25 eV. The short Co-O distance of 1.92 Å along with O-O distance lengthening from 1.21 Å for isolated O_2 to 1.28 Å when bound in the Co-TPP/Au **1** site confirms a stronger interaction (Table 1), for which 0.25 eV binding energy that is closer to physisorption in nature appears to be an underestimate [Table 1 near here]. This underestimation is derived from the fact that we compute binding energies with respect to the isolated Co-TPP on Au(111). When the O_2 binds to the Co center, its distance to Au lengthens from 2.84 Å in the unfunctionalized case to 3.11 Å, decreasing the Co-TPP binding energy to Au(111) by approximately 0.5 eV, thus producing a modest overall binding energy for O_2 on site **1**.

In contrast to molecular oxygen, atomic O interacts strongly with Co-TPP, preferentially occupying different binding sites to differing degrees. We will investigate shortly the reaction profile for O_2 dissociation at the catalytic Co metal center in Co-TPP to form free O atoms (see Sec. 4.4). Within heterogeneous catalysis, this phenomenon is typically known as spillover. Homolytic dissociation of O_2 and distribution of the oxygen atoms over two neighboring TPP molecules has been

reported in literature, for instance for MnCl-TPP on Au(111)[147] and HOPG[134] surfaces at the liquid-solid interface, and for Mn-TPP on Ag(111) in UHV at 78 K.[148] In order to compute O-atom binding energies for each ith configuration, we use a stable reference of a half of a triplet ground state O_2 molecule:

$$E_{rel}^i = E(\text{CO-TPP-O}(i)\,/\,\text{Au}) - \frac{1}{2}E(O_2) - E(\text{CO-TPP}\,/\,\text{Au}) \quad . \qquad (11)$$

Thus, a negative E_{rel}^i indicates binding is stable with respect to the ½ O_2 reference, whereas a positive value indicates the bound O is less stable. A free doublet oxygen atom is 3.2 eV higher in energy than the ½ triplet O_2 reference and therefore even positive values of E_{rel}^i correspond to strong binding to CoTPP/Au with respect to an O atom reference (full details of oxygen reference energetics are provided in Supplementary Material Table S1). Of the 12 initial configurations considered, geometry optimizations converged to 8 unique binding sites (Figure 13, see also Supplementary Material Table S2) [Figure 13 near here]. With the exception of site **1** (Co), double coordination was preferred with O forming two bonds to the CoTPP structure. For initial pyrrole ring configurations on a carbon atom (sites 3-6, and sites 8-11), the final optimized structures straddle two C-C sites with **9-10** (pulled away from Au) the most stable (E_{rel} = -0.55 eV) and **4-5** (angled toward Au) similarly stable at E_{rel} = -0.36 eV. We will refer to the **9-10** configuration as pyrrole (**Pyr**) in further analysis. Oxygen atom binding at the phenyl-linking carbon is shared between **12-8** or **12-3** with E_{rel} = 0.44 eV, which is more stable than the 5-6 or 3-4 binding on the pyrrole itself (E_{rel} = 0.79 eV). In contrast to the initial C-site adsorption, N-atom initial configurations **2** and **7** favor double coordination across the Co-N bond (referred to as the **Co-N** configuration in further analysis), with slightly lower energy for the pyrrole along the down-facing pyrrole coordinate (**1-7**, E_{rel} = 0.62 eV) due to the more

favorable orientation of Co and N along that bond. Finally, single coordination at the Co **1** center is weakly unfavorable (E_{rel} = 0.51 eV), which we will refer to as the **Co** configuration in further discussion.

The map of O binding on CoTPP thus highlights that the most stable configurations for binding are at the edge of the molecule along the downward-angled pyrrole, but stable binding configurations may form with the oxygen atom closer to the Co center, especially immediately following O-O bond cleavage. Analysis of geometric properties (Table 1) again reveals why single oxygen atom binding at Co is relatively unfavorable. With respect to the Co/O_2 configuration, oxygen atom binding on Co forms a stronger Co-O bond of 1.70 Å versus 1.92 Å for the molecular oxygen case, and this weakens the interaction of Co with the Au atom on the surface from 2.84 Å in the bare CoTPP and 3.11 Å in CoTPP/O_2 even further to 3.35 Å in CoTPP/O **1**. This phenomenon has recently been observed experimentally, particularly in one case to be so strong as to drive rearrangement of macrocycles to self-assemble differently when CO adsorbs at the metal center and weakens interaction with a metallic surface.[139] Overall, the relative instability of the CoTPP/O **1** configuration is likely derived in part by further reduction of the binding of the molecule to Au(111) by a total of 0.7 eV from the bare case. A comparison to the **Co-N** or **Pyr** configurations (Table 1) reveals that no such elongation occurs, despite symmetric C-O bonds in the **Pyr** of 1.47 Å and alternating 1.38 Å N-O and 1.90 Å Co-O distances in the **Co-N** configuration, the latter of which is comparable to the Co-O bond in the **O_2** adsorption case.

