#### CREATION AND CONTROL OF QUANTUM STATES IN LAYERED MATERIALS

Nathan C. Frey

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Supervisor of Dissertation

Vivek B. Shenoy Eduardo D. Glandt President's Distinguished Professor, Materials Science and Engineering, University of Pennsylvania

Graduate Group Chairperson



I-Wei Chen Skirkanich Professor of Materials Innovation, Materials Science and Engineering, University of Pennsylvania

Dissertation Committee Eric Detsi Professor, Materials Science and Engineering, University of Pennsylvania

Yury Gogotsi Professor, Materials Science and Engineering, Drexel University

Liang Feng Professor, Materials Science and Engineering, University of Pennsylvania

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To my parents and Kate.

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The behavior of large and complex aggregates of elementary particles, it turns out, is not to be understood in terms of a simple extrapolation of a few particles. Instead, at each level of complexity entirely new properties appear, and the understanding of the new behaviors requires research which I think is as fundamental in its nature as any other.

-Philip W. Anderson

The emergence of the earliest atoms / Transform to a level extremely hard to fathom. -GZA, Wu-Tang Clan

## ABSTRACT

#### CREATION AND CONTROL OF QUANTUM STATES IN LAYERED MATERIALS

#### Nathan C. Frey

#### Vivek B. Shenoy

The creation, control, and communication of information is the foundation of our digital economy. But as our demands for information processing continually increase, fundamental limitations in the current generation of electronics threaten to bottleneck progress towards increased computational power. A new paradigm of information processing based on coherent quantum states will sidestep these limitations entirely and have far-reaching impacts in fields ranging from energy consumption to computational modeling of new functional materials. The primary goal of this thesis is to use physicsinformed rational design to develop platforms for the creation and control of quantum states in layered materials. This challenge is addressed by 1) accelerating the synthesis of new functional materials with machine learning; 2) designing quantum materials with multiscale modeling and simple phenomenological models; and 3) engineering layered materials for ultra-compact solid-state devices that will enable efficient information processing and storage. A new type of semi-supervised machine learning was developed to predict newly synthesizable layered transition metal carbides and nitrides. A crystal field model was applied and an electro-mechanical model parameterized by first-principles calculations was developed to investigate the origins and control of magnetism in layered transition metal carbides and nitrides. The insights from these investigations, combined with high-throughput simulations and machine learning, were deployed at scale on a database of over 100,000 inorganic crystal structures to identify multi-order quantum materials with coexisting magnetic and topological orders. An analytic model, tightbinding, and continuum approaches were used to predict intrinsic confinement of Dirac fermions in lateral heterostructures of transition metal dichalcogenides and engineer device architectures for optimal confinement. Deep transfer learning and machine learning models were used to map monolayer materials and their point defect structures directly to key properties relevant for controllable two-level systems. We explained trends in defect formation energy within a minimal physical picture of defect formation and identified point defects that are of interest for quantum and neuromorphic information processing. We anticipate that the models, methods, and findings presented in this thesis will contribute to a greater understanding of engineerable quantum states in layered materials.

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## Preface

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 H. Kumar, N. C. Frey, L. Dong, B. Anasori, Y. Gogotsi, and V. B. Shenoy, ACS Nano 11, 7648 (2017).

[2] N. C. Frey, H. Kumar, B. Anasori, Y. Gogotsi, and V. B. Shenoy, ACS Nano 12, 6319 (2018).

[3] C. C. Price\*, N. C. Frey\*, D. Jariwala, and V. B. Shenoy, ACS Nano (2019).

[4] T. Schultz\*, N. C. Frey\*, K. Hantanasirisakul\*, S. Park, S. J. May, V. B. Shenoy, Y. Gogotsi, and N. Koch, Chem. Mater. (2019).

[5] N. C. Frey, J. Wang, G. I. Vega Bellido, B. Anasori, Y. Gogotsi, and V. B. Shenoy, ACS Nano 13, 3031 (2019).

[6] N. C. Frey, A. Bandyopadhyay, H. Kumar, B. Anasori, Y. Gogotsi, and V. B. Shenoy, ACS Nano 13, 2831 (2019).

[7] G. Deysher, C. E. Shuck, K. Hantanasirisakul, N. C. Frey, A. C. Foucher, K. Maleski,A. Sarycheva, V. B. Shenoy, E. A. Stach, B. Anasori, and Y. Gogotsi, ACS Nano (2019).

[8] Y. Yang, K. Hantanasirisakul, N. C. Frey, B. Anasori, R. J. Green, P. C. Rogge, I. Waluyo, A. Hunt, P. Shafer, E. Arenholz, V. B. Shenoy, Y. Gogotsi, and S. J. May, 2D Mater. 7, 025015 (2020).

[9] N. C. Frey, M. K. Horton, J. M. Munro, S. M. Griffin, K. A. Persson, V. B. Shenoy. Sci. Adv. 6, eabd1076 (2020).

[10] N.C. Frey, D. Akinwande, D. Jariwala, and V.B. Shenoy, ACS Nano acsnano.0c05267 (2020).

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The following publications that I co-authored during my Ph.D. are *not* presented in this thesis:

[1] N. C. Frey, B. W. Byles, H. Kumar, D. Er, E. Pomerantseva, and V. B. Shenoy, Phys. Chem. Chem. Phys. 20, 9480 (2018).

[2] D. Er, H. Ye, N. C. Frey, H. Kumar, J. Lou, and V. B. Shenoy, Nano Lett. 18, 3943 (2018).

[3] A. Bandyopadhyay, N. C. Frey, D. Jariwala, and V. B. Shenoy, Nano Lett. 19, 7793 (2019).

[4] M. Han, K. Maleski, C. E. Shuck, Y. Yang, J. T. Glazar, A. C. Foucher, K. Hantanasirisakul, A. Sarycheva, **N. C. Frey**, S. J. May, V. B. Shenoy, E. A. Stach, Y. Gogotsi, Tailoring Electronic and Optical Properties of MXenes through Forming Solid Solutions. J. Am. Chem. Soc. (2020), doi:10.1021/jacs.0c07395.

