AN OPTIMIZATION FRAMEWORK FOR NANOMATERIALS DESIGN

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ABSTRACT

Ongoing developments in the synthesis of nanostructured materials have led to a boom in the number of fabricatable nanomaterials. However, while there is a large body of work on how to fabricate increasingly complex nanostructures, there are relatively few systematic approaches for selecting *which* structures to fabricate so as to optimize for a particular functionality. In this thesis, we present a generic framework for modeling the design of nanostructured materials as mathematical optimization problems. Our work takes advantage of results from computationally demanding models (e.g. energies from quantum chemical calculations or kinetics from Monte Carlo simulations) from which it regresses simplified structure-function relationships that can be used in conjunction with a supervisory optimization algorithm to guide the design of highly functional nanostructures. We develop detailed mathematical optimization models for extended heterogeneous catalyst surfaces, doped perovskite oxygen carriers, and Wigner crystals while highlighting the ability of our approach to address a wide range of other material systems. In addition to detailed models, we have developed a general purpose Python package called MatOpt for streamlining the process of specifying optimizing materials and for lowering the barriers for applying mathematical optimization to materials problems. Our work provides systematic approaches for managing the combinatorial complexity of the nanomaterials design space and demonstrates the value of process systems engineering principles applied in new contexts.

PUBLICATIONS

The following papers related to the work presented in this thesis have been published, submitted, or are in preparation to be submitted in peer-reviewed journals:

- C. L. Hanselman and C. E. Gounaris. "A Mathematical Optimization Framework for the Design of Nanopatterned Surfaces." *AIChE Journal* 62.9 (2016), pp. 3250– 3263.
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1

INTRODUCTION

The field of process systems engineering has long recognized the importance of improving decision-making across all length scales of chemical engineering, from enterprisewide optimization down to molecular design [73, 207]. In this thesis, we show how the same principles that can be used to design chemical plants and supply chains can be applied at the nanoscale for the design of nanostructured materials. Importantly, we show how expertise in mathematical optimization can be applied to improve and systematically guide decision processes in the fields of materials science and catalysis.

1.1 NANOSTRUCTURED MATERIALS SYNTHESIS

Advances in nanotechnology have enabled the fabrication of materials with near-atomic scale precision. Specifically in the case of transition metals, there are a multitude of examples of particles synthesized with controlled sizes, shapes, and chemical orderings [14, 158, 238]. At the smallest scale, there are several approaches for synthesizing and manipulating atomically-precise clusters typically smaller than 50 atoms by introducing specially-designed protective ligands [55, 96, 133, 134]. At slightly larger length scales of ~10 nm to 500 nm, there are a plethora of controllable nanoparticle geometries including all types of convex polyhedra [237, 238], concave polyhedra [111, 239, 246, 247], cages [57, 77, 143, 170], stars [232, 243], dumbbells [138], and rings [101], among many others. These shape-controlled nanoparticles are typically created in solution but examples of detailed structures can also be found for supported nanoparticles [90, 211] or on annealed, nanofaceted surfaces [27, 39, 242]. Furthermore, at the micron scale there exist many methods for constructing, transferring, and replicating patterns on surfaces in a scalable way [63, 213].

As technological advances continue, our ability to tailor the properties of resulting nanostructures will only continue to grow. It is already possible to combine individual nanoparticles in sophisticated, hierarchically-assembled structures [91, 142, 244, 253]. Techniques for achieving these complex nanoscale assemblies include using functionalized facets [150, 187], templated surfaces [22, 115, 186, 213], and DNA [10, 174, 249, 254] to direct material organization via processes known as directed self-assembly [17, 74].

In conjunction with advances in synthesis techniques, it is becoming easier to interpret the structures of nanoparticles via advances in microscopy and image analysis [128, 135, 185, 196]. Interestingly, the same scanning tunneling microscopes for probing surfaces can also be used to individually manipulate atoms, leading to precise control of atom placement in some model systems [152]. While the approach of lining up atoms via a microscope is useful for investigative experiments, it is clear that more practical technologies are necessary to achieve scalable production of nanostructures.

1.2 NANOMATERIALS PROPERTIES & APPLICATIONS

Nano- and micro-structured materials typically have properties which are wildly different from their bulk properties, enhancing useful functionalities in a number of application contexts. For metallic nanoparticles in particular, recent work has highlighted enhanced catalytic activities [160, 222], unique optical properties [78, 237], and the potential for use in drug delivery [28, 41], among other exploitable properties. Motivated by the promise of exciting new material properties, developments in nanofabrication have benefited not only metallic nanoparticles [27, 238] but also a variety of material types including zeolites [35, 60], metal-organic frameworks [56, 130], and carbon allotropes [135] to name but a few.

In this thesis, we will typically focus on example applications related to catalysis due to the abundance of structure-function relationships linking catalytic turnover to nanostructure. However, we note that the general approaches developed in this work can similarly be applied to design the magnetic, optical, and structural properties of nanostructured materials. In the domain of heterogeneous catalysis, there are several example applications where nanostructures show significant potential for surpassing the capabilities of unstructured materials. Reactions on nanoparticulate catalyst surfaces have long been known to exhibit "structural sensitivity," whereby the size and shape of catalytic nanoparticles can have significant impact on the exhibited catalyst turnover [27, 118, 129]. One such case, the anodes and cathodes for polymer electrolyte fuel cells, has received

considerable attention due to its importance in sustainable energy conversion [53, 75, 228]. The possible turnover of the oxygen reduction reaction (a key limiting step) has been iteratively improved by controlling the size of supported Pt nanoparticles [62], introducing alloyed nanoframes [34], and by introducing structural defects [31, 36, 37].

1.3 COMPUTATIONAL MATERIALS EVALUATION

In parallel to synthesis efforts, theoretical and computational advances in the area of density functional theory (DFT) are enabling the design of materials from first principles [4, 51, 61, 81, 148, 163]. Specifically, DFT enables calculation of energy for chemical configurations via quantum mechanical models. The energies calculated by DFT provide a wealth of insight into the reactivity of catalytic systems.

For example, in the case of heterogeneous catalysis, the activation energy of reactions on the catalyst surface can typically be linearly correlated to differences in adsorption energies of reactive intermediates, which in turn can be correlated to the adsorption energies of simpler adsorbates [24, 162, 164]. Furthermore, the adsorption energies of small adsorbates have been demonstrated to correlate to geometric descriptors of sites on the surface, allowing predictions of catalytic activity from purely geometric considerations [30, 32, 154]. We defer detailed discussions about the structure-function relationships enabled by DFT to the relevant content chapters. In Chapter 2, we explain the linkage of DFT-calculated adsorption energies to turnover on a heterogeneous catalyst surface. In Chapter 4, we explain the linkage between DFT-calculated oxygen excess energy and the oxygen carrying capacity of perovskites.

The ubiquity of computational chemistry tools has enabled a wide variety of material material evaluations *in silico*. Standardized approaches have been demonstrated for simulating reactions and rearrangements of materials at the atomic via kinetic Monte-Carlo methods [105, 190, 204], molecular dynamics [117, 251], and microkinetic models such as the degree of rate control [206, 235].

1.4 HEURISTIC MATERIAL SCREENING

With this growing capability to manufacture metallic crystals to an ever-increasing precision comes the need to know which exact microstructures exhibit the best performance for their intended functionality. However, due to the combinatorially many ways with which matter can arrange itself, the best structures are unintuitive and likely impossible to identify without a systematic decision-making approach.

Several databases have been established to support screening of highly functional materials by comparing and interpolating data from both experimental and computational studies [45, 99, 126, 189]. Recently, high-throughput computational approaches [50, 71], chemical informatics [217, 229], and machine learning [69, 139, 218–220] have been used to massively increase the pace of calculations and to smartly sample the combinatorial material design space.

A key approach in materials screening has been to develop simplified structure-function relationships for the purpose of predicting catalyst activity as a function of simple geometric descriptors. Descriptors such as coordination number [154, 181, 226, 241], generalized coordination number [30, 32], orbitalwise coordination number [144, 227], surface angles [154], and effective coordination number [9, 65] have been demonstrated in the literature.

In addition to screening methods, there are several approaches that seek to optimize materials by applying numerical algorithms. These can be broadly classified as topology optimization algorithms and metaheuristic optimization algorithms [100]. Topology optimization involves solving a very specific form of optimization model over continuous material domains, typically with the goal of maximizing a function for an integral of the material properties over the domain [18, 94, 200]. These approaches are particularly useful for optimizing the shape of continuous, microscale material domains, but they can not be generically used to represent complex logical relationships that are prominent in discrete materials.

Several more approaches have utilized metaheuristic algorithms in conjunction with detailed material simulations to guide the design of some parameterized materials [151]. In Khaira et al. [109], the authors use an evolutionary algorithm to optimize a few parameters relevant to the design of block copolymer patterns. In Ruck et al. [183], the authors use a simple coordination-based structure-function relationship in conjunction with particle swarm optimization to design reactive, symmetric nanoparticles and rods. In Núñez and Vlachos [166], the authors used active learning in conjunction with a Monte-Carlo method for exploring the design space of bifunctional patchy catalyst surface. Similarly, in Núñez, Lansford, and Vlachos [165], the authors use a similar coordination-based structure-function with simulated annealing to design defects on nanostructured surfaces to increase surface reactivity. These approaches

leverage metaheuristic optimization methods to find good solutions, but still lack rigorous guarantees on the optimality of the identified designs.

1.5 MATHEMATICAL OPTIMIZATION FOR NANOMATERIALS DESIGN

In contrast to heuristic search procedures, exact mathematical optimization algorithms provide rigorous guarantees on the quality of identified designs. At the termination of exact optimization algorithms, the search procedure either provides guarantees that no better solution can be enumerated or provides an optimistic bound on the quality of designs not yet fully explored. In this way, exact optimization methods provide a unique advantage over heuristic optimization algorithms at the expense of requiring some mathematical structure for specifying the problem.

Mathematical optimization represents decision problems via variables, constraints, and an objective function. In Eqns. 1.1–1.4, we write the search for novel materials as a mathematical optimization model with generic notation. We denote a vector of variables for the design as d within a design space D (Eqn. 1.4). As an objective function (Eqn. 1.1) we generically write "Functionality," which can represent catalyst turnover, energies, desired site concentrations, or any other material property that can tractably encoded via algebraic functions of the design variables. In Eqns. 1.2 and 1.3, we represent constraints on the material via abstract functions for the "Stability" and "Fabricability" of designs. These constraints on the design space can represent crystallinity, composition bounds, geometric restrictions, thermodynamic relationships, reaction rates, or mass transport limitations. Though they are written as a single line in our model, these expressions typically require their own sub-models (i.e., structure-function relationships) for the properties of the material as functions of the design variables. Since the ability to solve the resulting optimization problem is closely tied to the number and complexity of constraints, there is a clear need to make good simplifying approximations so as to match chemical systems with suitable optimization model formulations.

$$\max_{d} \quad \text{Functionality}(d) \tag{1.1}$$

s.t. Stability(
$$d$$
) $\geq \varepsilon$ (1.2)

Fabricability
$$(d) \ge 0$$
 (1.3)

$$d \in D \tag{1.4}$$

In this abstract notation, there are no restrictions on the type or scale of materials that can be addressed; however, it is practically important to narrow down the scope of problems to focus on cases that are both chemically relevant and that can be tractably modeled. The common properties of nanostructured materials and chemistries of interest will serve to guide our focus towards a subset of systems that fall within the scope of materials optimization. In Chapter 5, we formally identify the properties of nanostructured materials optimization models that can be efficiently encoded via mixed integer linear programming. As an alternate perspective, in Chapter 6, we present an example design problem that takes the form of a nonlinear programming model and can be solved to identify materials in a continuous domain.

1.6 AIMS AND OUTLINE OF THE THESIS

The overarching aim of this thesis is to demonstrate ways in which mathematical optimization and other process systems engineering approaches can be applied to the design of nanostructured materials. To that end, we develop mathematical optimization models for several example systems and show how the principles identified therein can generically be applied to many other material systems. More specifically, throughout the thesis we aim to establish several key observations:

- 1. Mathematical optimization is well-suited to handle the combinatorial complexity of the nanostructured material design space.
- 2. Both discrete- and continuous-space nanostructured material geometries can be generically represented in optimization models.
- 3. A variety of simplified structure-function relationships can be encoded in mathematical optimization formulations.
- 4. Trade-offs of material properties can be efficiently explored in optimization models.
- 5. Results from mathematical optimization can inform future material synthesis efforts and accelerate the design of novel nanostructured materials.

The remainder of this thesis is organized as follows: In Chapter 2, we present the first application of mathematical optimization to design nanostructured catalytic surfaces. In Chapter 3, we build upon the surface design work by incorporating stability into our optimization models. This work relaxes several assumptions that were made in the earlier chapter and shows how a marginal increase in modeling complexity can result

in a more realistic and practically-relevant design space. In Chapter 4, we show how the same optimization principles can be applied to design of bulk materials, namely a doped perovskite that is used as an oxygen carrier for chemical looping combustion. Importantly, this application highlights the full design procedure starting from identifying optimization opportunities, regressing structure-function relationships from available computational data, and ending by solving relevant optimization models. In Chapter 5, we formalize a generic approach for conceptualizing nanostructured optimization problems as well as present a software package for automatically casting and optimizing the resulting models. In Chapter 6, we present an approach for optimizing the structure of Wigner crystals via nonlinear programming. This presents a contrasting example from our other work in that we relax the requirement that materials reside in discrete locations and instead consider the optimization of coordinates in a continuous domain. Finally, Chapter 7 summarizes the contributions of this work in addition to proposing several future research directions.

2

OPTIMIZING NANOSTRUCTURED CATALYST SURFACES

The recent explosion of capabilities to fabricate nanostructured materials to atomic precision has opened many avenues for technological advances but has also posed unique questions regarding the identification of structures that should serve as targets for fabrication. One material class for which identifying such targets is challenging are transition-metal crystalline surfaces, which enjoy wide application in heterogeneous catalysis. The high combinatorial complexity with which patterns can form on such surfaces calls for a rigorous design approach. In this chapter, we formalize the identification of the optimal periodic pattern of a metallic surface as an optimization problem, which can be addressed via established algorithms. We conduct extensive computational studies involving an array of crystallographic lattices and structure-function relationships, validating patterns that were previously known to be promising but also revealing a number of new, nonintuitive designs.

2.1 INTRODUCTION

The rational design of nanostructured metallic surfaces has recently received attention due to the potential for improving the catalysis of many important reactions. In the case of the oxygen evolution reaction in fuel cells [209, 228], for example, several studies have indicated that slight changes in the structure of a metallic surface can lead to a dramatic improvement in the achievable rate of reaction [116, 205]. Furthermore, a rigorously nanopatterned surface can provide chemical sensing capability via surface-enhanced Raman spectroscopy [15, 137, 234]. In this context, the shape and exact positioning of defects or decorations on an metallic surface leads to a nonlinear enhancement of local electric fields, referred to as "hot spots," which can be tuned to enhance the signal from Raman spectroscopy measurements [15, 114, 236]. The potential for such applications highlights the value of being able to control the structure of surfaces down to the nanoscale.

Nanostructured designs for metallic surfaces can be plausibly fabricated by a variety of techniques. Epitaxial methods [92] such as chemical layer deposition [177], atomic layer deposition [64], and dip-pen lithography [49] can be used to grow features on metallic surfaces. A combination of electron beam lithography and chemical etching [63] can be used to make very small features. On the atomic scale, pits and grooves can be formed from a metallic surface alloy via chemical dealloying of a metal or by galvanic displacement [31, 52, 116]. As the state of the art in the patterning of surface alloys improves, so will the capability to design nanostructured surfaces with controlled features. Similarly, advances in directed self-assembly will increase our capability to fabricate a variety of other material types with nano- or micro-structured features [17, 74, 201, 202].

In the context of heterogeneous catalysis on metallic crystalline surfaces several structurefunction relationships have been elucidated by a variety of tools [72, 118, 222]. More specifically, techniques such as density functional theory [81, 199], linear scaling relationships [2, 79, 223], and the degree of rate control approach [33, 206] have been employed towards correlating the structural, electronic, and reactive properties for a variety of material types and applications. These tools enable the prediction of adsorption energies, and therefore of a variety of other properties, as a function of the local surface site characteristics. Several site descriptors, such as the site's coordination number [13, 32], the number of available bonds [43], the d-band center [205], the average coordination number among neighboring sites [30], as well as the local surface curvature (e.g., various surface angles [154]) have been shown to correlate well with adsorption energies. Techniques for systematically identifying site descriptors have also been proposed [6, 146, 176].

The application of these types of structure-function relationships have been demonstrated for a variety of systems. For example, Zhang et al. [250] demonstrated an in-depth investigation of adsorption of ions at a variety of rutile-water interfaces. Kitchin et al. [112] described the potential to tailor the chemical properties of a platinum surface by introducing a subsurface metal alloy, while Calle-Vallejo et al. [31] used generalized coordination numbers to describe the reactivity of platinum surface sites for the oxygen reduction reaction.

The rate for the limiting step(s) in the overall conversion process can ultimately be correlated to the structure of the site, typically in the form of a volcano plot [163, 205]. Volcano plots arise due to *Sabatier's principle*, which states that catalytic surfaces perform

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best when they absorb reactive species neither too strongly, nor too weakly [164]. Importantly, the activation energy of a chemical reaction can be predicted from the adsorption energies of transition states [81]. Therefore, we can translate local site characteristics to adsorption energies (e.g., as provided by density functional theory computations) to activation energies. Using these demonstrated relationships, we can predict reaction rates of metal surface sites and, thus, be in position to design periodic surface patterns that maximize the total reactivity on a per area basis.

In this chapter, we intend to show how correlations that link performance (e.g., catalytic activity) to site descriptors, such as commonly available volcano plots, can be used to determine the optimal (i.e., of highest performance) periodic surface. As an illustration, we will use the average neighbor coordination number (also known as the generalized coordination number), denoted \overline{CN} , as an example site descriptor. This site descriptor has been chosen both due to its recent and emerging appearance in the literature [30, 31] as well as due to its interest from the mathematical modeling viewpoint. We should, however, emphasize that our approach can be readily adapted to handle a variety of other site descriptors as well.

In general, the collective performance of the catalytic surface can be attributed to a weighted average of the contributions by each of the surface sites, appropriately weighted via Boltzmann factors. In practice, however, it is typical to have volcano plots with steep sides, implying that only the "ideal" sites, i.e., those exhibiting features that lie very close to the peak of the volcano, contribute substantially to the overall reaction rate [31, 164]. With this observation in mind, the problem of designing the surface of highest reactivity simplifies to that of designing the surface that packs the most ideal sites in the unit area, essentially neglecting the contributions from the remaining, non-ideal sites.

In particular, when the material designs can be expressed via discrete variables, as is the case with materials conforming to well-defined crystalline lattices, and when appropriate site descriptors can be encoded via linear constraints and disjunctions, as is the case of descriptors based on site coordination numbers, we can cast mixed-integer linear programming (MILP) models and utilize well-developed MILP solvers [3, 76, 95] in order to determine the optimal surface packings. An ancillary advantage of using MILP solvers to address this design problem is that several optimal (or near-optimal) solutions can be collected via a solution pool approach [46]. In this way, multiple distinct, yet equivalent in terms of objective value, designs can be identified for comparison against some secondary criteria for further consideration by experts. Additionally, if one desires to maximize the selectivity of the surface for a particular reaction, an alternative objective

that maximizes the ratio of desired sites against competing sites may be employed. The resulting fractional objective function can then be linearized via well-established methods [245].

Another important consideration when designing catalytically active surfaces is their longer-term stability. In particular, we are concerned with the likelihood for rearrangement of low-coordinated atoms given the available energy released from reactions or from the process environment. At the interest of exposition, in this work we propose a very simple approach to postulate "stable" designs, acknowledging that a more sophisticated approach may be necessary to yield designs that are guaranteed to be stable under realistic process conditions. We discuss our current approach pertaining to stability as well as proposed alternatives later.

The remainder of this chapter is structured as follows. First, we formalize the design problem as a mathematical optimization problem and cast a suitable model to that purpose. We then highlight important algorithmic considerations, such as strategies for breaking model symmetry, after which we present results from a comprehensive study we conducted across a variety of crystallographic lattice types and a gamut of input volcano performance plots. Finally, we end with some concluding remarks that synopsize proposed next steps in this research.

2.2 METHODOLOGY

The effort to design a transition metal surface that features as many as possible ideal (i.e., maximally performing) local metal sites can be decomposed into two steps. In the first step, one needs to identify those target values for the site descriptors that would qualify a site as an ideal site. In most cases, when the performance of a site is governed by a volcano plot, the target value is the one that corresponds to the volcano's tip. However, as this value may not be exactly attainable by any physically realizable surface site, a more involved calculation may be needed. In Section 2.6, we present a rigorous approach that one can follow so as to identify target values for the site descriptors we consider in this study. Once the target values have been identified, the second step of the design process will be to determine the best feasible packing of surface sites that attain this maximal level of performance into a periodic pattern. This task can be formally cast as an MILP model and can, thus, be performed via use of well-established MILP optimization techniques. Below we present the derivation of this optimization model.



Figure 2.1: Example tile shapes and lattice locations of a design canvas. *Top:* Top-down views (shades of gray become darker as layer depth increases). *Bottom:* 3-D perspectives and full set of lattice locations.

2.2.1 Mathematical Model

The proposed model depends on a suitably defined graph, which serves as a "design canvas." The nodes of this graph constitute the lattice locations present in a periodic, space-filling tile of a horizontally-extending, thin crystal segment (see Fig. 2.1), while the edges of the graph signify those locations that are considered neighbors for determining a site's coordination number. Such a tile can be replicated ad infinitum (in practice, as many times as necessary) along the horizontal plane so as to form the complete design surface. Note that the periodic nature of the graph implies that certain locations that fall on the border of the tile will be equivalent to some other locations on the tile's "opposite" side. Figure 2.2 illustrates this property by depicting locations that are equivalent under periodicity principles.

Consequently, the area of the design surface occupied by a single tile is an important model consideration. This area can be parameterized by the integer number of lattice locations along the tile's horizontal edges, which we refer to as the tile's *size*. It should in fact be recognized that this parameter may induce limitations on the optimality of a design and, in general, calculations should be performed for a large enough tile size so that the results are not affected. We discuss the implication of finite tile size in more detail in our computational results section. An additional important parameter is the *depth* of the tile, which we define as the integer number of lattice location layers we consider in the direction perpendicular to the design surface. This parameter must be selected as follows. In cases where the thickness of the metallic surface is explicitly limited by the application, such as when only a thin film of the catalytically active metal



Figure 2.2: Periodicity of border locations in a hexagonal tile. Locations with the same number (color) are equivalent and are represented via common variables.

can be deposited on an underlying inert, the depth of the tile should be limited to the appropriate application-specific value. For applications where this is not the case, such as when one designs the optimal surface of a larger piece of crystal, the number of lattice location layers taken into account in the design computations should be allowed to be as large as necessary so as again not to affect the optimality of the design. For reference, the tiles depicted in Fig. 2.1 are all of size and depth equal to 5.

We denote the set of lattice locations as I, and we remark that only one index value is reserved for each set of periodically-equivalent locations; that is, we handle these equivalent locations as a single location and make use of common variables that correspond to the whole set. For each location $i \in I$, the set N_i is defined to include the locations that are neighboring to i; that is, locations that form an edge with node i. Note that, due to the periodicity considerations, locations on (or near) the border of the tile may have neighbors positioned on the tile's opposite side. Furthermore, locations below the bottom layer of the canvas graph are considered *filled*, i.e., always occupied by a metal atom (or an atom of the surface's support material, as appropriate), while locations above the top layer are considered *void*, i.e, not occupied by any atom. In this way, every location in Ihas every one of its neighbors well-defined, either being another location in I or being an extra-canvas location whose occupancy state is prefixed to either filled or void. For notational convenience, we denote with N_i^b the subset of location i's neighbors that are positioned in the layer below the layer of location i.

2.2 METHODOLOGY

The key decision variables in the model are a set of binary variables Y_i , which are defined for each $i \in I$ so as to indicate the presence or absence of a metal atom in location i.¹ In addition to this set of variables, we define a number of auxiliary variables that enable us to encode–and suitably restrict–various higher-level quantities while preserving linearity of the overall model. The optimal values of all auxiliary variables can be uniquely determined from the optimal values of variables Y_i . Given the presence of a metal atom in a lattice location i (i.e., $Y_i = 1$), a variety of site descriptors can be encoded for this location. For our example system, we encode the site's coordination number, CN_i , as well as the average coordination number of all neighbors, \overline{CN}_i . We remark that these variables are declared as continuous variables within appropriate bounds. We also introduce a new set of binary variables, denoted as Z_i , to indicate whether location i constitutes an ideal site. These variables are meant to be activated whenever (a) the site is indeed occupied by a metal atom, (b) this atom lies on the exposed surface of the crystal, and (c) the site descriptors attain the target values. Given the above definitions for model variables

¹ In the case of multi-metallic surfaces, this binary representation can be extended to a more general, discrete encoding.

and using logical propositions, we cast our surface patterning model in Eqns. 2.1–2.9. A comprehensive list of our notation is provided in the end of this chapter (Section 2.5).

$$\max_{\substack{Y_i, Z_i, \\ CN_i, CN_i}} \sum_{i \in I} Z_i$$
(2.1)

s.t.
$$\{Y_i = 1\} \Rightarrow \left\{ CN_i = \sum_{j \in N_i} Y_j \right\} \quad \forall i \in I$$
 (2.2)

$$\{Y_i = 0\} \Rightarrow \{CN_i = 0\} \qquad \forall i \in I$$
(2.3)

$$\overline{CN}_{i} = \frac{1}{CN_{\text{bulk}}} \sum_{j \in N_{i}} CN_{j} \qquad \forall i \in I$$
(2.4)

$$\{Z_{i} = 1\} \Rightarrow \left\{ \begin{array}{c} Y_{i} = 1\\ CN_{\min}^{\text{surf}} \leq CN_{i} \leq CN_{\max}^{\text{surf}}\\ |\overline{CN}_{i} - \overline{CN}^{*}| \leq \epsilon \end{array} \right\} \qquad \forall i \in I$$
(2.5)

$$\{Y_i = 1\} \Rightarrow \left\{ \bigwedge_{j \in N_i^b} (Y_j = 1) \right\} \qquad \forall i \in I \setminus I^{\text{bottom}}$$
(2.6)

$$0 \le \overline{CN}_i \le CN_{\text{bulk}} \qquad \forall i \in I \tag{2.7}$$

$$0 \le CN_i \le CN_{\text{bulk}} \qquad \forall i \in I \tag{2.8}$$

$$Z_i \in \{0,1\} \qquad \qquad \forall i \in I \qquad (2.9)$$

$$Y_i \in \{0, 1\} \qquad \qquad \forall i \in I \qquad (2.10)$$

In the above model, the objective 2.1 calls for maximizing the number of ideal sites present in the graph, which essentially maximizes their density in the designed surface. Note that only one copy of periodically-equivalent locations contributes to the objective, since only one index in the set *I* is reserved for the set of equivalent locations. Equations 2.2 and 2.3 define a location's coordination number, CN_i , noting that this quantity is defined to be equal to 0 for sites that are unoccupied. Given this definition for site descriptors CN_i , Eqns. 2.4 then define the site descriptors \overline{CN}_i , i.e., the average coordination number among all neighbors of a given location *i*. Equations 2.5 constitute the definitions of variables Z_i .² More specifically, these constraints ensure that the setting $Z_i = 1$ implies that all three criteria (a-c, see above) for the site *i* to be ideal are met. The first criterion will be met as long as the corresponding variable Y_i is activated. The second criterion will be met as long as the atom's coordination number falls inside an appropriate range that

² In the case of Eqns. 2.5, the forward implication suffices to enforce the full equivalence. Given the fact that the variable Z_i has a positive contribution to the maximization objective, the optimizer will select $Z_i = 1$ wherever possible; hence, we do not need to enforce the backward implication explicitly.

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depends on the type of lattice considered. For example, in the case of a face-centeredcubic lattice, where the coordination number of a bulk atom is $CN_{\text{bulk}} = 12$, an atom is considered to be on the exposed crystal surface if it has coordination number between $CN_{\text{min}}^{\text{surf}} = 3$ and $CN_{\text{max}}^{\text{surf}} = 9$, since having fewer than 3 neighbors would render the atom too unstable, while having more than 9 neighbors would render the atom too covered by other lattice atoms, prohibiting the site to receive significant adsorption. The third and final criterion will be met if the variable \overline{CN}_i attains a value close enough (within some small tolerance ϵ) to the target value, \overline{CN}^* , signifying that the site is ideal.

Equations 2.6 correspond to a set of constraints that are related to the fabricability and overall stability of the design. More specifically, these constraints mandate that, if location *i* is occupied, then all neighbors below this location, $j \in N_i^b$, must also be occupied. Consequently, we need not apply these constraints for locations *i* that are part of the bottom-most layer of the canvas graph, as doing so would be redundant. We remark that these simple constraints are in lieu of a more sophisticated approach to modeling the stability of the optimal design. We recognize that neglecting this consideration may result in optimal designs that are likely to rearrange under reaction conditions. However, at the interest of the framework's exposition, we have decided to not convolute our approach for identifying optimal surface patterns with a detailed scheme for modeling surface stability. As such, practitioners may apply their preferred structure-function relationship for stability in order to limit their search to stable designs (by augmenting constraints in a modular fashion). One can imagine encoding a requirement on stability as an upper bound on the thermodynamic energy of a design, or alternatively, as a constraint requiring at least some minimum energy barrier to move a given atom from one configuration to a neighboring configuration.

Finally, Eqns. 2.7–2.10 provide applicable bounds for the continuous variables and declare the binarity of the discrete variables. We remark that, although the variables CN_i are declared as continuous, the model constraints restrict them to only attain integer values in any feasible solution. We also highlight that, in the above model, references to quantities Y_j for extra-canvas, neighboring locations j, such as locations above the canvas's top layer or locations below the canvas's bottom layer, are to be interpreted as constants 0 or 1, respectively, so as to account for the void or filled status of those locations. Similarly, reference to quantities CN_j for these extra-canvas locations should be interpreted as either a constant 0, for the case of void locations above the canvas's top layer, or to an appropriate affine expression of variables Y_i , for the case of filled

2.2 METHODOLOGY

locations below the bottom layer of the canvas graph.³ We finally note that, for the sake of exposition, the above model was presented in a direct, conceptual form that involves various disjunctions and implications. In order to be addressable by off-the-shelf MILP optimization solvers, we would need to first apply some standard reformulation techniques so as to convert the model in an algebraic, MILP form. We present the fully reformulated model in Section 2.7.

2.2.2 Breaking Model Symmetry

We recognize that a surface patterning model like the one presented in Eqns. 2.1–2.10 is likely to admit multiple equivalently-optimal solutions, as there will typically exist several feasible combinations of values for the canvas occupancy variables, Y_i , that correspond to the same physical design. It is well-known that this kind of model symmetry, also referred to as *model isomorphism* [147], acts detrimentally to the numerical tractability of optimization processes that are based on branch-and-bound principles, such as the ones implemented in standard MILP solvers. To alleviate isomorphism in our model, we propose including a number of symmetry-breaking constraints, which we discuss in this section.

A prominent source of symmetry in our context is the rotational symmetry with respect to our ("two-dimensional") design surface. To that end, Eqns. 2.11 can be added to break this symmetry by requiring that more atoms be located in one half of the tile than the other. The relevant halves of the tile, denoted as location sets I_k^+ and I_k^- , are separated by a plane of symmetry (indexed by k), along which additional canvas locations, I_k^0 , may lie. Figure 2.3 illustrates the planes of symmetry for two example lattices and the associated partitioning of the tile into location subsets. Note that, in each case, constraints can be added for up to two linearly independent planes of symmetry.

$$\sum_{i \in I_k^+} p_i Y_i - \sum_{i \in I_k^-} p_i Y_i \ge 0 \quad \forall \, k \in \{1, 2\}$$
(2.11)

In Eqns. 2.11, the parameters p_i correspond to the inverse of the number of locations that are periodically-equivalent to location *i*. In other words, the existence of an atom in either side of the plane of symmetry must be weighted by the location's effective

³ Since the layer below the bottom layer represented in the graph is fully occupied, all layers further below it are also expected to be fully occupied. In fact, they are guaranteed to be bulk atoms or atoms of the support, and they always contribute to the evaluation of their neighbor's coordination number.



Figure 2.3: Canvas graph partitioning for symmetry breaking. Locations with '+' and '-' labels are in I_k^+ and I_k^- , while locations that fall on the plane of symmetry are in I_k^0 . *Top:* Symmetry planes for the FCC {111} lattice (only two may be used in conjunction). *Bottom:* Symmetry planes for the BCC {100} lattice.

presence in the tile. For example, in the case of a tile such as in Fig. 2.2, atoms 1 and 4 should be attributed a weight of $p_i = 1/3$, atoms 2, 3 and 5 a weight of $p_i = 1/2$, while all other (non-numbered) atoms should be given a full weight, $p_i = 1$.

Additionally, Eqn. 2.12 can be used to break symmetry with respect to translations of designs along the design surface. This works in conjunction with the above constraints that break rotational symmetry by bounding the imbalance in the two halves of the canvas by the sum of atoms directly along the symmetry plane. In practice, this reduces the number of isomorphic feasible solutions to only include those that are approximately balanced around the symmetry planes.

$$\sum_{i \in I_k^+} p_i Y_i - \sum_{i \in I_k^-} p_i Y_i \le \sum_{i \in I_k^0} p_i Y_i \quad \forall k \in \{1, 2\}$$
(2.12)

Finally, one may also eliminate symmetry in the direction perpendicular to the design surface. It should be noted that this symmetry is already partially broken by the setup of our optimization problem, as Eqn. 2.6 and the prefixing, respectively, of filled and void layers below and above our canvas graph effectively remove the potential for a design to flip along the perpendicular direction. However, there is still the possibility

for designs to translate up and down. To that end, we propose also the use of Eqn. 2.13, which requires the placement of at least one atom in the top-most layer of the canvas.

$$\sum_{i\in I^{\text{top}}} p_i Y_i \ge 1 \tag{2.13}$$

Alternatively, translation along the perpendicular direction can be broken via Eqn. 2.14, which simply enforces the presence of an atom in the center of the top layer. Note that, although this constraint fulfills the requirement of Eqn. 2.13, placing an atom in any specific position may over-constrain the feasible space in view of Eqns. 2.12. Hence, using Eqn. 2.14 comes at the expense of having to drop Eqns. 2.12 from the formulation.

$$Y_{\text{center}} = 1, \tag{2.14}$$

where i = center is an appropriate canvas location.