As we first described in the introduction, error cancellation among chemically-comparable oxygen-adsorption sites may be expected to occur. Therefore, the assignment of the **Pyr** configuration as the most stable C-coordinated oxygen species would be expected to hold independent of the xc functional choice, but we should

expect the relative binding stability of oxygen at the Co center to be highly sensitive to the treatment of exchange (e.g., with hybrid functionals or with DFT+U, in sec. 4.4).

4.2. Electronic Structure of CoTPPs

A critical component of any DFT surface chemistry analysis is to relate energetic properties to electronic descriptors that can help rationalize energetic trends. Comparison of the spin and partial charge on Co and adsorbed O atoms for oxygen in complex with CoTPP/Au or with the isolated CoTPP frozen in the adsorbed geometry for the representative **bare**, **Co**, **Co-N**, **Pyr**, and **O_2**-bound configurations reveals key differences in electronic structure (Table 2) [Table 2 near here]. The net spin on the cobalt center is comparable for the **bare** and **Pyr** configurations because in the latter the oxygen atom is distant from the Co center. Binding of a single oxygen atom at the Co center leads to enhanced overall spin from what is otherwise roughly a doublet system with absolute magnetization close to 1 Bohr in the bare case to a quartet-like system with absolute and total magnetization of 3.3 and 2.9 Bohr, respectively. This net spin in the **Co** configuration is distributed over Co (1.56 Bohr) and O (1.28 Bohr), which reflects an increase of 1 Bohr in net spin on Co versus the **bare** configuration. Binding of molecular oxygen has the opposite effect, with Co instead favoring a near-singlet like configuration (-0.10 Bohr on Co) and the majority of the magnetization residing on the O_2 molecule. In all cases, Co carries a weak partial charge of +0.09-0.28 *e*- versus oxygen typically carrying a negative charge around -0.24 to -0.32 *e*-.

The degree of charge transfer between the CoTPP and Au surface may also be determined from the difference in partial charges on frozen, isolated CoTPP and CoTPP/Au configurations (Supplementary Material Table S3). Charge transfer of around 1 *e*- is observed from the CoTPP to the Au surface across several configurations. Roughly 75% of the charge transfer occurs from the carbon and hydrogen atoms on the TPP macrocycle, and the partial charge on Co is unaffected in contrast to some earlier

work on adsorbed TPPs.[135, 136] Overall charge transfer is likely closely related to the pyrrole rings that are closer to the Au surface as a result of the saddle shape of the TPP.

Restricted spin doublet or quartet calculations reveal comparable partial charges and net spin on Co excluding most quartet isolated CoTPP configurations. Thus, comparison of spin-restricted and unrestricted CoTPP/Au properties suggest that the CoTPP is best described by a low-spin doublet configuration for **Co-N**, **Pyr**, and **bare** configurations with some of the spin delocalized, e.g. to O or Au surface atoms. An exception is the binding of an O atom to the Co center, which should nominally increase the oxidation state by two, favoring a higher spin quartet-like character in the **Co** configuration. Analysis of the projected density of states (PDOS) for the **Co-N**, **Pyr**, and **Co** configurations confirms these differences (Figure 14) [Figure 14 near here]. The frontier z^2 $3d$ orbital that is weakly occupied for the **Co-N** configurations becomes stabilized for spin up in both the **Pyr** and **Co** configurations. In all cases, hybridized x^2-y^2 and xy orbitals are first occupied followed by xz and/or yz orbitals with a narrow splitting (ca. 1 eV) for **Co-N** and **Pyr** configurations. This splitting is enlarged to around 2 eV in the **Co**-bound configuration, and the oxygen atom spin polarization is also apparent with frontier oxygen atom $2p$ states at the Fermi level.

Comparison of the **Co** and **Pyr** configuration total spin densities confirms the Co $3d$ z^2 and oxygen $2p$ character of the metal-centered spin-polarized states (Figure 15) [Figure 15 near here]. Some residual spin density is apparent in both cases on the pyrrole nitrogen atoms and phenyl-linking carbon atoms, consistent with previous results for TPP ring polarization upon surface adsorption.[135] The **Pyr** configuration is nominally similar to the bare CoTPP/Au case, but it is apparent that the presence of the oxygen atom does introduce asymmetry to the polarization on the TPP ring, with enhanced spin density on the side closer to the adsorbed oxygen atom. Surprisingly, for