# Chapter 1 Introduction

## 1.1 Information processing and storage

A bright vision of the future might include any number of technological revolutions enabled by novel nanomaterials. Arguably one of the most important potential revolutions is waiting in the field of information. The creation, control, storage, and communication of information is the foundation of our digital economy. We look to algorithms to curate and process information, and increasingly, to provide actionable insight and solutions to problems both scientific and societal. But as our demands for information processing continually increase, fundamental limitations in the current generation of electronics threaten to bottleneck progress towards increased computational power. A new paradigm of information processing based on coherent quantum states will sidestep these limitations entirely [1,2] and have far-reaching impacts in fields ranging from energy to medicine and beyond.

Conductor Graphene	Semimetal	Semiconductor		Insulator
	Graphene	WTe2	Black phosporus	MoS2
	TMDCs ne (WTe <sub>2</sub> ,TiSe <sub>2</sub> ,SnSe <sub>2</sub> ,etc.)	TMDCs (MoS <sub>2</sub> , WS <sub>2</sub> , MoSe <sub>2</sub> , WSe <sub>2</sub> ,etc)		
Graphene		Black ph	osphorus	h-BN
		Monoch (SnS, GaSe, G	alcogenides iaTe,InSe,etc.)	

Figure 1.1 Library of 2D materials. Reproduced with permission from [3].

### **1.2 Quantum states in layered materials**

Candidates for quantum information processing platforms include trapped ions [4], topological systems [5], and ultracoherent spintronics [6]. The persistent issue with these approaches is the requirement of extreme temperature and pressure conditions to prevent decoherence, which precludes inclusion of these technologies in practical devices. Twodimensional (2D) materials are a broad platform [7] (Figure 1.1) that host magnetic [8,9] and topological states [10], as well as quantum point defects (QPDs) with spin states that act as qubits [11]. Importantly, the interactions between layers can be engineered via van der Waals (vdW) stacking to control quantum states and produce entirely new phenomena. The library of available 2D materials is always expanding, but it remains a pressing problem to design and characterize new systems with desirable properties and guide experimental synthesis. One promising 2D materials family for exploring quantum phenomena is the collection of transition metal carbides, nitrides, and carbonitrides known as MX enes. MX enes are layered materials with the general formula  $M_{n+1}X_nT_x$  (M = early transition metal, X = C/N, T = O, OH, F, and n = 1-4). Transition metal dichalcogenides, with the formula MX<sub>2</sub>, and transition metal oxides are also promising model systems for investigating novel quantum states. The chemical and structural diversity of layered transition metal compounds, along with robustness to moisture and air, are major advantages over other platforms that allow for tuning electronic, topological, and magnetic properties.



Figure 1.2 Examples of quantum systems. Reprinted with permission from [12].

### **1.3 Multiscale modeling of layered materials**

Fundamentally, we want to understand the physics governing the properties of layered materials, at whatever length and time scales the properties of interest are relevant. To accomplish this, we adopt a multiscale modeling approach that bridges length scales from the fully atomistic to device-scale (Figure 1.2). In this way, we capture the relevant phenomena in quantum materials and apply the appropriate tool as needed to solve problems of interest. Model Hamiltonians, first-principles density functional theory, tight binding models, *ab initio* molecular dynamics, finite element methods, phenomenological models, and state-of-the-art machine learning are all used in this thesis to explore the rich diversity of phenomena exhibited by layered materials. In each chapter, we give an overview of the methods that are used and developed to model the systems of interest.



Figure 1.3 Multiscale modeling domains of applicability along time and length axes.

## 1.4 The goals of this thesis

The primary goal of this thesis is to use physics-informed rational design to develop platforms for the creation and control of quantum states in materials systems that exhibit 2D or quasi-2D phases. In this thesis, computational techniques that bridge length scales, from the atomistic to device-scale, are used to capture the relevant phenomena in quantum materials. We outline a holistic approach to theoretical materials discovery, synthesis, property prediction, and design, with the ultimate goal of achieving controllable quantum states in layered materials. This thesis is divided into three major sections:



**Figure 1.4** Schematic of the design goals of this thesis. Four principal mechanisms are investigated for applications from information storage to sensing and computing, spanning mono- and multi-layer materials systems.

# 1.4.1 Accelerating materials synthesis with positive and unlabeled machine learning

In **Chapter 2**, density functional theory is introduced in a high-throughput context. Machine learning as it applies to materials science, chemistry, and physics is introduced. A new type of semi-supervised positive and unlabeled machine learning is developed and applied to predict which new bulk MAX and 2D MXene phases are most likely to be synthesizable. Hybrid functionals and cluster expansion are used to calculate experimental

observables in MXene systems and draw direct comparison with experimental characterization of electronic structure.

# 1.4.2 Rational design of 2D magnetic materials and high-throughput discovery of composite quantum materials

In **Chapters 3** and 4, various models are introduced to understand the physics of magnetic phenomena in low dimensions arising from strong electron correlations. Namely, the crystal field theory of orbital energy degeneracy breaking, the Hubbard model and relativistic spin-orbit coupling within the DFT + U formalism, and the anisotropic Heisenberg model simulated with classical Monte Carlo. These models are used to develop a program for the rational design of 2D magnetic materials. A model for electro-mechanical control of 2D magnetism is developed. The effects of chemical, structural, and external degrees of freedom on magnetism in MXenes is explored and explained. These insights are then deployed at scale, with the development of automated computational workflows, to enable high-throughput screening for magnetic and topological order in inorganic composite quantum material candidates, including layered antiferromagnetic topological insulators, axion insulators, and ferromagnetic topological semimetals.

### 1.4.3 Engineering quantum confinement and point defects

In Chapter 5, a multiscale modeling approach for probing localized quantum states in layered materials is discussed. Atomistic simulations are used to obtain material parameters and to compute formation energies and band structures for both pristine 2D materials and point defect systems. A heterostructure device architecture hosting massive Dirac fermion is introduced. The physics of quantum confinement and the existence of fermionic bound states is understood through a simple two-band  $\mathbf{k} \cdot \mathbf{p}$  model, which is then solved for toy systems with a generalized tight binding model, and for realistic device geometries with the finite element method. Optimal material and device geometry combinations are proposed. Deep transfer learning and machine learning are used to predict experimentally

relevant parameters for point defects in 2D materials, which can be engineered to achieve controllable systems for quantum and neuromorphic computing. New, optimized point defect structures are proposed, and trends in defect formation are explained for atomically thin resistive switching materials.