In conclusion, two variants of symmetry-breaking constraints are proposed. The first utilizes Eqns. 2.11–2.13, while the second uses Eqns. 2.11 and 2.14. We remark that, despite the fact that employing these symmetry-breaking constraints (either of the two versions) may not entirely eliminate symmetry in certain cases, our experience suggests that adding them in the model always improves the solver's performance. We discuss the numerical benefits in more detail in our computational results section.

2.3 COMPUTATIONAL STUDIES

Our optimal surface patterning model of Eqns. 2.1–2.10 (in its MILP representation presented in Section 2.7) was instantiated and solved for a number of benchmark cases. These involved a total of five different combinations of crystallographic lattice types and orientations of the design surface. More specifically, we considered three face-centered cubic (FCC) lattices oriented such that the design surface is aligned with the {100}, {110} and {111} crystallographic planes, respectively, one body-centered cubic (BCC) lattice aligned with the {100} plane, and one hexagonal close-packed (HCP) lattice aligned with the {0001} plane. Note that the FCC, BCC and HCP lattices account cumulatively for the vast majority of transition metal-based, mono-metallic crystals, while the orientations chosen constitute the most stable crystallographic planes exhibited by such crystals [238].

Figure 2.1 depicts the chosen lattices, including representative periodic tiles and the set of lattice locations that the latter contain. Note that, in all five cases, the periodic tiles constitute either square, rectangular or hexagonal prisms. Also note that the border of the

	Table 2.11. Datalee Specific parameters.						
	FCC {100}	FCC {110}	FCC {111}	BCC {100}	HCP {0001}		
CN _{bulk}	12	12	12	8	12		
$CN_{\min}^{ m surf}$ 4 $CN_{ m max}^{ m surf}$ 9	4	4	3	4	3		
	9	9	9	6	9		
$\overline{CN}_{\min}^{\text{surf}}$	2.3	3.3	1.5	2.5	1.5		
$\overline{CN}_{\max}^{surf}$	$8.1\overline{6}$	8	8.5	5.5	8.5		

Table 2.1: Lattice-specific parameters.

tile is always drawn such that it aligns with certain lattice locations, ensuring that the tile is space-filling and consistent in view of periodicity. Table 2.1 summarizes the applicable values for model parameters that depend on the lattice type/orientation combination, such as the coordination number of a bulk atom, CN_{bulk} , as well as coordination number limits for an atom to be considered as part of the crystal's exposed surface, $CN_{\text{min}}^{\text{surf}}$ and $CN_{\text{max}}^{\text{surf}}$. In turn, these parameter choices give rise to attainable bounds on the site descriptor \overline{CN}_i of an atom *i* on the crystal exposed surface. We denote those bounds as $\overline{CN}_{\text{min}}^{\text{surf}}$ and $\overline{CN}_{\text{max}}^{\text{surf}}$. Consequently, with regards to target values for the ideal site descriptor, \overline{CN}^* , we considered all half-integer values that span the range $\left[\overline{CN}_{\min}^{\text{surf}}, \overline{CN}_{\max}^{\text{surf}}\right]$ that is applicable in each lattice type/orientation combination. We remark that, for applications where the target value is below the lower bound, the optimal result is the same as the result for the case of $\overline{CN}^* = \overline{CN}_{\min}^{\text{surf}}$ and, similarly, optimal solutions for the case of $\overline{CN}^* = \overline{CN}_{\max}^{\text{surf}}$ retain their status as optimal when the target value is above the upper bound.

As already mentioned, a tile of limited size and/or depth may adversely affect our ability to obtain the truly optimal design and, hence, one must choose a tile that is sufficiently large. Unless otherwise noted, the results reported in this chapter correspond to those tile sizes that yielded the best objective values attainable by a feasible design in light of the applicable computational resource limits. We discuss the effects of finite tile size later in this section. In each case, given a chosen tile size, the depth of the tile was selected such that the tile was deep enough for Eqns. 2.6 to induce full metal occupancy of the canvas graph's bottom layer. Specific values are provided in Table 2.2. Adding layers beyond this depth would have been meaningless, as all lattice positions in those extra layers would be occupied by atoms of the bulk and the optimal solutions would remain the same (as long as the tile sizes remain the same). We remark that our choice of tile depth

corresponds to contexts where there does not apply any application-related restriction on the thickness of the designed surface pattern. For cases where such restrictions must be taken into account, the depth can be appropriately limited. At the interest of brevity, we will refrain from studying this latter case. However, it should be noted that obtaining optimal solutions for cases with smaller tile depths is easier, in principle, as the resulting model sizes are smaller.

In all cases, the model was optimized using the MILP solver CPLEX 12.6.3 [95]. The relative optimality tolerance was set to zero, while the absolute optimality tolerance was set to the value 0.95, since our model's objective attains purely integer values and, hence, this setting guarantees the optimality of our solutions. A solution pool approach was enabled so as to additionally identify all equivalently-optimal designs, whenever these exist. All other solver settings were left at default values. All runs were conducted using 4 threads of an Intel Xeon E5-2680 (2.80 GHz) processor with 16 GB of available RAM. Finally, it should be mentioned that we used the value $\epsilon = \frac{1}{2CN_{\text{bulk}}}$, which is an appropriate value for the small tolerance in Eqns. 2.5.

2.3.1 Optimal Designs

Figure 2.4 presents the optimal designs for the FCC {111} canvas graph across the full spectrum of target values for the ideal site descriptor, \overline{CN}^* , corresponding to a wide range of catalysis applications. In general, the designs vary drastically as \overline{CN}^* values vary, featuring many transitions in the types of patterns they exhibit. This observation strengthens our motivation to devise a rigorous approach for determining optimal surface patterns.

Some basic trends can be noted. For low \overline{CN}^* values, the ideal sites tend to exist in the top layer of the designed surface. In some cases the optimal sites can be interpreted as the tips of small and closely-packed pyramids (e.g., Fig. 2.4a), while in other cases as lying on the ridge of parallel grooves (e.g., Fig. 2.4d). Conversely, for high \overline{CN}^* values, the ideal sites tend to appear in deeper layers, being located at the bottom of pits (e.g., Fig. 2.40). Intermediate values of \overline{CN}^* give rise to highly non-intuitive patterns, with sharp transitions between them. These intermediate values also tend to exhibit multiplicity of optimal solutions (only one representative design is presented in Fig. 2.4).

A notable case is that of $\overline{CN}^* = 7.5$, which is shown in Fig. 2.4m. Since the native \overline{CN} value of an unpatterned FCC {111} crystallographic plane is indeed equal to 7.5, the

	Tile		Model size			
	Size	Depth	I	# Bin. Vars.	# Cont. Vars.	# Constr.
~	3	4	48	33	96	594
{100	4	6	144	115	288	1,802
FCC	5	8	320	273	640	4,034
	6	10	600	531	1,200	7,602
~	5	3	112	93	224	1,330
[110	7	4	324	115	648	3,926
FCC	9	5	704	273	1,408	4,034
	11	6	1,300	531	2,600	7,602
~	3	4	48	64	96	542
[111	4	7	216	256	432	2,513
FCC	5	10	480	627	960	5,618
	6	13	1,050	1,248	2,100	12,377
~	5	4	64	93	128	770
(1 00	6	5	150	181	300	1,852
BCC	7	6	288	311	576	3,602
	8	7	490	491	980	6,176
1}	3	4	48	60	96	542
000}	4	7	216	217	432	2,513
HCP	5	10	480	524	960	5,618
	6	13	1,050	1,029	2,100	12,377

Table 2.2: Effect of tile dimensions on size of resulting model.

Note: The number of binary variables refers to those that remain free after variable fixing due to symmetry-breaking constraints. Number of constraints does not include variable bound constraints.


Figure 2.4: Optimal FCC {111} surface patterns for various target site descriptor values. Black spheres represent "ideal" sites, while gold spheres represent all other atoms.



Figure 2.5: Comparison of results relevant to the oxygen reduction reaction: (a) Design proposed in Calle-Vallejo et al. [31], (b) Best possible design on tile size 3, (c) Optimal design, and (d) Alternative optimal design.

unmodified surface is itself optimal in this case and, thus, every site on the unmodified surface is an ideal site. This is correctly identified by our model. Furthermore, the result shown in Figure 2.4n is reminiscent of the pattern proposed by Calle-Vallejo et al. [31] as to the optimal surface site for the oxygen reduction reaction with $\overline{CN}^* \approx 8$. For this reaction, an optimal catalyst must balance the energy of adsorption of the reactant oxygen against the energy of adsorption of the product water. The authors argue that introducing pits into the platinum FCC {111} surface results in an approximately threefold higher activity than the unmodified {111} facet, and they propose a pattern on a hexagonal tile of size 3. The periodic tiling of the pattern by Calle-Vallejo et al. [31] results into the design depicted in Figure 2.5a, which features 0.096 ideal sites per unit area. In comparison, our framework can identify a design that is similar to the one proposed in the aforementioned publication, but with the additional efficiency of packing as many as three ideal sites at the bottom of pits in the FCC {111} lattice. This design, which constitutes the best possible solution on a tile of size 3, is depicted in Figure 2.5b and features 0.289 ideal sites per unit area. However, even this design can be further improved by extending the canvas to consider tiles of size 4, leading to the best found design presented in Figure 2.5c with 0.385 ideal sites per unit area. Note that the optimal design in this case is not unique, as there exists the equivalently-optimal design shown in Figure 2.5d.



Figure 2.6: Maximum density of packable ideal sites for various lattices and target site descriptor values.

Our results further highlight the fact that there may be multiple different types of optimal sites that can be considered ideal for a specific application. Figures 2.4f, 2.4h and 2.4i exhibit patterns with two types of optimal sites, which both attain the same optimal site descriptor value. This exposes another important advantage of our framework, namely the ability to blend different optimal sites in a common design, as necessary. By doing so, we can identify better designs than what would have been possible by just attempting to replicate a single type of optimal site periodically.

The variety of optimal designs exhibited for the FCC {111} case is representative of the variety exhibited in the other lattice types and orientation combinations we considered. At the interest of conciseness, we report the full set of results in a more synopsized form via Fig. 2.6, where we present the objective values of the best known solutions we have encountered in each case we considered. More specifically, the plot reports the maximum number of ideal sites, normalized per unit area, as a function of target values for the ideal site descriptor, \overline{CN}^* . The unit of area considered here is α^2 , where α is the lattice's inter-atomic distance, a constant that depends on the specific chemistry of interest (i.e., type of transition metal).

There are no clear trends in optimal packings across the spectrum of \overline{CN}^* values. Intermediate values ($\overline{CN}^* \approx 4 - 6$) tend to have more feasible ways to pack together and, therefore, higher values for the optimal density can be attained in these cases. The overall maximal density that we found in our experiments, 1.154 ideal sites per α^2 of area, was exhibited for the target value of $\overline{CN}^* = 7.5$ by the unmodified FCC {111} and HCP {0001} crystallographic planes. This is a reasonable result, since both these planes expose atoms with a \overline{CN} value of exactly 7.5 and modifying such native–and already very closely-packed–surfaces may only lead to a decrease of the number of ideal sites per unit area. It is also noteworthy that the FCC {111} and the HCP {0001} planes exhibit the same optimal densities in the majority of cases, an observation that can be attributed to the similarly hexagonal nature of their corresponding canvas tiles.

2.3.2 Impact of Tile Size and its Periodicity

As demonstrated with the example of Figure 2.5, a larger tile size allows for the possibility of a more densely-packable pattern to be identified. However, it is obvious that adopting a larger tile size leads to an increase of the resulting MILP model's size in terms of both number of variables and constraints. A summary of tile and model sizes is given in Table 2.2. Our experience suggests that the CPU time required to solve the problem was highly dependent on the number of locations in the tile (i.e., the cardinality of set I). Additionally, the lattice structure and orientation made some instances easier to solve than others because of how prevalent the effects of variable dependency (via Eqns. 2.6) and symmetry-breaking constraints (predominantly, Eqns. 2.14) were in each case.

Ideally, the design tile should be small enough for the model to remain tractable and be optimized relatively quickly. At the same time, we would like to solve the optimization model on a design tile that is as large as possible so that the optimal solution is not adversely constrained by the finiteness of the canvas graph and its associated periodicity considerations. However, in most cases, it is not known a-priori what is the minimum size of the tile that admits the true optimal solution. Interestingly, it is not always clear whether such a minimum size tile exists or whether increasing the size of the tile always provides for a better design. To cope with this issue, we iteratively solved each benchmark example with increasing tile sizes until the problem was unable to be solved to optimality within a CPU time limit of 1 hour. Using this iterative approach, we identified as many tractable solutions as were possible, while getting a sense for the best solution found at the next larger scale. We can then use these results to infer whether or not a larger canvas graph would have yielded better designs.

The most popular trend is when the number of optimal sites per area increases until reaching a stable value at the limit of large tile size, at which point some negligible oscillations may appear due to periodicity effects. This trend is illustrated in Fig. 2.7,

which shows the increase of ideal site density as the tile size increases in the case of a BCC {100} canvas graph with a \overline{CN}^* target value equal to 2.5. As the size of the tile was increased from 4 to 5, the ability to pack ideal sites improved dramatically. However, at the next larger size, the optimal packing included relatively more non-ideal sites per area due to the fact that the true optimal design was not periodically-compatible with that particular tile size. As the size further increased to 7, the optimal packing was re-expressed, and this oscillation shall keep repeating as the size alternates between odd and even integer values. The true optimal density of ideal sites corresponds in this case to the value at odd tile sizes.

In contrast, we encountered some cases that did not stabilize around an optimal density value and, instead, the density showed a monotonic upward trend that is expected to continue as the tile size grows. Figure 2.8 illustrates the case of a BCC {100} canvas graph with a $\overline{CN}^* = 5$ target value. Increasing the tile size manifests in this case the possibility to grow zig-zag features that expose ideal sites on their slopes but not on their ridges and valleys. Designs that exploit the canvas in this way suggest that orienting the lattice along a different plane could serve as a better choice for that particular setting. Cases like this one highlight the fact that designs identified with our framework will generally be exogenously affected by the decision to align the surface with a particular crystallographic plane. To that end, care should be taken to appropriately interpret solutions and to possibly rethink the choice of inert support or base layer crystal cut that is employed.

2.3.3 Impact of Symmetry-Breaking Constraints

In this section we discuss the numerical tractability benefits provided by the incorporation of symmetry-breaking constraints. As already discussed, two versions of such constraints can be employed. Our computational experience determined that, although both approaches improved tractability compared to the practice of not breaking symmetry at all, it was more beneficial to employ the second version, i.e., to use Eqns. 2.11 and 2.14. This can be attributed to the fact that the use of Eqn. 2.14 in conjunction with Eqns. 2.6 leads the MILP presolver to determine that a large number of binary variables Y_i can be fixed (to the value of 1). More specifically, placing an atom at a location on the top layer of the canvas leads to the placement of atoms at below positions, cascading all the way to the bottom layer along a pyramid that accounts for approximately one-third of all locations in the tile.



Figure 2.7: Density of ideal sites in optimal designs across tile sizes. Case of BCC {100} lattice with $\overline{CN}^* = 2.5$.



Figure 2.8: Density of ideal sites in optimal designs across tile sizes. Case of BCC {100} lattice with $\overline{CN}^* = 5$. Two equivalently-optimal designs are presented for each of the cases (b) and (d).

2.4 CONCLUSIONS

Table 2.3 summarizes the difference in the time it took the MILP solver to prove optimality as well as the number of equivalently-optimal solutions found via the solution pool technique. The FCC {111} lattice with a tile size of 4 locations on edge was selected as a challenging problem size to compare computation times. For these cases, each instance was solved with a single thread in order to make a fairer comparison of computation times between models. Consequently, the CPU time limit was extended to eight hours. For the runs without symmetry-breaking constraints, the optimizer typically found the optimal solutions (as this was later shown by the run with symmetry-breaking enabled), but ran out of memory before proving the optimality of a design. With the inclusion of symmetry-breaking constraints, however, the framework's numerical tractability was significantly improved, and we were able to prove the optimal designs in all but two cases. We were also able to achieve a significant reduction in the number of equivalentlyoptimal solutions identified, which eventually reduces the burden for post-framework examination, validation and qualification of the proposed designs by expert opinion.

It should be noted that not all isomorphically-equivalent solutions were excluded from the feasible space when symmetry breaking was incorporated. In some cases, the design was balanced such that there were two or more feasible orientations or translations that satisfied Eqns. 2.11. For example, consider the case of $\overline{CN}^* = 8$, which yields a total of 7 optimal solutions after breaking symmetry. Out of these 7 solutions only 4 solutions were non-isomorphic, two of which are presented in Figures 2.5c and 2.5d. The 3 of the identified solutions were symmetric enough to not be disallowed by symmetry-breaking constraints, differing among each other in the orientation of their triangular pits or straight grooves. This opens the possibility for further strengthening the symmetry-breaking scheme and, hence, the potential for further improvements in overall tractability. It should of course be highlighted that the framework is inclusive in all cases, inasmuch as it shall never exclude all isomorphic representatives of an optimal pattern, providing guarantees that it shall always identify all of the non-isomorphic patterns qualified as optimal under the proposed objective.

2.4 CONCLUSIONS

In this chapter, we demonstrated a novel approach to designing microstructured surfaces of transition metal crystals via use of mixed-integer linear optimization techniques. We developed a surface patterning model, which incorporates the evaluation of appropriate surface site descriptors at every lattice location, and which detects the presence of ideal

	Without Symmetry Breaking				With Symmetry Breaking					
\overline{CN}^*	Opt.	# Opt.	t _{opt}	t _{pool}	Gap	Opt.	# Opt.	t _{opt}	t _{pool}	Gap
	Obj.	Sol.	(min)	(min)	(%)	Obj.	Sol.	(min)	(min)	(%)
1.5	3	≥99,999	1.08	\geq_5	0	3	2,364	≤0.01	0.04	0
2	6	1,431	24.0	58.4	0	6	24	0.214	0.162	0
2.5	9	21	68.9	238	0	9	1	0.652	1.31	0
3	≥ 9	-	≥150	-	39	9	15	5.94	17.7	0
3.5	≥13	-	≥185	-	32	13	34	1.81	9.34	0
4	≥12	-	≥480	-	45	12	5	45.9	97.6	0
4.5	≥10	-	≥134	-	150	10	\geq_7	283	≥197	0
5	≥18	-	≥152	-	30	18	2	12.0	9.19	0
5.5	≥12	-	≥480	-	94	≥12	-	≥480	-	8
6	≥12	-	≥480	-	96	≥12	-	≥188	-	36
6.5	≥ 9	-	≥ 83	-	240	12	\geq_1	306	≥174	0
7	≥ 8	-	≥ 98	-	268	12	\geq_1	405	≥74.9	0
7.5	27	8	19.5	18.5	0	27	1	0.865	0.566	0
8	≥ 9	-	≥118	-	134	9	7	24.7	16.4	0
8.5	3	≥99,999	153	≥56	0	3	2,444	1.14	0.864	0

Table 2.3: Effect of symmetry breaking on numerical tractability and solution multiplicity

Note: t_{opt} is the time spent proving the optimal design and t_{pool} is the additional time spent so as to identify all equivalently-optimal solutions. For cases when a time or memory limit was reached, we report the best known feasible solution and optimality gap by that point.

sites that perform optimally in view of some catalysis application. By packing such ideal sites as densely as possible in a periodic crystal lattice, we can identify catalytic surfaces that exhibit maximum activity.

A comprehensive suite of computational studies, conducted across an array of different lattice types and definitions of ideal lattice sites, demonstrated the effectiveness of the proposed approach in identifying optimal surface patterns. Our results revealed a number of non-intuitive optimal designs but, most importantly, showcased that the optimal surface patterns depend strongly on what type of site is considered to be ideal. To that end, it can be argued that a rigorous approach to identify them—such as the one proposed in this chapter—is necessary to unlock the full potential of the catalyst system.

2.5 NOTATION

Indices

i	canvas location		
j	neighboring canvas location		
k	symmetry plane		
υ	line of a volcano plot		
Sets			
Ι	unique (not periodically-equivalent) canvas locations		
N_i	neighbors to location <i>i</i>		
N_i^b	neighbors in the layer below location <i>i</i>		
Κ	set of planes of symmetry for definition of symmetry-breaking constraints		
I_k^+	locations strictly to the one side of symmetry plane k		
I_k^-	locations strictly to the other side of symmetry plane k		
I_k^0	locations laying directly on symmetry plane k		
I ^{top}	locations in the top layer of the canvas		
<i>I</i> ^{bottom}	locations in the bottom layer of the canvas		
V	set of lines constituting a volcano plot		
Binary V	/ariables		
Y_i	presence of a metal atom at canvas location <i>i</i>		
Z_i	presence of an ideal site at canvas location <i>i</i>		
Continuous Variables			

- CN_i coordination number of location *i*
- \overline{CN}_i average coordination number among location *i*'s neighbors
- *F*^{*} performance level for an ideal site

Parameters

CN _{bulk}	maximum possible coordination number (corresponding to crystal bulk)
CN_{\min}^{surf}	minimum coordination number of an atom in crystal's outer surface
CN_{\max}^{surf}	maximum coordination number of an atom in crystal's outer surface
$\overline{CN}_{\min}^{\text{surf}}$	minimum average neighbor coordination number of an atom in crystal's outer
	surface
$\overline{CN}_{\max}^{surf}$	maximum average neighbor coordination number of an atom in crystal's outer surface
\overline{CN}^*	average coordination number among neighbors of ideal site (target value)
ϵ	small positive number (tolerance)
p_i	inverse of the number of canvas locations that are periodically-equivalent to location \boldsymbol{i}
α	inter-atomic distance in crystallographic lattice
a_v, b_v	parameters of volcano plot lines

2.6 APPENDIX: IDENTIFICATION OF IDEAL SITE DESCRIPTOR VALUE

In this section, we discuss the approach one can follow so as to identify the site descriptors of the best realizable surface site (or sites). By realizable, we refer to the property that the site be admitted as a feasible site by the surface patterning optimization model presented in the Methodology Section. More specifically, given a volcano plot, $f(\overline{CN})$, that governs performance in the context of a given application of interest, we seek to determine a value for the site descriptor \overline{CN} that would maximize function f and qualify a site as an ideal site. The maximizer \overline{CN} value can then serve as a target value in the main model.

The approach presented here involves the modification of a reduced version of the surface patterning model itself. Let an ideal site i^* , which we consider to be occupied by an atom that lies on the crystal's exposed surface. In order to determine its site descriptor, \overline{CN}_{i^*} , we need only consider up to the second-nearest neighbors of location i^* . Therefore, let location set I include location i^* as well as the latter's first- and second-nearest neighbors. The set I can be easily extracted from some applicable canvas graph (without applying any location aliasing due to periodicity). As per the main model, we define occupancy variables Y_i for all $i \in I$, and we also define coordination number variables CN_i for all $i \in N_{i^*}$. The following model applies.

$$\max_{\substack{F^*,Y_i,\\CN_i,\overline{CN}_{i^*}}}$$

s.t.

 F^*

$$Y_{i^*} = 1$$
 (2.16)

$$CN_{\min}^{\text{surf}} \le \sum_{j \in N_i} Y_j \le CN_{\max}^{\text{surf}}$$
 (2.17)

(2.15)

$$\{Y_i = 1\} \Rightarrow \left\{ CN_i = \sum_{j \in N_i} Y_j \right\} \qquad \forall i \in N_{i^*}$$
(2.18)

$$\{Y_i = 0\} \Rightarrow \{CN_i = 0\} \qquad \forall i \in N_{i^*}$$
(2.19)

$$\overline{CN}_{i^*} = \frac{1}{CN_{\text{bulk}}} \sum_{j \in N_{i^*}} CN_j$$
(2.20)

$$\{Y_i = 1\} \Rightarrow \left\{ \bigwedge_{j \in N_i^b} (Y_j = 1) \right\} \qquad \forall i \in I \setminus I^{\text{bottom}}$$
(2.21)

$$F^* \le a_v \overline{CN}_{i^*} + b_v \qquad \qquad \forall v \in V \tag{2.22}$$

$$CN_{\min}^{\text{sum}} \le CN_{i^*} \le CN_{\text{bulk}} \tag{2.23}$$

$$0 \le CN_i \le CN_{\text{bulk}} \qquad \forall i \in N_{i^*}$$
(2.24)

$$Y_i \in \{0,1\} \qquad \qquad \forall i \in I \qquad (2.25)$$

In the above model, the objective (Eqn. 2.15) maximizes the auxiliary continuous variable F^* , which represents the performance level of site i^* , essentially evaluating the volcano plot at the value $\overline{CN} = \overline{CN}_{i^*}$; that is, $F^* = f(\overline{CN}_{i^*})$ in the optimal solution. Equations 2.16 and 2.17 qualify location i^* as a site occupied by a surface atom. Equations 2.18–2.20 apply variable definitions, as per the main model. Equations 2.21 are added to mirror the original constraints (Eqns. 2.6) of the main model. This is so as to guarantee that the ideal surface site remains feasible in the context of the main model and, hence, that the maximum performance level is indeed realizable. Equations 2.22 then enforce the definition of a volcano plot as the piecewise maximum of a number of linear functions, $f(\overline{CN}) = \max_{v \in V} \{a_v \overline{CN} + b_v\}$, where a_v and b_v are the coefficients that determine the v^{th} linear piece.⁴ Note that, in conjunction with the sense of the objective to maximize variable F^* , the inclusion of mere " \leq " inequalities suffice to correctly evaluate the volcano plot due to its concave nature. Finally, Eqns. 2.23–2.25 provide applicable bounds for the continuous variables and declare the binarity of the discrete variables.

⁴ A volcano plot is typically composed of only two pieces; that is, |V| = 2.

The solution of the above model identifies the maximum attainable performance by a physically-realizable site as well as the corresponding site descriptor value that exhibits this performance. Furthermore, it yields the structure of one possible ideal surface site. We must highlight, however, that we do not attempt to pack the occurrence of this particular site in the subsequent, main step, where we solve the surface patterning model. This is because we recognize that typically more than one ideal surface site structures may exist and, thus, our intention in the main step is to maximize the cumulative occurrence of all ideal structures and not the occurrence of any particular one of them.

2.7 APPENDIX: MIXED INTEGER LINEAR PROGRAMMING FORMULATION

 $CN_i \leq CN_{\text{bulk}}Y_i$

Below we present the actual optimal surface patterning model that we used in this study. This model implements the conceptual model of Eqns. 2.1–2.10 in an equivalent, yet fully algebraic, MILP form that is compatible to be optimized by an off-the-shelf MILP solver.

$$\max_{Y_i,Z_i, \\ CN_i,\overline{CN}_i} \sum_{i \in I} Z_i$$
(2.26)

s.t.
$$CN_i \leq \sum_{j \in N_i} Y_j$$
 $\forall i \in I$ (2.27)
 $CN_i \geq \sum Y_i - CN_i = (1 - Y_i)$ $\forall i \in I$ (2.28)

$$CN_i \ge \sum_{j \in N_i} Y_j - CN_{\text{bulk}} (1 - Y_i) \qquad \forall i \in I$$
(2.28)

$$\overline{CN}_{i} = \frac{1}{CN_{\text{bulk}}} \sum_{j \in N_{i}} CN_{j} \qquad \forall i \in I$$
(2.30)

 $\forall i \in I$

(2.29)

$$Y_i \ge Z_i \qquad \qquad \forall i \in I \qquad (2.31)$$

$$CN_{i} \leq CN_{\max}^{\text{surf}}Z_{i} + CN_{\text{bulk}} (1 - Z_{i}) \qquad \forall i \in I \qquad (2.32)$$
$$CN_{i} \geq CN_{\min}^{\text{surf}}Z_{i} \qquad \forall i \in I \qquad (2.33)$$

$$\overline{CN}_{i} - \overline{CN}^{*} \leq +\epsilon Z_{i} + \left(CN_{\text{bulk}} - \overline{CN}^{*}\right)(1 - Z_{i}) \qquad \forall i \in I$$
(2.34)

$$\overline{CN}_{i} - \overline{CN}^{*} \ge -\epsilon Z_{i} - \overline{CN}^{*} (1 - Z_{i}) \qquad \forall i \in I \qquad (2.35)$$

$$Y_{i} \ge Y_{i} \qquad \forall i \in N^{b} \quad \forall i \in I \setminus I^{\text{bottom}} \qquad (2.26)$$

In the above model, Eqns. 2.27 and 2.28 implement the original constraint (Eqn. 2.2) by setting the variable CN_i to the value $\sum_{j \in N_i} Y_j$ only when the binary variable Y_i is activated. Equations 2.29 then implement constraints 2.3 by setting CN_i to the value of 0 whenever Y_i is not activated. The constant CN_{bulk} serves here as a tight big-M coefficient. Equations 2.31–2.35 implement the original constraints 2.5, namely they ensure that the setting $Z_i = 1$ implies all three constraints in the implication's right-hand-side. Finally, Eqns. 2.36 implements the implications of original constraints 2.6.

3

OPTIMIZATION ACTIVE AND STABLE NANOSTRUCTURED SURFACES

Mathematical optimization is well-suited to search this design space with algorithms that provide guarantees of optimality that are not possible with sampling algorithms. In this work, we develop several formulations for catalytic activity and stability as part of mathematical optimization models for designing nanostructured surfaces. Using the oxygen reduction reaction as an example, we show how optimization-based design can be used to efficiently explore the trade-off of activity against stability of surfaces. We furthermore demonstrate how nanostructuring can be applied to increase the expected activity of surfaces under various constraints on the coverage and over-binding of adsorbates. Our approach can be generally applied to other chemistries of interest, and is suitably parameterized such that a wide array of systems can be considered, enabling evaluation of the sensitivity of different systems to constraints on the design space.

3.1 INTRODUCTION

Advances in catalysis are enabling the development of technologies such as proton exchange membrane fuel cells [197, 205, 228], solar-powered hydrogen conversion [124, 230], and catalytic conversion of CO₂ [48, 102, 203]. In each of these cases, nanomaterials have been demonstrated as possible avenues for achieving more active catalysts, with new and complex nanoparticles being synthesized by increasingly sophisticated techniques [34, 77, 111, 139, 242, 248]. However, identifying which nanostructure is optimal for a given application is not straightforward, due to the combinatorial number of possible materials. Many approaches study the variation in nanoparticle reactivity by scanning over simple nanoparticle geometries and correlating the number of exposed sites to reactivity in a "top-down" approach [106, 179, 193, 214]. In a complimentary way, one can study reactions on specific sites of model crystalline surfaces [71, 163, 164] and optimize surfaces in a "bottom-up" manner to exhibit favorable site characteristics. In both cases, computational approaches have been developed to speed up materials discovery and manage the combinatorial complexity of the resulting search space [26, 58, 103, 191, 218–221].

Previous works have demonstrated advantages when tailoring the nanostructure of heterogeneous catalysts. In Calle-Vallejo et al. [31], for example, it was shown that the introduction of pits formed by dealloying, galvanic displacement, or electrochemical destruction on a platinum surface improved the observed reaction rate threefold over the unmodified face-centered cubic (FCC) {111} surface. The authors highlighted the importance of structure on the reactivity, demonstrating that the optimally reactive surface may not be a simple crystal surface. Additionally, Kozlov and Neyman [120] found significant differences in the activation energies of methane activation reactions between nanocluster sites and their respective model crystal surfaces, while Tran and Ulissi [217] identified dozens of non-ideal catalyst surfaces that are active for CO_2 reduction and hydrogen evolution. More recently, Núñez, Lansford, and Vlachos [165] studied the trade-offs between the expected performance of catalysis on perfect surfaces, randomly defected surfaces, and engineered defected surfaces. Arguably, tuning the activity of a surface via means of alloying, applying strain, or introducing defects is viewed as a plausible practice.

While we can theoretically imagine manipulating individual atoms via a microscope [152], the likelihood of industrial relevance will depend on scalable synthesis techniques. In Solis, Barton, and Stephanopoulos [201] the authors formalize the mathematical algorithms for systematically forming complex nanostructures via top-down directed assembly methods such as electric fields. Scalable formation of simple patterns may become practical as we gain more control over the formation of ordered near surface alloys [29, 110]. Regardless of the possible advances in synthesis routes, there is a clear need for systematic ways to search the potential material design space to narrow down the focus on materials that are expected to be high-performing.

In the previous chapter, we showcased how a mathematical optimization approach could address the design of nanostructured materials and how the resulting mixed-integer linear programming (MILP) formulations could be solved for a variety of parameterized example systems. This prior work constituted a first approach for rigorously solving simple nanostructure optimization problems and was demonstrated under a relatively idealistic set of simplifying assumptions. More specifically, the reactivity of catalyst surfaces was approximated by simply trying to pack "ideal" reactive sites, while also assuming that all sites experienced adsorption, effectively ignoring the impact of site coverage. It was also assumed that any designs could be fabricated and would be stable over time scales of interest. Each of these assumptions served to simplify our optimization models and generally led to optimistic nanostructure designs. While these idealized structures are certainly of value as theoretical targets for material performance, we can obtain progressively more realistic targets by making modular additions to our framework. In this work, we demonstrate several approaches that can be used to relax our original simplifying assumptions and obtain more realistic designs.

Firstly, we improve upon the modeling of reactivity by using Boltzmann factors for reaction turnover on surface sites instead of simply counting "ideal" sites. Secondly, we regress and incorporate a model for the surface energy of proposed designs, giving us the capability to constrain the design space to only consider designs that satisfy a threshold of stability. Thirdly, we adopt an approach that considers how over-binding sites may interfere with active sites and thereby deactivate a surface. Using the developed models, we first present a general overview of optimization results over the range of model parameterizations. Finally, we present a case study on the oxygen reduction reaction (ORR) to illustrate the potential insights from such a materials design approach.