the **Pyr** case, spin density is also observed on the Au surface atom closest to the Co center with apparent $3d\,z^2$ character as well. The Au surface atoms should be nominally d^{10}, and the presence of this spin polarization on Au is suggestive of charge transfer from the Au to Co centers through overlap of the respective $3d\,z^2$ orbitals. Thus, the negligible spin density on Au observed for the **Co** configuration is likely due to decreased CoTPP-Au interaction strength that was indicated by a longer Co-Au bond distance with respect to the other configurations (see Table 1). Thus, structural, energetic, and electronic properties provide a cohesive picture of the relationship between oxygen-CoTPP interactions and CoTPP-Au interactions although we may expect quantitative components such as the exact degree of charge transfer or spin polarization to be sensitive both to the model choice (i.e., number of layers of Au in the slab) and xc functional choice (i.e., self-interaction error increasing electron delocalization between metal and CoTPP).

4.3. Double Oxygen Atom Binding

In addition to the single oxygen binding characteristics, we aim to provide some insight into the probable mechanism for single oxygen atom adsorption on CoTPP/Au monolayers, which is through O_2 adsorption, dissociation, and spillover to other atoms on that or adjacent porphyrins based on experimental observations for related porphyrins.[147, 148] In order to investigate any unique properties of double oxygen atom adsorption cases, we carried out geometry optimizations of eight representative configurations. In analogy to the lowest-energy single O-atom adsorption **Pyr** site, oxygen atoms on opposite pyrroles (**Pyr-op**) or on the same pyrrole C-C bond (**Pyr-adj**) were studied alongside a slight variation (**Pyr-ver**) in which oxygen atoms were adsorbed to the **5-6** site of the pyrrole on opposite sides of the CoTPP. Modifications of the favorable single atom Co and Co-N configurations were double Co-N adsorption (**Co-N-op**) and Co or Co-N adsorption combined with phenyl carbon linker (**12-8**)

adsorption (**Co, Ph** or **Co-N, Ph**). Finally, alternate configurations of double phenyl carbon linker adsorption in opposite orientations around the Co center (**Ph-d1** and **Ph-d2**) were also considered. In all cases, these configurations were fully geometry optimized and found to be stable local minima (structures shown in Figure 16, see Supplementary Material for coordinates of all structures) [Figure 16 near here]. Qualitative trends in the relative binding energies of the double oxygen atom cases with respect to bare CoTPP/Au and triplet O_2 are consistent with previous observations for single oxygen atom binding (Figure 15).

The **Pyr-op** configuration is the most stable of the eight configurations considered at -1.53 eV with respect to desorbed triplet O_2. The **Pyr-adj** structure represents a unique configuration wherein two oxygen atoms with an O-O distance of 1.51 Å are adsorbed at sites **9** and **10** with each forming a single 1.48 Å bond to a pyrrole carbon. In this configuration, the O-O bond is intermediate between the equilibrium value in the gas phase of 1.2 Å and full dissociation. Although **Pyr-adj** is higher in energy (E_{rel} = -0.56 eV) than the **Pyr-op** case, it remains stable with respect to desorbed O_2, likely due to the partial bonding character between the neighboring oxygen atoms.   All other combinations of previously considered single-oxygen adsorption sites are positive, i.e., less stable than desorbed O_2 and bare CoTPP, ranging from 0.33 eV (or ca. 0.17 eV per oxygen atom) for **Pyr-ver** to 0.64 eV for **Ph-d2**.

Overall, the double oxygen atom cases are slightly more stable than adding single oxygen atom adsorption energetics would have suggested by around 0.4 eV, although this difference is enhanced to as much as 0.75 eV for the **Co-N-op** configuration (E_{rel} = 0.48 eV).   Comparison of structural properties reveals that the CoTPP-Au interactions are strengthened in the **Co-N-op** structure, as indicated by a Co-Au bond of 2.7 Å versus the typical range observed around 2.8-2.85 Å for most

configurations (see Table 1). The simultaneous formation of two pairs of O-Co and O-N bonds around 1.88 Å and 1.36 Å, respectively, pushes the Co center toward the Au metal adsorption site, strengthening surface bonding and increasing stability of this configuration. Although closer than other configurations, the 2.5 Å distance between the two oxygen atoms is likely too far to retain any bonding character. The Co-Au bonds in five of the double oxygen configurations fall in the range of 2.81-2.85 Å with the only other outliers, **Co-Ph** and **Co-N, Ph**, instead having elongated 3.28 and 2.92 Å Co-Au distances, respectively, consistent with single oxygen atom adsorption cases (Table 1). Magnetization of the CoTPP/Au assemblies is highest (1.02-1.57 Bohr) for Co-adjacent oxygen configurations and lower (0.00-0.43 Bohr) for the remaining configurations, consistent with single oxygen atom observations (Table 1). In total, geometries and energetic trends in preferred adsorption sites are comparable for the single and double oxygen atom adsorption cases, with the exception of very close oxygen-oxygen adsorption distances that alter the preferred adsorption geometries (**Co-N-op** and **Pyr-adj**).