# Chapter 2 Accelerating materials synthesis with positive and unlabeled machine learning

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N. C. Frey, J. Wang, G. I. Vega Bellido, B. Anasori, Y. Gogotsi, and V. B. Shenoy, ACS Nano 13, 3031 (2019),

T. Schultz\*, N. C. Frey\*, K. Hantanasirisakul\*, S. Park, S. J. May, V. B. Shenoy, Y. Gogotsi, and N. Koch, Chem. Mater. (2019),

G. Deysher, C. E. Shuck, K. Hantanasirisakul, N. C. Frey, A. C. Foucher, K. Maleski, A.

Sarycheva, V. B. Shenoy, E. A. Stach, B. Anasori, and Y. Gogotsi, ACS Nano (2019), and

Y. Yang, K. Hantanasirisakul, N. C. Frey, B. Anasori, R. J. Green, P. C. Rogge, I. Waluyo, A. Hunt, P. Shafer, E. Arenholz, V. B. Shenoy, Y. Gogotsi, and S. J. May, 2D Mater. 7, 025015 (2020).

\* Denotes equal contribution.

### **2.1 Introduction**

In this chapter we discuss what is in many ways the zeroth order aim of theoretical materials science. Before we can move on to developing understanding of quantum states and exploiting that understanding for rational design of materials, we would like to address the problem of synthesizing and characterizing materials in the laboratory. While theory and computation oftentimes yield impressive predictions, the predictions and guidance offered by theory cannot be realized without experiment. Here, we adapt the method of positive and unlabeled (PU) machine learning (ML) to quantify the synthesizability of novel MAX and MXene phases based on descriptors derived from structure, stoichiometry, and first-principles calculations. We will review density functional theory (DFT) and take a more extensive look at how ML can be applied in materials science. Briefly, we discuss efforts to couple theory and experiment to characterize and discover new materials systems.

## 2.2 Methods

### 2.2.1 Density functional theory

There are something like Avogadro's number of DFT explainers and texts available (maybe not quite, but approaching that number). Here, we give a hopefully succinct review of the fundamentals of DFT and summarize when it is useful and when it is not. Later (in Chapter 4), DFT is used to study many more materials in a high-throughput context and further explanation will be given.

DFT is concerned with the problem of solving the many-body problem for electrons in solids and molecules. Typically, this problem is formulated with a time-independent Schrödinger equation in the Born-Oppenheimer approximation, giving an eigenvalue equation for N electrons of the form

$$H\Psi = E\Psi, \tag{2.1}$$

where *E* is the total energy,  $\Psi$  is the electron wavefunction depending on spatial coordinates  $r_i \dots r_N$  and spin degrees of freedom  $s_i \dots s_N$ . The Hamiltonian (*H*) is given by

$$H = T_e + V_{n-e} + V_{n-n} + V_{e-e}, (2.2)$$

$$T_e = -\sum_i \frac{\hbar^2}{2m_i} \nabla_{r_i}^2, \qquad (2.3)$$

$$V_{n-e} = -\frac{e^2}{4\pi\epsilon_0} \sum_j \sum_i \frac{Z_j}{|\mathbf{R}_j - \mathbf{r}_i|},$$
(2.4)

$$V_{n-n} = \frac{e^2}{8\pi\epsilon_0} \sum_{i\neq j} \frac{Z_i Z_j}{|\boldsymbol{R}_i - \boldsymbol{R}_j|},$$
(2.5)

$$V_{e-e} = \frac{e^2}{8\pi\epsilon_0} \sum_{i\neq j} \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|},$$
(2.6)

where  $T_e$  is the electron kinetic energy, and  $V_{n-e}$ ,  $V_{n-n}$ , and  $V_{e-e}$  are the nuclei-electron, nuclei-nuclei, and electron-electron interactions, respectively.  $R_i$  and  $r_i$  are the spatial coordinates of the *i*-th nucleus and electron, and the constants are defined as is typical. The boundary conditions for Eq. 2.1 are periodic for solids and in 0D systems the wavefunction decays to zero. There is a normalization condition  $\langle \Psi | \Psi \rangle = 1$ , and  $\Psi$  is antisymmetric under interchanges of electron coordinates. *E* can be obtained as the expectation value of the Hamiltonian,

$$E[\Psi] = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}.$$
(2.7)

There is no known analytical solution to obtain the ground state wavefunction  $\Psi_0$  that minimizes Eq. 2.7. There are many approximate solutions to the problem, and DFT is one such method.

DFT is rooted in two theorems due to Hohenberg and Kohn [13] that can be stated simply as 1) the ground state potential  $v_{ext}(\mathbf{r})$  is determined uniquely by the ground state electron density  $\rho(\mathbf{r})$ ; and 2)  $\rho(\mathbf{r})$  can be determined from the ground state energy functional  $E[\rho(\mathbf{r})]$  by application of the variational principle. These theorems transform the intractable many-body problem into a tractable problem of specifying an energy functional.

Kohn and Sham proposed using non-interacting orbitals that make the evaluation of the kinetic energy term trivial, portioning the many-body interactions into a separate term [14]. They wrote the energy functional as

$$E[\rho] = T[\rho] + V[\rho] + E_{xc}[\rho]$$
(2.8)

with  $T[\rho]$  as the kinetic energy,  $V[\rho]$  as the classical Coulomb repulsion, and  $E_{xc}[\rho]$  the "exchange-correlation" energy. This defines a new Kohn-Sham effective potential

$$v_{eff}(\mathbf{r}) = v_{ext}(\mathbf{r}) + \frac{\delta V[\rho]}{\delta \rho} + \frac{\delta E_{xc}[\rho]}{\delta \rho}.$$
(2.9)

In terms of this effective potential, the Kohn-Sham equations can be written with an effective single particle Hamiltonian as

$$h_{eff}\Psi_i = \left(-\frac{1}{2}\nabla^2 + \nu_{eff}\right)\Psi_i = \varepsilon_i\Psi.$$
 (2.10)

So we see that the many-body problem has been cast to a single particle problem in a mean field,  $v_{eff}$ . All the difficulty has been hidden in the form of  $E_{xc}[\rho]$ , and there are many

flavors of DFT that differ in how they approximate the exchange-correlation. Here, we will restrict the discussion to three general classes of functional that are used in this thesis.