3.2 MODELING METHODOLOGY

Many of the basic framework concepts introduced in Hanselman and Gounaris [82] are particularly applicable to this work, and are therefore reiterated here. As a design space, we considered the space of possible periodic patterns of defects in a base crystallographic plane. We defined a "canvas" that consisted of several layers of lattice locations at the surface of a simple crystallographic plane. The canvas was defined in a periodically consistent way, producing infinitely tillable patterns. We then modeled surface atoms' contributions to reactivity via simple structure-function relationships and optimized the placement of atoms on the surface to expose sites with higher reactivity than the unmodified surface. Figure 3.1 illustrates some example optimal nanostructured surfaces that are attainable from this approach. The figure also highlights the fact that the space of possible surface nanostructures is highly combinatorial, often leading to non-intuitive patterns.



Figure 3.1: Example optimal nanostructures obtainable from the approach in Hanselman and Gounaris [82]. Target generalized coordination numbers for reactive sites are labeled below each image (\overline{CN}^*) . Atoms colored in black correspond to sites attaining those numbers exactly.

3.2.1 Modeling Reaction Turnover

Our approach to designing nanostructured surfaces relies on the presence of a relationship between atomic structure and activity. Typically, this relationship is built up from a series of linear scaling relationships that link activity to reaction intermediate adsorption energy and activation energy [80, 81, 164]. These important descriptors of reactivity have also been shown to correlate well with geometric site descriptors, such as the coordination number [32, 42, 180] and generalized coordination number [11, 30, 184, 252]. In simple cases, the series of structure-function relationships results in a volcano plot that demonstrates the Sabatier principle.

In our previous work, we took advantage of the fact that volcano plots are often "steep," meaning that a relatively specific type of reactive site is expected to dominate the turnover on the catalyst surface. An example FCC system is plotted below in Figure 3.2 for the case where $\overline{CN}^* = 8$, demonstrating the fact that sites in a relatively narrow band of descriptors contribute exclusively to reaction turnover. We therefore simplified the goal of the nanostructure design problem to pack as many "ideal" reactive sites as possible.

In this work, we intend to lift this simplification. Instead of a single, most reactive type of site at the tip, or sufficiently near the tip, of the volcano plot, we model an array of types, even if they are to contribute to the overall reaction turnover to a lesser extent. To this end, each type of site is associated with a parameter for its turnover relative to the turnover on the most reactive site, effectively resulting in a Boltzmann factor for reaction turnover. Given a volcano plot, we can enumerate the possible types of reactive sites that

exhibit relative turnover greater than a threshold (we used 0.01), and account for each one's contribution to the overall reactivity. Details on the implementation of this in the context of the optimization model are discussed in Section 3.3. For now, it suffices to highlight that, for the example volcano plot in Figure 3.2, the enumeration results in 15 types of contributing reactive sites.



Figure 3.2: Example volcano plot parameterization and calculated turnover rates, demonstrated for $\overline{CN}^* = 8$.

3.2.2 Modeling Stability

There typically exists a clear trade-off between the activity of metal surfaces and their stability. Recently, in fact, Núñez, Lansford, and Vlachos [165] used metaheuristic optimization techniques coupled with simplified models of surface properties to design defected surfaces that form a Pareto-optimal frontier of activity against stability. As a metric for the latter, the authors used a simple model for surface energy of the defected slabs, effectively assuming that surfaces with low surface energy are less likely to rearrange compared to higher energy surfaces. In this work, we build upon this paradigm by embedding surface energy predictions in an exact (as opposed to heuristic) optimization approach.

Recognizing that the coordination number of metal atoms has been shown to be a useful descriptor for the energy of nanostructured slabs and clusters [181], we regressed surface energies as a function of surface atom coordination and developed a tailored model for the surface energy of our designs that can be directly embedded in our MILP formulation. As a database for exploring the impact of nanostructuring on surface energy, we exhaustively enumerated the set of possible 3 atom \times 3 atom slabs that

result from modifications to the FCC {111} surface. These slabs were formed by stacking atoms layer-by-layer without forming hollow pockets below any atom, thereby leading to plausible surfaces. This process resulted in over one hundred symmetrically-distinct nanostructured slabs to consider. In order to calculate slab surface energies, we employed the approach of Fiorentini and Methfessel [59]. The details of this calculation are deferred to Section 3.7.

The slab formation energies were calculated using the Generalized Adsorption Simulator for Python (GASpy) [216] with the Vienna Ab-initio Simulation Package (VASP) [122, 123], as implemented in the Atomic Simulation Environment (ASE) [93]. Calculations were performed using the Perdew-Burke-Ernzerhof for solids (PBEsol) [173] functional along with the default pseudopotential supplied by VASP version 5.4. Bulk relaxations were performed with a k-point grid of $10 \times 10 \times 10$, an energy cut off of 500 eV, and with only isotropic relaxations allowed, while slab relaxations were performed with a k-point grids of $4 \times 4 \times 1$ and an energy cutoff of 350 eV. For slab relaxations, we fixed atoms more than 3 Å from the top and bottom of the slabs in the scaled Z-direction. No spin magnetism or dispersion corrections were included.

Stability Model Regression

Given the database of slab surface energy calculations, we were able to regress a simple bond-counting model for predicting the surface energy of larger slabs. As descriptors, we considered the count of atoms on the nanostructured surface with coordination between 3 and 11, normalized against the number of atoms in the FCC {111} plane (i.e., 9 for the 3×3 slab). This linear predictor takes the form of Eqn. 3.1, where D_p are the counts of atoms with coordination p, A_p are the coefficients for coordination p, and A_0 is the model intercept.

$$E^{\text{surf}} = A_0 + \sum_{p=3}^{11} A_p D_p \tag{3.1}$$

In Figure 3.3 we summarize the regressed linear model for surface energy against surface atom coordination, while we provide the exact coefficient values in the Supporting Information.

Notably, two important features of the surface energy model allow us to more efficiently encode Eqn. 3.1 in MILP models. First, the contributions to surface energy can be broken down into a per-site basis. Secondly, the model contributions are roughly linear with respect to coordination number. Using these features, we can reinterpret the model by



Figure 3.3: Linear regression of surface energy against coordination

breaking up contributions to the surface energy on a per atom basis and using simpler expressions based on coordination number. For this, we transform the model, from variables D_p for the count of sites with a given coordination, to a model with variables CN_i for the coordination of each site $i \in I^{\text{surf}}$, where I^{surf} is the set of surface sites in a given design. The rearranged model is given below in Eqn. 3.2 and, with minor modification, can be embedded directly in our MILP surface design models, since the latter already features the necessary variables to encode coordination numbers as part of the structure-activity relationship. A summary of the identified coefficients is provided in Section 3.8.

$$E^{\text{surf}} = A_0 + \sum_{i \in I^{\text{surf}}} \left(\beta C N_i + \gamma\right)$$
(3.2)

3.2.3 Modeling Coverage

Many density functional theory (DFT) adsorption studies include data from simple planar or stepped surfaces of a single metal, displaying one or a few types of sites [72]. More precisely, these surfaces may display multiple potential binding sites (i.e., on top, hollow, bridge), but the strongest binding site is typically dominant in low-coverage environments due to relatively low barriers between binding configurations. In this way, the metric of activation energy plotted on the traditional volcano plot is the activation energy of particular binding configuration on a surface. In some cases, the adsorption energy can be shown to be significantly dependent on surface coverage, and therefore, activation

energies should be evaluated for the expected coverage and surface configuration. [25, 113, 194]

When considering nanostructured materials, the volcano plot still serves to reflect the dependence of activation energy on site descriptors; however, the reactivity of the nanostructured surface may not be directly inferred from the volcano plot. With multiple types of sites present on a surface, the overall surface reactivity should be a weighted combination of the reactivity on each type of site. At the extreme of 100% coverage, all sites should contribute to the turnover of the reaction according to their individual site activation energies (i.e., overall reactivity is determined by equally weighting all sites). At the extreme of low coverage, the presence of stronger-binding sites and the mobility of adsorbates on the surface becomes important to model.

The impact of coverage on adsorption energies and associated chemical reaction pathways is commonly studied for the case of planar surfaces, [108, 194, 240] but poorly described on nanostructured or defected surfaces. In Bray, Smith, and Schneider [25], the authors identify a wide range of adsorption configurations across different coverage levels for a low-symmetry stepped surface. Notably, the authors highlight the increased complexity of modeling coverage on low-symmetry surfaces as well as the sensitivity to adsorption on surface kinks. In Xu and Kitchin [240], the authors identify some scaling relations that hold for adsorption energies across a range of coverages, but the conclusions are particular to specific similarities in geometries of adsorption sites.

In general, we would like to model the likelihood of adsorption and diffusion [70, 171] on the catalyst surface but observe that this would become prohibitively complicated to encode in MILP models. For our optimization models, we propose two simple ways to approximately incorporate the effect of coverage. As a starting point, we can formulate our MILP to prohibit adsorption sites that bind too strongly according to the volcano relationships. This can be thought of as reducing the count of such sites to fall below a budget. In this way, even if some adsorbates irreversibly bind to attractive sites on the surface, some fraction of adsorbates may still be able to adsorb on more reactive sites. A second, stricter approach is to require that the reactive sites also be the strongest adsorbing sites on the surface. This pessimistic approximation is expected to be particularly useful in modeling the situation at the limit of low coverage. The implementation of these two approaches is described in more detail in Section 3.3.3 below.

3.3 MATHEMATICAL OPTIMIZATION FORMULATION

Given a model for the activity and stability of catalyst surfaces, our approach calls for formulating mathematical optimization models to identify optimal nanostructure designs. We first present a base model that takes as input a function that predicts activity from atom coordination. Then, we present several sets of modular constraints that encode the effects of surface energy, surface deactivation from over-binding sites, and adsorbate surface coverage. The model is generically parameterized such that optimal designs can be found in a range of systems of interest and for a series of increasingly restrictive constraints. In all cases, the models include discrete decisions and linear constraints, leading to MILPs that we present here via implication logic. In several cases, there are additional modeling efficiencies that can be employed. The more efficient MILP formulation that we actually used in our computational studies is presented in detail in the Supporting Information.

3.3.1 Packing Reactive Sites

The key decision variables, Y_i , correspond to the choice of atoms at lattice sites $i \in I$, where *I* represents the periodic slab locations used as the "canvas" for the design. From the placement of atoms, the coordination number, CN_i , can be counted via Eqns. 3.4 and 3.5. The generalized coordination number, \overline{CN}_i , is counted via Eqn. 3.6. The presence of a reactive site in location *i* is indicated via a binary variable Z_i and imposes several requirements on the site (Eqn. 3.7) that can be generically expanded to match the application of interest. Here, it requires that an atom be present in the specific location, that this atom's coordination be within reasonable bounds to be considered on the surface, and that the generalized coordination number be within bounds to be considered reactive. The identity of reactive sites is further refined by assigning a type of reactive site, indicated by X_{ic} for all sites $i \in I$ as well as all types $c \in C$. In Eqns. 3.8 and 3.9, we assign types of active sites based on their value of generalized coordination number and link them to the broader definition of reactive sites. In Eqn. 3.10 we require that atoms be stacked on top of each other, forming well-connected surfaces and disallowing low-coordinated atoms. Finally, in Eqns. 3.11–3.15 we declare the type and place bounds on this optimization model's variables.

As the objective function (Eqn. 3.3), we consider a general weighting of the variables X_{ic} , indicating the contribution of different conformations to the reactivity of the surface. For example, one could choose α_c weights as pure zeros and ones, aiming to only pack "ideal" conformations on the surface, as we previously demonstrated in Hanselman and Gounaris [82]. Alternatively, a set of weights for the relative turnover rate of sites can be modeled, allowing for less than ideal contributions to reactivity.

Similar to our observation in Hanselman and Gounaris [82], we found that the high degree of symmetry in our design space hindered our ability to optimize designs on practically sized tiles. This symmetry is due to the fact that multiple equivalent translations and rotations of fully-formed designs are feasible in the original design space. This requires the optimization algorithm to search a branch and bound tree that is several times larger than necessary, exponentially increasing the difficulty of solving the optimization problem [147]. In this work, we broke symmetry by choosing to fix a single atom in the top plane of the design canvas. This resulted in a pyramid of locations below the fixed atom that were immediately also fixed as a result of Eqn. 3.10, anchoring the design and reducing the number of possible equivalent translations and rotations.

While we tested several other approaches for breaking symmetry, none outperformed this simple variable fixing, and therefore are not presented here.

$$\max_{\substack{Y_i, CN_i, CN_i, \\ X_{ic}, Z_i}} \sum_{c \in C} \alpha_c \sum_{i \in I} X_{ic}$$
(3.3)

s.t.
$$\{Y_i = 1\} \Rightarrow \left\{ CN_i = \sum_{j \in N_i} Y_j \right\} \quad \forall i \in I$$
 (3.4)

$$\{Y_i = 0\} \Rightarrow \{CN_i = 0\} \qquad \forall i \in I$$
(3.5)

$$\overline{CN}_{i} = \frac{1}{CN^{\text{bulk}}} \sum_{i \in I} CN_{i} \qquad \forall i \in I$$
(3.6)

$$\{Z_{i} = 1\} \Rightarrow \left\{ \begin{array}{c} Y_{i} = 1\\ CN_{LB}^{\text{surf}} \leq CN_{i} \leq CN_{UB}^{\text{surf}}\\ \overline{CN}_{LB}^{*} \leq \overline{CN}_{i} \leq \overline{CN}_{UB}^{*} \end{array} \right\} \quad \forall i \in I$$

$$(3.7)$$

$$\{X_{ic} = 1\} \Rightarrow \left\{ \overline{CN}_{LB}^{c} \le \overline{CN}_{i} \le \overline{CN}_{UB}^{c} \right\} \qquad \forall i \in I, \forall c \in C$$

$$\sum_{c \in C} X_{ic} = Z_{i} \qquad \forall i \in I$$

$$(3.8)$$

$$\forall i \in I$$

$$(3.9)$$

$$\{Y_i = 1\} \Rightarrow \{Y_j = 1\} \qquad \forall i \in I, \forall j \in N_i^{\text{below}}$$
(3.10)
$$\forall i \in I, \forall j \in N_i^{\text{below}}$$
(3.11)

$$Y_i \in \{0, 1\} \qquad \qquad \forall i \in I \qquad (3.11)$$

$$CN \in [0, CN^{\text{bulk}}] \qquad \qquad \forall i \in I \qquad (3.11)$$

$$CN_i \in \begin{bmatrix} 0, CN^{\text{bulk}} \end{bmatrix} \qquad \forall i \in I \qquad (3.12)$$

$$\overline{CN}_i \in \begin{bmatrix} 0, CN^{\text{bulk}} \end{bmatrix} \qquad \forall i \in I \qquad (3.13)$$

$$Z_i \in \{0,1\}$$
 $\forall i \in I$ (3.14) $X_{ic} \in \{0,1\}$ $\forall i \in I, \forall c \in C$ (3.15)

3.3.2 Encoding Surface Energy

Motivated by the surface energy model identified in Eqn. 3.2, we formulated a generic block of constraints to encode the contribution from surface atoms via a logical implication. In Eqn. 3.16 we break down the prediction of the surface energy, E^{surf} , into contributions on a per site basis, denoted as E_i . In Eqns. 3.17 and 3.18, we require that any placed atom have a contribution greater than a piecewise linear function and that empty sites have zero contribution. The variable bounds of the two types of introduced variables are given in Eqns. 3.19 and 3.20, respectively.

The upper bound on surface energy serves to constrain the design space to include only lower energy–and therefore more stable–surfaces. Choosing a value for this bound is not straightforward, but may be inferred from an analysis similar to the Wulff construction for determining nanoparticle shape [16]. More specifically, the highest energy facet of a nanoparticle that is exhibited in the application of interest is a plausible upper bound, as we can imagine replacing that nanoparticle facet with our nanostructured surface. Furthermore, we find that it is informative to parametrically optimize the resulting optimization models and identify a hierarchy of optimal designs under increasingly tight constraints on surface energy, establishing the trade-off (Pareto) frontier between activity and stability.

$$E^{\text{surf}} = A_0 + \sum_{i \in I} E_i$$
(3.16)

$$\{Y_i = 1\} \Rightarrow \{E_i \ge \beta C N_i + \gamma\} \quad \forall i \in I$$
(3.17)

$$\{Y_i = 0\} \Rightarrow \{E_i = 0\} \qquad \forall i \in I \tag{3.18}$$

$$E_i \in [E_{LB}, E_{UB}] \qquad \qquad \forall i \in I \tag{3.19}$$

$$E^{\text{surf}} \in \left| E_{LB}^{\text{surf}}, E_{UB}^{\text{surf}} \right|$$
 (3.20)

3.3.3 Accounting for Adsorbate Coverage

In our models we assume that all surface sites can potentially experience adsorption and are equally accounted for in the objective. However, at the limit of low coverage, the sites with the strongest adsorption energies will be covered first and may modify the adsorption energies of other nearby sites, thereby changing and possibly reducing their contribution to activity. We have developed two approaches to better account for reactivity at the low coverage regime. In the first approach, we attempt to mitigate the effect of strongly-adsorbing sites by constraining the number of such sites to be below a budget. In the second approach, we pessimistically assume that only the strongest adsorbing sites contribute to the reactivity of the surface and appropriately modify the constraints for indicating reactive sites.

Budgeting Over-binding Sites

In this approach, we seek nanostructured surface designs that avoid strongly-binding sites, which are assumed to be relatively unreactive for reactions of interest. More

specifically, if a site falls below some tolerance, $\Delta \overline{CN}^{ob}$, from the target generalized coordination number, this can be indicated via an auxiliary binary variable Q_i that we introduce to the model for this purpose. The count of such sites can then be constrained to be below an "allowable" budget. This corresponds to the assumption that adsorbates will prefer to adsorb on strong-binding sites before spilling over to other adsorption sites. By setting $\Delta \overline{CN}^{ob}$ to a large number, we are only prohibiting sites that very strongly bind the reaction intermediates, whereas if we choose a small value, we can prohibit any sites that are slightly more attractive than the ideal reaction sites.

In Eqn. 3.21, we define a simple cutoff in terms of generalized coordination number, but our model can more generally support more complicated descriptions of over-binding sites, as required. In Eqn. 3.22 we indicate the presence of an over-binding site with binary variable Q_i . In Eqn. 3.23 we limit the presence of such sites to be below a budget N^{ob} , effectively requiring most of the adsorption to take place on reactive sites.

$$\overline{CN}^{\rm ob} = \overline{CN}^* + \Delta \overline{CN}^{\rm ob}$$
(3.21)

$$\left\{\overline{CN}_{i} \leq \overline{CN}^{\text{ob}}\right\} \Rightarrow \left\{Q_{i} = 1\right\} \quad \forall i \in I$$
(3.22)

$$\sum_{i \in I} Q_i \le N^{\text{ob}} \tag{3.23}$$

$$Q_i \in \{0,1\} \qquad \qquad \forall i \in I \qquad (3.24)$$

Requiring Coverage of Reactive Sites

Using similar MILP logic, we can incorporate a more explicit model for the expected adsorption on the nanostructured surface. As a first approximation, we can model adsorption as only taking place on the lowest-coordinated sites, which tend to be the stronger-binding sites. More specifically, we introduce a new binary variable C_i to encode the fact that a location *i* is covered. Then, in Eqn. 3.25 we identify the lowest value of the generalized coordination number for the sites with atoms present, \overline{CN}^{cov} , while in Eqn. 3.26 we require that sites considered as covered have coordination equal to

 \overline{CN}^{cov} . Finally, in Eqn. 3.27, we require that reactive sites only be counted if they are also expected to be covered.

$$\{Y_i = 1\} \Rightarrow \left\{\overline{CN}^{cov} \le \overline{CN}_i\right\} \qquad \forall i \in I$$
(3.25)

$$\{C_i = 1\} \Rightarrow \begin{cases} \overline{CN}_i \le \overline{CN}^{\text{cov}} \\ Y_i = 1 \end{cases} \quad \forall i \in I$$
(3.26)

$$\{Z_i = 1\} \Rightarrow \{C_i = 1\} \qquad \forall i \in I \qquad (3.27)$$

$$\overline{CN}^{\text{cov}} \in \left[0, CN^{\text{bulk}}\right] \qquad \forall i \in I$$
(3.28)

$$C_i \in \{0,1\} \qquad \qquad \forall i \in I \qquad (3.29)$$

3.4 RESULTS AND DISCUSSION

The formulated MILP models were parameterized so that they can represent an array of volcano plots, stability thresholds, number of over-binding sites, and coverage. Specific MILP formulations are provided in Section 3.9. Here, we present some general observations for example systems, illustrating the flexibility of the modeling framework.

As an example of a design space, we chose to use a slab of size 4×4 and 7 layers to allow for any design that satisfies Eqn. 3.10. Regarding the use of a volcano plot to govern activity, there are several parameters of interest that could be investigated. At the interest of simplicity of the exposition, however, we shall adopt throughout our computations the shape (i.e., the slopes and minimum activation energy value) of the volcano plot for the oxygen reduction reaction presented in Calle-Vallejo et al. [31], while sliding its tip horizontally to mimic a possible variety of application chemistries. Then, for each target generalized coordination number of interest, we computed turnover rates at room temperature for the activation energy defined in the corresponding volcano plot by solving our optimization model.

We consider three general cases of models. First, we solved the base formulation (Eqns. 3.3–3.15) with the additional constraints on surface energy (Eqns. 3.16–3.20). Next, we solved models with the base formulation, stability constraints, and the block of constraints on the number of over-binding sites given in Eqns. 3.21–3.24. Finally, as an alternative to modeling over-binding sites, we solved models with the base formulation, stability constraints, and coverage constraints defined in Eqns. 3.25–3.29.

Our models were parameterized with a description of ideal reactive sites (CN^*) , a maximum allowable values for surface energy (E_{UB}^{surf}) , a definition of over-binding sites (\overline{CN}^{ob}) , and a corresponding budget of such sites (N^{ob}) , where applicable. In all cases, the optimization solver CPLEX 12.8.0 was able to either identify optimal solutions or prove infeasibility of the model within the one hour time limit on a standard desktop computer.

Figure 3.4 summarizes some example results. On each plot, we show the objective value (corresponding to multiples of turnover on ideal reactive site) for various levels of the surface energy constraint. Lines that are lower on the plot have lower surface energy and therefore are more stable but exhibit fewer reactive sites. In general, nanostructuring is able to introduce additional ideal reactive sites that are unavailable in low surface energy structures. Figure 3.5 demonstrates this trend for the case of $\overline{CN}^* = 3.5$. However, there are some exceptions where the optimal design for the target application is both stable and reactive. For example, in the cases of $\overline{CN}^* = 7.5$ and $\overline{CN}^* = 6.5$, the optimal design is the base FCC {111} plane or a singly defected {111} plane, respectively.

Scanning across Figures 3.4a–3.4c, we notice a general decrease in the achievable reactivity due to increasingly stringent constraints on over-binding sites and coverage. By comparing Figure 3.4b and Figure 3.4c, we observe a drastic reduction in the objective values for cases with $\overline{CN}^* = 6$, 7, or 8 due to the constraints disallowing any over-binding sites. Similarly, across Figure 3.4c and Figure 3.4d, most of the designs remain the same or decrease in quality when coverage is explicitly modeled. However, in one case, $\overline{CN}^* = 8$, the optimal design improves slightly because non-ideal sites that were previously considered over-binding (and thus were forbidden) can serve as the explicitly-modeled adsorption sites. Similar comparisons can be made in many cases, providing hints about the sensitivity of each application to the various constraints on the design space and allowing practitioners to determine the relative importance of off-target reactivity, over-binding sites, coverage, and stability.

3.4.1 Case Study: Oxygen Reduction Reaction

As demonstrated in the previous section, our optimization framework is generically able to address a variety of systems. In this section, we focus on a particular example to demonstrate the possible insights that can be gained from the optimal solutions. Specifically, we are considering the oxygen reduction reaction (ORR), a key limiting reaction in proton exchange membrane fuel cells [195]. As identified in Calle-Vallejo et al.



Figure 3.4: Trends in quality of designs for a range of descriptions of ideal reactive site and constraints on the design space. Each line represents a different constraint on surface energy. Parameters for constraints on over-binding sites and coverage are given below each graph.

[31], the ideal reaction site has generalized coordination $\overline{CN}^* = 8.0$. The commonly used baseline material for comparison is the platinum FCC {111} surface with generalized coordination $\overline{CN}^* = 7.5$. Here, we aim to identify nanostructured surfaces that expose sites with slightly higher generalized coordination number than the base FCC {111} surface.

In the entirely unrestricted case (i.e., no constraints on surface energy, over-binding sites, or coverage), we find a pitted surface with highly reactive sites around closely packed pits on the surface (see Figure 3.6a). Upon adding a constraint on the number of allowed over-binding sites ($\overline{CN}^{ob} = 4.5$, $N^{ob} = 0$), we find a different structure with reactive sites at the bottom of ridges in the surface (see Figure 3.6b). Note how, in the first case, the design has 6 ideally reactive sites per 4 × 4 tile, while the design in the second case



Figure 3.5: Example optimal surfaces for $\overline{CN}^* = 3.5$ under increasingly restrictive surface energy constraints. In each figure the sites that contribute to reactivity are colored black.

exhibits 4 ideal reactive sites per such tile. Furthermore, when we incorporate a constraint on the surface energy, the optimal design changes to a pattern of adatoms on the FCC $\{111\}$ plane (see Figure 3.6c). In this case, there are no sites with ideal site descriptors, but several sites that partially contribute, resulting in an objective value corresponding to 1.22 ideally reactive sites per tile. If we instead choose to model coverage only on the lowest coordinated sites, each of these solutions are sub-optimal, since they each contain unreactive, low-coordinated sites. In this case, the optimal solution defaults to the unmodified FCC $\{111\}$ surface, with an objective value of 0.39 ideal reaction site equivalents (see Figure 3.6d).

These results highlight a recurring theme arising from our optimization-based design framework. In the most optimistic case, we have nanostructured surfaces that tend to exhibit relatively complicated patterns and are high in energy. As more realistic constraints are applied, the high-energy sites are prohibited and the optimal patterns become simpler. Eventually, only simple crystal planes are stable enough to satisfy the most stringent requirements. Importantly, the spectrum of optimal designs under various restrictions should all be collected and analyzed via some secondary criteria. Those nanostructured designs that pass further screening can serve as targets for future material synthesis efforts, as they constitute non-intuitive solutions that may improve upon the simple planar surfaces.

In general, one of the key benefits of the proposed mathematical optimization approach is its ability to systematically search the design with guarantees that we shall find the best design up to the level of detail with which the system is modeled. In particular, we have shown how to encode in the model detailed considerations about the activity, stability, and coverage, leading to better screening of candidate material structures.







Figure 3.6: Example optimal designs for the ORR case. In each figure, the sites that contribute to reactivity are colored black.

Furthermore, when higher-fidelity comparisons are needed, the proposed approach allows for the collection of sequences of high-performing designs (beyond the optimal one) by employing the so-called "solution pool" feature of state-of-the-art optimization solvers. Collecting such sequences enables additional screening against criteria that might not have been explicitly accounted for in the optimization model.

3.5 CONCLUSIONS

3.5 CONCLUSIONS

In this work, we demonstrated several techniques for designing nanostructured reactive surfaces via mathematical optimization models. We considered the trade-off of activity versus stability for defected surfaces and rigorously optimized to identify patterns that are provably optimal. We showed how to model general contributions to surface reactivity by using indicators for multiple types of reactive sites. Additionally, we regressed a simplified model for the surface energy of defected surfaces that was embedded directly into the optimization formulation, while we proposed enhancements of the latter to account for the effects of adsorbate coverage. Our results for the oxygen reduction reaction highlighted the variety of designs that can be reactive under different assumptions. Overall, the approach of designing nanostructures via mathematical optimization establishes optimistic targets of material performance and can serve as a systematic guide for future synthesis efforts.

3.6 NOTATION

Indices

р	term in surface energy model
i, j	canvas site
С	type of active site
Sets	
Ι	canvas sites
$I^{\rm surf}$	surface sites in a given design
N_i	canvas sites neighboring to site <i>i</i>
N_i^{below}	canvas sites below site i
С	types of active sites

Variables

D_p	count of sites with coordination p
Y_i	presence of an atom at site <i>i</i>
CN_i	coordination number of site i
\overline{CN}_i	generalized coordination number of site \boldsymbol{i}
Z_i	presence of a reactive site at i
X_{ic}	presence of reactive site of type c at site i
E^{surf}	surface energy of slab
E_i	contribution of site i to slab surface energy
Q_i	presence of over-binding site at i
\overline{CN}^{cov}	generalized coordination of covered sites
C_i	presence of coverage at site <i>i</i>
Parameters

A_0, A_p	coefficients of regressed surface energy model
α _c	contribution to objective function of reactive site of type c
CN^{bulk}	coordination of bulk lattice
$CN_{LB}^{ m surf}$, $CN_{UB}^{ m surf}$	lower, upper bounds on coordination number for surface sites
$\overline{CN}_{LB}^*, \overline{CN}_{UB}^*$	lower, upper bounds on generalized coordination for reactive sites
$\overline{CN}_{LB}^{c}, \overline{CN}_{UB}^{c}$	lower, upper bounds on generalized coordination number for reactive sites of
	type c
β,γ	coefficients of per atom contributions to surface energy
E_{LB}, E_{UB}	lower, upper bounds on per atom contribution to surface energy
$E_{LB}^{ m surf}$, $E_{UB}^{ m surf}$	lower,upper bounds on slab surface energy
$\overline{CN}^{\mathrm{ob}}$	maximum generalized coordination number of over-binding sites
$\Delta \overline{CN}^{\mathrm{ob}}$	offset in generalized coordination number between ideal
	and over-binding site
N^{ob}	number of permitted over-binding sites

3.7 APPENDIX: SURFACE ENERGY CALCULATION

In order to accurately calculate slab surface energy, we employed the approach of Fiorentini and Methfessel [59]. Here, we briefly review the calculation steps. First, we calculated the slab formation energies for a series of slabs with increasing number of bulk layers. By fitting a linear regression between the DFT-calculated zero-point energies and the number of atoms in the slab, we can identify the "zero-thickness" energy, which is equivalent to the surface energy due to both sides of the slab. We then subtract out the contribution to surface energy from the FCC {111} plane on the bottom of the slab to obtain the surface energy to create the nanostructured surface. As the FCC {111} energy, we use $0.128 \text{ eV}/\text{Å}^2$. An example set of 3×3 slabs with linear regression of zero-thickness energy are shown below in Figure 3.7.



(e) Di l'energies

Figure 3.7: Example extrapolation of DFT calculations to identify zero-thickness surface energy.

3.8 APPENDIX: SURFACE ENERGY MODEL REGRESSION

Given a set of calculations for the surface energy of nanostructured slabs, we can regress a model for the surface energy as a function of site coordination numbers. This is conceptually similar to a simple bond-breaking model, where each bond is given weighting according to the coordination atom of each atom.

In this regression, we first tabulated the number of sites with a given coordination number. Because of the way that slabs were chosen, no sites with coordination number 1 or 2 were present in the dataset. Additionally, we exclude the sites with coordination 12, as they are irrelevant to the formation of surfaces. The count of sites was then normalized by the number of sites in the FCC{111} surface (9 for the 3×3 slabs). The coefficients of the resulting model are given in the below table.

р	A_p	Units
0	1.01E-1	eV/Å ²
3	2.74E-1	$eV/{\rm \AA^2}$ per normalized count
4	2.47E-1	$eV/{\rm \AA^2}$ per normalized count
5	2.03E-1	$eV/{\rm \AA^2}$ per normalized count
6	1.73E-1	$eV/Å^2$ per normalized count
7	1.17E-1	$eV/{\rm \AA^2}$ per normalized count
8	6.63E-2	$eV/{\rm \AA^2}$ per normalized count
9	2.55E-2	$eV/{\rm \AA^2}$ per normalized count
10	-2.38E-2	$eV/{\ensuremath{\mathring{A}}}^2$ per normalized count
11	-5.18E-2	eV/Å ² per normalized count

 Table 3.1: Surface energy model parameters

Note how the values of the regressed coefficients of the slab surface energy model were approximately linear with respect to coordination number (see also Figure 3.3b). Although, in principle, a general piecewise linear model for the site contributions to surface energy could be embedded in our MILP formulation, we decided to exploit the fact that the trend was roughly linear and to instead embed a simpler set of linear



Figure 3.8: Graphical interpretation of the simplified constraints for surface energy

constraints (Eqns. 3.49–3.51). The parameters for the the latter are given in the below table, while the constraints themselves are graphically illustrated in the associated figure.