4.4. Energetics of Binding and Spillover: GGA, DFT+U, and Hybrid functionals

Thus far, we have identified a number of both single oxygen and double oxygen atom adsorption configurations that are favorable with respect to bare CoTPP/Au and triplet O_2. In contrast, we found that triplet O_2 solely adsorbs to the Co center on CoTPP/Au. Using this information, we can piece together a possible pathway by which molecular oxygen may adsorb, dissociate and then spill over to form stable configurations on CoTPP/Au assemblies. However, binding energies are sensitive to the class of exchange-correlation (xc) functional employed. The generalized-gradient approximation (GGA) employed here is no exception, as the lack of cancellation of self-interaction error (SIE) in this functional potentially leads to overestimates of binding

energetics. We therefore now consider the effect of partial SIE-correction through the DFT+U approach.

Here, we are interested in calculating the U for the Co center in CoTPPs in order to determine if a DFT+U treatment alters binding energetics. Au also has occupied $3f$ states but is generally metallic, and following common practice, we will not apply any U corrections to the Au metal slab. Although U may be calculated on systems for which the total spin is unrestricted, the potential shift applied may cause evolution of the electronic state in an unpredictable manner. Thus, for numerical stability, we constrain the multiplicity of the overall system to either doublet or quartet and calculate U values for both isolated CoTPPs, which are frozen in their adsorbed geometries, and CoTPP/Au assemblies (Table 3) [Table 3 near here]. We may then compare electronic properties obtained at both fixed and unrestrained spin (Table 2) to identify which fixed magnetization calculations are most comparable to the unrestrained results.

Overall, isolated quartet CoTPP molecules have the lowest calculated U values at around 5.8 eV and range from 4.8 to 6.7 eV. Doublet isolated CoTPP and both spin states for CoTPP/Au are instead much more comparable with averages of 7.2-7.5 eV and ranges spanning 6.3 to 8.4 eV (Table 3). Regardless of spin state, calculated U values are generally highest for the configurations with oxygen proximal to the Co center (**Co**, **Co-N**, and **Co-O₂**). Comparing the electronic properties (Table 2) for the unrestricted CoTPP/Au calculations with fixed spin results suggested that all configurations except for the **Co** configuration are well described by doublet spin states. Thus, suitable U values for the **Co** configuration should be around 7.0 eV, whereas suitable values for the other configurations likely range from 6.3-7.9 eV.

Total energies at different values of U cannot be compared because the xc functional is no longer the same, although interpolation schemes have been

developed[126] to overcome this limitation. Here, we will take a pragmatic approach of i) comparing energetic trends with U values and ii) applying a U corresponding to global average values of 6.0 eV for isolated CoTPP and 6.4 eV for CoTPP/Au. The effect of varying U by around 1 eV has been shown to have a much smaller variation in relative energetics around 0.1 eV[169], and there is a relatively narrow range of calculated U values compared to observed variations obtained from altering the metal center identity.[170] The functional form of DFT+U is well-known to alter GGA low-spin state preference and recover high-spin ground states. This observation may be explained by the fact that the low-spin ground state is typically more fractional than a high-spin state due to an increase in the number of hybridized orbitals occupied in the former with respect to the latter.

The effect of U on binding energetics is less clear and also sensitive to the nature of the isolated ground state CoTPP versus the case where the oxygen atom is bound. Thus, we calculated the doublet-quartet spin state splittings and relative oxygen binding energetics with increasing U in the isolated molecular state where the doublet and quartet spin states are well-defined (Figure 17) [Figure 17 near here]. Here, we have computed DFT+U energies on GGA optimized structures, although DFT+U is known to alter some geometric properties[108, 126, 169] (see Supplementary Material Tables S4-8). As suggested by our previous analysis, **Pyr**, **bare**, and **Co-N** configurations strongly prefer doublet configurations by at least 0.5 eV with GGA, but the **Co** configuration weakly favors the quartet state by around 0.2 eV. Increasing values of U shift preference for the three doublet configurations (**Pyr**, **bare**, and **Co-N**) toward the quartet states, producing a preferred quartet state for $U = 4$ eV and higher in the **Co-N** geometry. The **Co** configuration doublet and quartet states become conversely nearly degenerate. In the range of average U values, the qualitative spin state ordering and

relative magnitude of splitting is unchanged from GGA except for the changed preference for high-spin instead of low-spin **Co-N** by about 0.25 eV.