The first is the generalized gradient approximation (GGA) [15] which includes terms from the local density approximation (LDA) [14], namely, the exact exchange energy density of a uniform electron gas and an approximate correlation energy density fit from quantum Monte Carlo (QMC) calculations. As might be expected from the name, GGA also includes terms involving the gradient of the electron density. Particular implementations of GGA including Perdew-Burke-Ernzerhof (PBE) [15] and PBEsol [16] are used in this thesis as the workhorse methods for calculating ground state energies, forces, and equilibrium structures of solid-state materials.

The next level of approximation is the hybrid functional. Hybrid functionals incorporate a tunable portion of exact exchange from Hartree-Fock (HF) theory and either *ab-initio* or empirical exchange-correlation. This has been shown to give improved accuracy for many properties, most notably electronic properties like band gaps in semiconductors. In this thesis we use the Heyd-Scuseria-Ernzerhof (HSE) functional [17,18] primarily for computing band structures. HSE uses a screened Coulomb potential where two parameters, a and  $\omega$ , control the amount of mixing between HF and PBE exchange and the cutoff for the short-range interaction, respectively. HSE06 uses values of a = 1/4 and  $\omega = 1/5$  that are empirically found to give reasonable results for most systems.

Finally, we make use of so-called meta-GGAs. Naturally following from the GGA, meta-GGAs make use of the Laplacian of the orbitals, or the kinetic energy density. We use the Strongly Constrained and Appropriately Normed (SCAN) [19] functional, which further improves accuracy of electronic property prediction through its semilocal approximation to the exchange-correlation energy. SCAN strikes a balance between computational efficiency (being less expensive than hybrid methods) and outperforming older methods in some domains (structure and energetics) [20,21]. Still, SCAN fails to capture much of the interesting physics of strongly correlated electrons [22].

DFT is our method of choice for calculating fundamental materials properties in an *ab initio* way, but often as inputs to other models or methods, because DFT is an extremely limited method. Depending on computational resources and implementation details, DFT can handle systems of hundreds or thousands of electrons. This brief exploration of the "ladder of chemical accuracy" with regards to exchange-correlation approximation methods illustrates the complexity of multiscale modeling – we have not even left the domain of small length scale quantum mechanical calculations! And extensions to these methods will be required to handle electron correlations, relativistic effects, and other complications. These extensions will be introduced as needed throughout this thesis.

#### 2.2.2 Positive and unlabeled machine learning

In this section we discuss our adaptation of a machine learning (ML) method called positive and unlabeled (PU) learning [23–26]. Most ML approaches are either "supervised" or "unsupervised" methods; that is, an ML model is trained on data that is completely labeled and perfectly characterized (supervised) or on data that has no labels, where the model must "discover" the labels (unsupervised). In reality, most problems are somewhere inbetween, in the sense that we (humans) have only partial or incomplete knowledge of how to label or classify the data, so some of the inputs are unlabeled. In this situation, semisupervised methods like PU learning are used. This is particularly relevant for the problem of materials synthesis, where synthesized samples can be thought of as "positive" (labeled) and materials that have not yet been synthesized are "unlabeled."

Our method is a variant of the transductive bagging support vector machine (SVM) [24]. SVMs are a fundamental type of ML classifier that look at data represented as points in a high-dimensional feature space and find a hyperplane that maximally separates categories of data. Bagging (also called bootstrapping) is a technique for creating ensembles of base classifiers to improve stability and accuracy while reducing overfitting. Transductive means that the model will attempt to correctly label the unlabeled data.

Bagging can be applied to other classifiers, so we switch from SVMs to decision trees [27,28], which are more widely used in modern ML because of their power and flexibility. The entire PU learning scheme is shown schematically in Figure 2.1. For some set of data, we denote P the set of positive (labeled) samples and U the set of unlabeled samples. K is the number of positive samples and T is the number of bootstraps (the bagging size). In each one of T iterations, a decision tree classifier is constructed and a random subsample of U, denoted  $U_s$ , is treated as negative samples. The classifier is trained on P and  $U_s$  then predicts the likelihood that each remaining sample in  $U \setminus U_s$  is positive or negative. The size of  $U_s$  is chosen to be the same as K to ensure balanced training. After T iterations are complete, the final score x of an unlabeled sample is given by averaging over all the scores predicted by decision trees that did not see that sample during training. If the score x > 0.5, then the sample is labeled positive; else it is labeled negative. This threshold is arbitrary and more granular detail can be seen by examining individual scores or distributions of scores.



Figure 2.1 Positive and unlabeled learning workflow. Reprinted with permission from [29].

In practice, this procedure is repeated with k-fold cross-validation, so that the dataset is split k times and the training occurs only on k-1 splits so that the predictive performance can be tested on the remaining split. This is repeated for every possible training/testing split of the k folds. Moreover, the entire process detailed thus far is repeated up to 1,000 times. Increasing the bagging size and number of folds only incidentally increases the training time, but the model stability must be tested over many iterations, which substantially increases the runtime of the training.
The PU learning method has been implemented in the Python package *Positive and Unlabeled Materials Machine Learning (pumml)* and is available on github: https://github.com/ncfrey/pumml.

We also implement a different PU learning approach and repeat the analysis using the robust ensemble SVM (RESVM) method [25]. RESVM uses class weighted SVMs with empirically tuned misclassification penalties for positive and unlabeled samples,  $C_P$ and  $C_U$ , where  $C_P > C_U$ . During training, random samples of size  $n_P$  and  $n_U$  are drawn from **P** and **U**, respectively, and  $C_P$  is determined using a model hyperparameter,  $w_P$ according to

$$C_P = \frac{C_U w_P n_U}{n_P}.$$
(2.11)

Another hyperparameter,  $\gamma$ , controls the radial basis functions during the optimization. The hyperparameters are tuned using a grid search, starting from the suggested values in Ref. [25]. Similar to the approach outlined above, RESVM builds an ensemble of models, with individual models predicting scores for samples they have not been trained on. This ensemble approach reduces the bias of individual models and prevents overfitting. The final score for an unlabeled sample x is obtained by aggregating the scores from the ensemble and using majority voting. The fraction of positive votes is given by

$$v(x) = \frac{1}{2} + \frac{1}{n} \sum_{i} sgn(\psi_i(x)), \qquad (2.12)$$

where *n* is the number of SVM models and  $\psi_i$  is the decision function of *i*-th model. As above, v > 0.5 is assigned a positive label, while v < 0.5 is assigned negative.