Term	Value	Units
A_0	1.01E - 1	eV/Å ²
eta^1	-4.29E-2	eV/Å ² per CN per site
γ^1	4.15E-1	$eV/Å^2$ per site
β^2	5.18E-2	$eV/Å^2$ per CN per site
γ^2	-6.21E-1	eV/Å ² per site

Table 3.2: Simplified surface energy model parameters

3.9 APPENDIX: DETAILED MIXED INTEGER LINEAR PROGRAM FORMULATION

Base Model

$$\begin{array}{ll} \max_{Y_{i} \in N_{i} \in N_{i}} & \sum_{c \in C} \alpha_{c} \sum_{i \in I} X_{ic} & (3.30) \\ \text{s.t.} & CN_{i} \leq \sum_{j \in N_{i}} Y_{j} & \forall i \in I & (3.31) \\ & CN_{i} \geq \sum_{j \in N_{i}} Y_{j} - CN^{\text{bulk}} (1 - Y_{i}) & \forall i \in I & (3.32) \\ & CN_{i} \leq CN^{\text{bulk}} Y_{i} & \forall i \in I & (3.33) \\ & \overline{CN}_{i} = \frac{1}{CN^{\text{bulk}}} \sum_{i \in I} CN_{i} & \forall i \in I & (3.34) \\ & Z_{i} \leq Y_{i} & \forall i \in I & (3.35) \\ & CN_{i} \geq Z_{i}CN_{LB}^{\text{suff}} + (1 - Z_{i})CN^{\text{bulk}} & \forall i \in I & (3.37) \\ & \overline{CN}_{i} \geq Z_{i}\overline{CN}_{LB}^{\text{suff}} + (1 - Z_{i})CN^{\text{bulk}} & \forall i \in I & (3.38) \\ & \overline{CN}_{i} \geq Z_{i}\overline{CN}_{LB}^{\text{suff}} + (1 - Z_{i})CN^{\text{bulk}} & \forall i \in I & (3.39) \\ & \overline{CN}_{i} \geq X_{ic}\overline{CN}_{LB}^{c} + (1 - X_{ic})CN^{\text{bulk}} & \forall i \in I & (3.40) \\ & \overline{CN}_{i} \leq X_{ic}\overline{CN}_{UB}^{c} + (1 - X_{ic})CN^{\text{bulk}} & \forall i \in I, \forall c \in C & (3.40) \\ & \overline{CN}_{i} \leq X_{ic}\overline{CN}_{UB}^{c} + (1 - X_{ic})CN^{\text{bulk}} & \forall i \in I, \forall c \in C & (3.41) \\ & \sum_{c \in C} X_{ic} = Z_{i} & \forall i \in I, \forall c \in C & (3.42) \\ & Y_{i} \leq Y_{j} & \forall i \in I, \forall i \in I & (3.42) \\ & Y_{i} \leq Y_{j} & \forall i \in I, \forall i \in I & (3.43) \\ & Y_{i} \in \{0, 1\} & \forall i \in I & (3.45) \\ & \overline{CN}_{i} \in [0, CN^{\text{bulk}}] & \forall i \in I & (3.46) \\ & Z_{i} \in \{0, 1\} & \forall i \in I & (3.47) \\ & \forall i \in$$

 $X_{ic} \in \{0,1\} \qquad \qquad \forall i \in I, \, \forall c \in C \qquad (3.48)$

Encoding Surface Energy

$$E^{\text{surf}} = A_0 + \sum_{i \in I} E_i$$
 (3.49)

$$E_i \ge \beta^1 C N_i + \gamma^1 Y_i \quad \forall i \in I$$
(3.50)

$$E_i \ge \beta^2 C N_i + \gamma^2 \qquad \forall i \in I \tag{3.51}$$

$$E_i \in [E_{LB}, E_{UB}] \qquad \forall i \in I \tag{3.52}$$

$$E^{\text{surf}} \in \left[E_{LB}^{\text{surf}}, E_{UB}^{\text{surf}} \right]$$
(3.53)

Budgeting Over-binding Sites

$$\overline{CN}_i \ge \overline{CN}^{\text{ob}} (1 - Q_i) \quad \forall i \in I$$
(3.54)

$$\sum_{i \in I} Q_i \le N^{\text{ob}} \tag{3.55}$$

$$Q_i \in \{0, 1\} \qquad \forall i \in I \tag{3.56}$$

Requiring Coverage of Reactive Sites

$$\overline{CN}^{\text{cov}} - \overline{CN}_i \le CN^{\text{bulk}} \left(1 - Y_i\right) \quad \forall i \in I$$
(3.57)

$$\overline{CN}_i - \overline{CN}^{\text{cov}} \le CN^{\text{bulk}} (1 - C_i) \quad \forall i \in I$$
(3.58)

$$C_i \le Y_i$$
 $\forall i \in I$ (3.59)

$$Z_i \le C_i \qquad \qquad \forall i \in I \qquad (3.60)$$

$$\overline{CN}^{\text{cov}} \in \left[0, CN^{\text{bulk}}\right] \qquad \forall i \in I$$
(3.61)

$$C_i \in \{0,1\} \qquad \qquad \forall i \in I \qquad (3.62)$$

4

OPTIMIZING OXYGEN VACANCY FORMATION IN DOPED PEROVSKITES

Perovskite materials are being considered for a variety of applications due to their demonstrated capacity to rapidly transport lattice oxygen. Importantly, controlling the dopant concentration in the perovskite lattice has been shown to tune the oxygen vacancy formation energy, an important descriptor for oxygen ion diffusivity. In this chapter, we utilize $BaFe_{1-x}In_xO_{3-\delta}$ as a model perovskite for investigating the role that atomic-scale patterns of substitutional doping at the B-site has on the formation of oxygen vacancies. Using this model material, we demonstrate a framework for evaluating the atomic-scale properties of possible dopant motifs exhibited within a doped perovskite lattice. For each relevant motif, we calculate via density functional theory the oxygen excess energy, which is a robust descriptor for evaluating the bulk oxide ion diffusion. We then formulate and solve a mathematical optimization model to identify patterns of dopant placement that yield materials with desirable properties. These results provide optimistic targets for material performance and may inform future material synthesis efforts.

4.1 INTRODUCTION

Facile oxygen transport is of great importance in a variety of transformative energy technologies. For example, oxygen carriers for transporting oxygen from air into chemical reactors are of the utmost importance for chemical looping combustion and reforming processes [89, 159, 188, 192]. In the context of fuel cells, mixed ion and electron conductors for oxygen transport and reduction have received attention as they alleviate the need for traditional precious-metal catalysts [178, 182, 210]. Similarly, novel oxygen-permeable membranes are of interest in general for oxygen separation and purification [54, 140].

Ceramic materials based on perovskites have been identified as excellent candidates for each of these applications due to their superior stability and tunability.

Perovskites are a family of mixed oxides with the general formula ABO₃, where the "A-site" is typically an alkaline earth metal or lanthanide and the "B-site" is typically a transition metal. Prior research has illustrated the introduction of dopant in either site can have a dramatic impact on the material's performance in various process contexts. In general, it has been observed that the size of dopant in the A-site affects size and distortion of the unit cell, while the choice of B-site dopant impacts the non-stoichiometry available to the material, catalytic properties, and bulk oxide conductivity [157]. In the context of ion conductors for fuel cells, Ishihara, Matsuda, and Takita [98] showed that choices of dopant on both A-sites and B-sites could increase the concentration of oxygen vacancies in the lattice, thereby improving the diffusion of oxygen through the material. Taskin, Lavrov, and Ando [212] showed that introducing a second A-site metal could form a layered structure that improved oxygen diffusion through the lattice significantly. Motohashi et al. [153] demonstrated that double perovskite BaYMn₂O_{5+ δ} was able to release an equivalent of one oxygen atom per (double perovskite) unit cell, a remarkable extent of reduction, in a rapid and reversible fashion.

In this chapter, we aim to consult very localized, atomic level information from traditional computational chemistry tools, such as density functional theory (DFT), and use this information to design "patterns" across much larger size scales. However, due to the vast, combinatorially-complex design space that arises from the many choices for perovskite composition and the possibility of patterned atomic placement of dopant in the lattice, an exhaustive search becomes intractable. To circumvent this challenge and facilitate the search for novel materials, we propose applying rigorous optimization frameworks that are more commonly utilized in the field of process systems engineering research. In order to translate the search for high-performing perovskites into a formal mathematical optimization problem, we first need to establish the impact of dopant structure on the performance of perovskites. Given such a structure-function relationship derived from first-principles, the search for the design of a nanostructured perovskite material that performs optimally in view of some application can then be cast as a mixed-integer linear programming (MILP).

The use of MILP for the design of perovskites becomes possible due to the crystalline nature of such materials, where the atomic placement is restricted to well-defined locations on a lattice, and it is especially advantageous from a numerical perspective due to the great advances in the ability of modern MILP solvers to address relatively large

4.1 INTRODUCTION

scale models. Such benefits have, for example, been demonstrated in Hanselman and Gounaris [82], where the design of patterned nanostructured transition metal surfaces was also cast as an MILP model, allowing the identification of non-intuitive designs out of the myriad possible configurations for such crystalline materials.

Here, we consider a $BaFe_{1-x}In_xO_{3-\delta}$ material that was selected based on previous reports of interesting structure changes in this system [140]. Based on this report and an initial experimental screening of substituted perovskites with the general formula $BaFe_{1-x}M_xO_{3-\delta}$ (M=Al, Co, Cu, In, Mn, Ni, Sr, Ti), indium substitution was found to be the most promising avenue for continued research [132]. Experimental results demonstrated that oxygen desorption could be tuned in the $BaFe_{1-x}In_xO_{3-\delta}$ material with increasing indium concentration resulting in more oxygen production from the material at lower temperatures.

Because the performance of perovskite candidates is intimately related to facile oxygen transport, higher oxygen diffusivity is desirable. The mechanism of diffusion occurs via a hopping mechanism facilitated by vacancies through which the relatively large oxygen anion may travel [66, 156]. The energetics of oxygen vacancy formation energy has been strongly correlated to the ability of these materials to generate vacant sites within the lattice that would allow for oxygen diffusion [12, 47]. This vacancy formation energy has been shown to depend on the local dopant environment, but only relatively simple configurations (i.e., variation in nearest B-sites) have been studied to date. Given the central role played by this descriptor and its attendant effect on chemical looping combustion and reforming efficiency, its precise estimation is required. Such calculations have been previously done in perovskite using empirical interatomic potential based methods [40, 104]. These methods, however, rely on particular parametrization of the potential and are therefore system-specific. In contrast, a first-principles quantum mechanics approach based on DFT provides reliable predictions, as it incorporates the correct physics in the underlying framework. The Hubbard DFT+U method, in particular, has been used to calculate oxygen vacancy formation energies in bulk perovskites that are free from self-interaction errors inherent in conventional electron-correlation functional for mid to late transition metal oxides [136].

In this chapter, we first establish a first-principles understanding of the impact that dopant structure has on the reducibility of our perovskite material. We perform DFT calculations over a set of structural motifs spanning the space of possible dopant configurations around a lattice oxygen. Then, we use the identified structure-function information to formulate mathematical optimization models that identify structures of dopant that

optimize the lattice properties. Finally, we compare our nanostructured results against the expected performance of randomly doped perovskites.

4.2 COMPUTATIONAL METHODS

4.2.1 Predicting Oxygen Excess Energy

Periodic spin-polarized DFT calculations were performed with the Vienna Ab Initio Simulation Package code, version 5.3.5 [121]. The generalized gradient approximation (GGA) formulation of Perdew, Burke and Enzerhoff was employed [172]. The inner core electrons of each atom were described by the projector-augmented wave method [107] and Ba $5s^2/5p^6/6s^2$, Fe $4s^2/3d^6$, O $2s^2/2p^4$ and In $5s^2/5p^1$ electrons were considered as valence electrons. The Kohn-Sham one electron valence eigenstates were expanded in terms of plane-wave basis sets with a cutoff energy of 520 eV using Monkhorst-Pack k-point grid [169]. The drawback of GGA in treating localized partially filled d states was adjusted by using the DFT+U method which uses a Hartree-Fock-type intra-atomic electron-electron interaction, U, properly balanced by the so-called double counting correction [136]. A U value of 4.0 eV was included for Fe derived from previous studies of structural and electronic properties of Fe-based perovskite oxides [131]. To validate the DFT model, we calculated the bulk properties of the parent cubic BaFeO₃ material. The predicted lattice constant is 4.02Å which compares well with the experimental values of 3.97 – 3.99Å [88, 155]. Our calculations indicate that the ferromagnetic (FM) ordering is the most stable with the A-type, C-type and G-type anti-ferromagnetic (AFM) states strongly unfavorable by 2.69, 2.72 and 2.76 eV/formula unit, respectively. The calculated total magnetization of 4.17 μ_B is in good agreement with 3.50 μ_B obtained from experiments [88].

We employed cubic perovskite supercells (see Fig. 4.1) as the structural model, since it was found experimentally that partial introduction of In in BaFeO₃ leads to the stabilization of the cubic phase [140]. To address the role of In substitution, the set of rotationally-unique dopant motifs was enumerated. There are two B-sites that are nearest neighbors to a perovskite lattice oxygen, 8 B-sites that are second-nearest, and 10 B-sites that are third-nearest. In a compromise of complexity against accuracy, we chose to only consider the first two of those B-site shells (i.e., 10 nearest B-sites) in our definition of a motif. This choice has the advantage of keeping the number of possible conformations to a manageable level, while at the same time, allowing motifs to be modeled by supercells



Figure 4.1: Example perovskite cubic unit cell.

that are of a tractable size for DFT calculations. Experimental results suggest that we are interested in materials that have between 10% and 30% dopant, a range which we expand to consider motifs with between 0 and 5 dopant atoms out of the 10 B-sites in the motif. From this space of possible dopant conformations, we enumerated all of the possible ways to incorporate between 0 and 5 dopant atoms in a motif. This resulted in a total of 74 symmetrically unique-configurations to consider.

The energy cost for oxygen removal can be quantified using the following equation:

$$\Delta E_{\rm vac} = E_{\rm defective} - E_{\rm perfect} - \frac{1}{2}E_{O_2}, \tag{4.1}$$

where $E_{\text{defective}}$, E_{perfect} and E_{O_2} represent the energy of the supercell with an oxygen vacancy, energy of the perfect supercell and the energy of the gas phase O_2 molecule in its triplet ground state. The simplest approximation to the vacancy formation energy is the excess energy that only accounts for the first two terms and neglects the energy of the oxygen:

$$E_{\text{excess}} = E_{\text{defective}} - E_{\text{perfect}}.$$
 (4.2)

For each motif, the lattice parameter and the atomic positions were allowed to relax below the maximum force threshold of 0.03 eV/Å. The free energy of oxygen vacancy formation was computed according to:

$$\Delta G_{\rm vac} = G_{\rm defective} - G_{\rm perfect} - \frac{1}{2}G_{O_2}.$$
(4.3)

The Gibbs free energy for the gaseous species is obtained by adding zero-point energy (E_{zpe}) , thermal energy (E_{th}) , *PV* work term, and entropic contributions (*TS*) to the calculated DFT+U electronic energy (E_{el}) : $G_{O_2} = E_{el} + E_{zpe} + E_{th} + PV - TS$ [23]. The E_{th}

term is the sum of translational, rotational and vibrational contributions to the internal energy. The *PV* term can be replaced by *RT*, assuming an ideal gas. The term E_{zpe} and the vibrational component of the entropies of the defective and perfect solid were calculated from the vibrational frequencies using standard methods [44]. The entropy contribution (vibrational entropy) is given by:

$$S = k_B \sum_{i}^{3N} \left[-\ln\left(1 - e^{-\beta\varepsilon_i}\right) + \frac{\beta\varepsilon_i}{e^{\beta\varepsilon_i} - 1} \right], \qquad (4.4)$$

where $\varepsilon_i = hv_i$. The vibrational frequencies are derived from the Hessian matrix using finite difference methods. For the perovskite, the PV term is ignored due to its small contribution as do the translational and rotational components of E_{th} and S. Therefore, only the vibrational component of E_{th} and S are considered. For the defective lattice case, the normal mode frequencies of the first neighbor atoms around the vacancy are computed while the rest are fixed in their relaxed positions. For the perfect counterpart, the retained oxygen atom was included in the normal mode calculations. A supercell with a maximum periodicity of $4 \times 4 \times 4$ containing 320 atoms was used for the energetic calculations. The calculations were performed on the Joule Supercomputer of the National Energy Technology Laboratory (NETL). Housed at NETL's Simulation Based Engineering User Center, the machine achieves 503 TFlops and enables DFT simulations requiring extensive computational resources. Structural optimization, vacancy formation energy evaluation, and vibrational frequency calculations required approximately 330 CPU hours per motif on this computing resource. Overall, we find the numerical convergence of the calculated excess energies to be very good, thus not affecting the physical conclusions drawn (see Appendix 4.6).

4.2.2 Mathematical Optimization Model

Given evaluations of the free energy of oxygen release for each possible motif, we formulated a mathematical optimization model that identifies dopant patterns that pack as many sites with a target oxygen vacancy formation energy as possible. More generally, this model can be used to design patterns of dopant that maximally pack oxygen sites with desired motifs for a variety of energetic objectives. For a design space, we consider a periodic supercell of the perovskite lattice with the placement of dopant in each B-site $j \in J$ as the key decision variable, Y_j . From these variables for dopant placement, we can indicate as variable Z_{ic} the presence of a target conformation $c \in C$ around each oxygen atom $i \in I$ by imposing suitable constraints, Eqns. 4.6-4.7. Here, *C* is the set of feasible

conformations we wish to consider, *I* is the set of oxygen sites in the lattice, and *J* is the set of B-sites in the lattice. The parameter ζ_{ijc} is 1, if conformation *c* features a dopant atom in a B-site *j* around an oxygen atom *i*. The sets of B-sites neighboring to each oxygen atom are denoted as N_i and appropriately account for periodically equivalent locations across the boundary of the supercell. The objective function, Eqn. 4.5, is the number of target oxygen conformations present in the lattice optionally weighted by parameter α_c . Constraints on the local (i.e., around each oxygen location) and global (i.e., across the entire material) dopant concentration can also be imposed through Eqns. 4.8 and 4.9, respectively. The values of L_{loc} , U_{loc} , L_{glob} , and U_{glob} can be adjusted to explore different constrained designs, but the values chosen to best match our perovskite were o and 5 B-site substitutions per motif, and 10% to 30% B-site substitutions across the whole lattice [132].

$$\max_{Y_j, Z_{ic}} \sum_{i \in I} \sum_{c \in C} \alpha_c Z_{ic}$$
(4.5)

s.t.
$$\sum_{\substack{c \in C: \\ \{\xi_{ijc}=1\}}} Z_{ic} \le Y_j \qquad \forall i \in I, \forall j \in N_i$$
(4.6)

$$\sum_{\substack{c \in C: \\ \{\xi_{ijc}=0\}}} Z_{ic} \le 1 - Y_j \qquad \forall i \in I, \forall j \in N_i$$
(4.7)

$$L_{\text{loc}} \le \sum_{j \in N_i} Y_j \le U_{\text{loc}} \qquad \forall i \in I$$
 (4.8)

$$L_{\text{glob}} \le \sum_{j \in J} Y_j \le U_{\text{glob}} \tag{4.9}$$

$$Z_{ic} \in \{0,1\} \qquad \qquad \forall i \in I, \forall c \in C \qquad (4.10)$$

$$Y_j \in \{0,1\} \qquad \qquad \forall j \in J \qquad (4.11)$$

If the set of conformations, *C*, includes all feasible conformations (i.e., the set is mutually exclusive and collectively exhaustive), then we can additionally include Eqn. 4.12 to tighten the model. This constraint requires exactly one conformation variable to be indicated at each oxygen location.

$$\sum_{c \in C} Z_{ic} = 1 \quad \forall i \in I$$
(4.12)

An important feature of this mathematical formulation is the ability to generically represent a variety of target physical properties. For example, we can model the material that packs as many motifs with lowest oxygen energy as possible, corresponding to

	# Binary Variables	# Constraints
$3 \times 3 \times 3$	51,705	1,784
4 imes 4 imes 4	122,560	4,226
$5 \times 5 \times 5$	239,375	8,252

Table 4.1: Formulation size for instances involving all conformations (|C| = 638)

materials with the lowest temperature for the onset of reduction. Alternatively, we can optimize for the material with the lowest average oxygen excess energy across all oxygen sites, corresponding to the material with the lowest oxygen release temperature overall. Finally, we can optimize for the material with a custom weighting, giving preference for sites with low oxygen excess energy and decreasing preference for sites with higher excess energies. We found that, for this application, encoding contributions to material performance by indicating conformations generally resulted in more tractable models than the approach of regressing simplified structure-function relationships from geometric descriptors [83]. This approach of encoding conformation variables can be thought of as an extreme case of using high-dimensional geometric descriptors, resulting in unique descriptions for each material conformation. These descriptors result in tighter logical implication constraints, improving the tractability of these models.

Because the model includes binary variables with linear constraints, this optimization problem constitutes a mixed-integer linear program, which can be solved by standard general-purpose solvers. More specifically, all optimization models were solved on a desktop computer using the MILP optimization software CPLEX 12.8.0 under a time limit of 1 hour [95]. We were able to solve instances to provable optimality for supercell sizes of up to $4 \times 4 \times 4$, noting that there was an extreme increase in difficulty with increasing supercell size. Table 4.1 illustrates the cubic growth in both the number of binary variables and constraints, resulting in an exponential growth in the number of feasible solutions. Problems with supercells of size $3 \times 3 \times 3$ or below could be solved in seconds, while supercells of size $4 \times 4 \times 4$ were solved in approximately an hour. Supercells of size $5 \times 5 \times 5$ displayed very slow progress in the upper bound of the branch and bound tree, and were only able to achieve an approximately 30% relative gap within reasonable time limits. In general, we observed that CPLEX was able to quickly find good feasible solutions and that most of the computational effort was spent subsequently to prove the optimality of those solutions.

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In order to clearly see the potential benefit of nanostructuring, we compared our optimal identified designs against designs formed by randomly placed dopant in the lattice. We predicted the probability of the presence of a particular oxygen conformation as the joint probability of each neighboring location having the correct choice of dopant or un-doped site. We assumed that the presence of dopant was independent of neighboring sites, and thus the probability of neighboring dopant was simply given as the total dopant fraction. Then, the prevalence of a given motif is simply the sum of probabilities of the conformations (i.e., equivalent rotations) that contribute to a motif. Using these probabilities, we developed distributions of several characteristics of oxygen sites in the lattice to use as a baseline against which we compare the optimal nanostructured design.

4.3 RESULTS AND DISCUSSION

Since there exists no experimental method to directly measure oxygen excess energy for a target oxygen atom, we relied upon DFT calculations to approximate this quantity. Several iterations of these calculations for different supercell sizes and k-point grids were performed to ensure calculation convergence (see Appendix 4.6 for details). Inspecting the results from the converged DFT calculations, we can rank the oxygen excess energy of relevant motifs and make several observations (Fig. 4.2). First, the motifs with the lowest oxygen excess energy tend to have dopant in the second shell of B-sites, and none in the two nearest B-sites (Fig. 4.3). The motif with the highest oxygen excess energy (and thus, the hardest oxygen to remove from the lattice) is the motif with both nearest B-sites doped and without any other doping further away (Fig. 4.4). These observations suggest that indium binds strongly to neighboring oxygen and weakens bonds to oxygen in the lattice further away.

The evaluation of oxygen excess energy was extended to reflect process temperatures by carrying out vibrational energy calculations and calculating the Gibbs free energy (Fig. 4.5). A key observation was that the free energy of oxygen removal at 973K per motif largely followed the same ordering as the energy at oK. This observation is likely to hold for a variety of other cubic perovskites, even if the impact of dopant structure on excess energies is different. Because of this, we can use the oK oxygen excess energy as a robust ranking of free energy of oxygen removal when considering applications at any temperature. For reference, the oxygen excess energy evaluations along with the relevant dopant locations are tabulated in Appendix 4.7.



Figure 4.2: Sorted evaluations of oxygen excess energy for all 74 motifs considered in this study.



Figure 4.3: Motifs with oxygen excess energy between 4.05 - 4.25 eV. See Table 4.2 of Appendix 4.7



Figure 4.4: Motifs with oxygen excess energy between 5.39 - 6.49 eV. See Table 4.2 of Appendix 4.7

Using the general model formulation presented in Eqns. 4.5–4.11, we were able to optimize for several objectives targeting different energetic properties of the perovskite. First, we targeted the three motifs with lowest oxygen excess energy as desirable, seeking the material with the highest concentration of oxygen vacancies at low temperature. Secondly, we chose to minimize the average excess energy across the lattice. Thirdly, we chose weightings $\alpha_c = \exp(-(\Delta E_{\text{vac}} - \Delta E_{\text{vac}}^{\min})/(k_B T))$ to represent a Boltzmann factor at



Figure 4.5: Comparison of free energy of oxygen removal at oK and 973K.

973 K for the expected fraction of oxygen vacancies relative to the motif with the lowest excess energy. We present each of these possible choices of objective function to highlight the flexibility of mathematical optimization modeling. Using this approach, our model can be generalized to a variety of systems and target material properties.

We solved each model over a range of increasing supercell sizes and were generally able to prove optimality for supercells of size $4 \times 4 \times 4$ and below, while solutions from larger sizes can only be qualified as good solutions. In Fig. 4.6 we present the optimal periodic cell across all investigated cell sizes for each of the example objectives.

4.3.1 Maximizing Number of Target Motifs

Since our goal is to identify materials with facile oxygen removal, we first considered patterns that packed as many sites with low oxygen excess energy as possible. The objective function in this case corresponds to the collective count of "target" conformations, where only target conformations are given a weight of one in the objective function. The

optimal dopant pattern for packing oxygen sites with low excess energy is presented in Fig 4.6a, demonstrating 50% of oxygen sites as one of the three motifs with lowest oxygen excess energy. The optimal design consists of a repeating $2 \times 2 \times 2$ cell, regularly spacing dopant throughout the lattice. This result can be interpreted as maximizing the number of oxygen sites that have two dopant sites in their second shell of neighbors, while minimizing the number of sites that are immediately next to dopant. Additionally, by solving a slightly relaxed version of the optimization model, we can prove that this design is optimal over any even-sized supercell (i.e., $4 \times 4 \times 4$, $6 \times 6 \times 6$, etc.).

4.3.2 Minimizing Average Oxygen Excess Energy

We next considered minimizing the average oxygen excess energy across the lattice. This particular objective function is generally of interest when considering macroscopic material properties that are a simple combination across the available lattice sites. In the domain of oxygen carriers, this corresponds to a material that releases oxygen over a potentially broad range of temperatures, but the lowest range overall. With the goal of minimizing the average excess energy, we identify the design in Fig. 4.6b with an average oxygen excess energy of 4.45 eV. Importantly, this design clusters dopant in such a way to avoid motifs of the highest oxygen excess energy.

4.3.3 Maximizing Sum of Boltzmann Factors

Our third objective function aims to maximize the sum of Boltzmann factors for the oxygen excess energy of sites across the lattice. This is proportional to the likelihood of forming the first oxygen vacancy, and furthermore, should be proportional to the likelihood of forming subsequent vacancies. Overall, this represents the reducibility of the material at a given temperature. Importantly, this objective function highlights the capability to model more complex physical situations by simply changing model coefficients. The optimal design presented in Fig. 4.6c has an objective value of 96.01 out of a total of 192 oxygen sites. This corresponds to roughly 50% of the sites as performing as a site with the lowest oxygen excess energy. In fact, this design places the best motif in 50% of the sites and is also an optimal solution to our first example model. However, the first example had no motivation to prefer one of the three motifs over another. In

general, the choice to use Boltzmann weighting should serve to break those ties and lead to more informative results.



(a) Maximizing the number of sites displaying one of the three motifs





(b) Minimizing the average oxygen excess energy of sites in the lattice.



(c) Maximizing a sum of Boltzmann factors.

Figure 4.6: Example optimal periodic doped perovskite dopant patterns.

The results from each of these optimization models can be used to suggest future directions for synthesis of precisely-structured perovskite nanoparticles, possibly fabricated via a layer-by-layer approach [198]. To highlight the potential benefit that nanostructuring can have, we predicted the performance of randomly doped perovskite lattices. We found that as dopant fraction increased from 10% to 30%, the prevalence of oxygen sites with the lowest oxygen excess energy increased slightly, while the prevalence of motifs of intermediate excess energy decreased (Fig. 4.7, see Appendix 4.8 for more details). Importantly, these trends in the distribution of oxygen excess energy can be compared against the distribution present in optimally-doped lattices. Our optimal design for the objective of packing motifs with the lowest excess energy (Presented in Fig. 4.6a) displays significantly more oxygen sites at lower oxygen excess energies (50% vs. approx. 5%), which is expected to correspond to a larger extent of reduction occurring at lower temperatures. The differences in characteristics of randomly doped perovskites and our optimal design highlight the impact that controlling not only dopant amount, but also placement can potentially have on the achievable performance of doped perovskites.

4.4 CONCLUSIONS

In this chapter, we investigated the impact that indium dopant can have on the release of oxygen from a BaFeO₃ perovskite. We identified motifs that capture all the possible ways in which dopant can be presented to a particular oxygen atom within some reasonable limits on the local dopant concentration. These limitations could be relaxed and more motifs could be identified for further investigation, if desired.

For each identified motif, we embedded the particular arrangement of dopant in a periodic supercell and evaluated the oxygen excess energy via density functional theory. We demonstrate that our density functional theory results converge to an evaluation that can be trusted to be free of artifacts from supercell size or algorithmic parameters.

The density functional theory calculations were used to identify dopant motifs that lead to highly reducible material. In general, we observed that oxygen sites directly next to indium tend to have higher oxygen excess energy, while oxygen sites further away have slightly lowered oxygen excess energy. This supports the hypothesis that incorporation of indium into the lattice leads to more reducible material by binding to nearby oxygen and weakening bonds to oxygen further away in the lattice. We then formulated and solved a set of mathematical optimization models that identify patterns of dopant that result in materials with desirable distributions of easily removed oxygen. These results were compared against the expected quality of designs from randomly doped lattices, highlighting the benefits that nanostructuring can offer in this context. While these precise patterns may be impractical to consider synthesizing today to sufficient atomic precision, the optimal results are useful to elucidate trends in material structure and

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4.4 CONCLUSIONS

function, serve as theoretical bounds on the performance of the material class under investigation as a whole, as well as guide the development of future synthesis methods.

This work demonstrates a generic framework that can be readily adapted to other crystalline material design contexts. The procedure of defining a motif, enumerating possible material conformations, and then calculating energetic properties of interest from first principles can be generically used to identify structure-function relationships for other materials. Given the appropriate material understanding in the form of a suitable such relationship, it is then possible to cast a rigorous optimization model, similar in terms of its mathematical structure to the one presented in this chapter, in order to obtain promising material designs to serve as targets for synthesis and further investigation. Mathematical optimization serves to formalize and guide the search for novel materials in a way that identifies unintuitive results and provides strong guarantees of optimality of resulting designs.



(a) Maximizing the number of sites displaying one of the three motifs with lowest oxygen excess energy.



(b) Minimizing the average oxygen excess energy of sites in the lattice.



- (c) Maximizing a sum of Boltzmann factors at 973 K for the expected fraction of oxygen vacancies relative to the motif with the lowest excess energy.
- Figure 4.7: Comparison between distributions of oxygen excess energies in optimal and randomly doped perovskites.

4.5 NOTATION

Indices

i	oxygen site
j	B-site
С	conformation
Sets	
Ι	oxygen sites in canvas
J	B-sites in canvas
N_i	neighbor B-sites to oxygen site i
С	oxygen conformations

Binary Variables

Y_j	presence of dopant at B-site j
Z_{ic}	presence of conformation c at oxygen site i

Parameters

α_c	objective weighting parameter for oxygen conformation <i>c</i>
ξ _{ijc}	1 if a dopant atom in B-site j if conformation c would be present at site i , otherwise o
$L_{\rm loc}, U_{\rm loc}$	lower and upper bound on local (i.e., neighboring) dopant concentration

 $L_{\text{glob}}, U_{\text{glob}}$ lower and upper bound on global (i.e., canvas-wide) dopant concentration

4.6 APPENDIX: DENSITY FUNCTIONAL THEORY CONVERGENCE

We first compared the impact of embedding motifs in a supercells of size $3 \times 3 \times 3$ unit cells (135 atoms) versus supercells of size $4 \times 4 \times 4$ unit cells (320 atoms) on the evaluation of oxygen excess energy. This showed poor convergence, with a average absolute error of 0.73eV between the two approaches (Fig. 4.8a). These results suggested that the number of k-points should also be increased to improve the reliability of calculations. Upon increasing the number of k-points in the 135 atom supercells from $3 \times 3 \times 3$ to $5 \times 5 \times 5$, the results were relatively unchanged while the 320 atom supercells exhibited a dramatic difference going from $3 \times 3 \times 3$ to $4 \times 4 \times 4$ k-points. Using the higher numbers of k-points, the difference between the two supercell sizes was significantly smaller, indicating the satisfactory convergence of our computational results (Fig. 4.8b).



Figure 4.8: Convergence of DFT results with respect to supercell size and k-points.

4.7 APPENDIX: OXYGEN EXCESS ENERGY EVALUATIONS



Figure 4.9: Reference B-site location numbering.

	DC	Dopant presence in neighboring sites									
Motif #	0	1	2	3	4	5	6	7	8	9	EE @ oK
0											4.656
1	X										5.028
2	X	Х									5.797
3			Х								4.267
4	X		Х								4.756
5		Х	Х								5.219
6	X	Х	Х								5.377
7			Х	Х							4.525
8	X		Х	Х							4.992
9		Х	Х	Х							5.115
10	X	Х	Х	Х							5.494
11			Х		Х						4.061
12	X		Х		Х						4.659
13		Х	Х		Х						5.360
14	X	Х	Х		Х						5.553
15			Х	Х	Х						4.366
16	X		Х	Х	Х						4.780

 Table 4.2: Oxygen excess energy as a function of dopant placement.

 Dopant process in neighboring sites

		pan	i pi	esei		n ne	igin	JOIN	ig si	lies	
Motif #	0	1	2	3	4	5	6	7	8	9	EE @ oK
17		Х	Х	Х	Х						5.395
18	X	Х	Х	Х	Х						4.622
19			Х	Х	Х	Х					4.941
20	X		Х	Х	Х	Х					4.727
21		Х	Х	Х	Х	Х					5.079
22			Х				Х				4.367
23	X		Х				Х				4.732
24	X	Х	Х				Х				4.462
25				Х			Х				4.918
26	X			Х			Х				5.332
27	X	Х		Х			Х				4.135
28			Х	Х			Х				4.888
29	X		Х	Х			Х				4.960
30		Х	Х	Х			Х				4.988
31	X	Х	Х	Х			Х				4.413
32					Х		Х				4.548
33	X				Х		Х				5.197
34	X	Х			Х		Х				5.362
35			Х		Х		Х				4.477
36	X		Х		Х		Х				4.871
37		Х	Х		Х		Х				4.991
38	Х	Х	Х		Х		Х				6.488
39				Х	Х		Х				4.826
40	X			Х	Х		Х				4.578
41		Х		Х	Х		Х				5.035
42	X	Х		Х	Х		Х				5.065
43			Х	Х	Х		Х				5.207
44	X		Х	Х	Х		Х				4.544
45		Х	Х	Х	Х		Х				4.717
46				Х		Х	Х				4.055

Table 4.2: Oxygen excess energy as a function of dopant placement (cont.)