Relative oxygen binding energies may be computed for each configuration in both spin states, although only one of the two spin states would correspond to the ground state of the molecule (Figure 17). The E_{rel} for the most stable binding configuration for CoTPP/Au (**Pyr**) is mostly invariant in either spin state to Hubbard U because the Co center electronic structure is unchanged from the bare reference molecule. Conversely, relative binding energies of the GGA ground state doublet **Co-N** and **Co** quartet decrease with increasing values of U. However, at high values of U, the ground state spin of the **Co-N** configuration becomes a quartet, which has a somewhat lower relative binding energy of about 0.25 eV above the ½ triplet O_2 reference. Additionally, DFT+U strongly destabilizes O adsorption on Co in the quartet ground state from a relative energy around -1.0 eV in GGA up to 0.75 eV at $U = 6$ eV. DFT+U does not alter the most stable binding configuration (**Pyr**) or its relative binding energy substantially, but it does shift preference for relative binding from quartet **Co** to the adjacent quartet **Co-N** configuration while simultaneously weakening the relative binding energies of both configurations. A similar analysis on the full CoTPP/Au system (Supplementary Material Figure S3 and Tables S9-S13) is consistent with previous observations (Table 2) and molecule-only trends. Namely, we observe: i) close doublet-quartet energy splittings with doublet ground states except for a quartet **Co** configuration that becomes a doublet at U above the average value of 6.3 eV and ii) the most stable **Pyr** relative binding energy is invariant to changing U but **Co** and **Co-N** binding configurations are both weakened, with **Co-N** becoming favored over **Co**.

Using the refined energetics we generated both at the GGA and DFT+U levels of theory, we can now piece together a plausible energetic landscape to explain how O_2

might bind and react with CoTPPs adsorbed on Au(111) and compare it to isolated CoTPP frozen in the structure optimized in the presence of the surface (Figure 18) [Figure 18 near here]. The GGA molecular structures show consistently stronger binding (more negative relative energies) than the adsorbed molecules, but DFT+U with an average value of U reverses this trend and makes the two curves more comparable, likely due to decreased hybridization between Co and Au in the adsorbed DSFT+U molecules, making isolated CoTPP and CoTPP/Au more comparable with DFT+U. After O_2 binds strongly (or slightly unfavorably) with GGA (DFT+U), the highest energy barrier is associated with formation of the **Co** geometry through dissociation of the O-O bond to form a free oxygen atom taken as either a ½ O_2 reference or isolated oxygen, where the former is roughly 3 eV more stable than the latter. For GGA, the **Co** formation is only weakly unfavorable, whereas for DFT+U it becomes prohibitive and a **Co-N** structure may be preferred instead. Thus, more plausible mechanisms for adsorption may be through dissociation of O_2 across Co and formation of the **Co-N-op** double oxygen atom adsorption structure (Figure 16). Regardless, once molecular oxygen is dissociated and adsorbed at a site away from the Co center, the remaining energetics (e.g., to form one or more **Pyr** oxygen atom adsorption sites) are downhill and favorable with respect to the isolated CoTPP or adsorbed CoTPP/Au reference. Overall, stabilization of CoTPP by Au(111) does not appear to mediate oxygen adsorption and dissociation beyond what would be possible in isolation because oxygen binding appears to sometimes weaken and destabilize CoTPP/Au interactions. However, adsorption of oxygen to CoTPPs immobilized on Au should be favorable in a number of configurations following formation of free oxygen atoms from Co-mediated O_2 dissociation.

As we introduced previously, hybrid exchange correlation functionals within

DFT are well-known to provide superior energetics over semi-local approximations for isolated molecules (see review in Ref. [34] and references therein), but when studying extended, metallic systems, these approximations may fare poorer than a semi-local exchange correlation approximation. The DFT+U approximation may be interpreted as a local approximation to Hartree-Fock exchange, and the similarity in energetics of the two methods has recently been quantified in some surface science applications.[171] In order to examine the extent to which DFT+U and hybrid treatments comparably impact self-interaction error in transition metal complexes, we now compare CoTPP properties predicted with the B3LYP hybrid functional that contains 20% Hartree-Fock exchange. Owing both to the limited accuracy of hybrid functionals for metals (i.e., the Au(111) slab in this study) and the increased computational cost of around 1-2 orders of magnitude in periodic hybrid functional calculations, we again limit our comparison to the isolated CoTPP frozen in the geometry of the CoTPP/Au. A further motivating reason for restricting the comparison to CoTPP was the observation that CoTPP and CoTPP/Au energetics were comparable across the spillover reaction coordinate (see Figure 18). Both the choice to focus only on the molecule and freeze it in a single geometry rather than carrying out geometry optimizations could introduce bias if the extent to which a geometry is away from the B3LYP minimum on the potential energy surface varies. Thus, we focus here on qualitative comparisons.