## 2.2.3 k-means clustering

*k*-means clustering [30] is a standard "unsupervised" machine learning method, where samples are not labelled in any way, and the algorithm's goal is to identify clusters of similar samples. It is a simple but powerful technique to quickly group data, especially when labelling is impractical or impossible. Samples are described by vectors of features, and the algorithm partitions the samples into k clusters based on the distance between each sample and the mean of the cluster. This is stated mathematically as

$$argmin\sum_{i=1}^{k}\sum_{\mathbf{x}\in S_{i}}\left|\left|\mathbf{x}-\boldsymbol{\mu}_{i}\right|\right|^{2}=argmin\sum_{i=1}^{k}\left|S_{i}\right| Var S_{i}$$
(2.13)

where x is the set of feature vectors,  $S_i$  is the *i*-th set of samples, and  $\mu_i$  is the mean of samples in  $S_i$ . This minimizes the variance within each cluster, or equivalently minimizes the pairwise deviations between points within each cluster.

The basic implementation of naive k-means randomly chooses k observations and uses their means to initialize k clusters. Then, the samples are iterated through, assigning each one to the cluster its mean is closest to, and then updating the cluster mean (centroid) values. The procedure is repeated until the sample assignments do not change, but this is not guaranteed to find optimal clusters. In practice, there are more sophisticated initialization schemes that accelerate convergence, and testing must be done to identify the true number of clusters that best describes the data set, if this is not known *a priori*.

#### 2.2.4 Cluster expansion

To compute thermodynamic properties for alloys and disordered solid solutions, we combine first-principles DFT calculations with an ML-like representation of alloy energetics called cluster expansion [31]. Cluster expansion enables the prediction of the energy for any configuration, based on calculated energies of a small number of known configurations (< 50). In the simple case of a binary alloy defined by a parent lattice, each site in the lattice has an occupation variable  $\sigma_i$ , where  $i \in \{1, -1\}$  and depends on the type

of atom occupying the site. This spin-like representation allows any alloy configuration to be represented by a vector of spins,  $\sigma$ . The cluster expansion is a parameterization of the energy per atom of the alloy as a polynomial in  $\sigma_i$ :

$$E(\sigma) = \sum_{\alpha} m_{\alpha} J_{\alpha} \left\langle \prod_{i \in \alpha'} \sigma_i \right\rangle$$
(2.14)

where  $\alpha$  is a set of sites *i* (a cluster),  $J_{\alpha}$  are the effective cluster interaction (ECI) coefficients, and  $m_{\alpha}$  are the multiplicities. The sum is over all clusters that are not symmetrically equivalent under an operation of the space group of the parent lattice, and the average is taken over all clusters  $\alpha'$  that are symmetrically equivalent to  $\alpha$ . The multiplicity is the number of clusters equivalent to  $\alpha$  divided by the number of lattice sites.

The cluster expansion converges rapidly, such that usually sufficient accuracy can be achieved only by including short-range pair and small triplet interactions.  $J_{\alpha}$  values are obtained by fitting to a small number of configurations. We use the cluster expansion construction as implemented in the MIT *Ab initio* Phase Stability (MAPS) code [32] included in the Alloy Theoretic Automated Tookit (ATAT) package [33].

## 2.3 Results

## **2.3.1 Dataset preparation**

With the PU learning model introduced above, the challenge is two-fold: 1) identify trends in synthesized materials and predict new synthesizable materials; and 2) validate these predictions. First, although the mathematical details of the model are presented above, we will discuss the particulars of applying the method to a particular materials problem. Setting up the problem involves identifying a suitable family of materials that has enough chemical diversity to provide ample not-yet-synthesized unlabeled samples and an adequate number of synthesized examples for training.

The family of 2D transition metal carbide and nitride MXenes and their parent bulk MAX phases are ideal for this purpose. MXenes have the general formula  $M_{n+1}X_nT_x$  (n =

1-4) and MAX phases are layers of MXene interleaved with A-group elements. With the large variety of chemical compositions, solid solutions, number of layers, and variable surface chemistry, MXenes provide a huge chemical search space for ML models. More than 20 theoretically predicted MXenes have been successfully synthesized [34]. The space of accessible solid solutions is so vast that for this initial work we restrict the search to the 66 single M atom MXenes and their 792 MAX phase precursors. At the time this work was completed, 63 MAX phases and 10 single M MXenes had been reliably synthesized.

Having defined the search space and ML problem, the next task is to acquire a dataset. In order to make a predictive model, we need to provide descriptors that are linked in a non-trivial way to synthesizability. If the connection was trivial, we could exploit it simply guess which materials should be synthesized next. Of course, there is no such trivial predictor, which motivates the use of machine learning. Still, we can use our physical and chemical intuition and understanding of MAX and MXene synthesis to suggest useful descriptors that should be collected. MXenes are synthesized via chemical etching of MAX phase, which exploits the reactivity of the metallic M-A bonds compared to the more inert M-X bonds [35]. Acidic solutions are used to selectively etch the A layer, which is almost always aluminum. Empirically, it has been observed that MAX phases with larger n and heavier M atoms require longer etching times and stronger solutions, which may be related to the number of valence electrons [36]. Based on these observations, we might expect certain descriptors to be of particular importance: features related to bond strengths like interlayer distances, bond lengths, and charge distributions; atomic masses and number of layers; and of course, thermodynamic data related to enthalpies of formation. To characterize each material, we collect exhaustive information on its structural and chemical properties from elemental data, as well as DFT-derived properties. DFT calculations for each material were used to obtain interlayer distances, bond lengths, formation energies, and charge densities. Over 80 features were collected to describe each material.

To evaluate the internal model performance, the true positive rate (TPR) is defined as the percentage of correctly classified samples according to the metric

$$TPR = \frac{1}{R} \sum_{i}^{R} \frac{1}{K} \sum_{k=1}^{K} TPR_{k,r}, \qquad (2.13)$$

where R is the number of total model training repetitions and K is the number of splits. The TPR is computed first from the predictions of out-of-fold validation samples, then averaged over all k folds, and finally averaged over all the model training cycles. The model training is repeated for both MAX and MXene, varying the number of repetitions, bagging size, and number of splits systematically while holding the other two at a sufficiently large value. Once the models have been internally tested as much possible and "converged" with respect to these three hyperparameter values, we examine the maximum TPRs and begin model interpretation.