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	Dopant presence in neighboring sites										
Motif #	0	1	2	3	4	5	6	7	8	9	EE @ oK
47	X			Х		Х	Х				4.975
48		Х		Х		Х	Х				5.114
49	X	Х		Х		Х	Х				5.174
50			Х	Х		Х	Х				4.307
51	X		Х	Х		Х	Х				4.735
52		Х	Х	Х		Х	Х				4.808
53				Х	Х	Х	Х				4.867
54	X			Х	Х	Х	Х				4.553
55		Х		Х	Х	Х	Х				4.739
56			Х	Х	Х	Х	Х				4.832
57			Х	Х			Х	Х			4.368
58	X		Х	Х			Х	Х			4.363
59			Х		Х		Х	Х			4.807
60	X		Х		Х		Х	Х			4.299
61		Х	Х		Х		Х	Х			4.997
62				Х	Х		Х	Х			4.402
63	X			Х	Х		Х	Х			4.782
64			Х	Х	Х		Х	Х			4.247
65					Х	Х	Х	Х			4.944
66	X				Х	Х	Х	Х			4.588
67			Х		Х	Х	Х	Х			4.361
68			Х		Х		Х		Х		4.251
69	X		Х		Х		Х		Х		4.400
70			Х	Х	Х		Х		Х		4.280
71				Х		Х	Х		Х		4.293
72			Х		Х	Х		Х			5.011
73		Х	Х		Х	Х		Х			4.248

Table 4.2: Oxygen excess energy as a function of dopant placement (cont.)

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4.8 APPENDIX: RANDOMLY DOPED PEROVSKITE ANALYSIS

Currently, standard synthesis methods for doped perovskites are not able to precisely control the placement of dopant in the lattice, but rather, lead to random arrangements of dopant subject to a total dopant concentration. To predict the expected performance of randomly doped lattices, we calculated the likelihood of each motif using a product of Bernoulli distributions as a function of overall dopant concentration. The probability of each of the 74 motifs considered in this study is plotted below in Figure 4.10a, with each line corresponding to the distribution at various levels of dopant. Displayed as Motif # 74 is the cumulative probability of all other motifs (i.e., those containing more than 5 dopant atoms per 10 nearest-B-sites) for which we did not evaluate the oxygen excess energy.

Given the prevalence of motifs and their evaluation of oxygen excess energy, we plot in Figure 4.10a the cumulative probability density of motifs over a range of oxygen excess energies.



(a) Prevalence of motifs over various dopant levels. Motif #74 incorporates all other motifs not listed in Appendix 4.7.



(b) Probability density function of oxygen excess energy.

Figure 4.10: Distribution of oxygen sites in randomly doped lattices

5

MATOPT: A PYTHON PACKAGE FOR NANOMATERIALS DISCRETE OPTIMIZATION

Novel nanostructured materials are being enabled by advances in synthesis techniques that achieve ever better control over the atomic-scale structure of materials. The pace of materials development has been further increased by high-throughput computational experiments guided by informatics and machine learning. In the previous chapters, we have demonstrated complimentary approaches using mathematical optimization models to search through highly combinatorial design spaces of atomic arrangements, guiding the design of materials. In this chapter, we formalize the common features of materials optimization problems that can be efficiently modeled via mixed-integer linear optimization models. To take advantage of these commonalities, we have produced MatOpt, a Python package that formalizes the process of representing the materials designs space and formulating optimization models. This tool serves to bridge the gap between practitioners with expertise in nanostructured materials and those with expertise in solving optimization in nanostructured materials problems.

5.1 INTRODUCTION

While there are many approaches obtaining better predictions of nanoparticle reactivity and control over the nanostructure, there are relatively few systematic methods for designing nanomaterials algorithmically. In Calle-Vallejo et al. [31], the authors used a model for activity as a function of generalized coordination number to design defects on nanostructured surfaces. However, this approach relies on chemist intuition to identify reactive sites and does not provide any guarantees on the quality of identified surfaces. In Ruck et al. [183], the authors use a similar coordination-based structure-function relationship in conjunction with particle swarm optimization to design symmetric nanoparticles and rods. In Núñez, Lansford, and Vlachos [165], the authors use another coordinationbased structure-function model in conjunction with simulated annealing to design defects on nanostructured surfaces. These approaches leverage metaheuristic optimization methods to find good solutions, but still lack rigorous guarantees on the optimality of the identified designs.

We seek provably optimal designs by applying exact mathematical optimization algorithms to arrange nanostructured materials from their fundamental building blocks. Previously, we have developed mathematical optimization models for the design of nanostructured surfaces [82, 85], doped perovskites [84], and metallic nanoclusters [97]. In each case, we showed how mathematical optimization was well-suited to search the combinatorial design space of nanostructures by formulating appropriate models.

In this chapter, we first summarize the common elements of materials optimization problems. Specifically, we describe the common features of material domains of interest and show how these commonalities result in simple patterns for modeling materials via mathematical optimization. Then, we describe the implementation of MatOpt, a Python-based toolkit for specifying and solving these types of material optimization problems. Finally, we provide two case studies to illustrate the use of MatOpt in a catalyst optimization problem.

5.2 COMMONALITIES AMONG MATERIAL GEOMETRIES

Nanostructured materials generally share a few characteristics that lead to the complexity of the design space and thus, the combinatorial difficulty of finding optimal structures. These common material characteristics provide a basis for defining the scope for our optimization framework and result in simplifying assumptions for our framework to take advantage of. Specifically, we benefit from the discrete nature of lattices, local descriptors of functionality, and periodicity of designs.

5.2.1 Discrete Lattices

We generically denote the individual components of the design as "building blocks." In the example case of nanostructured transition metal catalyst surfaces, the building block can be thought of as an atom, while in larger systems such as metal organic frameworks or supramolecular assemblies the building block can be a molecule.

Conceptually, one could optimize the design of materials by choosing the *x*, *y*, *z* coordinates for the building blocks of interest. However, at the nanoscale, many solid materials tend to form architectures with atoms placed on lattices with specific, discrete locations. While exceptions to this observation are inevitable (i.e., lattice relaxations around defects, atomic restructuring on nanoclusters), we note that this observation can serve as a good first approximation in many systems of interest. We note that while we typically work with regular crystalline lattices, our approaches can be applied to other design spaces where the possible placement of matter is ordered but does not satisfy strict definitions of a lattice (i.e., five-fold symmetry around icosahedral nanoclusters). The discrete nature of nanomaterials can let us simplify the search space to only require "yes" or "no" decisions on the choices of building blocks to place in the design. These binary decisions tend to lead to simpler models since we can preprocess geometric information and avoid encoding nonlinear constraints in our optimization models, generally formulating mixed-integer linear programming (MILP) models that are significantly more efficient to solve than their nonlinear counterparts.

5.2.2 Local Functionality Descriptors

Given a set of discrete points on which building blocks can be placed, there are also a discrete number of interactions that can contribute to the functionality of a design. In many cases, the desired functionality of the material can be broken down into contributions from sites in the material. Furthermore, it is also typically the case that the functionality of a site is dependent on the presence of building blocks in a small subset of sites that can be thought of as "neighbors." Strictly speaking, the definition of neighbors does not need to be based on the physical distance between sites, though this is typically a good first approximation of relevant sites. The combination of discrete sites and neighborhoods leads to the basic data structure that we denote as a "canvas."

The canvas data structure is generically composed of a list of site coordinates in conjunction with a graph with nodes for each site and directed arcs for the neighbor connections. The connections are considered directed because, in general, it is possible for site functionality to depend on other sites asymmetrically. In addition to the standard components of the graph data structure, the canvas specifies an ordering of neighbors to represent specific types of connections. This is useful for the ability to represent the specific alignment of neighbors in the lattice, which is necessary when trying to indicate a particular configuration of atoms in a design. In Figure 5.1, we present an example canvas with the corresponding data structure for the neighborhoods.



Site	Neighbor											
i	п											
	0	1	2	3								
0	4	1	None	None								
1	5	2	None	0								
2	6	3	None	1								
3	7	None	None	2								
4	8	5	0	None								
5	9	6	1	4								
6	10	7	2	5								
7	11	None	3	6								
8	12	9	4	None								
9	13	10	5	8								
10	14	11	6	9								
11	15	None	7	10								
12	None	13	8	None								
13	None	14	9	12								
14	None	15	10	13								
15	None	None	11	14								

Figure 5.1: Example ordered neighbor connections for a simple canvas.

5.2.3 Material Periodicity

Nanostructured materials are typically modeled in simulation cells containing periodicity between o to 3 dimensions, corresponding to clusters, wires, surfaces, and bulk materials, respectively. From an implementation standpoint, the presence of periodicity can lead to non-intuitive neighborhoods with connections that cross periodic boundaries. These connections can be identified from the combination of the canvas sites with a set of rules for transforming points that cross the tiling boundaries. Given a fixed canvas, these connections can be tabulated prior to formulating a mathematical optimization model

and care should be taken to ensure that the canvas neighborhoods are geometrically consistent. In general, the same site can appear as a neighbor for multiple connections when considering multiple periodic directions, especially for small tiles.

Figure 5.2 illustrates a simple two dimensional lattice with connections defined by the periodicity of the canvas. In this example, the shape of the periodic tile is denoted with the dashed red parallelogram and neighbors crossing the tile edge are shown with directed arcs.



Figure 5.2: Example neighbor connections across the boundary of a periodically-tiled canvas. The red, dashed parallelogram represents the boundary of the periodic tile, slightly shifted down and to the left to unambiguously distinguish between sites in and outside of the tile.

The size of the canvas to be considered as the design space constrains the resulting optimization model and may lead to the best design being missed if the canvas is too small. However, in the case of periodic designs, a natural algorithm for quickly identifying good solutions is to iteratively expand the size of the periodic canvas and re-solve until computational resources are expended or until a satisfactory design is found. While we may not know the truly best solution *a priori*, a typical observation may be to see the same (likely to be truly best) design repeated as the optimal solution at multiple sizes that are consistent with the periodicity of the design (see Sec. 2.3.2).

5.3 MODELING ELEMENTS

Given the commonalities in the materials of interest, there are several optimization modeling patterns that we can use to modularly formulate models. The discrete nature of the design space leads to formulations that naturally employ binary variables and implication logic. In cases where complex or nonlinear structure-function relationships are of interest, there are several strategies to exactly encode the same information via linear constraints and implication logic.

5.3.1 Basic Variables

The common features of nanostructured materials lead to a natural set of basic variables from which mathematical optimization models can be formulated. Below, we present four types of basic variables in addition to several more variables representing their aggregation.

Presence of Building Blocks

The presence of a building block of a given type at a particular site is the most fundamental variable in the optimization model. In Eqn. 5.1, we denote as Y_{ik} the presence of a building block of type *k* in site *i*. We write the set of sites in the canvas as *I*, and we write the set of building blocks as *K*.

$$Y_{ik} \in \{0,1\} \quad \forall i \in I, \forall k \in K$$
(5.1)

Presence of Bonds

Given the variables for the presence of specific building block types, we can encode information about the connections between building blocks. For convenience, we refer to these variables as "bond" type variables, but in general, they do not have to correspond to bonds in the chemical sense. In Eqns. 5.2–5.5, we denote as X_{ijkl} the presence of a bond between a building block of type k at site i and a building block of type l at site j. To denote the set of neighboring sites to location i, we use N_i .

$$X_{ijkl} \le Y_{ik} \qquad \forall i \in I, \forall j \in N_i, \forall k \in K, \forall l \in K$$
(5.2)

$$X_{ijkl} \le Y_{jl} \qquad \forall i \in I, \forall j \in N_i, \forall k \in K, \forall l \in K$$
(5.3)

$$X_{ijkl} \ge Y_{ik} + Y_{jl} - 1 \quad \forall i \in I, \, \forall j \in N_i, \, \forall k \in K, \, \forall l \in K$$
(5.4)

$$X_{ijkl} \in \{0,1\} \qquad \forall i \in I, \forall j \in N_i, \forall k \in K, \forall l \in K$$
(5.5)

Neighbor Counts

Applications at the nanoscale often correlate functionality to counts of neighbors around a particular type of site. In general, this functionality can also be broken down into contributions from sites and neighbors of particular types. In Eqns. 5.6–5.7, we denote as C_{ikl} the count of bonds between a building block of type k at site i and neighboring building blocks of type l. In this definition, if there is not a building block of type k at site i, then all C_{ikl} counts are set to zero.

$$C_{ikl} = \sum_{j \in N_i} X_{ijkl} \quad \forall i \in I, \forall k \in K, \forall l \in K$$
(5.6)

$$C_{ikl} \in [0, |N_i|] \quad \forall i \in I, \forall k \in K, \forall l \in K$$
(5.7)

Aggregate Variables

Variables with type-dependent information may not always be necessary or useful for modeling. For example, many descriptors are expressed with conditionals such as the presence of "any atom" or "any bond" being present in the material. For each of the type-dependent variables previously discussed, we also present aggregated versions that indicate the presence of any atom, bond, or count of neighbors. In Eqns. 5.8–5.17 we denote as Y_i the presence of any atom at site *i*, we denote as X_{ij} the presence of any type
of bond between sites i and j, and we denote as C_i the count of any type of neighbor next to any type of building block present at site i.

$$Y_i \in \{0,1\} \qquad \forall i \in I \tag{5.8}$$

$$X_{ij} \le Y_i \qquad \forall i \in I, \forall j \in N_i$$
(5.9)

$$X_{ij} \le Y_j \qquad \forall i \in I, \, \forall j \in N_i \tag{5.10}$$

$$X_{ij} \ge Y_i + Y_j - 1 \quad \forall i \in I, \, \forall j \in N_i$$
(5.11)

$$X_{ij} \in \{0,1\} \qquad \forall i \in I, \forall j \in N_i$$
(5.12)

$$C_i = \sum_{j \in N_i} X_{ij} \qquad \forall i \in I$$
(5.13)

$$C_i \in [0, |N_i|] \qquad \forall i \in I \tag{5.14}$$

$$V_i = \sum V_i \qquad \forall k \in K \tag{5.15}$$

$$Y_i = \sum_{k \in K} Y_{ik} \qquad \forall k \in K \tag{5.15}$$

$$X_{ij} = \sum_{k \in K} \sum_{l \in K} X_{ijkl} \quad \forall i \in I, \forall j \in N_i$$
(5.16)

$$C_i = \sum_{k \in K} \sum_{l \in K} C_{ikl} \quad \forall i \in I$$
(5.17)

Presence of Conformations

In addition to variables for indicating bonds and neighbor counts, we also encode basic variables for indicating specific combinations of neighbors, or "conformations." In Eqns. 5.18–5.21, we denote Z_{ic} as the presence of a conformation of type c at site i. We use the parameter ξ_{icjl} to indicate if a conformation of type c located at site i should have a building block of type l in neighboring location j.

$$Z_{ic} \leq Y_{jl} \qquad \qquad \forall i \in I, \forall c \in C, \\ \forall j \in N_i, \forall l \in K : \xi_{icjl} = 1 \qquad (5.18)$$

$$Z_{ic} \leq 1 - Y_{jl} \qquad \qquad \forall i \in I, \forall c \in C, \\ \forall j \in N_i, \forall l \in K : \xi_{icjl} = 0 \qquad (5.19)$$

$$Z_{ic} \ge 1 - \sum_{\substack{j \in N_i \ l \in K \\ \xi_{icjl} = 1}} \sum_{l \in K} \left(1 - Y_{jl} \right) - \sum_{\substack{j \in N_i \ l \in K \\ \xi_{icjl} = 0}} \sum_{l \in K} Y_{jl} \quad \forall i \in I, \forall c \in C$$
(5.20)

$$Z_{ic} \in \{0,1\} \qquad \forall i \in I, \forall c \in C$$
(5.21)

5.3.2 Common Constraint Patterns

Given the set of basic variables, a wide variety of additional, application-specific descriptors can be defined. In this section, we provide several basic patterns of constraints used to define new descriptors and to implement restrictions on the design space. In each case, we present a basic pattern, noting that there are a variety of ways to apply these patterns for combinations of site and bond types.

Linear & Piecewise Linear Constraints

The most straightforward constraints to incorporate in MILP models are simple linear equalities or inequalities. In our models, these often take the form of budget constraints or summations. Similarly, we can incorporate piecewise linear expressions into the model by introducing additional binary variables and implication logic.

Because the basic decision variables are discrete, all subsequent variables are also discrete and we can conceptually use piecewise linear constraints to incorporate any nonlinear function into material design models without introducing approximation error. We achieve this by encoding breakpoints to coincide with the discrete feasible points, illustrated in Figure 5.3. This can be used to exactly encode nonlinear functions without sacrificing accuracy if the number of required breakpoints is not too large. In other cases, it may still be necessary to estimate the original function to avoid a significant increase in computational difficulty. In Eqns. 5.22–5.23 we present the general notation for representing simple constraints, where g(x) and P(x) denote linear and piecewise linear expressions, respectively. Here, x represents the variables and parameters used in the expression. Although Eqns. 5.22–5.23 are written as ≤ 0 constraints, we generally model any combination of =, \geq , and non-zero parameters by simple modeling techniques.

$$g(x) \le 0 \tag{5.22}$$

$$P(x) \le 0 \tag{5.23}$$

Site & Bond Descriptor Implications

Frequently, material descriptors are defined in terms of logical predicates or conclusions. In such cases, we can use implication logic to conditionally apply constraints on the design space. We identify three general patterns of logical implications that are encountered



Figure 5.3: Example piecewise linear function to exactly encode a nonlinear function over a discrete domain.

in material design optimization models. In each case, a linear expression is conditionally set to zero if a binary indicator variable is active (i.e., equal to 1).

The first general type of logical constraint enforces a constraint only if a given condition is true for the site. In Eqn. 5.24, $g_i(x)$ corresponds to a general linear expression that is required to be equal to 0 if binary indicator Z_i is equal to 1 at site *i*. The parameters M^{LB} and M^{UB} are can be automatically calculated to correctly encode the design space in the case that the binary indicator is inactive. An example of this pattern could be to require a site's generalized coordination number to be equal to a target value if the site is considered a reactive site.

Similarly, logical implication constraints can be written for expressions and indicator variables indexed by bonds in the canvas (Eqn. 5.26). An example of this pattern is requiring the binding energy to be equal to an expression only if a bond is actually present between two sites.

$$M^{\text{LB}}(1-Z_i) \le g_i(x) \le M^{\text{UB}}(1-Z_i) \quad \forall i \in I$$
 (5.24)

$$Z_i \in \{0,1\} \qquad \qquad \forall i \in I \tag{5.25}$$

$$M^{\text{LB}}\left(1-Z_{ij}\right) \le g_{ij}(x) \le M^{\text{UB}}\left(1-Z_{ij}\right) \quad \forall i \in I, \, \forall j \in N_i$$
(5.26)

$$Z_{ij} \in \{0,1\} \qquad \qquad \forall i \in I, \, \forall j \in N_i \tag{5.27}$$

Site Combination Implications

The second pattern of logical implications involves combinations of neighboring sites. In this case, we show how indicator variables can be indexed over the set of neighbor pairs in a canvas to create individual constraints on each of the sites. This pattern is used to encode the basic variables for the presence of bonds and can also be used in user-defined descriptors for encoding neighboring pairs of conformations.

$$M^{\text{LB}}\left(1-Z_{ij}\right) \le g_i(x) \le M^{\text{UB}}\left(1-Z_{ij}\right) \quad \forall i \in I, \, \forall j \in N_i \tag{5.28}$$

$$M^{\text{LB}}\left(1-Z_{ij}\right) \le g_j(x) \le M^{\text{UB}}\left(1-Z_{ij}\right) \quad \forall i \in I, \, \forall j \in N_i \tag{5.29}$$

$$Z_{ij} \in \{0,1\} \qquad \qquad \forall i \in I, \forall j \in N_i \tag{5.30}$$

Neighborhood Implications

The third pattern of logical implications introduces constraints on all neighboring sites to a location in the canvas. This pattern is used to encode the basic variables for the presence of conformations and is also generally useful for introducing more complicated constraints on combinations of sites in the canvas.

$$M^{\text{LB}}(1-Z_i) \le g_j(x) \le M^{\text{UB}}(1-Z_i) \quad \forall i \in I, \forall j \in N_i$$
(5.31)

$$Z_i \in \{0,1\} \qquad \forall i \in I \tag{5.32}$$

5.4 MATOPT TOOLKIT IMPLEMENTATION DETAILS

The developed toolkit formalizes and simplifies the process for carrying out nanostructured materials optimization via two major contributions. First, we provide several modeling tools for specifying the materials design space from simple input. Secondly, we provide a framework for specifying simplified structure-function relationships without needing a detailed understanding of the underlying mathematical optimization model.

5.4.1 Materials Representation Objects

Several existing tools provide interfaces for setting up and analyzing materials at the atomic scale [127, 168, 175]. They typically include "optimization" routines that serve to minimize the energy of atomic configurations by relaxing the atomic coordinates in

the vicinity of lattice sites (not equivalent to the mathematical optimization of interest in this chapter). These codes are tailored to work for more traditional workflows in computational materials screening and therefore do not immediately adapt to the same level of generality that we aspire to. As a first approach, we have created our own basic data structures for representing the materials design space to the level of detail that we require in our optimization modeling. In the future, it may be of interest to incorporate connections between other open-source packages and our optimization modules.

The first major contribution of the toolkit is the ability to easily instantiate data structures necessary to represent nanoscale materials from simple input. Figure 5.4 illustrates the interactions between several objects and data structures to represent nanostructured material designs. While the explanation given here is conceptual, we encourage the interested reader to refer to the detailed documentation and open source code available online as part of the Institute for the Design of Advanced Energy Systems (IDAES) code distribution [161].

The basic data structure required to cast an optimization model is a Canvas, which essentially is a list of Cartesian points coupled with a graph of nodes for sites and arcs for bonds. This object establishes a mapping from the abstract, mathematical modeling of materials as graphs to the geometry of the material lattice. The list of points and neighbor connections necessary to create a Canvas object can be obtained from the combination of Lattice, Shape, and Tiling objects.

The Lattice object encodes methods for determining which Cartesian coordinates to consider as sites on an infinite crystal lattice. The Lattice can be constructed from a point on the lattice (i.e., a shift from the origin), an alignment (i.e., rotation from a nominal orientation), and appropriate scaling factors. With these attributes, we generally support the translation, rotation, and rescaling of lattices. Additionally, Lattice objects include a method for determining which sites should be considered neighbors. In the simplest case, these rules for indicating neighbors can be simple cutoff distances, but we also note cases where asymmetric definitions of neighbors can be useful for representing materials. For example, in Chapter 4, we utilized an asymmetric definition of neighbors to establish different definitions of neighbors around oxygen atoms compared to metallic B-site atoms.

A collection of Shape objects are included in the toolkit. These objects include methods for determining if a Cartesian coordinate lies in the interior or on the face of shapes. In this way, we can identify the sites (out of an infinite lattice) that fall in the geometry of interest. Shape objects also include methods for translation, rotation, and rescaling,



Figure 5.4: Flow of information for creating objects when representing materials.

allowing for flexible representation of the geometries of nanoclusters. In conjunction with Shape objects, we provide Tiling objects for identifying neighbors that are periodicallyconsistent across Shape boundaries. Using Tiling objects, we can systematically identify the transformation of coordinates outside of the tile shape to a coordinate inside the tile. Additionally, we can use Tiling objects to replicate our designs periodically, facilitating the visualization of patterns.

While a Canvas object holds topological and geometric information, a Design object is composed of a Canvas in conjunction with a list of building blocks placed in the sites of the material. The Design object provides methods for querying the distribution of building blocks in a structure, including methods for counting neighbors of a site by building block type, methods for identifying the count of building blocks over the whole design, and methods for determining the equivalence of Design objects.

The necessary attributes of a building block are encoded in the BuildingBlock class, and can in principle be extended to represent many materials. As a starting point, we have implemented the Atom class that is of interest in our work. Additionally, we implement several parsers for creating standard crystal structure files from Design objects filled with Atom objects.

5.4.2 Algebraic Modeling Language Features

While the goal of MatOpt's material modeling modules is to help organize and create prerequisite data structures, the goal of the optimization modules is to enable users to cast optimization models from minimal input. One of the key features of our modeling approach is the automatic encoding of logical expressions into MILP models. Additionally, we automatically generate indexed expressions for a wide variety of patterns encountered in material optimization models. To interface with optimization solvers,

we take advantage of Pyomo [86, 87], an algebraic modeling language for representing mathematical optimization models in Python. By specializing our modeling objects to represent common materials optimization patterns, our tool can be used by practitioners without a background in mathematical optimization.

Given a defined Canvas and a list of BuildingBlocks to place in the design, we start by automatically generating the set of basic descriptors for the presence of building blocks, bonds, neighbor counts, and conformations. Then, we enable users to specify additional descriptors using a combination of Expression and Rule objects. The general flow of information for specifying a model is presented in Figure 5.5.

Expression objects are generated from basic or user-defined descriptors via a set of predefined patterns. Two examples include SumSites and SumBonds to allow simple summations. A more complicated example is SiteCombination which creates expressions indexed over bonds by adding contributions from descriptors at two neighboring sites.

Expression objects are used in conjunction with Rule objects to define descriptors and to generate constraints on the design space without requiring the user to specify the details of the underlying constraints or necessary reformulations. Then, when the user requests to optimize the model, the code can automatically interpret Rule objects to generate a Python Optimization Modeling Objects (Pyomo) optimization model. Several example Rules include LessThan, EqualTo, GreaterThan, and Implies. A full list of available expression, rule patterns, and example use cases is provided in Appendix 5.9, with the expectation that additional patterns can be introduced as part of ongoing open-source development.

Several rules (e.g., LessThan, EqualTo, GreaterThan) can be immediately interpreted as linear constraints in the model. Other rules require reformulation to be used in mathematical optimization models. The Implies rule creates implication constraints that are enforced only if the site descriptor is true (e.g., if a site is present, if a bond is present, etc.). The FixedTo rule is included to allow descriptors to be explicitly fixed to a value. While, in principle, the same effect could be achieved by introducing equality constraints into the model, the FixedTo routines have the additional efficiency of fixing logically-implied basic variables when possible. The PiecewiseLinear rule allows the user to specify the variable domain, values, and breakpoints to equate a descriptor to a piecewise linear function. When generating constraints, the MatOpt framework converts PiecewiseLinear rules to specialized objects in Pyomo. This generically leverage advances in Pyomo and optimization solvers and enables interested users to quickly try several alternate formulations provided by Pyomo.



Figure 5.5: Flow of information for instantiating MatOpt optimization models.

One of the useful features of our modeling framework is the automatic handling of expression and rule indexes. For example, if a user-defined variable is indexed over a subset of sites in the canvas (e.g., over only the oxygen sites in a lattice), then the derived expressions and constraints are likewise indexed over that subset. Alternatively, if a variable indexed over canvas sites is multiplied by a parameter that is indexed over site types, then the resulting expression is automatically indexed over the set product of sites with site types. Figure 5.6 presents an example descriptor definition and highlights the data structures for indexing that are maintained for each descriptor, expression, and rule in the model. As an example descriptor, we present an abstract structure-function relationship that assigns the bond energy (BE_{ii}) , programmatically m.BEij) to an expression formed from a weighted combination of the coordination number (C_i , programmatically m.Ci) conditional on the type of bond that is present (X_{iikl} , programmatically m.Xijkl). The constraint includes bond-type-indexed parameters (A_{kl} , programmatically m. Akl) that abstractly represent the weighting contributions. While this example was artificially constructed to demonstrate a complex pattern, similar functions involving weighted functions of coordination can be found in literature [42, 181, 241].

The last component necessary to specify an optimization model is a single expression to minimize or maximize as an objective function. While optimization solvers typically only accept a single objective, we note that it is possible to combine multiple objectives via a weighted sum implemented as a LinearExpr object. One of our case study below exemplifies this and illustrates how optimization models can be used to generate Paretooptimal frontiers.

As a demonstration of the MatOpt framework, we present two example case studies. In the first example, we describe the simple syntax for creating a nanocluster optimization model. This serves as an example of the minimal Python and mathematical optimization



Figure 5.6: Example creation of site descriptor rules. Example code is given in the top row and the equivalent mathematical notation is given in the middle. Attributes implied by automatic indexing are presented on the bottom row.

knowledge necessary to begin using the MatOpt tool. In the second example, we show how the approach can be extended to model a bifunctional catalyst design problem inspired by recent literature. This example demonstrates the flexibility of the tool to be able to quickly model a more complex system with a marginal increase in programming effort.

5.5 CASE STUDY: NANOCLUSTER COHESIVE ENERGY MAXIMIZATION

The recent work of Isenberg et al. [97] demonstrates the use of mathematical optimization models to identify cohesive nanoclusters via a set of tailored algorithms. Here, we present a simplified version of their models as an example system prior to applying the tailored algorithms that they develop. As the structure-stability relationship, we consider a normalized version of the Tománek model for cohesive energy [215], given below in Eqn. 5.33. In this equation, \hat{E}^{coh} corresponds to the normalized cohesive energy of a nanocluster (1 corresponding to bulk cohesive energy, 0 corresponding to isolated atoms) and C_i corresponds to the coordination number of atom *i*.

$$\hat{E}^{\text{coh}} = \frac{1}{N\sqrt{12}} \sum_{i \in I} \sqrt{C_i}$$
(5.33)



Figure 5.7: Conceptual flowchart for MatOpt workflows.

Figure 5.7 presents the conceptual steps that we will be following for specifying this nanocluster energy minimization problem. In the first steps, we import the MatOpt module and provide input about the materials system of interest. Then, we specify the relevant structure-function and constraint information for defining an optimization problem. Finally, we invoke the optimizer and output the identified designs.

The following section, we present the minimal code necessary to setup and solve the optimization problem. First, we import the MatOpt package and standard Python modules.

- 1 from math import sqrt
- 2 from matopt import *
- 3 import numpy as np

Next we define the objects necessary to represent the material information in the problem. We create a Lattice object (scaled to the interatomic distance) which specifies the rules for neighbor connections and sites to consider adding to the design space.

4 Lat = FCCLattice(IAD=2.77044437)

In lines 5–7 we build a Canvas object composed of three shells of face-centered cubic (FCC) lattice locations around the origin. Note that since we are using a lattice defined in three-dimensional space, the expected data type of a point is a NumPy [167] array with floating point precision.

```
5 Canv = Canvas()
6 Canv.addLocation(np.array([0,0,0],dtype=float))
7 Canv.addShells(3,Lat.getNeighbors)
```

In the next lines, we define a parameter, N, to be the number of atoms to consider in nanocluster. Additionally, we define the set of Atom objects to place in the design.

8 N = 20
9 Atoms = [Atom('Pt')]

Once the material information is specified, we can begin to generate a mathematical optimization model via an object of class MatOptModel. The model object is initialized from a Canvas and a list of Atom objects from which we can identify index sets for sites, bonds, site types, and bond types. These index sets are automatically used as new descriptors are defined.

```
10 m = MatOptModel(Canv,Atoms)
```

In the following steps, we introduce material descriptors to encode the structure-stability relationship as well as to constrain the design space of interest. First, we introduce a descriptor for the square root of the coordination number defined by a piecewise linear rule. Note that since the input descriptor, the coordination number (m.Ci), is indexed over all sites, the resulting rule and descriptor are also indexed over all sites.

11	<pre>m.addSitesDescriptor('CNRi',bounds=(0,sqrt(12)),integer=False,</pre>
12	<pre>rules=PiecewiseLinear(values=[sqrt(CN) for CN in range(0,13)],</pre>
13	<pre>breakpoints=[CN for CN in range(0,13)],</pre>
14	<pre>input_desc=m.Ci))</pre>

Next, we introduce the descriptor for the normalized cohesive energy (m.Ecoh). As a normalizing coefficient, we take by the number of atoms in the cluster, N, and the square root of the bulk coordination number, 12.

```
15 m.addGlobalDescriptor('Ecoh',
16 rules=EqualTo(SumSites(desc=m.CNRi,
17 coefs=(1/(N*sqrt(12)))))
```

Finally, we introduce a a descriptor for the size of the nanocluster. By setting the bounds on the descriptor to be equal, we constrain the nanocluster to be a specific size. This could have been achieved by several approaches (e.g., by fixing the variable or by equating the variable to a constant), but it is expected that each would be interpreted efficiently by MILP solvers.

```
18 m.addGlobalDescriptor('Size',bounds=(N,N),
19 rules=EqualTo(SumSites(desc=m.Yi)))
```

At this point, the feasible space for the optimization model is fully specified. We finalize the model and begin to solve it by specifying a maximizing objective. In this example, the maximizing objective is a single material descriptor, m.Ecoh, but any Expression object can be used in general.

```
20 D = m.maximize(m.Ecoh,tilim=60,keepfiles=False,tee=False,disp=True)
```

If the optimization solver is successful, a Design object is returned that can be written to standard material file formats. Here, we create a Protein Data Bank (PDB) file [19], but other parsers are implemented and can be used as necessary.

```
21 if(D is not None):
22 D.toPDB('result_{}.pdb'.format(N))
```

While the example presented above is intentionally terse, there are many ways to modify the script to collect and analyze a variety of results. The most obvious extension is to place the model generation and solution in a loop to generate designs for a range of sizes. In Figure 5.8, we present a few example results from solving the simple model in a loop. The code can be further tailored by changing the contributions to cohesive energy to specially-regressed coefficients to better represent a metal of interest. Additionally, the Canvas shape can by recreated and adapted across several optimizations, as presented in Isenberg et al. [97].

5.6 CASE STUDY: BIFUNCTIONAL CATALYST DESIGN

In Núñez and Vlachos [166], the authors presented a machine-learned model for predicting surface reactivity of ammonia decomposition on a patchy Ni-Pt bifunctional catalyst



Figure 5.8: Example optimally cohesive nanoclusters.

and then designed a surface by applying a simulated annealing optimization algorithm. While their approach is tailored to make accurate predictions of reactivity, there are no guarantees that simulated annealing indeed produced the optimal design. In this case study, we present our optimization model as a complimentary approach that can identify provably optimal structures for a simplified version of the relevant chemistry.