Overall, comparisons of CoTPP intermediate energies along the same reaction coordinate considered earlier (see Figure 18) reveals similarity between B3LYP and DFT+U energetics computed at the globally averaged U of 6 eV, especially compared to GGA results (Table 4) [Table 4 near here]. Namely, molecular or atomic oxygen binding at the Co center is less stabilized with respect to binding on the ring for both hybrids and DFT+U. This trend is also apparent for the **Co-N** species, which are

destabilized with both DFT+U and B3LYP with respect to GGA.

We quantify this agreement in a root-mean-squared error (RMSE) over the four species where oxygen is bound to the Co center because we know that configurations with oxygen distant from the Co center should not be shifted by DFT+U with respect to the reactants that have all been aligned at a relative energy of zero (see Table 4). This RMSE over the **Co-O$_2$**, **Co-O**, **Co-Pyr1**, and **Co-N1** configurations (conf.) is computed as:

$$\text{RMSE} = \frac{1}{4}\sqrt{\sum_{\text{conf.}}(E(\text{method}) - E(\text{B3LYP}))^2} \quad . \tag{12}$$

The GGA RMSE of 0.65 eV is reduced to 0.23 eV with DFT+U. We also may identify the value of U that minimizes this RMSE with respect to the B3LYP reference by interpolating the linear fit relationships of DFT+U energies. The U value that minimizes the RMSE is observed to be 5.4 eV, quite close to the global average of computed linear response values of U, and the reduction in RMSE to 0.21 eV is modest. This analysis, however, suggests that either incorporation of Hartree-Fock exchange in a hybrid functional or DFT+U have comparable behavior. The agreement between the two approximately-SIE-correcting methods suggests that GGA overstabilizes oxygen binding at the Co center and that more peripheral oxygen atom binding should instead be favorable.

The results for our worked example highlight the necessity to evaluate the sensitivity of surface chemistry predictions made with a GGA to more advanced treatments of exchange and correlation. Although in organic molecules, the hierarchy of the "Jacob's ladder" of exchange-correlation approximations is well-established[34], this ordering is less clear in surface chemistry and often necessitates a multi-faceted approach.

5. Conclusions

We began this article by introducing some of the challenges facing computational chemists who wish to study surface chemistry phenomena quantitatively with an aim towards providing equal partnership and predictive power in experimental collaborations or in studying phenomena in previously uncharted waters. Some of these challenges, such as the limitations of computational efficiency for very large systems, have lessened over time as codes have become faster and available computing power has increased dramatically. Nevertheless, with the sky still not the limit, the computational chemist must choose prudently the system size and level of theory. We then highlighted some of the challenges associated with just getting started in carrying out simulations through the considerations that must be made when generating complex adsorbate supercells. In addition to the presently available codes, we provided our own addition that specifically leverages molecular building tools to enable complex adsorbate-adsorbate interactions and precise positioning of adsorbates on surfaces. Of all of the challenges, the accuracy of the exchange-correlation approximation within DFT, particularly for large system sizes needed for studying surface phenomena, remains the most outstanding challenge.

Although a semi-local GGA DFT study may be sufficient for studying organic extended systems, self-interaction errors in transition-metal-containing materials can dramatically alter both qualitative and quantitative predictions of relative energetics and degree of charge transfer. We provided a worked example of CoTPP on Au interacting with oxygen adsorbates. We highlighted and confirmed the portions of our reaction coordinate we expected to be insensitive to exchange-correlation approximation (i.e., relative oxygen-carbon interaction energetics on the macrocycle) and those we expected to be over-stabilized within the GGA approximation (i.e., binding interactions at the Co metal center). We related observations in energetic trends to electron density descriptors, which are a critical component of any surface chemistry analysis. We finally identified and compared results obtained from a GGA to those obtained with both DFT+U and hybrid functionals. Although no silver bullet is yet available for practical DFT to study systems with hundreds of atoms and thousands of valence electrons, insight into imbalances of common DFT approximations can inform evaluations of which predictions

should be trusted and which should be tested.

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Table 1. Bond distances of O atom or O_2 molecule adsorption geometries: the distance (*d*) of the oxygen atom to the first (P1) and/or second (P2) closest sites on the porphyrin, Co center to the closest Au surface atom, and O-O distance in the case of adsorbed molecular oxygen, all in Å.

Distance	Co	Co-N	Pyr	Bare	Co (O_2)
d(O-P1)	1.70	1.38	1.47	--	1.92
d(O-P2)	--	1.90	1.47	--	--
d(Co-Au)	3.35	2.88	2.82	2.84	3.11
d(O-O)	--	--	--	--	1.28

Table 2. Net spin and partial charge on Co and O for doublet and quartet CoTPP isolated molecule and doublet, quartet, and unrestricted CoTPP/Au. In the unrestricted case, the total/absolute magnetization (mag.) is indicated as well.