**Figure 2.2** Model feature importance graphs for (a) MAX and (b) MXene models. Reprinted with permission from [29].

## 2.3.2 Model evaluation

The graphs in Figure 2.2 show the top 50 most important features for the MAX and MXene models. The feature importance reveals how useful each feature is in determining the synthesizability of samples. For the MAX phases, the five most important features are the formation energy, number of layers, M atom Bader charge, system mass, and cohesive energy. The X atom Bader charge, M atom ionization potentials, and c lattice constant are also among the 10 most important features. These features encode information about thermodynamic stability and strength of the M-X bond, which is in line with our chemical intuition. Feature importance for the MXene model is also consistent with empirical

observations. The most important features include M–X bond length, cohesive and formation energies, per-atom mass, and the Bader charges for the M and X atoms. Again, strength of the M–X bond and the overall thermodynamic stability are of paramount importance. Interestingly, the simple metric of number of M atom valence electrons is not important, although this feature is generally highly correlated with the M atom Bader charge; previous experiments have suggested this feature is strongly tied to synthesis success [37].

The trained models predict that 111 of the 729 unlabeled MAX phases are synthesizable. This reduces the chemical search space for MAX synthesis to 17% of its original size, significantly narrowing the search for new viable materials, while still providing many candidates and plenty of chemical variety to explore. We find ten of the 11 possible M species are represented – no compounds containing W were predicted positive, but W may be stabilized in solid solutions. All 12 possible A species and all three n = 1, 2, 3 layer thicknesses are also accounted for. Nitrides account for 29 predicted positives, including Mn<sub>2</sub>AlN, although no Mn-based MAX phases have been successfully synthesized as of yet. We emphasize the nitride and Mn-based compounds due to the possibility that they might be precursors for MXenes with superior magnetic properties, for which no parent phases are currently available.

To evaluate the model's predictive power, beyond the internal hyperparameter tuning and cross-validation, we consider three physics-informed stability tests: 1) thermodynamic, 2) dynamical, and 3) binary-phase. 87% of predicted positives are "viable crystals," satisfying the thermodynamic criterion of negative heat of formation (compared to most stable unary phases of constituent elements) and the Cauchy-Born elastic stability criteria [38]. We further tested the phase stability of predicted positive M<sub>2</sub>AX compounds against their competing binary phases using the MaterialsWeb [39] database. 89% of the predicted positives are stable or metastable by this criterion. These physical tests of crystal stability give confidence that the model predictions are based on relevant physical and chemical data and are therefore able to capture the underlying factors that determine synthesizability.

#### 2.3.3 Synthesizability predictions

Of the 56 unlabeled MXenes, 18 are predicted positive by the model and these compounds are listed in Table 2.1. Fourteen of the 18 have formation energies below 200 meV/atom, so they are considered stable by the general threshold for 2D material stability [40]. The four unstable systems (W<sub>4</sub>C<sub>3</sub>, Ta<sub>2</sub>C, W<sub>3</sub>C<sub>2</sub>, and Mo<sub>4</sub>C<sub>3</sub>) may be stabilized by surface functionalization or as solid solutions; W and Mo in particular are known to be stabilized with alloying of other elements [41]. As a further check, we find that 16 of the compounds have medium or high elastic stability reported in the Computational 2D Materials Database (C2DB) [42].

Hf <sub>4</sub> C <sub>3</sub>	Sc <sub>2</sub> C	Zr <sub>4</sub> C <sub>3</sub>
Ta <sub>4</sub> N <sub>3</sub>	Ta <sub>3</sub> C <sub>2</sub>	$Sc_4C_3$
Sc <sub>3</sub> C <sub>2</sub>	Ti <sub>4</sub> C <sub>3</sub>	Mo <sub>4</sub> C <sub>3</sub>
Nb <sub>3</sub> C <sub>2</sub>	$W_3C_2$	Ti <sub>2</sub> N
Ta <sub>2</sub> C	$W_4C_3$	Hf <sub>4</sub> N <sub>3</sub>
Zr <sub>2</sub> C	Hf <sub>2</sub> C	Nb <sub>2</sub> N

Table 2.1 Predicted synthesizable single-M MXenes.

The model predicts many synthesizable systems that do not have close analogs in the set of already available materials, including Ta, Hf, and Nb nitrides, as well as Sc- and W-based MXenes. To access these compounds (for which no MAX precursors exist), ongoing research is being done on nanolaminated ternary phases like (W, Ti)<sub>4</sub>C<sub>4-x</sub> [43] and other alloys.

The scaled errors of machine learning model predictions decrease with increasing sample size. Data sets for machine learning in materials science typically use between 100 and 104 training samples [44]. Additionally, traditional *k*-fold cross-validation is overly optimistic when evaluating materials discovery machine learning models, because materials data sets are often skewed and the goal is to detect materials with anomalous characteristics or performance [45]. With these points in mind, it is particularly important

and necessary in this study to compare the model predictions to external measures of validation like experiments, especially because of the small number of available samples in this study.

With this in mind, next we test our model predictions against experimental observations by comparing the MXenes that are predicted to be difficult to synthesize to compounds for which we have unsuccessfully attempted synthesis. The lack of available MAX phase precursor is responsible for the lack of success in synthesizing many MXenes. For example, there are no reported MAX phase precursors for Hf<sub>3</sub>N<sub>2</sub>, Cr<sub>3</sub>C<sub>2</sub>, Cr<sub>3</sub>N<sub>2</sub>, or Mo<sub>3</sub>N<sub>2</sub>. Even when MAX phases do exist, the attempted wet-chemical etching in hydrofluoric acid (HF)- containing aqueous solutions is not always successful. Although the Cr<sub>2</sub>AlC MAX phase has been available for many years [46], all attempts to make Cr<sub>2</sub>C via HF etching have been unsuccessful. To our knowledge, no selective etching of Al is observed for any concentration of HF; instead, the MAX phase powder is dissolved [47]. This suggests that  $Cr_2C$  is unlikely to be synthesized by the HF route. Similarly,  $Ti_4N_3$ dissolved in HF, but it was synthesized via molten salt etching [48]. However, molten salt etching has not been successful for Cr<sub>2</sub>C (not published). These experimental findings agree with our predictions that materials with low synthesizability scores are difficult to synthesize. Indeed, Cr<sub>2</sub>C has a low synthesizability score of 0.25. Generally, many nitride MXenes have low scores, which also agrees with experimental observations that these compounds tend to dissolve in solution or simply do not have available precursors.