The problem involves trying to identify the optimal patterning of a single layer of Ni atoms on top of a Pt {111} surface. The placement of Ni atoms creates facet and edge sites that contribute to the turnover of the ammonia decomposition reaction. As a first order approximation of the microkinetic model presented in Núñez and Vlachos [166], we simply assume that slab reactivity is proportional to the sum of pairs of edge sites immediately next to a facet site. This simplified viewpoint neglects contributions to reactivity from adsorbates that take a longer path diffusing across the catalyst surface between sites further away than nearest neighbors. However, we remark that more complicated contributions could be conceptually represented via additional variables, constraints, and parameters for the turnover on the catalyst surface.



Figure 5.9: Relevant material conformations in bifunctional catalyst example.

We employ basic variables for conformation indication (Eqns. 5.18–5.21), which are automatically encoded by MatOpt to indicate the presence of facet or edge sites. In Figure 5.9 we show the conformations including the facet site and the six orientations of edge sites. To represent our simplified model of catalyst turnover, we define new material descriptors to indicate the conjunction of a conformation of type "A" (i.e., a facet site) next to conformation of type "B" (i.e., an edge site).

Additionally, we model the surface energy of the resulting patterns with the goal of mapping the Pareto-optimal frontier of activity against stability in this design space. As a model for the surface energy, we employ the square-root trend from the Tománek model (Eqn. 5.33), only including sites in the top two layers of the canvas. The sum of these contributions results in a normalized evaluation of cohesive energy which can in turn serve as an approximation of surface energy after dividing by a unit area.

The MatOpt implementation of this model is available in Section 5.10 and the equivalent mathematical optimization model is presented in Section 5.11. While the code is more complex than the first case study, it illustrates several features that are commonly utilized in models. For example, we create a canvas from a periodic tile, we introduce descriptors over a subset of the sites in the canvas, and we fix part of the design to certain atoms. We include a loop to solve the model for a range of constraints on the surface activity, we save the results, and then we repeat for different sizes of the periodic tile to explore designs with different periodicity. In this way, we can build a Pareto frontier of the activity against the stability of the nanostructured surfaces, presented in Figure 5.10. A few Pareto-optimal solutions identified on tiles of size 8 atoms \times 8 atoms are plotted below in Figure 5.11. We note that the maximally active design was equivalent to the design proposed by Núñez and Vlachos [166], suggesting that, at least to a first approximation, their identified design was in fact optimally active.

5.7 CONCLUSIONS

In this chapter, we present a general-purpose approach to designing nanostructured materials. We compile a set of shared features of nanomaterial design problems and then develop modular variables and constraints to represent the basic features of the their respective optimization models. From these general approaches, we have created MatOpt, a Python module for casting mathematical optimization models in Pyomo from simple material input. We describe the object-oriented classes for specifying material information and for representing material optimization models. A detailed example of



Figure 5.10: Pareto-optimal frontier for the bifunctional catalyst design example.



Figure 5.11: Example Pareto-optimal results for the bifunctional catalyst example. Normalized activity and surface energy values are given below each tile.

the module applied to a nanocluster cohesive energy minimization problem illustrates the basic syntax and logic for creating models. An implementation of a bifunctional catalyst surface problem illustrates several more complex features of the tool and demonstrates an approach to generate Pareto-optimal results. The resulting MatOpt tool is distributed as part of the IDAES software distribution and will enable rigorous mathematical optimization in the domain of nanostructured material design.

5.8 NOTATION

Indices

i, j	canvas location				
k,l	building block type				
С	conformation				
Sets					
Ι	canvas locations				
N_i	neighbors to canvas location <i>i</i>				
Κ	building block types				
С	conformations				
Binary	Binary Variables				
Y_{ik}	presence of a building block of type k at site i				
Y_i	presence of any building block at site <i>i</i>				
X_{ijkl}	presence of building blocks of type k and l at sites i and j , respectively				
X_{ij}	presence of building blocks of any type at sites i and j				
Z_{ic}	presence of conformation <i>c</i> at site <i>i</i>				
Z_i , Z_{ij}	indicator variables to represent a condition at site i or for a pair of sites (i, j)				
Integer	Integer Variables				
C_{ikl}	count of building blocks of type l next to a building block of type k at site i				
C_i	count of any type of building block next to site <i>i</i>				

Expressions

P(x)	piecewise linear function of input variable <i>x</i>
$g(x), g_i(x), g_j(x), g_{ij}(x)$	linear expressions indexed over various combinations of sites or
	bonds
Parameters	
ξicjl	1 if a building block of type l is present at site j if a conformation
	of type c would be present at site i , otherwise o
ξicj	1 if a building block of any type is present at site <i>j</i> if a
	conformation of type c would be present at site i , otherwise o
$M^{ m LB}$, $M^{ m UB}$	big-M values for the lower and upper bounds on implication
	constraints, respectively

5.9 APPENDIX: KEY FRAMEWORK OBJECT CLASSES

5.9.1 Expressions

Table 5.1: Explanation of MatOpt Expression objects.

Expression Name	Definition & Example Use Case
	Summation of contributions across
LinearExpr	multiple descriptors & coefficients plus an offset
	Scaling and normalizing surface energy
SiteCombination	an expression at site i and an expression at neighboring site j
	Counting bond energy from function of coordination at neighbor sites
SumSites	sites (per site type)
	Counting number of Pt in nanocluster
SumBonds	bonds (per bond type)
	Counting contributions to energy by bonds
SumSiteTypes	site types (per site)
	Counting presence of any atom at a site
SumBondTypes	bond types (per bond)
	Counting bond type-dependent contributions to bond energy
${\tt SumSitesAndTypes}$	sites and site types
	Counting number of atoms in nanocluster
${\tt SumBondsAndTypes}$	bonds and bond types
	Counting multi-metallic bond contributions to cohesive energy
${\tt SumConfs}$	conformation types (per site)
	Counting presence of conformation of type "A"
SumSitesAndConfs	sites and conformation types
	Counting conformation-specific contributions to turnover
SumNeighborSites	neighboring sites (per neighbor site type)
	Counting local atom concentration
SumNeighborBonds	bonds to neighboring sites (per bond type)
	Counting number of bonds of specific types around a site

5.9.2 Descriptor Rules

Tab	le 5.2: Explanation of MatOpt Rule objects.
Rule Name	Definition & Example Use Case
LessThan	Descriptor less than or equal to an Expression
	"surface energy should be less than a threshold"
EqualTo	Descriptor equal to an Expression
	"surface energy should be equal to a linear expression"
GreaterThan	Descriptor greater than or equal to an Expression
	"stability must be greater than a linear expression"
FixedTo	Descriptor fixed to a scalar value
	"subset of canvas sites should be fixed to specific atoms"
PiecewiseLinear	Descriptor equal to the evaluation of a piecewise linear expression
	"descriptor follows the square root of coordination number"
Implies	Indicator (binary) descriptor that imposes other constraints if the descriptor is one
	"if an atom is placed on the surface, then there must be an atom placed beneath it"
NegImplies	<i>Indicator (binary) descriptor that imposes other constraints if the descriptor is zero</i>
	"if an atom is not present at a site, then then no bond can be present"
ImpliesSiteCombination	Indicator (binary) bond descriptor that imposes constraints on the two sites in the bond
	"this combination of reactive sites requires a conformation of type A and a conformation of type B"
ImpliesNeighbors	Indicator (binary) site descriptor that imposes constraints on all neighbor sites
	"if a conformation is present, then each neighboring site must match the conformation pattern"

5.10 APPENDIX: BIFUNCTIONAL CATALYST DESIGN CODE

```
1 import numpy as np
    from matopt import *
    IAD = 2.828
 5 Lat = FCCLattice.alignedWith111(IAD)
    nUnitCellsOnEdge = 4
    nLayers = 4
    a = b = nUnitCellsOnEdge*IAD
    c = nLayers*Lat.FCC111LayerSpacing
10 alpha = beta = np.pi/2
    gamma = np.pi/3
    S = Parallelepiped.fromEdgesAndAngles(a,b,c,alpha,beta,gamma)
    S.shift(np.array([-0.01*a,-0.01*b,-0.01*c]))
    T = PlanarTiling(S)
15 Canv = Canvas.fromLatticeAndTilingScan(Lat,T)
    iToSetNi = [[3,4,5,6,7,8],[3,4,5,6],[4,5,6,7],[5,6,7,8],[6,7,8,3],[7,8,3,4],[8,3,4,5]]
    iToSetPt = [[9,10,11]]*7
    Confs = [[(Atom('Ni') if i in iToSetNi[c] else (Atom('Pt') if i in iToSetPt[c] else None))
20
              for i in range(12)] for c in range(7)]
    I = range(len(Canv))
    LocsToFixPt = [i for i in I if Canv.Points[i][2] < Lat.FCC111LayerSpacing*2.5]
    LocsToExcludePt = [i for i in I if i not in LocsToFixPt]
    CanvMinusTwoBotLayers = [i for i in I if Canv.Points[i][2] > Lat.FCC111LayerSpacing*1.5]
25 OneLocToFix = [min(LocsToExcludePt)]
    maxNormSurfE = 999
    Atoms = [Atom('Ni'),Atom('Pt')]
    for SumActiveSitesLB in range(nUnitCellsOnEdge**2):
30
        m = MatOptModel(Canv,Atoms,Confs)
        m.Yik.rules.append(FixedTo(1,sites=LocsToFixPt,site_types=[Atom('Pt')]))
        m.Yik.rules.append(FixedTo(0,sites=LocsToExcludePt,site_types=[Atom('Pt')]))
        m.Zic.rules.append(FixedTo(1,sites=OneLocToFix,confs=[0]))
        m.Zic.rules.append(Implies(concs=(m.Yik,EqualTo(1,site_types=[Atom('Ni')])))
        SumAConfs = SumConfs(m.Zic,confs_to_sum=[0])
35
        SumBConfs = SumConfs(m.Zic,confs_to_sum=[1,2,3,4,5,6])
        m.addBondsDescriptor('SiteCombinations', binary=True,
                             rules=ImpliesSiteCombination(Canv,
                                                           (SumAConfs, GreaterThan(1)),
                                                           (SumBConfs,GreaterThan(1))))
40
        m.addGlobalDescriptor('SumActiveSites', bounds=(SumActiveSitesLB,None),
                              rules=EqualTo(SumBonds(m.SiteCombinations)))
        m.addSitesDescriptor('Ei',rules=PiecewiseLinear(values=[1-sqrt(CN/12) for CN in range(13)],
                                                        breakpoints=[CN for CN in range(13)],
                                                         input_desc=m.Ci),
45
                             sites=CanvMinusTwoBotLayers)
        m.addGlobalDescriptor('NormEsurf',
                              rules=EqualTo(SumSites(m.Ei,coefs=1/(nUnitCellsOnEdge**2))))
        D = m.minimize(m.NormEsurf):
50
        if(D is None):
            break
        D.toCFG('result_{}.cfg'.format(SumActiveSitesLB),BBox=S)
```

5.11 APPENDIX: BIFUNCTIONAL CATALYST DESIGN MODEL

As part of our example, we also show how to incorporate simple constraints for modeling the stability of designs. These constraints are based on the Tománek model for cohesive energy [215], recently exemplified in Núñez, Lansford, and Vlachos [165]. In this model, each atom contributes to the cohesive energy by a square root dependence on coordination number. In Eqn. 5.34 we present the descriptor for the total cohesive energy of the slab \hat{E}^{stab} as a function of coordination number C_i at site *i*. We have normalized the values of surface energy and the per-atom contributions so that they all lie between o and 1, with a value of o corresponding to isolated atoms and a value of 1 corresponding to the bulk cohesive energy.

$$\hat{E}^{\text{stab}} = \frac{1}{|I|} \sum_{i \in I} \left(1 - \sqrt{\frac{C_i}{12}} \right)$$
(5.34)

The resulting optimization model is presented below in Eqns. 5.35– 5.42, in conjunction with the definitions for the basic variables in Eqns. 5.8–5.14. As the objective function (Eqn. 5.35), we have taken a weighted sum of the terms for normalized catalyst activity and the normalized cohesive energy. In Eqn. 5.36 we define the normalized catalyst activity A^{act} as a normalized sum of reactive pairs of sites, each denoted as ϕ_{ij} . In Eqn. 5.38 we define the normalized catalyst stability as a normalized sum of contributions from sites, each denoted as \hat{E}_i . To incorporate the square root function, we utilize the piecewise linear rule in MatOpt, abstractly represented in Eqn. 5.39 as a function of coordination number C_i , noting that additional variables and constraints will be modularly included by Pyomo to correctly encode that function. The set of basic variables are automatically added to satisfy the requirements of the user-specified constraints. In this example, since there is only one type of atom being placed, the variables for building block type $(Y_{ik}, X_{ijkl}, C_{ikl})$ can be preprocessed out so that only the type-agnostic variables remain (Y_i, X_{ij}, C_i) .

$$\max_{\substack{A^{\hat{a}ct}, \phi_{ij}, \hat{E}^{stab}, \hat{E}_{i}, \\ Z_{ici}, C_i, X_{ii}, Y_i}}$$

$$w^{\text{act}} \hat{A^{\text{act}}} + (1 - w^{\text{act}}) \hat{E}^{\text{stab}}$$
(5.35)

 Z_{ic}, C_i, X_{ij}, Y_i

s.t.
$$A^{\text{act}} = \frac{2}{\sum_{i \in I} |N_i|} \sum_{i \in I} \sum_{j \in N_i} \phi_{ij}$$
 (5.36)

$$\{\phi_{ij}\} \Rightarrow \left\{ \left(\bigvee_{c \in C_1 \subset C} Z_{ic}\right) \land \left(\bigvee_{c \in C_2 \subset C} Z_{jc}\right) \right\} \quad \forall i \in I, \forall j \in N_i$$
 (5.37)

$$\hat{E}^{\text{stab}} = \frac{1}{|I|} \sum_{i \in I} \hat{E}_i$$
(5.38)

$$\hat{E}_i \in f(C_i) \qquad \qquad \forall i \in I \qquad (5.39)$$

$$A^{\hat{a}ct} \in [0,1] \tag{5.40}$$

$$\phi_{ij} \in \{0,1\} \qquad \qquad \forall i \in I, \forall j \in N_i \qquad (5.41)$$

$$\hat{E}^{\text{stab}} \in [0, 1] \tag{5.42}$$

$$(5.8) - (5.14)$$

6

OPTIMIZING WIGNER CRYSTAL BILAYERS

In this chapter, we present an alternative to the paradigm in the previous sections by showing how mathematical optimization can also be used to identify patterns of materials in a continuous space. Specifically, we consider the problem of identifying minimum energy configurations for Wigner crystal bilayers. This involves optimizing the precise placement of point charges on two periodic, infinite plates. For some simple setups of the problem, the optimal patterns are well known, but for more complex situations there are no guarantees that the best known patterns are indeed optimal. We present a simplified mathematical optimization model that approximates the complex equations for Coulomb interactions in the Wigner bilayer problem and that can be used to quickly identify good solutions to the problem. However, we also identify cases where the truncation error in the approximate model leads to spurious results, and therefore, we also develop a numerical optimization approach that more closely encodes the complex equations governing the energy of Wigner crystals. The approaches developed in this work can be used to more systematically identify Wigner crystal patterns in situations where intuition and heuristic algorithms fail.

6.1 INTRODUCTION

Self-assembly of building blocks at the atomic scale has long been identified as an important route for controlling the formation of useful nanostructures [208, 224, 231]. Often, the self-assembly process can be better controlled or scaled-up by applying external forces in a process known as directed self-assembly [74]. Currently, much effort is spent developing robust techniques for arranging two-dimensional nanostructures, with the goal of utilizing these advances to hierarchically assemble three-dimensional nanostructures [253]. Example approaches for forming two-dimensional self-assemblies

include the use of anisotropic interactions between colloidal particles [20, 21, 38], assembly by DNA [5], and flow over templated surfaces [186]. One application of interest is assembling nanoparticles for surface-enhanced Raman scattering [114].

In this chapter, we focus on a specific phenomenon that has potential applications in the self-assembly at surfaces. Specifically, we will consider the assembly of charges confined to conductive plates to form lattice structures known as Wigner crystals [233]. Wigner crystals have long been of interest in the physics community as a way to explain observations of phenomena originating from the quantum nature of materials at extremes of low temperature and small length scale [67]. Our interest in Wigner crystals is due to the fact that they form a wide array of stable patterns which can be tuned by controlling relatively simple parameters related to their confinement. Specifically, the parameters of charge density and plate separation can be controlled at the microscale and used to form patterns of charged particles which can in turn be transfered to more permanent patterns in other nearby materials.

Similarly-charged particles interacting via a Coulomb potential will repel each other to form an evenly-spaced, hexagonally-packed lattice on an infinite plate but will form complex patterns under other conditions. When confined on other shapes (e.g., circular disks), the minimal-energy lattice can be distorted to form other patterns [119]. Similarly, when a second charged plate is brought parallel to the first plate, a series of patterns form as a function of plate separation [68]. The key observation is that the optimal charge pattern is no longer hexagonal (as in the case of a single, infinite plate), but instead transitions through several stable lattices with rectangular and square patterns in the intermediate plate separations. This setup is referred to as the *symmetric* Wigner bilayer, since the two plates were studied with equal charges on the two plates.

More recently, optimal patters have been considered for unequal charges on the two plates, in a setup referred to as *asymmetric* Wigner bilayers [7, 8, 141]. By introducing another tunable parameter in the formation of Wigner crystals, the asymmetric bilayer problem has created a significantly more complex space of nanoscale patterns. Ludwig et al. [141] used a Monte Carlo approach to approximately identify the stable structures while Antlanger et al. [7] used a variation of genetic algorithms to heuristically optimize the crystal patterns.

In this chapter, we apply mathematical optimization to optimize the structure of Wigner bilayers. We first define the problem of finding the minimum energy Wigner bilayer crystal pattern and present the prerequisite expressions necessary to calculate the potential energy. Then, we present a nonlinear programming (NLP) model to represent the energy minimization of the Wigner bilayer system with truncation on the Coulomb interactions considered. We characterize the results of the NLP model and highlight the need for numerical optimization of the more rigorous expression for the potential energy. We present preliminary results on the application of numerical optimization algorithms and outline an algorithm for generally optimizing the Wigner crystal structure via mathematical optimization.

6.2 PROBLEM STATEMENT & PRELIMINARIES

We consider a problem setup equivalent to the one presented in Antlanger et al. [8], restated here for convenience. Let L_1 and L_2 represent two infinite parallel plates with point charges of elementary charge -e at specified densities. We define a periodic tile to distribute the charges with area A, such that the number of charges per tile on the two plates, N_1 and N_2 , and the density of charges, σ_1 and σ_2 , are given by:

$$N_1 = \sum_{i \in L_1} 1$$
(6.1)

$$N_2 = \sum_{i \in L_2} 1$$
(6.2)

$$\sigma_1 = \frac{N_1}{A} \tag{6.3}$$

$$\sigma_2 = \frac{N_2}{A} \tag{6.4}$$

To satisfy electroneutrality, we assume that the two plates are also uniformly charged with charge densities $\sigma_1 e$ and $\sigma_2 e$. The two plates are separated by a distance *d* which can be normalized to a dimensionless parameter η .

$$\eta = d\sqrt{\left(\sigma_1 + \sigma_2\right)/2} \tag{6.5}$$

The coordinates of the point charges can be generically represented by the position of a charge in one "central" tile plus an offset for the periodic images of of the tile. We denote the position of charges in the central tile as r_i and the vector between two charges in the central tile as r_{ij} . Both of these vectors are defined in three-dimensional space, however, we can simplify the geometry by choosing to align the plates normal to the z direction and fixing the bottom plate at z = 0 and the top plate at z = d. Then, we define two-dimensional versions of the charge position as s_i and the difference vectors as s_{ij} . The offset for periodic image n is given as S_k and defined by multiples of lattice

vectors A and B in the *xy* plane. Similarly, multiples of the reciprocal lattice vectors for the periodic tile are written as G_k

$$\boldsymbol{S_k} = i_k \boldsymbol{A} + j_k \boldsymbol{B} \tag{6.6}$$

$$\boldsymbol{G}_{\boldsymbol{k}} = i_{\boldsymbol{k}} \frac{2\pi\boldsymbol{B} \times \hat{\boldsymbol{e}}_{\boldsymbol{z}}}{A} + j_{\boldsymbol{k}} \frac{2\pi\hat{\boldsymbol{e}}_{\boldsymbol{z}} \times \boldsymbol{A}}{A}$$
(6.7)

Finally, we denote the charge density as a function of position $\rho(\mathbf{r})$ that simply represents the sum of several Dirac delta functions for point charges and the background charge at a specific position. Given this notation, we can define the energy of our system in Eqn. 6.8. In the first line, we include the infinite summation of repulsive interactions between point charges across the periodic images of the tile.¹ In the second line, we include the summation of favorable interactions between point charges and the neutralizing plate charge by integrating over the surface of the plates. In the third line, we include integrals for the energy of the neutralizing plate charges interacting unfavorably with each other.²

$$E = \frac{e^2}{2} \sum_{i \in L_1 \cup L_2} \sum_{j \in L_1 \cup L_2} \sum_{S_k} \frac{1}{\|r_{ij} + S_k\|} - \frac{e^2}{2} \sum_{i \in L_1 \cup L_2} \int_{L_1 \cup L_2} dr \sum_{S_k} \frac{\rho(r)}{\|r_i - r + S_k\|} + \frac{e^2}{2} \int_{L_1 \cup L_2} dr' \int_{L_1 \cup L_2} dr \sum_{S_k} \frac{\rho(r)\rho(r')}{\|r - r' + S_k\|}$$
(6.8)

6.2.1 Ewald Summation

The expression for energy defined in Eqn. 6.8 is problematic due to the infinite summation of contributions across periodic tiles. In general, this would require a large series to add up contributions from periodic images as the interaction terms tend towards zero. However, for the Coulomb potential, the terms in the summation does not converge and instead become dependent on the choice of boundary conditions for the summation. Fortunately, we can utilize a technique called Ewald summation in conjunction with the

1 We denote the summation across all (infinite) periodic images by \sum_{S_k} . For the central tile, k = 0, we should not include an interaction for i = j. We denote this exclusion as $\sum_{S_k}^{j'}$.

² We take the outer integral over all points on the plates except for the point considered in the inner integral. We denote this as $\int_{L_1 \cup L_2} dr'$

electroneutrality condition to break the summation into two parts, yielding a result that is insensitive to the bounds on the summation [149].

Ewald summation breaks the potential energy into "real space" and "reciprocal space" contributions with an arbitrary parameter, α , that dictates the relative weight to give the reciprocal space contributions. The derivation of the contributions is explained in Mazars [149], and here we just reiterate the resulting equations. In Eqn. 6.9 we denote the total energy as the summation of real- and reciprocal-space interactions within the same plate as well as interactions between the two plates. In Eqns. 6.10–6.14 we present the four types of contributions as well as an auxiliary function. Note that *i* refers to the imaginary number and *G*_k refers to multiples of the two-dimensional reciprocal lattice vectors defined in Eqn. 6.7.

$$E = \sum_{l=1,2} E_{\text{intra},l}^{\text{real}} + \sum_{l=1,2} E_{\text{intra},l}^{\text{recip}} + E_{\text{inter}}^{\text{real}} + E_{\text{inter}}^{\text{recip}}$$
(6.9)

$$E_{\text{intra},l}^{\text{real}} = \frac{e^2}{2} \sum_{i,j \in L_l} \sum_{\boldsymbol{S}_k} \frac{\operatorname{erfc}\left(\alpha \left\|\boldsymbol{s}_{ij} + \boldsymbol{S}_k\right\|\right)}{\left\|\boldsymbol{s}_{ij} + \boldsymbol{S}_k\right\|}$$
(6.10)

$$E_{\text{intra},l}^{\text{recip}} = \frac{\pi e^2}{A} \sum_{\boldsymbol{G}_{\boldsymbol{k}} \neq 0} \frac{\text{erfc}\left(\|\boldsymbol{G}_{\boldsymbol{k}}\|/2\alpha\right)}{\|\boldsymbol{G}_{\boldsymbol{k}}\|} \left\|\sum_{j \in L_l} \exp\left(i\boldsymbol{G}_{\boldsymbol{k}} \cdot \boldsymbol{s}_{\boldsymbol{j}}\right)\right\|^2 - \frac{\sqrt{\pi}N_l^2 e^2}{\alpha A} - \frac{\alpha N_l e^2}{\sqrt{\pi}}$$
(6.11)

$$E_{\text{inter}}^{\text{real}} = e^2 \sum_{i \in L_1} \sum_{j \in L_2} \sum_{\mathbf{S}_k}' \frac{\operatorname{erfc}\left(\alpha \sqrt{\|\mathbf{s}_{ij} + \mathbf{S}_k\|^2 + d^2}\right)}{\sqrt{\|\mathbf{s}_{ij} + \mathbf{S}_k\|^2 + d^2}}$$
(6.12)

$$E_{\text{inter}}^{\text{recip}} = \frac{\pi e^2}{A} \sum_{\boldsymbol{G_k} \neq 0} F\left(\boldsymbol{G_k}, \alpha, d\right) \operatorname{Re}\left[\left(\sum_{j \in L_1} \exp\left(i\boldsymbol{G_k} \cdot \boldsymbol{s_j}\right)\right) \left(\sum_{j \in L_2} \exp\left(-i\boldsymbol{G_k} \cdot \boldsymbol{s_j}\right)\right)\right] \\ - \frac{\pi N_1 N_2 e^2}{A} \left[\frac{\exp\left(-\alpha^2 d^2\right)}{\alpha \sqrt{\pi}} + d \operatorname{erf}(\alpha d)\right] \\ - \pi e^2 \sigma_2 d \left[\sigma_1 A - 2N_1\right] - \pi e^2 \sigma_1 d \left[\sigma_2 A - 2N_2\right]$$
(6.13)

$$F(\boldsymbol{G}_{\boldsymbol{k}}, \alpha, d) = \frac{1}{\|\boldsymbol{G}_{\boldsymbol{k}}\|} \exp\left(\|\boldsymbol{G}_{\boldsymbol{k}}\|\,d\right) \operatorname{erfc}\left(\frac{\|\boldsymbol{G}_{\boldsymbol{k}}\|}{2\alpha} + \alpha d\right) \\ + \frac{1}{\|\boldsymbol{G}_{\boldsymbol{k}}\|} \exp\left(-\|\boldsymbol{G}_{\boldsymbol{k}}\|\,d\right) \operatorname{erfc}\left(\frac{\|\boldsymbol{G}_{\boldsymbol{k}}\|}{2\alpha} - \alpha d\right)$$
(6.14)

The introduction of the Ewald parameter α enables the potential energy of the system to be robustly calculated by considering a finite set of periodic images, beyond which each of the terms in the summation should have decayed to zero. For a chosen numerical



Figure 6.1: Example Ewald summation calculations as a function of parameter α . The problem and tile parameters are given below each plot.

tolerance, the choice of a suitable Ewald parameter and the set of periodic images to consider requires some tuning. In Figure 6.1 we present the trend in several example calculations as a function of α for summations of periodic images up to 100 copies away from the central tile. For choices of small α , energies are overestimated due to non-converging contributions of real-space interactions while at large α the error is due to nonzero reciprocal-space contributions at the limits of the summation. At intermediate values of α (~ 5–50), the results are relatively insensitive to this arbitrary parameter choice and therefore provide best setting for avoiding truncation errors. For the remainder of our calculations, we choose $\alpha = 10$ in conjunction with summation bounds of ± 100 periodic tiles away from the central tile.

6.3 NONLINEAR PROGRAMMING MODEL

The Ewald summation for evaluating the potential energy of Wigner crystals converges to a real number. However, the equations include complicated terms that can not be encoded in typical NLP models. As an alternate approach, we choose to neglect the interactions between the neutralizing plate and the point charges. Furthermore, we truncate the summation of Coulomb interactions to only include a smaller subset of periodic images with the hypothesis that even if energy evaluations fail to converge, the truncation may form a good approximation of the true potential energy surface. In Figure 6.2, we illustrate the set of charged particle-particle interactions considered across tile images indexed by k out of the finite set of images K.

In general, we would like to co-optimize the placement of charges as well as tile parameters. However, when considering a truncated set of contributions, the optimizer will be motivated to skew the tile (e.g., by choosing small interior angle and aspect ratio ≤ 1) to separate charges and take advantage of truncation errors. As an alternative, we can optimize tile geometry by simply scanning over a collection of results from problems with fixed tile parameters and then selecting the best. The tile geometry can be fully specified by four parameters, A_x , A_y , B_x , and B_y illustrated in Figure 6.3. Without loss of generality, we can choose to fix one of the vertices of the tile at the origin and choose one lattice vector to be aligned with the *x*-axis (Eqn. 6.15). Then, we normalize the tile area to 1 (Eqn. 6.16), we define an interior angle of the tile as θ (Eqn. 6.17), and we define the aspect ratio of the tile as χ (Eqn. 6.18).

$$0 = A_y \tag{6.15}$$

$$1 = A_x B_y \tag{6.16}$$

$$\tan \theta = \frac{B_y}{B_x} \tag{6.17}$$

$$\chi = \frac{\|\boldsymbol{A}\|}{\|\boldsymbol{B}\|} \tag{6.18}$$

With the goal of optimizing the placement of charged particles within this set of periodically-consistent tiles, we define an NLP model in Eqns. 6.19–6.29. We use set *I* to represent the set of point charges, and we use set *K* to represent the set of periodic tile images. In Eqns. 6.20–6.21, we define the variables for periodic copies of charges as a function of the central tile charge positions and offsets defined by combinations of lattice vector parameters. We define integer combinations of tile directions as parameters v_k^A and v_k^B for each periodic image *k*. From these basic variables, we define variables r_{ijk} for the

distance between charge *i* in the central tile to charge *j* in tile *k* via Eqn. 6.22. To represent the displacement in the *z* direction, we utilize parameter d_{ij} which is equal to 0 if charge *i* is on the same plate as charge *j* and equal to the plate separation *d* otherwise. The objective function, Eqn. 6.19, minimizes a sum of inverse distances that is proportional to the Coulomb potential energy from particle-particle interactions. In addition to the definitions of variables, we include four sets of constraints (Eqns. 6.23–6.26) to represent the boundaries of the periodic tile for the charges in the central image. Additionally, we can generally choose to fix one electron in the system to the origin, breaking translational symmetry of the point charges.

$$\min_{x_{ik}, y_{ik}, r_{ijk}} \sum_{i \in I} \sum_{\substack{j \in I \\ j \neq i}} \frac{1}{r_{ij0}} + \sum_{i \in I} \sum_{j \in I} \sum_{\substack{k \in K \\ k \neq 0}} \frac{1}{r_{ijk}}$$
(6.19)

s.t.
$$x_{ik} = x_{i0} + v_k^A A_x + v_k^B B_x$$
 $\forall i \in I, \forall k \in K : k \neq 0$ (6.20)
 $y_{ik} = y_{i0} + v_k^A A_y + v_k^B B_y$ $\forall i \in I, \forall k \in K : k \neq 0$ (6.21)

$$r_{ijk}^{2} = (x_{i0} - x_{jk})^{2} + (y_{i0} - y_{jk})^{2} + d_{ij}^{2} \quad \forall i \in I, \forall j \in I,$$

$$\forall k \in K : i \neq j \lor k \neq 0$$
 (6.22)

$$\forall i \in I$$
 (6.23)

$$y_{i0} \le B_y \qquad \qquad \forall i \in I \qquad (6.24)$$

$$y_{i0} \leq \frac{y}{B_x} x_{i0} \qquad \forall i \in I \qquad (6.25)$$

$$y_{i0} \geq \frac{B_y}{B_x} x_{i0} - \frac{A_x B_y}{B_x} \qquad \forall i \in I \qquad (6.26)$$

$$r_{ijk} \in \begin{bmatrix} r_{ijk}^{\text{LB}}, r_{ijk}^{\text{UB}} \end{bmatrix} \qquad \forall i \in I, \forall j \in I, \forall k \in K : k \neq 0 \qquad (6.27)$$

$$x_{ik} \in \begin{bmatrix} x_{ik}^{\text{LB}}, x_{ik}^{\text{UB}} \end{bmatrix} \qquad \forall i \in I, \forall k \in K \qquad (6.28)$$

$$\forall i \in I, \, \forall k \in K \tag{6.29}$$

6.3.1 NLP Model Results

 $y_{ik} \in \left[y_{ik}^{\text{LB}}, y_{ik}^{\text{UB}}\right]$

 $y_{i0} \geq 0$

The model presented in Eqns. 6.19–6.29 constitutes a non-convex NLP that is expected to have multiple local optima. In a preliminary investigation, we found that global optimizers had significant difficulty in solving problems for relatively small systems (i.e., 4 point charges or less). However, we found that the local optimizer IPOPT [225] coupled



Figure 6.2: Illustration of contributions to periodic tile energy. Each tile is labeled by an index, *k*. Red circles represent charges on the bottom plate and blue circles represent charges on the top plate. Black, double-headed arrows represent intra-tile interactions and gray, single headed arrows represent example inter-tile interactions between tiles o and 7.



Figure 6.3: Explanation of periodic tile boundary constraints. Constraints in the optimization model are noted next to each boundary.

with a grid multi-start algorithm could consistently find the global optimum confirmed by inspecting the potential energy surface. A few cases of identified patterns are plotted in Figure 6.4. In the first three cases (Figs. 6.4a–6.4c), the pattern roughly corresponds to symmetric patterns expected by intuition, and the deviation from the expected patterns could be used to quantify the quality of the truncation in the model. However, the fourth case highlights the major limitation of the truncation approach.