Property	Co	Co-N	Pyr	Bare	Co (w/ O_2)
			doublet CoTPP		
Co spin	0.36	0.71	1.14	1.14	-0.19
Co q	0.25	0.19	0.26	0.26	0.17
O spin	0.69	0.09	0.00	--	0.52 / 0.66
O q	-0.29	-0.31	-0.35	--	0.07 / -0.08
			quartet CoTPP		
Co spin	1.64	2.33	2.50	2.47	1.36
Co q	0.30	0.33	0.40	0.37	0.22
O spin	1.34	0.23	0.00	--	0.79 / 0.82
O q	-0.28	-0.33	-0.33	--	0.00 / 0.09
			doublet CoTPP/Au		
Co spin	0.56	0.29	0.52	0.56	-0.11
Co q	0.23	0.14	0.13	0.13	0.09
O spin	0.81	0.05	0.00	--	0.52 / 0.65
O q	-0.23	-0.27	-0.33	--	0.06 / -0.08
			quartet CoTPP/Au		
Co spin	1.54	0.30	0.56	0.61	-0.09
Co q	0.27	0.15	0.13	0.13	0.09
O spin	1.30	0.05	0.00	--	0.53 / 0.65
O q	-0.23	-0.27	-0.33	--	0.06 / -0.08
			unrestricted CoTPP/Au		
Co spin	1.56	0.0	0.50	0.55	-0.10
Co q	0.28	0.14	0.13	0.13	0.09
O spin	1.28	0.00	0.00	--	0.52 / 0.64
O q	-0.24	-0.26	-0.32	--	0.06 / -0.08
mag.	2.9 / 3.3	0.0 / 0.0	0.4 / 1.0	0.5 / 1.1	1.1 / 1.5

Table 3. Calculated U values (in eV) for CoTPP on Au and isolated CoTPP for the listed oxygen binding configurations with average, maximum, and minimum grouped by model and spin multiplicities (doublet or quartet).

Multiplicity	CoTPP/Au		CoTPP	
	2	4	2	4
Co	8.4	7.0	7.6	6.7
Co-N	7.9	7.8	7.2	5.9
Pyr	6.5	6.6	7.3	4.8
Bare	6.3	6.5	7.3	5.1
Co (w/ O_2)	7.9	7.9	8.0	6.5
avg.	7.4	7.2	7.5	5.8
max.	8.4	7.9	8.0	6.7
min.	6.3	6.5	7.2	4.8

Table 4. B3LYP relative energetics (in eV) for isolated doublet CoTPP with the listed oxygen binding configurations listed along side the energetics with GGA and DFT+U for a U of 5.4 eV that maximized correspondence with B3LYP results and the global average U of 6 eV. Co-O refers to O on the Co configuration, and Co-Pyr1 (Co-Pyr2) or Co-N1 (Co-N2) refer to Co-Pyr and Co-N, respectively, with only one (two) oxygen atom(s) in that configuration. Root-mean-squared error (RMSE) with respect to B3LYP reference in eV is reported for GGA and DFT+U results for the four steps that directly involve Co-coordination by oxygen (**Co-O$_2$, Co-O, Co-Pyr1, Co-N1**).

	GGA	U=5.4	U=6.0	B3LYP
Bare + O$_2$	0.00	0.00	0.00	0.00
Co-O$_2$	-0.84	0.46	0.60	0.06
Co-O + ½ O$_2$	-0.03	1.53	1.71	1.16
Co-Pyr1+Co-O	-0.31	0.38	0.46	0.95
Co-Pyr2	-0.89	-0.91	-0.91	-0.41
Co-N1+Co-O	0.65	2.05	2.21	2.37
Co-N2	1.35	1.73	1.78	2.41
RMSE (eV)	0.65	0.21	0.23	--

Figure Captions

Figure 1. Comparison of typical semi-local functional E vs. N curvature (blue curve) for an atomic or small molecular system (left) to that for a large system or extended solid (right). The exact piecewise linear behaviour is shown as a gray dashed line in both cases.

Figure 2. Cartoon representation of how electron density (red for the isolated atom, blue for the surface) delocalizes from an isolated atom or molecule to a surface when the atom or molecule adsorbs on the surface.

Figure 3. Cartoon comparison of CO adsorbed on an atop site or an fcc hollow site on Pt(111). The number of partners over which electron density delocalizes in the atop case (one, yellow) is reduced with respect to the fcc hollow case (three, purple).