**Figure 2.3** Violin plots of synthesis probabilities as a function of atomic species. Nitrides are shown in blue, carbides are shown in green. MAX phase synthesizability versus (a) M atom and (b) A atom. (c) MXene synthesizability versus M atom. Reprinted with permission from [29].

We can examine the model predictions across constituent atomic species to identify broad trends in synthesizability. Figure 2.3 shows violin plots of the synthesis probability distributions. Distributions for carbides (green) are always equal to or higher than for nitrides (blue), which is expected because less than 15% of successfully synthesized MAX phases are nitrides. The lack of synthesized nitrides certainly biases the models towards carbides, but it also underscores the importance of identifying synthesizable nitrides to unlock new areas of chemical space. Most of the violin plots show a larger distribution at lower synthesizability, and smaller distributions at higher values. This also agrees with intuition from empirical results, which suggest that most of the not-yet synthesized compounds are more difficult to synthesize.

There is an apparent trend of decreasing synthesizability in the MAX phases with increasing M atom group number, such that group 4 Ti-, Zr-, and Hf-based compounds have much higher synthesizability than group 6 Mo- and W-based compounds. The A atom dependence is less clear, with scores spreading out over large ranges. It is clear that MXenes with V, Mn, and Cr have the lowest synthesizability, although this may be an artifact because compounds with strongly correlated 3*d* block electrons are likely to be magnetic, which was not accounted for in the calculations. We also find that synthesizable MAX phases have Bader charges that are  $\sim 2 e^{-1}$  less on the M atom than those that are predicted negative. This agrees with experimental observations that heavier M atoms with more valence electrons require stronger etching conditions and are more difficult to synthesize.

To overcome the relative scarcity of available data, we take advantage of the fact that these systems come as (MAX, MXene) pairs that can be treated as individual (precursor, 2D material) samples. By considering the 111 predicted positive MAX phases, we generate 111 (MAX, MXene) pairs and try to identify the most promising synthesis pathways, where novel MAX and MXenes may be synthesized together. A simple descriptor that characterizes chemical etching is the static exfoliation energy [49], which is defined as

$$E_{etch} = \frac{E_{MAX} - 2E_{MX} - 2\mu_A}{4S}$$
(2.14)

where  $E_{MAX}$  is the total energy of the MAX phase,  $E_{MX}$  is the energy of a MXene unit cell,  $\mu_A$  is the chemical potential of the A atom referenced to its most stable unary phase, and  $S = \frac{\sqrt{3}a^2}{2}$  is the surface area, with *a* the MAX phase in-plane lattice constant. For simplicity, we neglect surface terminations, which are known to affect MXene formation and etching energies [40]. The etching energy is used along with the MAX and MXene predicted synthesizability scores as inputs to *k*-means clustering in order to group (MAX, MXene) pairs and identify clusters of highly synthesizable, novel precursors and 2D materials.



**Figure 2.4** *k*-means clustering of (MAX, MXene) pairs. Predicted positive samples are shown in light green, predicted negative samples are orange, and the top 20 predicted positive samples are in dark green. Three representative samples are highlighted. Reprinted with permission from [29].

In Figure 2.4 we plot the clusters with the etching energy on the *z*-axis to aid the visualization. With clustering, we identify 20 pairs of not-yet-synthesized MAX phase and corresponding MXene that can both be synthesized with high probability. At the time this work was published, only A = AI MAX phases had been successfully etched into MXenes, but in line with our predictions, MAX phases with Ga and Si A layers have been successfully etched [50]. This provides further guidance to experiment, suggesting that of the 111 predicted positive MAX candidates, these 20 have the best possibility of also being chemically etched into new MXenes.

## 2.3.4 Characterizing electronic properties

Next, we will briefly discuss efforts to synthesize new MAX and MXene materials, as well as characterize their electronic structure, with the goal of understanding fundamental material properties that enable rational design strategies discussed in the next chapter. Recent success in synthesis has yielded the first n = 4 MAX phase, Mo<sub>4</sub>VAlC<sub>4</sub> and 2D Mo<sub>4</sub>VC<sub>4</sub> with five atomic layers of transition metal [41]. This material is a disordered solid solution that possibly crystallizes in a structure never before seen in MAX phases. This unlocks the possibility for new M'<sub>4</sub>M''AlC<sub>4</sub> phases with different transition metals.



**Figure 2.5** Calculated formation energies for M'<sub>4</sub>M''AlC<sub>4</sub> phases. (a) Comparison between ordered and disordered Mo<sub>4</sub>VAlC<sub>4</sub> structures. (b) Ordered M'<sub>4</sub>M''AlC<sub>4</sub> formation energies. Reprinted with permission from [41].

DFT calculations were used to determine the stabilities of O-, F-, and OHterminated Mo<sub>4</sub>VC<sub>4</sub>, 18 quasirandom solid-solution configurations of Mo<sub>4</sub>VAlC<sub>4</sub>, as well as an ordered configuration with one layer of V sandwiched between four layers of Mo (two layers of Mo on each side). Each of these phases were predicted to be stable, with Ohtermination the most favorable for the MXene, in agreement with experimental results. For Mo<sub>4</sub>VAlC<sub>4</sub>, there are solid-solution configurations that are more stable than the ordered configuration, suggesting that Mo<sub>4</sub>VAlC<sub>4</sub> is a solid-solution. The most stable solid-solution configuration that we calculated had *a* and *c* lattice parameters of 3.04 and 28.52 Å, respectively. This agrees well with our experimental results obtained with X-ray diffraction (a = 2.99 and c = 28.22 Å). DFT calculations were also performed to determine the thermodynamic stability of other  $M_5AlC_4$  MAX phases. The formation energies of ordered compositions were calculated where M' and M'' were Hf, Zr, Ti, Ta, Nb, V, Sc, Mo, and W. A summary of the predicted stability of these phases is shown in Figure 2.5(b). It is expected for many of the compositions that there may be at least one solid-solution structure that is more stable than the compositionally equivalent ordered structure. We present calculations for ordered MAX structures as a simple exploration of stability trends.