The pattern plotted in Figure 6.4d shows that the optimum of the NLP model was at the boundary of the tile when the true optimum of the problem on an infinite plate is at the center of the tile. This discrepancy is due to the fact that the optimizer is motivated to separate the charges as much as possible in the limited periodic images, and therefore, places charges on the top plate (blue points) at the rightmost edge where some tile images (e.g., the ~ 8 on the edge of the truncation) lack neighbors. This "cheating" is expected to impact all cases to some degree, but may contribute more when tiles have a small aspect ratio (\ll 1). The potential energy surface of this case is further illustrated in Figure 6.5, showing that the result identified by the NLP model was in fact a saddle point of the true potential energy surface. We furthermore show that the gradient in the *x* direction was relatively small for the true energy evaluation, explaining why truncation error in the NLP could distort the landscape to lead to the optimum at the edge of the tile.

Having identified specific cases that yield poor results with the NLP model, we further quantify the parity between the simplified, truncated objective function and the full Ewald summation evaluation (considered the "truth"). In Figure 6.6, we plot the Ewald summation evaluations against the objective of the NLP model for 1080 cases (drawn from 15 charge positions, 9 tile angles, 8 aspect ratios) of a simple 2-particle system. From these results, it is clear that the simplified objective value is a weak predictor of the true potential energy function.

6.4 BLACK-BOX NUMERICAL OPTIMIZATION APPROACH

While it is not possible to embed the exact equations for Ewald summation directly in a mathematical optimization model, we can still use numerical optimization to guide the placement of point charges in a "black box" approach. We accomplish this by using potential energy function evaluations in conjunction with automatic differentiation tools to calculate derivatives. Specifically, we utilize Autograd [145], an automatic differentiation package in Python, and cyIPOPT [125], a Python interface to the IPOPT solver [225].



(a) N = 2, $N^{\text{top}} = 1$, $\eta = 0.2$, $\theta = 90^{\circ}$, $\chi = 1.0$



(b) N = 2, $N^{\text{top}} = 1$, $\eta = 0.2$, $\theta = 60^{\circ}$, $\chi = 1.0$



(c) N = 3, $N^{\text{top}} = 1$, $\eta = 0.2$, $\theta = 60^{\circ}$, $\chi = 1.0$



(d) N = 2, $N^{\text{top}} = 1$, $\eta = 0.2$, $\theta = 90^{\circ}$, $\chi = 0.5$

Figure 6.4: Example solutions from the NLP optimization model. Red points correspond to charges on the bottom plate, blue points correspond to the top plate. The number of charges *N*, number of charges on the top plate N^{top} , dimensionless plate separation η , tile angle θ , and tile aspect ratio χ are given below each case.



(a) Isometric view of scaled potential energy surface.



(b) View perpendicular to the steepest gradients.



(c) Close-up of the curvature in *x*.

Figure 6.5: Potential energy surface for the case: N = 2, $N^{top} = 1$, $\eta = 0.2$, $\theta = 90^{\circ}$, $\chi = 0.5$. The red dot indicates the solution of the NLP approximation model, while the black dot indicates the optimum found by the numerical optimization approach.



Figure 6.6: Comparison of NLP objective values to calculated potential energies for a range of tile angles, tile aspect ratios, and charge positions.

While IPOPT is typically used to solve equation-oriented models (from which it automatically calculates derivatives), it can also accept function and derivative evaluations programmatically. In this way, we can optimize directly on the true potential energy surface without surrogate models.

However, this approach has the drawback of being computationally intensive. For small systems of 2 point charges, we found that the time to evaluate a derivative (\sim minutes) was an order of magnitude more expensive than evaluating the function for potential energy (\sim seconds). Additionally, the memory usage when using Autograd was significant (\sim 4 GB), presumably due to the need to store the calling tree for programmatically evaluating derivatives. These computational challenges were not investigated in detail, but it is clear that even after tuning, numerical optimization via function calls to the Ewald summation will be significantly more computationally expensive than optimization of a truncated version of the model.

In Figure 6.7, we plot the potential energy of solutions identified by numerical optimization given the NLP model solution as a starting point for tiles generated from 4 choices of tile angle and 8 choices of tile aspect ratio. In all cases, the numerical optimization approach was able to improve the solution identified by the NLP model. All together, these solutions allow us to identify the energy minimum placement of point charges and tile parameters for the specified plate separation and charge densities.



Figure 6.7: Improvement in potential energy of designs optimized by the black-box numerical optimization method given the NLP solution as a starting point. N = 2, $N^{\text{top}}=1$, $\eta = 0.1$.

We graphically analyze the results from several 2-electron systems by plotting the potential energies as a function of tile parameters, shown in Figure 6.8. In general, the trends of energy as a function of tile parameters are unintuitive and can exhibit optima at extremes or intermediate values of tile parameters. Importantly, we recreate the trend in optimal patterns of symmetric Wigner bilayers that are well-known in the literature [1, 68]. Specifically, at small (but nonzero) plate separation, we identify the rectangular tile arrangement know as the II phase (Figure 6.8a). At intermediate plate separation, the optimal pattern shifts to a square pattern known as the III phase (Figure 6.8b). And finally, at larger separation the optimal patterns are hexagonal close-packed layers known as the V phase (Figure 6.8c).

6.5 CONCLUSIONS

In this chapter, we have presented an approach for systematically identifying low-energy configurations of Wigner crystal bilayers. We first identified a nonlinear programming model that approximates the potential energy of the crystals by considering a truncated set of Coulomb interactions. We analyzed the results of this optimization model and identified cases where the truncation error significantly changes the optimal solutions to


(c) $\eta = 1.0$ (large separation)

Figure 6.8: Example optimal results of the 2-electron problem across tile parameters. The normalized plate separation, η , is given below each plot and the tile aspect ratio that attained the minimum energy is marked by a vertical arrow below the corresponding point.

the problem. To avoid such errors, we developed a numerical optimization approach to directly optimize the complex equations of the physically accurate model. We recreated some expected trends of stable crystalline phases, illustrating how the overall algorithm could be repeated to identify optimal patterns and tilings for general instances of the problem.

7

CONCLUSIONS AND FUTURE WORK

In this thesis, we have developed mathematical optimization approaches to guide the design of nanostructured materials. Models were derived for several types of material optimization problems, and in doing so, we identified common features that can be generically encoded so as to make our approaches applicable to a wide range of material applications. We have shown how materials science concepts like lattices, atoms, and structure-function relationships can be systematically translated into mathematical optimization models. In this way, we have lowered the barrier for rigorous mathematical optimization to be applied by material experts. In the following sections, we summarize the key contributions of our work and then present several directions for future research.

7.1 CONTRIBUTIONS

In Chapter 2, we showed how mathematical optimization can be used to systematically identify modifications to a transition metal heterogeneous catalyst surface to produce highly active nanostructured surfaces.

- We showed how transition metal crystal systems exhibiting the Sabatier principle and adhering to a discrete lattice can be modeled by implication logic via mixed integer linear programming models.
- We demonstrated that the quality of optimization results on finite canvases tends to be sensitive to the size of the canvas. Results tend to improve as canvas size increases due to additional degrees of freedom, however, we identified a significant increase in problem difficulty as the number of locations increased.

- We identified translational and rotational symmetry in our design space that had an adverse impact on the ability to solve optimization models. We also identified symmetry-breaking constraints that led to a significant improvement in the tractability of the resulting optimization problems.
- In some cases, we confirmed intuitively optimal designs, but in many more cases we identified non-intuitive designs that maximized the desired material reactivity through complex nanostructure patterns. In the motivating case of the oxygen reduction reaction, we identified a novel pattern that was significantly more reactive than the design from recent literature which was identified via intuition.

In Chapter 3, we identified several sub-models for better representing heterogeneous catalysts, lifting many of the simplifying assumptions that we had utilized previously.

- We showed how implication logic can be used to account for partial reactivity of catalyst sites.
- We regressed a simplified structure-function relationship for the surface energy of nanostructured tiles that was amenable to be embedded in mathematical optimization models.
- We introduced additional constraints to indicate the formation of "over-binding" sites in the material as an approach to approximately represent the coverage on nanostructured surfaces. As a more restrictive approximation, we also introduced formulations that model coverage only on the strongest-adsorbing sites.
- We showed how results from our optimization models can be parametrically collected and analyzed to indicate the sensitivity of reaction turnover to the various constraints on the material design space.

In Chapter 4, we demonstrated a complete workflow for materials design on a bulk metallic oxide starting by first proposing computational chemistry experiments and ending with analysis of optimization results.

- We demonstrated a general modeling strategy for attributing material functionality in a doped perovskite to local neighborhoods of sites termed motifs.
- We showed how density functional theory evaluations can be incorporated into mathematical optimization models via binary variables to indicate motifs in the material.

- We highlighted the flexibility of the conformation indication formulation by presenting three related optimization models that could be interchanged by simply modifying model coefficients.
- We compared our results to those expected from randomly synthesized materials, quantifying both the value of controlling the material nanostructure and designing via mathematical optimization.

In Chapter 5, we identified the common features of nanostructured material design problems that can be efficiently modeled in mixed-integer linear programming models. From these commonalities, we developed a Python package to streamline the specification of the materials design space and automate the formulation of optimization models.

- We identified a set of basic variables that are common to many types of material design problems and can be used to quickly build more complicated models.
- We developed a Python package, MatOpt, for streamlining the process of specifying nanostructured materials optimization models.
 - We defined several object classes for constructing and manipulating the material information necessary to populate the optimization model data structures.
 - We created another set of objects for specifying material descriptors and structure-function relationships from simple input, automatically managing the details of indexed constraints.
 - We provided simple routines for automatically converting implication logic to mixed-integer linear programming formulations and for solving the resulting optimization problems.
- We demonstrated the effectiveness of using MatOpt in the context of two case studies, illustrating both the simple syntax and flexibility of the module.

In Chapter 6, we demonstrated how mathematical optimization can be applied to systematically identify patterns of point charges in Wigner crystal bilayers.

- We developed a simplified nonlinear programming model formulation to represent a truncated summation of Coulomb interactions on infinite plates.
- We analyzed the results of the approximate model to identify errors stemming from the truncation. In particular, we identified the fact that the truncated model can not be reliably used to co-optimize the placement of point charges and tile parameters in a single formulation.

• We proposed a numerical optimization approach to optimize the placement of point charges inside fixed, periodic tiles. By iterating over tile parameters, we mapped out several minimum energy patterns and reproduced a series of optimal patterns from the literature.

7.2 FUTURE DIRECTIONS

Several ideas can be generically explored that apply to each of the research areas presented in this thesis.

- Decomposition methods and other algorithm development can be further explored to improve the tractability of material optimization problems. We experimented with a few decomposition techniques but were never able to outperform general-purpose mixed-integer linear programming solvers.
- A systematic way to derive symmetry-breaking constraints would be valuable. We manually identified several such constraints, but we recognize opportunities for more systematic treatments that could improve the tractability of the model formulations.

In the design of nanostructured transition metal slabs, there are several avenues to extend the work to address more structure-function relationships.

- The developed models can be adapted to work in bimetallic materials. This will involve finding relevant structure-function relationships (e.g., volcano plots) that take into account a combination of coordination number and atom identity. This may potentially involve regression if no such models currently exist.
- There is an opportunity to formally model with parametric uncertainty the inability to reliably implement the optimal nanostructured solution (in addition to the modeling of stability, covered in Chapter 3). While the optimal nanostructured design may introduce the most active sites, a slightly less optimal design may be less susceptible to deactivation by atomic rearrangements and better overall.

In the context of models for stability and coverage of nanostructured catalysts, there is ample opportunity to model the relevant physics with higher fidelity.

• The model for stability demonstrated in Chapter ₃ can be modified to take into account corrective terms that are more complicated than coordination number. For

example, Roling, Li, and Abild-Pedersen [181] included a term for atoms in the first subsurface layer of metal slabs.

• The models for over-binding and coverage can be replaced by a simplified representation a microkinetic modeling trends. We provided several ways to approximate the relevant chemistry, but a tailored model for coverage would be useful to embed in the mathematical optimization model.

In the design of doped perovskites, there are opportunities for additional model development.

- There is an opportunity to model additional contributions to the vacancy formation energy as a function of dopant placement, improving the predictions of the simplified structure-function relationship. We considered the removal of the first oxygen atom, neglecting interactions between vacancies in the lattice. Additional modeling would improve predictions of subsequent oxygen removals from the lattice.
- The implementation uncertainty when synthesizing perovskites can be modeled to better represent the current synthesis capabilities. While the optimization model we considered in Chapter 4 resulted in optimistic targets for material performance, it would be useful to formulate a model that does not assume control over the precise placement of dopant atoms.

There are several opportunities to continue improving the MatOpt interface for translating nanostructured materials design problems into optimization models.

- We have provided several basic objects for modeling materials, but many more such objects can be defined. For example, additional nanocluster shapes, lattices, and building blocks can be created as new applications require them.
- The implementation of descriptor rules was limited by our current understanding of possible structure-function relationships. Additional rules may be needed to represent more complicated structure-function relationships that we have yet to consider.

For the design of Wigner crystals, several key extensions will be needed to fully demonstrate the advantages of applying mathematical optimization.

• We demonstrated several proof of concept results, but a much broader set of optimization results would be valuable (i.e., by considering more tile angles, aspect ratios, and point charges). This will likely require tuning the codes for Ewald summation to speed up the computation of potential energy and its derivatives.

- Our approach can be readily extended to obtain similar results for other types of potentials. For example, the Yukawa potential (also referred to as a screened Coulomb potential [149]) is of interest because it decreases faster than the Coulomb potential. Importantly, this functional form may yield acceptable results from a truncated nonlinear programming model, avoiding the need for numerical optimization of a complex Ewald summation.
- We designed Wigner crystals subject to a common periodic boundary on the top and bottom plate. While this is generically sufficient to represent any tiling, it may be more computationally efficient to consider distinct tile boundaries for each plate, enabling smaller tiles to represent the same periodic patterns.

- L. Aamaj and E. Trizac. "Critical phenomena and phase sequence in a classical bilayer Wigner crystal at zero temperature." *Physical Review B - Condensed Matter and Materials Physics* 85.20 (2012), pp. 1–15.
- [2] F. Abild-Pedersen et al. "Scaling properties of adsorption energies for hydrogencontaining molecules on transition-metal surfaces." *Physical Review Letters* 99.1 (2007), pp. 4–7.
- [3] T. Achterberg. "SCIP: Solving constraint integer programs." *Mathematical Programming Computation* 1.1 (July 2009), pp. 1–41.
- [4] A. V. Akimov and O. V. Prezhdo. "Large-Scale Computations in Chemistry: A Bird's Eye View of a Vibrant Field." *Chemical Reviews* 115.12 (2015), pp. 5797–5890.
- [5] F. A. Aldaye, A. L. Palmer, and H. F. Sleiman. "Assembling Materials with DNA as the Guide." *Science* 321.5897 (2008), pp. 1795–1799.
- [6] A. N. Andriotis et al. "Informatics guided discovery of surface structure-chemistry relationships in catalytic nanoparticles." *Journal of Chemical Physics* 140.9 (2014).
- [7] M. Antlanger, G. Kahl, M. Mazars, L. Šamaj, and E. Trizac. "Rich Polymorphic Behavior of Wigner Bilayers." *Physical Review Letters* 117.11 (2016), pp. 1–6.
- [8] M. Antlanger, G. Kahl, M. Mazars, L. Šamaj, and E. Trizac. "The asymmetric Wigner bilayer." *Journal of Chemical Physics* 149.24 (2018).
- [9] M. Attarian Shandiz. "Effective coordination number model for the size dependency of physical properties of nanocrystals." *Journal of Physics Condensed Matter* 20.32 (2008), p. 325237.
- [10] E. Auyeung et al. "DNA-mediated nanoparticle crystallization into Wulff polyhedra." *Nature* 505.7481 (2014), pp. 73–7.
- [11] S. Back, M. S. Yeom, and Y. Jung. "Understanding the Effects of Au Morphology on CO₂ Electrocatalysis." *Journal of Physical Chemistry C* 122.8 (2018), pp. 4274– 4280.
- [12] Z. M. Baiyee, C. Chen, and F. Ciucci. "A DFT+U study of A-site and B-site substitution in BaFeO_{3-δ}." *Phys. Chem. Chem. Phys.* 17.36 (2015), pp. 23511–23520.

- [13] T. A. Baker, C. M. Friend, and E. Kaxiras. "Atomic Oxygen Adsorption on Au(111) Surfaces with Defects." *The Journal of Physical Chemistry C* 113.8 (2009), pp. 3232– 3238.
- [14] F. Baletto. "Structural properties of sub-nanometer metallic clusters." *Journal of Physics Condensed Matter* 31.11 (2019), p. 113001.
- [15] M. J. Banholzer, J. E. Millstone, L. Qin, and C. a. Mirkin. "Rationally designed nanostructures for surface-enhanced Raman spectroscopy." *Chemical Society reviews* 37.5 (2008), pp. 885–897.
- [16] G. D. Barmparis, Z. Lodziana, N. Lopez, and I. N. Remediakis. "Nanoparticle shapes by using Wulff constructions and first-principles calculations." *Beilstein Journal of Nanotechnology* 6.1 (2015), pp. 361–368.
- [17] J. V. Barth, G. Costantini, and K. Kern. "Engineering atomic and molecular nanostructures at surfaces." *Nature* 437.7059 (2005), pp. 671–679.
- [18] M. P. Bendsøe and O. Sigmund. "Material interpolation schemes in topology optimization." Archive of Applied Mechanics 69.9-10 (1999), pp. 635–654.
- [19] H. M. Berman et al. "The protein data bank." Acta Crystallographica Section D: Biological Crystallography 58.6 I (2002), pp. 899–907.
- [20] E. Bianchi, C. N. Likos, and G. Kahl. "Self-assembly of heterogeneously charged particles under confinement." ACS Nano 7.5 (2013), pp. 4657–4667.
- [21] E. Bianchi, C. N. Likos, and G. Kahl. "Tunable assembly of heterogeneously charged colloids." *Nano Letters* 14.6 (2014), pp. 3412–3418.
- [22] C. T. Black et al. "Polymer self assembly in semiconductor microelectronics." IBM Journal of Research and Development 51.5 (2007), pp. 605–633.
- [23] D. W. Blaylock, T. Ogura, W. H. Green, and G. J. O. Beran. "Computational Investigation of Thermochemistry and Kinetics of Steam Methane Reforming on Ni (111) under Realistic Conditions." J. Phys. Chem. C 111 (2009), pp. 4898–4908.
- [24] T. Bligaard et al. "The Brønsted-Evans-Polanyi relation and the volcano curve in heterogeneous catalysis." *Journal of Catalysis* 224.1 (2004), pp. 206–217.
- [25] J. M. Bray, J. L. Smith, and W. F. Schneider. "Coverage-dependent adsorption at a low symmetry surface: DFT and statistical analysis of oxygen chemistry on kinked Pt(321)." *Topics in Catalysis* 57.1-4 (2014), pp. 89–105.
- [26] F. Brockherde et al. "Bypassing the Kohn-Sham equations with machine learning." *Nature Communications* 8.1 (2017), p. 872.

- [27] C. Burda, X. Chen, R. Narayanan, and M. A. El-Sayed. "Chemistry and properties of nanocrystals of different shapes." *Chemical Reviews* 105.4 (2005), pp. 1025–1102.
- [28] M. Caldorera-Moore, N. Guimard, L. Shi, and K. Roy. "Designer nanoparticles: incorporating size, shape and triggered release into nanoscale drug carriers." *Expert Opinion on Drug Delivery* 7.4 (2010), pp. 479–495.
- [29] F. Calle-Vallejo, M. T. M. Koper, and A. S. Bandarenka. "Tailoring the catalytic activity of electrodes with monolayer amounts of foreign metals." *Chemical Society Reviews* 42.12 (2013), pp. 5210–30.
- [30] F. Calle-Vallejo, J. I. Martinez, J. M. Garcia-Lastra, P. Sautet, and D. Loffreda. "Fast prediction of adsorption properties for platinum nanocatalysts with generalized coordination numbers." *Angewandte Chemie - International Edition* 53.32 (2014), pp. 8316–8319.
- [31] F. Calle-Vallejo et al. "Finding optimal surface sites on heterogeneous catalysts by counting nearest neighbors." *Science* 350.6257 (2015), pp. 185–189.
- [32] F. Calle-Vallejo, D. Loffreda, M. T. M. Koper, and P. Sautet. "Introducing structural sensitivity into adsorption-energy scaling relations by means of coordination numbers." *Nature Chemistry* 7.5 (2015), pp. 403–410.
- [33] C. T. Campbell. "Future Directions and Industrial Perspectives Micro- and macrokinetics: Their relationship in heterogeneous catalysis." *Topics in Catalysis* 1.3 (1994), pp. 353–366.
- [34] M. Carlo. "Highly Crystalline Multimetallic Nanoframes with Three-Dimensional Electrocatalytic Surfaces." *Science* 343.6177 (2014), pp. 1339–1343.
- [35] J. Cejka, A. Corma, and S. Zones. *Zeolites and Catalysis: Synthesis, reactions and applications*. Wiley-VCH Verlag GmbH & Co. KGaA, 2010.
- [36] R. Chattot et al. "Beyond Alloying Effects: Microstrain-Induced Enhancement of the Oxygen Reduction Reaction Kinetics on Various PtNi/C Nanostructures." *Submitted* (2016).
- [37] R. Chattot et al. "Surface distortion as a unifying concept and descriptor in oxygen reduction reaction electrocatalysis." *Nature Materials* 17.September (2018), pp. 1–7.
- [38] Q. Chen, S. C. Bae, and S. Granick. "Directed self-assembly of a colloidal kagome lattice." *Nature* 469.7330 (2011), pp. 381–384.
- [39] W. Chen, H. Wang, and R. A. Bartynski. *Nanofaceted Metal Surfaces: Structure, Reactivity, and Applications*. Elsevier Inc., 2015, pp. 301–338.

- [40] M. Cherry, M. Islam, and C. Catlow. "Oxygen Ion Migration in Perovskite-Type Oxides." *Journal of Solid State Chemistry* 118.1 (1995), pp. 125–132.
- [41] B. D. Chithrani, A. a. Ghazani, and W. C. W. Chan. "Determining the size and shape dependence of gold nanoparticle uptake into mammalian cells." *Nano Letters* 6.4 (2006), pp. 662–668.
- [42] T. S. Choksi, L. T. Roling, V. Streibel, and F. Abild-Pedersen. "Predicting Adsorption Properties of Catalytic Descriptors on Bimetallic Nanoalloys with Site-Specific Precision." *The Journal of Physical Chemistry Letters* (2019), pp. 1852–1859.
- [43] A. R. Cholach, A. A. Bryliakova, A. V. Matveev, and N. N. Bulgakov. "Resonant active sites in catalytic ammonia synthesis: A structural model." *Surface Science* 645 (2016), pp. 41–48.
- [44] C. J. Cramer. Essentials of Computational Chemistry: Theories and Models. John Wiley & Sons, 2013.
- [45] S. Curtarolo et al. "AFLOW: An automatic framework for high-throughput materials discovery." *Computational Materials Science* 58 (2012), pp. 218–226.
- [46] E. Danna, M. Fenelon, Z. Gu, and R. Wunderling. "Generating Multiple Solutions for Mixed Integer Programming Problems." In: *Proceedings of the Twelfth Conference on Integer Programming and Combinatorial Optimization*. Springer-Verlag Berlin Heidelberg, 2007, pp. 280–294.
- [47] R. A. De Souza and J. A. Kilner. "Oxygen transport in La_{1-x}Sr_xMn_{1-y}Co_yO_{3±δ} perovskites: Part II. Oxygen surface exchange." *Solid State Ionics* 126 (1999), pp. 153– 161.
- [48] J. Dean, Y. Yang, N. Austin, G. Veser, and G. Mpourmpakis. "Design of Copper-Based Bimetallic Nanoparticles for Carbon Dioxide Adsorption and Activation." *ChemSusChem* 11.7 (2018), pp. 1169–1178.
- [49] L. M. Demers et al. "Direct Patterning of Modified Oligonucleotides on Metals and Insulators by Dip-Pen Nanolithography." Science 296.5574 (2002), pp. 1836– 1838.
- [50] A. A. Emery, J. E. Saal, S. Kirklin, V. I. Hegde, and C. Wolverton. "High-Throughput Computational Screening of Perovskites for Water Splitting Applications." *Chemistry of Materials* 28 (2016), pp. 5621–5634.
- [51] A. Erba, J. Baima, I. Bush, R. Orlando, and R. Dovesi. "Large-Scale Condensed Matter DFT Simulations: Performance and Capabilities of the CRYSTAL Code." *Journal of Chemical Theory and Computation* 13.10 (2017), pp. 5019–5027.

- [52] J. Erlebacher, M. J. Aziz, A. Karma, N. Dimitrov, and K. Sieradzki. "Evolution of nanoporosity in dealloying." *Nature* 410.6827 (2001), pp. 450–453.
- [53] M. Escudero-Escribano, K. D. Jensen, and A. W. Jensen. "Recent advances in bimetallic electrocatalysts for oxygen reduction: design principles, structurefunction relations and active phase elucidation." *Current Opinion in Electrochemistry* 8 (2018), pp. 135–146.
- [54] M. Ezbiri, K. M. Allen, M. E. Gàlvez, R. Michalsky, and A. Steinfeld. "Design principles of perovskites for thermochemical oxygen separation." *ChemSusChem* 8.11 (2015), pp. 1966–1971.
- [55] J. Fang et al. "Recent advances in the synthesis and catalytic applications of ligand-protected, atomically precise metal nanoclusters." *Coordination Chemistry Reviews* 322 (2016), pp. 1–29.
- [56] O. K. Farha and J. T. Hupp. "Rational design, synthesis, purification, and activation of metal-organic framework materials." *Accounts of Chemical Research* 43.8 (2010), pp. 1166–1175.
- [57] J. Feng, X. Wang, Q. Zhang, Y. Yin, and Y. Bai. "Synthesis, Properties, and Applications of Hollow Micro-/Nanostructures." *Chemical Reviews* 116.18 (2016), pp. 10983–11060.
- [58] S. Fias, K. Y. S. Chang, and O. A. von Lilienfeld. "Alchemical normal modes unify chemical space." *The Journal of Physical Chemistry Letters* 10 (2018), pp. 30–39.
- [59] V. Fiorentini and M Methfessel. "Extracting convergent surface formation energies from slab calculations." *Journal of Physics: Condensed Matter* 8 (1996), pp. 6525– 6529.
- [60] E. L. First, C. E. Gounaris, J. Wei, and C. A. Floudas. "Computational characterization of zeolite porous networks: an automated approach." *Physical Chemistry Chemical Physics* 13.38 (2011), pp. 17339–17358.
- [61] B. Garlyyev et al. "Theoretical and experimental identification of active electrocatalytic surface sites." *Current Opinion in Electrochemistry* 14 (2018), pp. 206– 213.
- [62] B. Garlyyev et al. "Optimizing the Size of Platinum Nanoparticles for Enhanced Mass Activity in the Electrochemical Oxygen Reduction Reaction." Angewandte Chemie - International Edition (2019), pp. 9596–9600.
- [63] M. Geissler and Y. Xia. "Patterning: Principles and Some New Developments." Advanced Materials 16.15 (2004), pp. 1249–1269.

- [64] S. M. George. "Atomic Layer Deposition: An Overview." Chemical Reviews 110.1 (2010), pp. 111–131.
- [65] P. Ghosh, R. Pushpa, S. De Gironcoli, and S. Narasimhan. "Effective coordination number: A simple indicator of activation energies for NO dissociation on Rh(100) surfaces." *Physical Review B - Condensed Matter and Materials Physics* 80.23 (2009), p. 233406.
- [66] M. Gilleßen et al. "Oxygen-storage materials BaYMn₂O_{5+ δ} from the quantumchemical point of view." *Chemistry of Materials* 24.10 (2012), pp. 1910–1916.
- [67] V. J. Goldman, M. Santos, M. Shayegan, and J. E. Cunningham. "Evidence for Two-Dimensional Quantum Wigner Crystal." *Physical Review Letters* 65.17 (1990), pp. 2189–2192.
- [68] G. Goldoni and F. Peeters. "Stability, dynamical properties, and melting of a classical bilayer Wigner crystal." *Physical Review B - Condensed Matter and Materials Physics* 53.8 (1996), pp. 4591–4603.
- [69] B. R. Goldsmith, J. Esterhuizen, J.-X. Liu, C. J. Bartel, and C. Sutton. "Machine learning for heterogeneous catalyst design and discovery." *AIChE Journal* 64.7 (2018), pp. 2311–2323.
- [70] M. A. Gosálvez et al. "Low-coverage surface diffusion in complex periodic energy landscapes: Analytical solution for systems with symmetric hops and application to intercalation in topological insulators." *Physical Review B* 93.7 (2016), p. 075429.
- [71] J. Greeley, T. F. Jaramillo, J. Bonde, I. B. Chorkendorff, and J. K. Nørskov. "Computational high-throughput screening of electrocatalytic materials for hydrogen evolution." *Nature Materials* 5.11 (2006), pp. 909–13.
- [72] A. Gross. "Adsorption at nanostructured surfaces." *Journal of Computational and Theoretical Nanoscience* 5.5 (2008), pp. 894–922.
- [73] I. E. Grossmann and a. W. Westerberg. "Research challenges in Process Systems Engineering." AIChE Journal 46.9 (2000), pp. 1700–1703.
- [74] M. Grzelczak, J. Vermant, E. M. Furst, and L. M. Liz-Marzán. "Directed Self-Assembly of Nanoparticles." ACS Nano 4.7 (2010), pp. 3591–3605.
- [75] S. Guo, S. Zhang, and S. Sun. "Tuning nanoparticle catalysis for the oxygen reduction reaction." Angewandte Chemie - International Edition 52.33 (2013), pp. 8526– 8544.
- [76] Gurobi Optimization, Inc. Gurobi Optimizer Reference Manual. http://www.gurobi. com. 2019.

- [77] M. Hajfathalian et al. "A Wulff in a Cage: The Confinement of Substrate-Based Structures in Plasmonic Nanoshells, Nanocages, and Nanoframes Using Galvanic Replacement." ACS Nano 10.6 (2016), pp. 6354–6362.
- [78] N. J. Halas. "Playing with Plasmons: Tuning the Optical Resonant Properties of Metallic Nanoshells." MRS Bulletin 30.5 (2005), pp. 362–367.
- [79] B. Hammer, L. Hansen, and J. Nørskov. "Improved adsorption energetics within density-functional theory using revised Perdew-Burke-Ernzerhof functionals." *Physical Review B* 59.11 (1999), pp. 7413–7421.
- [80] B. Hammer and J. K. Nørskov. "Electronic factors determining the reactivity of metal surfaces." Surface Science 343.3 (1995), pp. 211–220.
- [81] B. Hammer and J. Nørskov. "Theoretical Surface Science and Catalysis Calculations and Concepts." *Advances in Catalysis* 45 (2000), pp. 71–129.
- [82] C. L. Hanselman and C. E. Gounaris. "A Mathematical Optimization Framework for the Design of Nanopatterned Surfaces." *AIChE Journal* 62.9 (2016), pp. 3250– 3263.
- [83] C. L. Hanselman et al. "Design of Doped Perovskite Oxygen Carriers Using Mathematical Optimization." In: 13th International Symposium on Process Systems Engineering (PSE 2018) (July 1, 2018–July 5, 2018). Ed. by M. R. Eden, M. Ierapetritou, and G. P. Towler. San Diego: Elsevier B.V., 2018, pp. 2461–2466.
- [84] C. L. Hanselman et al. "A Framework for Optimizing Oxygen Vacancy Formation in Doped Perovskites." Computers & Chemical Engineering 126 (2019), pp. 168–177.
- [85] C. L. Hanselman, W. Zhong, K. Tran, Z. W. Ulissi, and C. E. Gounaris. "Optimization-based Design of Active and Stable Nanostructured Surfaces." *Under Review* (2019).
- [86] W. E. Hart, J.-P. Watson, and D. L. Woodruff. "Pyomo: modeling and solving mathematical programs in Python." *Mathematical Programming Computation* 3.3 (2011), pp. 219–260.
- [87] W. E. Hart et al. Pyomo-optimization modeling in python. Second. Vol. 67. Springer Science & Business Media, 2017.
- [88] N. Hayashi et al. "BaFeO₃: A ferromagnetic iron oxide." *Angewandte Chemie International Edition* 50.52 (2011), pp. 12547–12550.
- [89] F. He et al. "The use of $La_{1-x}Sr_xFeO_3$ perovskite-type oxides as oxygen carriers in chemical-looping reforming of methane." *Fuel* 108 (2013), pp. 465–473.

- [90] Y. He et al. "Size-dependent dynamic structures of supported gold nanoparticles in CO oxidation reaction condition." *Proceedings of the National Academy of Sciences* 115.30 (2018), pp. 7700–7705.
- [91] J. Henzie, M. Grünwald, A. Widmer-Cooper, P. L. Geissler, and P. Yang. "Selfassembly of uniform polyhedral silver nanocrystals into densest packings and exotic superlattices." *Nature Materials* 11.2 (2011), pp. 131–137.
- [92] M. A. Herman, W. Richter, and H. Sitter. *Epitaxy: Physical Principles and Technical Implementation*. Ed. by R. Hull, J. Parisi, R. J. Osgood, and H. Warlimont. Springer-Verlag Berlin Heidelberg, 2004.
- [93] A. Hjorth Larsen et al. "The atomic simulation environment—a Python library for working with atoms." *Journal of Physics: Condensed Matter* 29.27 (2017), p. 273002.
- [94] X. Huang, Y. M. Xie, B. Jia, Q. Li, and S. W. Zhou. "Evolutionary topology optimization of periodic composites for extremal magnetic permeability and electrical permittivity." *Structural and Multidisciplinary Optimization* 46.3 (2012), pp. 385–398.
- [95] IBM Corp. IBM ILOG CPLEX Optimizer. https://www.ibm.com/analytics/cplexoptimizer. 2019.
- [96] T. Imaoka et al. "Platinum clusters with precise numbers of atoms for preparativescale catalysis." *Nature Communications* 8.1 (2017), p. 688.
- [97] N. E. Isenberg et al. "Identification of Optimally Stable Nanocluster Geometries via Mathematical Optimization and Density-Functional Theory."
- [98] T Ishihara, H Matsuda, and Y Takita. "Effects of Rare-Earth Cations Doped for La Site on the Oxide Ionic-Conductivity of LaGaO₃-Based Perovskite-Type Oxide." Solid State Ionics 79 (1995), pp. 147–151.
- [99] A. Jain et al. "The Materials Project: A materials genome approach to accelerating materials innovation." *APL Materials* 1.1 (2013), p. 011002.
- [100] A. Jain, J. A. Bollinger, and T. M. Truskett. "Inverse Methods for Material Design." AIChE Journal 60.8 (2014), pp. 2732–2740.
- [101] H. Y. Jang, H. J. Jang, D. K. Park, W. S. Yun, and S. Park. "Fabrication of shapecontrolled reduced graphene oxide nanorings by Au@Pt nanoring lithography." *Nanoscale* 7.2 (2015), pp. 460–464.
- [102] H. R. M. Jhong, S. Ma, and P. J. Kenis. "Electrochemical conversion of CO₂ to useful chemicals: Current status, remaining challenges, and future opportunities." *Current Opinion in Chemical Engineering* 2.2 (2013), pp. 191–199.