Figure 4. Schematic of shift in molecular or extended states from semi-local DFT (e.g., a GGA) to DFT+U. Bonding states (shown in blue) are destabilized with DFT+U, antibonding states (shown in pink) are stabilized if they are occupied, and unoccupied states are destabilized. The Fermi energy (E_f) is indicated with a gray bar.

Figure 5. Occupation matrix eigenvalues and eigenvectors for an example low-spin (left) and high-spin) molecule (here, Co tetraphenylporphyrin with O atom adsorbed). The fractional nature of eigenvalues is indicated in a symmetric coloring scheme that is red at 0.5 and white at both 0 and 1.

Figure 6. Calculated linear response values of U for Pt(111) surfaces with adsorbed CO in atop, bridge, hcp hollow, and fcc hollow configurations. The unique atoms in the unit cell are shown in the shaded parallelogram. The range of computed values is indicated by the color bar (4.9 eV in red to 6.5 eV in blue) and compared to the U values computed in the pristine case at top right.

Figure 7. Degree of charge transfer between Cu(111) and Co-tetrabromophenyl porphyrin. Sites with reduced charge density are shown in blue and enhanced are shown in red with respect to a reference isolated Cu(111) slab. Reproduced from J. Chem. Phys. 142, 240901 (2015), with the permission of AIP Publishing.

Figure 8. CoTPP orientation on Au(111). The angle of the N-Co-N axis with respect to the [$1\bar{1}0$] direction (40°) is indicated in green. The unit cell and dimensions are shown in yellow.

Figure 9. Saddle geometry of CoTPP on a single unit cell of the Au(111) surface. The angle of the pyrrole H to the Co-N-containing plane and an example dihedral of the phenyl group with respect to the porphine base are both annotated in green.

Figure 10. Location of selected adsorption sites for oxygen atom and/or dioxygen on the porphyrin structure color-coded by site type: pyrrole carbons are shown in green, pyrrole nitrogens are shown in blue, cobalt center is shown in purple, and the phenyl-connecting carbon is shown in orange. The pyrroles angled away from the Au(111) surface are at the top and bottom.

Figure 11. Example of fcc supercell replication from primitive unit cell in the supercell builder extension to molSimplify. The unit cell vectors and angles are labelled (left), and the replicated atoms along each vector are color-coded accordingly (right).

Figure 12. Flowchart of the surface placement tool for generating 3D coordinates of aligned adsorbates on a slab.

Figure 13. Oxygen atom binding positions and GGA binding energies relative to half of a triplet O_2 molecule ranging from -1.2 eV (green, more stable) to +1.2 eV (orange, less stable).

Figure 14. Co and O projected density of states (PDOS) from GGA for a) oxygen bound on Co-N bond, b) oxygen bond on the C-C bond of a pyrrole group, and c) oxygen

bound at the Co center, with the Fermi energy set to zero in all cases. Total PDOS for Co (black, solid line) and O (black dashed line) is indicated along with each d orbital (as shown in legend). The curves on the right-hand side of each plot are for the spin up states and the left-hand side for the spin down states.

Figure 15. Spin density of the Co-centered oxygen atom binding mode (left) and pyrrole centered oxygen atom binding mode (right) with both side (top) and top view (bottom). The isosurfaces represent ± 0.002 e-, with red corresponding to positive spin and blue to negative spin. The Au closest to Co is spin polarized in the pyrrole case (top right).

Figure 16. Double oxygen atom binding configuration structures and relative energy with respect to separated CoTPP/Au and triplet O_2.

Figure 17. a) The doublet-quartet spin state energetics (in eV) versus Hubbard U (in eV) for isolated CoTPP with no bound oxygen atoms (None, red squares), oxygen bound to Co (Co, purple circles), oxygen bound on the Co-N bond (Co-N, blue triangles), and oxygen bound on the pyrrole C-C edge (Pyr, green diamonds). b) The relative binding energies of oxygen atoms with respect to a half triplet O_2 molecule dissociation limit in doublet or quartet Co, Co-N, and Pyr doublet and quartet configurations. The ground state spin at a given U value is indicated by a solid line, whereas the higher energy spin state is indicated with a dashed line. Only Co-N configurations change spin state, and all spin states are labelled adjacent to the plot. In both a) and b), Calculated values at quartet (stars) and doublet (crosses) U values are indicated on the plot. Values beyond U = 6 eV are extrapolated with a dotted line.

Figure 18. Model of possible adsorption events on CoTPP/Au (black line) and CoTPP (red line) with a) DFT+U using an average value of U and b) GGA. The intermediates at each point are indicated in the bottom panel with cartoon descriptions. The high energy dissociated O radical is excluded from a) to keep scales comparable, and the Co-N adsorption energies are indicated with faded dashed lines. The last two points correspond to two Co-N or two Pyr adsorbed oxygen atoms.