- [103] R. Jinnouchi and R. Asahi. "Predicting Catalytic Activity of Nanoparticles by a DFT-Aided Machine-Learning Algorithm." *The Journal of Physical Chemistry Letters* (2017), pp. 4279–4283.
- [104] A. Jones and M. S. Islam. "Atomic-scale insight into LaFeO₃ perovskite: Defect nanoclusters and ion migration." *Journal of Physical Chemistry C* 112.12 (2008), pp. 4455–4462.
- [105] M. Jørgensen and H. Grönbeck. "Scaling Relations and Kinetic Monte Carlo Simulations to Bridge the Materials Gap in Heterogeneous Catalysis." ACS Catalysis 7.8 (2017), pp. 5054–5061.
- [106] M. Jørgensen and H. Grönbeck. "The Site-Assembly Determines Catalytic Activity of Nanoparticles." Angewandte Chemie - International Edition (2018), pp. 5086–5089.
- [107] D. Joubert. "From ultrasoft pseudopotentials to the projector augmented-wave method." *Physical Review B - Condensed Matter and Materials Physics* 59.3 (1999), pp. 1758–1775.
- [108] I. Katsounaros, M. C. Figueiredo, X. Chen, F. Calle-Vallejo, and M. T. M. Koper. "Structure- and Coverage-Sensitive Mechanism of NO Reduction on Platinum Electrodes." ACS Catalysis (2017), pp. 4660–4667.
- [109] G. S. Khaira et al. "Evolutionary Optimization of Directed Self-Assembly of Triblock Copolymers on Chemically Patterned Substrates." ACS Macro Letters 3.8 (2014), pp. 747–752.
- [110] D. Kim et al. "Electrochemical Activation of CO2through Atomic Ordering Transformations of AuCu Nanoparticles." *Journal of the American Chemical Society* 139.24 (2017), pp. 8329–8336.
- [111] M. E. King and M. L. Personick. "Bimetallic Nanoparticles with Exotic Facet Structures via Iodide-Assisted Reduction of Palladium." *Particle & Particle Systems Characterization* 34.5 (2017), p. 1600422.
- [112] J. R. Kitchin, J. K. Nørskov, M. A. Barteau, and J. G. Chen. "Modification of the surface electronic and chemical properties of Pt(111) by subsurface 3d transition metals." *Journal of Chemical Physics* 120.21 (2004), pp. 10240–10246.
- [113] J. R. Kitchin. "Correlations in coverage-dependent atomic adsorption energies on Pd(111)." *Physical Review B - Condensed Matter and Materials Physics* 79.20 (2009), p. 205412.
- [114] H. Ko, S. Singamaneni, and V. V. Tsukruk. "Nanostructured surfaces and assemblies as SERS media." Small 4.10 (2008), pp. 1576–1599.

- [115] S. Koh. "Strategies for Controlled Placement of Nanoscale Building Blocks." English. Nanoscale Research Letters 2.11 (2007), pp. 519–545.
- [116] S. Koh and P. Strasser. "Electrocatalysis on bimetallic surfaces: Modifying catalytic reactivity for oxygen reduction by voltammetric surface dealloying." *Journal of the American Chemical Society* 129.42 (2007), pp. 12624–12625.
- [117] M. Konuk and S. Durukanoğlu. "Shape-controlled Growth of Metal Nanoparticles: An Atomistic View." *Phys. Chem. Chem. Phys.* 18.3 (2016), pp. 1876–1885.
- [118] M. T. M. Koper. "Structure sensitivity and nanoscale effects in electrocatalysis." Nanoscale 3.5 (2011), pp. 2054–2073.
- [119] A. A. Koulakov and B. I. Shklovskii. "Charging spectrum of a small Wigner crystal island." Philosophical Magazine B: Physics of Condensed Matter; Statistical Mechanics, Electronic, Optical and Magnetic Properties 77.5 (1998), pp. 1235–1247.
- [120] S. M. Kozlov and K. M. Neyman. "Insights from methane decomposition on nanostructured palladium." *Journal of Catalysis* 337 (2016), pp. 111–121.
- [121] G. Kresse and J. Hafner. "Ab initio molecular-dynamics simulation of the liquidmetal-amorphous-semiconductor transition in germanium." *Physical Review B* 49.20 (1994), pp. 14251–14269.
- [122] G. Kresse and J. Furthmüller. "Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set." *Computational Materials Science* 6.1 (1996), pp. 15–50.
- [123] G. Kresse and J. Hafner. "Ab initio molecular dynamics for liquid metals." *Physical Review B* 47.1 (1993), pp. 558–561.
- [124] R. van de Krol, Y. Liang, J. Schoonman, Y. Liang, and J. Schoonman. "Solar hydrogen production with nanostructured metal oxides." *Journal of Materials Chemistry* 18.20 (2008), pp. 2311–2320.
- [125] M. Küemmerer. cyIPOPT: Python wrapper for IPOPT. https://github.com/ matthias-k/cyipopt.
- [126] D. D. Landis et al. "The computational materials repository." *Computing in Science* & Engineering 14.6 (2012), p. 51.
- [127] A. H. Larsen et al. "The atomic simulation environment—a Python library for working with atoms." *Journal of Physics: Condensed Matter* 29.27 (2017), p. 273002.

- [128] J. V. Lauritsen, R. T. Vang, and F. Besenbacher. "From atom-resolved scanning tunneling microscopy (STM) studies to the design of new catalysts." 111 (2006), pp. 34–43.
- [129] I. Lee, F. Delbecq, R. Morales, M. a. Albiter, and F. Zaera. "Tuning selectivity in catalysis by controlling particle shape." *Nature Materials* 8.2 (2009), pp. 132–138.
- [130] J. Lee et al. "Metal-organic framework materials as catalysts." *Chemical Society Reviews* 38.5 (2009), pp. 1450–1459.
- [131] Y.-L. Lee, J. Kleis, J. Rossmeisl, Y. Shao-Horn, and D. Morgan. "Prediction of solid oxide fuel cell cathode activity with first-principles descriptors." *Energy & Environmental Science* 4.10 (2011), pp. 3966–3970.
- [132] J. W. Lekse et al. "Tuning the Structure and Oxygen Storage Properties of $BaFeO_{3-d}$ Perovskites via Indium Substitution" (2018). Under review.
- [133] Q. Li et al. "Molecular 'surgery' on a 23-gold-atom nanoparticle." *Science Advances* 3.5 (2017), e1603193.
- [134] Q. Li et al. "Reconstructing the Surface of Gold Nanoclusters by Cadmium Doping." *Journal of the American Chemical Society* 139 (2017), pp. 17779–17782.
- [135] Z. Li, Z. Liu, H. Sun, and C. Gao. "Superstructured Assembly of Nanocarbons: Fullerenes, Nanotubes, and Graphene." *Chemical Reviews* 115.15 (2015), pp. 7046– 7117.
- [136] A. I. Liechtenstein, V. I. Anisimov, and J. Zaanen. "Density-functional theory and strong interactions: Orbital ordering in Mott-Hubbard insulators." *Physical Review B* 52.8 (1995), pp. 5467–5471.
- [137] N. C. Lindquist, P. Nagpal, K. M. McPeak, D. J. Norris, and S.-H. Oh. "Engineering metallic nanostructures for plasmonics and nanophotonics." *Reports on Progress in Physics* 75.3 (2012), p. 036501.
- [138] D. Liu et al. "Three-dimensional controlled growth of monodisperse sub-50 nm heterogeneous nanocrystals." *Nature Communications* 7 (2016), p. 10254.
- [139] X. Liu and D. Astruc. "From Galvanic to Anti-Galvanic Synthesis of Bimetallic Nanoparticles and Applications in Catalysis, Sensing, and Materials Science." *Advanced Materials* 29.16 (2017), p. 1605305.
- [140] Y. Lu et al. "Investigation of In-doped BaFeO_{3- δ} perovskite-type oxygen permeable membranes." *J. Mater. Chem. A* 3.11 (2015), pp. 6202–6214.

- [141] P. Ludwig, A. Filinov, Y. E. Lozovik, H. Stolz, and M. Bonitz. "Crystallization in mass-asymmetric electron-hole bilayers." *Contributions to Plasma Physics* 47.4-5 (2007), pp. 335–344.
- [142] J. Luo, J. Gao, A. Wang, and J. Huang. "Bulk Nanostructured Materials Based on Two-Dimensional Building Blocks: A Roadmap." ACS Nano 9.10 (2015), pp. 9432– 9436.
- [143] S. Luo, M. Tang, P. K. Shen, and S. Ye. "Atomic-Scale Preparation of Octopod Nanoframes with High-Index Facets as Highly Active and Stable Catalysts." *Advanced Materials* 29.8 (2017), p. 1601687.
- [144] X. Ma. "Orbitalwise Coordination Number for Predicting Adsorption Properties of Metal Nanocatalysts." *Physical Review Letters* 118.3 (2017), p. 036101.
- [145] D. Maclaurin, D. Duvenaud, M. Johnson, and J. Townsend. Autograd Python Package. https://github.com/HIPS/autograd.
- [146] N. Madaan, N. R. Shiju, and G. Rothenberg. "Predicting the performance of oxidation catalysts using descriptor models." *Catal. Sci. Technol.* 6.1 (2016), pp. 125– 133.
- [147] F. Margot. "Symmetry in Integer Linear Programming." In: 50 Years of Integer Programming 1958-2008: From the Early Years to the State-of-the-Art. Ed. by M. Jünger et al. Springer Berlin Heidelberg, 2010. Chap. 17, pp. 647–686.
- [148] R. J. Maurer et al. "Advances in Density-Functional Calculations for Materials Modeling." Annual Review of Materials Research 49 (2019), pp. 1–30.
- [149] M. Mazars. "Long ranged interactions in computer simulations and for quasi-2D systems." *Physics Reports* 500.2-3 (2011), pp. 43–116.
- [150] J. A. Millan, D. Ortiz, and S. C. Glotzer. "Effect of shape on the self-assembly of faceted patchy nanoplates with irregular shape into tiling patterns." *Soft Matter* 11 (2015), pp. 1386–1396.
- [151] M. Z. Miskin, G. Khaira, J. J. de Pablo, and H. M. Jaeger. "Turning statistical physics models into materials design engines." *Proceedings of the National Academy* of Sciences 113.1 (2016), pp. 34–39.
- [152] K. Morgenstern, N. Lorente, and K.-H. Rieder. "Controlled manipulation of single atoms and small molecules using the scanning tunnelling microscope." *Physica Status Solidi* (B) 250.9 (2013), pp. 1671–1751.

- [153] T. Motohashi et al. "Remarkable oxygen intake/release capability of BaYMn₂O_{5+δ}: Applications to oxygen storage technologies." *Chemistry of Materials* 22.10 (2010), pp. 3192–3196.
- [154] G. Mpourmpakis, A. N. Andriotis, and D. G. Vlachos. "Identification of descriptors for the CO interaction with metal Nanoparticles." *Nano Letters* 10.3 (2010), pp. 1041–1045.
- [155] O. Muller and R. Roy. *The major ternary structural families*. Springer, 1974.
- [156] A. B. Muñoz-García, M. Pavone, and E. A. Carter. "Effect of antisite defects on the formation of oxygen vacancies in Sr₂FeMoO₆: Implications for ion and electron transport." *Chemistry of Materials* 23.20 (2011), pp. 4525–4536.
- [157] A. B. Muñoz-García, A. M. Ritzmann, M. Pavone, J. A. Keith, and E. A. Carter. "Oxygen transport in perovskite-type solid oxide fuel cell materials: Insights from quantum mechanics." *Accounts of Chemical Research* 47.11 (2014), pp. 3340–3348.
- [158] C. B. Murray, C. R. Kagan, and M. G. Bawendi. "Synthesis and characterization of monodisperse nanocrystals and close-packed nanocrystal assemblies." *Annual Review of Materials Science* 30.1 (2000), pp. 545–610.
- [159] L. Nalbandian, A. Evdou, and V. Zaspalis. " $La_{1-x}Sr_xM_yFe_{1-y}O_{3-\delta}$ perovskites as oxygen-carrier materials for chemical-looping reforming." *International Journal of Hydrogen Energy* 36.11 (2011), pp. 6657–6670.
- [160] R. Narayanan and M. A. El-Sayed. "Shape-dependent catalytic activity of platinum nanoparticles in colloidal solution." *Nano Letters* 4.7 (2004), pp. 1343–1348.
- [161] National Energy Technology Laboratory. *Institute for the Design of Advanced Energy* Systems (IDAES). www.idaes.org.
- [162] J. K. Nørskov et al. "The nature of the active site in heterogeneous metal catalysis." *Chemical Society reviews* 37.10 (2008), pp. 2163–71.
- [163] J. K. Nørskov, T. Bligaard, J. Rossmeisl, and C. H. Christensen. "Towards the computational design of solid catalysts." *Nature Chemistry* 1.1 (2009), pp. 37–46.
- [164] J. Nørskov et al. "Universality in Heterogeneous Catalysis." *Journal of Catalysis* 209.2 (2002), pp. 275–278.
- [165] M. Núñez, J. L. Lansford, and D. G. Vlachos. "Optimization of the facet structure of transition-metal catalysts applied to the oxygen reduction reaction." *Nature Chemistry* 11.5 (2019), pp. 449–456.

- [166] M. Núñez and D. G. Vlachos. "Multiscale Modeling Combined with Active Learning for Microstructure Optimization of Bifunctional Catalysts." *Industrial & Engineering Chemistry Research* 58 (2019), pp. 6146–6154.
- [167] T. E. Oliphant. *Guide to NumPy*. Vol. 1. Trelgol Publishing, 2006.
- [168] S. P. Ong et al. "Python Materials Genomics (pymatgen): A robust, open-source python library for materials analysis." *Computational Materials Science* 68 (Feb. 2013), pp. 314–319.
- [169] J. D. Pack and H. J. Monkhorst. "Special points for Brillouin-zone integrations." *Physical Review B* 13.12 (1976), pp. 5188–5192.
- [170] J. Park et al. "Hollow nanoparticles as emerging electrocatalysts for renewable energy conversion reactions." *Chemical Society Reviews* 47.22 (2018), pp. 8173–8202.
- [171] G. Peng and M. Mavrikakis. "Adsorbate Diffusion on Transition Metal Nanoparticles." Nano Letters 15.1 (2015), pp. 629–634.
- [172] J. P. Perdew, K. Burke, and M. Ernzerhof. "Generalized gradient approximation made simple." *Physical Review Letters* 77.18 (1996), pp. 3865–3868.
- [173] J. P. Perdew et al. "Restoring the Density-Gradient Expansion for Exchange in Solids and Surfaces." *Physical Review Letters* 100.13 (2008), p. 136406.
- [174] A. V. Pinheiro, D. Han, W. M. Shih, and H. Yan. "Challenges and opportunities for structural DNA nanotechnology." *Nat Nano* 6.12 (2011), pp. 763–772.
- [175] S. Plimpton. "Fast parallel algorithms for short-range molecular dynamics." Journal of Computational Physics 117.1 (1995), pp. 1–19.
- [176] E.-J. Ras, M. J. Louwerse, and G. Rothenberg. "New tricks by very old dogs: Predicting the catalytic hydrogenation of HMF derivatives using Slater-type orbitals." *Catalysis Science & Technology* 2.12 (2012), pp. 2456–2464.
- [177] M. S. Rill et al. "Photonic metamaterials by direct laser writing and silver chemical vapour deposition." *Nat Mater* 7.7 (2008), pp. 543–546.
- [178] A. M. Ritzmann, A. B. Muñoz-García, M. Pavone, J. A. Keith, and E. A. Carter. "Ab Initio DFT+U analysis of oxygen vacancy formation and migration in $La_{1-x}Sr_xFeO_{3-\delta}$ (x = 0, 0.25, 0.50)." *Chemistry of Materials* 25.15 (2013), pp. 3011– 3019.
- [179] B. Roldan Cuenya and F. Behafarid. "Nanocatalysis: Size- and shape-dependent chemisorption and catalytic reactivity." *Surface Science Reports* 70.2 (2015), pp. 135–187.

- [180] L. T. Roling and F. Abild-Pedersen. "Structure-Sensitive Scaling Relations: Adsorption Energies from Surface Site Stability." *ChemCatChem* 10.7 (2018), pp. 1643– 1650.
- [181] L. T. Roling, L. Li, and F. Abild-Pedersen. "Configurational Energies of Nanoparticles Based on Metal-Metal Coordination." *The Journal of Physical Chemistry C* 121.41 (2017), pp. 23002–23010.
- [182] S. Royer et al. "Perovskites as substitutes of noble metals for heterogeneous catalysis: Dream or reality." *Chemical Reviews* 114.20 (2014), pp. 10292–10368.
- [183] M. Ruck, A. Bandarenka, F. Calle-Vallejo, and A. Gagliardi. "Fast identification of optimal pure platinum nanoparticle shapes and sizes for efficient oxygen electroreduction." *Nanoscale Advances* 1.8 (2019), pp. 2901–2909.
- [184] M. Rueck, A. S. Bandarenka, F. Calle-Vallejo, and A. Gagliardi. "Oxygen Reduction Reaction: Rapid Prediction of Mass Activity of Nanostructured Platinum Electrocatalysts." *Journal of Physical Chemistry Letters* 9.15 (2018), pp. 4463–4468.
- [185] F. Ruiz-Zepeda et al. "Atomically resolved anisotropic electrochemical shaping of nano-electrocatalyst." *Nano Letters* 19.8 (2019), pp. 4919–4927.
- [186] M. Rycenga, P. Camargo, and Y. Xia. "Template-assisted self-assembly: a versatile approach to complex micro- and nanostructures." *Soft Matter* 5.6 (2009), pp. 1129– 1136.
- [187] M. Rycenga, J. M. McLellan, and Y. Xia. "Controlling the Assembly of Silver Nanocubes through Selective Functionalization of Their Faces." *Advanced Materials* 20.12 (2008), pp. 2416–2420.
- [188] M. Rydén et al. "Novel oxygen-carrier materials for chemical-looping combustion and chemical-looping reforming; $La_xSr_{1-x}Fe_yCo_{1-y}O_{3-\delta}$ perovskites and mixedmetal oxides of NiO, Fe₂O₃ and Mn₃O₄." *International Journal of Greenhouse Gas Control* 2.1 (2008), pp. 21–36.
- [189] J. E. Saal, S. Kirklin, M. Aykol, B. Meredig, and C. Wolverton. "Materials design and discovery with high-throughput density functional theory: The open quantum materials database (OQMD)." JOM 65.11 (2013), pp. 1501–1509.
- [190] M. Salciccioli, M. Stamatakis, S. Caratzoulas, and D. G. Vlachos. "A review of multiscale modeling of metal-catalyzed reactions: Mechanism development for complexity and emergent behavior." *Chemical Engineering Science* 66.19 (2011), pp. 4319–4355.

- [191] K. Saravanan, J. R. Kitchin, O. A. V. Lilienfeld, and J. A. Keith. "Alchemical Predictions for Computational Catalysis: Potential and Limitations." J. Phys. Chem. Lett. 8 (2017), pp. 5002–5007.
- [192] Z. Sarshar, F. Kleitz, and S. Kaliaguine. "Novel oxygen carriers for chemical looping combustion: $La_{1-x}Ce_xBO_3$ (B = Co, Mn) perovskites synthesized by reactive grinding and nanocasting." *Energy & Environmental Science* 4.10 (2011), pp. 4258–4269.
- [193] K. Sawabe, T. Koketsu, J. Ohyama, and A. Satsuma. "A Theoretical Insight into Enhanced Catalytic Activity of Au by Multiple Twin Nanoparticles." *Catalysts* 7.6 (2017), p. 191.
- [194] D. E. Schipper et al. "Effects of Catalyst Phase on the Hydrogen Evolution Reaction of Water Splitting: Preparation of Phase-Pure Films of FeP, Fe₂P, and Fe₃P and Their Relative Catalytic Activities." *Chemistry of Materials* 30.10 (2018), pp. 3588–3598.
- [195] Z. W. Seh et al. "Combining theory and experiment in electrocatalysis: Insights into materials design." *Science* 355.6321 (2017), eaad4998.
- [196] M. Setvín et al. "Surface point defects on bulk oxides: atomically-resolved scanning probe microscopy." Chem. Soc. Rev. 39 (2017), pp. 3959–3968.
- [197] M. Shao, Q. Chang, J.-P. Dodelet, and R. Chenitz. "Recent Advances in Electrocatalysts for Oxygen Reduction Reaction." *Chemical reviews* 116.6 (2016), pp. 3594– 3657.
- [198] J. H. Shim et al. "Process-property relationship in high-k ALD SrTiO₃ and BaTiO₃: A review." J. Mater. Chem. C (2017), pp. 8000–8013.
- [199] D. Sholl and J. A. Steckel. Density functional theory: A practical introduction. John Wiley & Sons, 2011.
- [200] O. Sigmund and S. Torquato. "Design of Materials With Extreme Thermal Expansion Using a Three-Phase Topology." *Journal of the Mechanics and Physics of Solids* 45.6 (1997), pp. 1037–1067.
- [201] E. O. P. Solis, P. I. Barton, and G. Stephanopoulos. "Controlled Formation of Nanostructures with Desired Geometries. 1. Robust Static Structures." *Industrial* & Engineering Chemistry Research 49.17 (2010), pp. 7728–7745.
- [202] E. O. P. Solis, P. I. Barton, and G. Stephanopoulos. "Controlled formation of nanostructures with desired geometries. 2. Robust dynamic paths." *Industrial and Engineering Chemistry Research* 49.17 (2010), pp. 7746–7757.

- [203] C. Song. "Global challenges and strategies for control, conversion and utilization of CO₂ for sustainable development involving energy, catalysis, adsorption and chemical processing." *Catalysis Today* 115.1-4 (2006), pp. 2–32.
- [204] M. Stamatakis and D. G. Vlachos. "A graph-theoretical kinetic Monte Carlo framework for on-lattice chemical kinetics." *Journal of Chemical Physics* 134.21 (2011), p. 214115.
- [205] V. Stamenkovic et al. "Changing the activity of electrocatalysts for oxygen reduction by tuning the surface electronic structure." Angewandte Chemie - International Edition 45.18 (2006), pp. 2897–2901.
- [206] C. Stegelmann, A. Andreasen, and C. T. Campbell. "Degree of rate control: How much the energies of intermediates and transition states control rates." *Journal of the American Chemical Society* 131.23 (2009), pp. 8077–8082.
- [207] G. Stephanopoulos and G. V. Reklaitis. "Process systems engineering: From Solvay to modern bio- and nanotechnology.: A history of development, successes and prospects for the future." *Chemical Engineering Science* 66.19 (2011), pp. 4272–4306.
- [208] N. Stephanopoulos, E. O. P. Solls, and G. Stephanopoulos. "Nanoscale process systems engineering: Toward molecular factories, synthetic cells, and adaptive devices." *AIChE Journal* 51.7 (2005), pp. 1858–1869.
- [209] I. E. L. Stephens, A. S. Bondarenko, U. Grønbjerg, J. Rossmeisl, and I. Chorkendorff. "Understanding the electrocatalysis of oxygen reduction on platinum and its alloys." *Energy & Environmental Science* 5.5 (2012), pp. 6744–6762.
- [210] J. Suntivich et al. "Design principles for oxygen-reduction activity on perovskite oxide catalysts for fuel cells and metal-air batteries." *Nature Chemistry* 3.7 (2011), pp. 546–550.
- [211] H. Tang et al. "Classical strong metal-support interactions between gold nanoparticles and titanium dioxide." *Science Advances* 3.10 (2017), e1700231.
- [212] A. A. Taskin, A. N. Lavrov, and Y. Ando. "Achieving fast oxygen diffusion in perovskites by cation ordering." *Applied Physics Letters* 86.9 (2005), pp. 1–3.
- [213] S. Tawfi et al. "Engineering of Micro- and Nanostructured Surfaces with Anisotropic Geometries and Properties." Advanced Materials 24 (2012), pp. 1628– 1674.
- [214] M. G. Taylor, N. Austin, C. E. Gounaris, and G. Mpourmpakis. "Catalyst Design Based on Morphology- and Environment-Dependent Adsorption on Metal Nanoparticles." ACS Catalysis 5.11 (2015), pp. 6296–6301.

- [215] D. Tomanek, S. Mukherjee, and K. H. Bennemann. "Simple theory for the electronic and atomic structure of small clusters." *Phys. Rev. B* 28.2 (1983), pp. 665– 673.
- [216] K. Tran, A. Palizhati, and Z. W. Ulissi. "Dynamic Workflows for Routine Materials Discovery in Surface Science." *Journal of Chemical Information and Modeling* 58 (2018), pp. 2392–2400.
- [217] K. Tran and Z. W. Ulissi. "Active learning across intermetallics to guide discovery of electrocatalysts for CO₂ reduction and H₂ evolution." *Nature Catalysis* 1.9 (2018), pp. 696–703.
- [218] Z. W. Ulissi, A. R. Singh, C. Tsai, and J. K. Nørskov. "Automated Discovery and Construction of Surface Pourbaix Diagrams using Machine Learning." J. Phys. Chem. Lett. 7 (2016), pp. 3931–3935.
- [219] Z. W. Ulissi et al. "Machine-Learning Methods Enable Exhaustive Searches for Active Bimetallic Facets and Reveal Active Site Motifs for CO₂ Reduction." ACS Catalysis 7.10 (2017), pp. 6600–6608.
- [220] Z. W. Ulissi, A. J. Medford, T. Bligaard, and J. K. Nørskov. "To address surface reaction network complexity using scaling relations machine learning and DFT calculations." *Nature Communications* 8 (2017), p. 14621.
- [221] E. Vignola et al. "A machine learning approach to graph-theoretical cluster expansions of the energy of adsorbate layers." *The Journal of Chemical Physics* 147.5 (2017), p. 054106.
- [222] F. Viñes, J. R. B. Gomes, and F. Illas. "Understanding the reactivity of metallic nanoparticles: beyond the extended surface model for catalysis." *Chemical Society Reviews* 43.14 (2014), pp. 4922–4939.
- [223] V. Vorotnikov and D. G. Vlachos. "Group additivity and modified linear scaling relations for estimating surface thermochemistry on transition metal surfaces: Application to furanics." *Journal of Physical Chemistry C* 119.19 (2015), pp. 10417– 10426.
- [224] D. M. Vriezema et al. "Self-Assembled Nanoreactors." Chemical Reviews 105.4 (2005), pp. 1445–1490.
- [225] A. Wächter and L. T. Biegler. "On the implementation of an interior-point filter line-search algorithm for large-scale nonlinear programming." *Mathematical programming* 106.1 (2006), pp. 25–57.

- [226] S. Wang, N. Omidvar, E. Marx, and H. Xin. "Coordination numbers for unraveling intrinsic size effects in gold-catalyzed CO oxidation." *Physical Chemistry Chemical Physics* 20.9 (2018), pp. 6055–6059.
- [227] S. Wang, N. Omidvar, E. Marx, and H. Xin. "Overcoming Site Heterogeneity in Search of Metal Nanocatalysts." ACS Combinatorial Science 20.10 (2018), pp. 567– 572.
- [228] Y.-J. Wang et al. "Carbon-Supported Pt-Based Alloy Electrocatalysts for the Oxygen Reduction Reaction in Polymer Electrolyte Membrane Fuel Cells: Particle Size, Shape, and Composition Manipulation and Their Impact to Activity." *Chemical Reviews* 115.9 (2015), pp. 3433–3467.
- [229] L. Ward and C. Wolverton. "Atomistic calculations and materials informatics: A review." Current Opinion in Solid State and Materials Science 21.3 (2017), pp. 167– 176.
- [230] S. C. Warren et al. "Identifying champion nanostructures for solar water-splitting." *Nature Materials* 12.9 (2013), pp. 842–849.
- [231] G. M. Whitesides and B. Grzybowski. "Self-Assembly at All Scales." Science 295.5564 (2002), pp. 2418–2421.
- [232] L. Whittaker, J. M. Velazquez, and S. Banerjee. "A VO-seeded approach for the growth of star-shaped VO2 and V2O5 nanocrystals: facile synthesis, structural characterization, and elucidation of electronic structure." *CrystEngComm* 13.17 (2011), pp. 5328–5336.
- [233] E. Wigner. "On the interaction of electrons in metals." *Physical Review* 46.11 (1934), pp. 1002–1011.
- [234] K. A. Willets and R. P. Van Duyne. "Localized Surface Plasmon Resonance Spectroscopy and Sensing." Annual Review of Physical Chemistry 58.1 (2007), pp. 267– 297.
- [235] C. A. Wolcott, A. J. Medford, F. Studt, and C. T. Campbell. "Degree of rate control approach to computational catalyst screening." *Journal of Catalysis* 330 (2015), pp. 197–207.
- [236] K. L. Wustholz et al. "Structure-activity relationships in gold nanoparticle dimers and trimers for surface-enhanced Raman spectroscopy." *Journal of the American Chemical Society* 132.31 (2010), pp. 10903–10910.
- [237] Y. Xia and N. J. Halas. "Shape-Controlled Synthesis and Surface Plasmonic Properties of Metallic Nanostructures." MRS Bull. 30.5 (2005), pp. 338–348.

- [238] Y. Xia, Y. Xiong, B. Lim, and S. Skrabalak. "Shape-Controlled Synthesis of Metal Nanocrystals: Simple Chemistry Meets Complex Physics?" Angewandte Chemie International Edition 48.1 (2009), pp. 60–103.
- [239] X. Xie et al. "Large-Scale Synthesis of Palladium Concave Nanocubes with High-Index Facets for Sustainable Enhanced Catalytic Performance." Sci. Rep. 5 (2015), p. 8515.
- [240] Z. Xu and J. R. Kitchin. "Probing the coverage dependence of site and adsorbate configurational correlations on (111) surfaces of late transition metals." *Journal of Physical Chemistry C* 118.44 (2014), pp. 25597–25602.
- [241] Z. Yan, M. G. Taylor, A. Mascareno, and G. Mpourmpakis. "Size-, Shape-, and Composition-Dependent Model for Metal Nanoparticle Stability Prediction." *Nano Lett.* 18.4 (2018), pp. 2696–2704.
- [242] X. Yang, B. E. Koel, H. Wang, W. Chen, and R. A. Bartynski. "Nanofaceted C/Re(1121): Fabrication, structure, and template for synthesizing nanostructured model Pt electrocatalyst for hydrogen evolution reaction." ACS Nano 6.2 (2012), pp. 1404–1409.
- [243] E. Ye, M. D. Regulacio, S.-Y. Zhang, X. J. Loh, and M.-Y. Han. "Anisotropically branched metal nanostructures." *Chem. Soc. Rev.* 44 (2015), pp. 6001–6017.
- [244] Y. Yu, Q. Zhang, Q. Yao, J. Xie, and J. Y. Lee. "Architectural design of heterogeneous metallic nanocrystals-principles and processes." *Accounts of chemical research* 47.12 (2014), pp. 3530–3540.
- [245] D. Yue, G. Guillen-Grosalbez, and F. You. "Global Optimization of Large-Scale Mixed Integer Linear Fractional Programming Problems: A Reformulation-Linearization Method and Process Scheduling Applications." AIChE Journal 59.11 (2013), pp. 4255–4272.
- [246] H. Zhang, M. Jin, and Y. Xia. "Noble-Metal Nanocrystals with Concave Surfaces: Synthesis and Applications." Angewandte Chemie International Edition 51.31 (2012), pp. 7656–7673.
- [247] J. Zhang, Q. Kuang, Y. Jiang, and Z. Xie. "Engineering high-energy surfaces of noble metal nanocrystals with enhanced catalytic performances." *Nano Today* 11.5 (2016), pp. 661–677.
- [248] L. Zhang et al. "Platinum-based nanocages with subnanometer-thick walls and well-defined, controllable facets." *Science* 349.6246 (2015), pp. 412–416.

- [249] Y. Zhang, F. Lu, K. G. Yager, D. van der Lelie, and O. Gang. "A general strategy for the DNA-mediated self-assembly of functional nanoparticles into heterogeneous systems." *Nat Nano* 8.11 (2013), pp. 865–872.
- [250] Z. Zhang et al. "Ion adsorption at the rutile-water interface: Linking molecular and macroscopic properties." *Langmuir* 20.12 (2004), pp. 4954–4969.
- [251] H. Zhao, J. Gui, J. Cao, and C. Zheng. "Molecular Dynamics Simulation of the Microscopic Sintering Process of CuO Nanograins Inside an Oxygen Carrier Particle." *Journal of Physical Chemistry C* 122.44 (2018), pp. 25595–25605.
- [252] Z. Zhao, Z. Chen, X. Zhang, and G. Lu. "Generalized Surface Coordination Number as an Activity Descriptor for CO₂ Reduction on Cu Surfaces." *The Journal* of *Physical Chemistry C* 120.49 (2016), pp. 28125–28130.
- [253] W. Zhou and Z. Wang. *Three-dimensional nanoarchitectures*. Springer New York, 2011.
- [254] W. Zhou, Q. Y. Lin, J. A. Mason, V. P. Dravid, and C. A. Mirkin. "Design Rules for Template-Confined DNA-Mediated Nanoparticle Assembly." Small 14.44 (2018), p. 1802742.