Interestingly, other phases containing Hf, Zr, and Ta, are predicted to be more stable than the synthesized Mo<sub>4</sub>VAlC<sub>4</sub>. The effect that the M' element has on the stability was determined to be much greater than that of M''. W- and Mo-containing compositions are the least stable and are the only two M' elements that produce some unstable compositions. For both Mo- and W-based MAX phases specifically, it is known that Mo and W avoid stacking with C in a face-centered cubic structure (FCC) [51], so alloying with another element that occupies some of the FCC sites relieves stress in the crystal. These calculations also show that most of the M elements can achieve higher stability when they are combined with another M element. The only exception to this is Hf which is most stable when M' = M''. Higher stability occurs when Hf, Zr, Ti, and Ta are the M' or M'' element. This agrees with other studies where these elements were predicted to stabilize MAX phases [52], and the lower formation energies were correlated with the difference in ionic radius between the M atoms [39].

To thoroughly explore the configuration space of the Mo<sub>4</sub>VAlC<sub>4</sub> system, we performed cluster expansion calculations around the concentration  $x_{Mo} = 0.8$ . The converged ground-state solid-solution structure has an energy 15.8 meV/atom lower than the ordered symmetric phase. The low energy structures generated during the cluster expansion calculations show that V avoids the middle layer in solid-solution. In this composition range, V prefers to occupy layers 2 and 4 in order to maximize the number of favorable Mo–V bonds and stabilize the crystal structure. Based on the crystal structure observed with transmission electron microscopy (TEM), we considered a nontypical MAX phase structure: Mo<sub>4</sub>VAlC<sub>4</sub> with *P6m2* symmetry, rather than the traditional *P6<sub>3</sub>/mmc*  space group [53], because this space group exhibits a herringbone-type structure like that observed with TEM. Mo<sub>4</sub>VAlC<sub>4</sub> with  $P\overline{6m2}$  symmetry also prefers a disordered solid-solution, with a solid-solution ground-state energy that is 67.8 meV/atom lower than the ordered, symmetric phase. The low energy structures exhibit the same Mo-rich middle layers. Interestingly, the ground state in the  $P\overline{6m2}$  geometry is 31.8 meV/atom lower in energy than the ground state in the  $P6_3/mmc$  geometry. This indicates that further study, both experimentally and theoretically, is required to confirm the structure of Mo<sub>4</sub>VAlC<sub>4</sub> and other theoretically predicted quaternary M<sub>5</sub>AlC<sub>4</sub> phases. However, the disordered structure and Mo-rich inner layer are independent of the space group.

The disordered structure and surface chemistry of MXenes makes it something of a challenge to correlate experimental observations with theoretical predictions. However, by systematically investigating four Ti-based MXenes,  $Ti_2CT_x$ ,  $Ti_3C_2T_x$ ,  $Cr_2TiC_2T_x$ , and  $Mo_2TiC_2T_x$ , we are able to map out their most fundamental electronic structures and identify robust properties and resolve contributions of individual species to electronic properties.



**Figure 2.6** Densities of states and band structures of Ti-based MXenes. Ti unoccupied *d*-orbital PDOS for (a) surface Ti<sub>2</sub>AlC / Ti<sub>2</sub>CT<sub>x</sub>, (b) surface and sub-surface Ti<sub>3</sub>AlC<sub>2</sub> / Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, and (c) sub-surface Cr<sub>2</sub>TiAlC<sub>2</sub> / Cr<sub>2</sub>TiC<sub>2</sub>T<sub>x</sub>. Reprinted with permission from [54]. (d) Band structure for Ti<sub>3</sub>C<sub>2</sub>O<sub>2</sub> (O occupying bridge site) and Ti<sub>3</sub>C<sub>2</sub>F<sub>2</sub> (F occupying A site). Reprinted with permission from [55].

In Figure 2.6(a-c), we present the Ti *d*-orbital-derived partial density of states (PDOS) above the Fermi level ( $E_F$ ) (the region of electronic structure probed by X-ray Absorption Spectroscopy (XAS))for three types of MAX phases (Ti<sub>2</sub>AlC, Ti<sub>3</sub>AlC<sub>2</sub>, and Cr<sub>2</sub>TiAlC<sub>2</sub>) and the corresponding O- and F-terminated MXenes. The PDOS of surface layer Ti atoms in MXenes is systematically shifted to lower energies compared to the MAX phase, which is qualitatively reproduced in XAS measurements. New peaks also emerge depending on the surface termination, while these effects are not seen for sub-surface Ti atoms.

Similarly, to probe the occupied states in MXenes, we performed exhaustive hybrid functional calculations of band structures of  $Ti_3C_2T_x$  with O, F, and OH terminations in four different high symmetry sites on the MXene surface: bridge, top, FCC (A), and hexagonal close packed (HCP-B) for a total of 12 band structures. By closely comparing the calculated band structures and comparing them to angle-resolved photoemission spectroscopy (ARPES) measurements, we identified signatures in the calculated band structures that reveal the surface chemistry and structure of MXene. Low-lying bands from F at FCC sites and dispersive features due to O at bridge sites (Figure 2.6(d)) were found in the ARPES measurements and used to determine the electronic structure-property relationship. By closely comparing first principles electronic structure of Ti-based MXenes. Based on these results, we propose that sub-surface M atoms are robust to the disordered MXene surface chemistry and n > 1 MXenes can be engineered with sub-surface layers to display surface invariant electronic and magnetic properties.

# **2.4 Conclusions**

We adapted positive and unlabeled machine learning to predict the synthetic accessibility (synthesizability) of novel bulk and 2D materials. We applied the method to the model materials system of 2D transition metal carbides and nitrides (MXene) and their bulk phase

precursors (MAX). The large dimensionality, chemical variety, and numerous successfully synthesized materials in this family makes these systems ideal for a machine learning study. Elemental data and density functional theory calculations were used to featurize each material and extensive testing was performed to optimize model hyperparameters and avoid overfitting. Our implementation of transductive bagging with decision tree base classifiers provides easily interpretable synthesizability scores between 0 and 1, and analyzing the results revealed that the trained models used features related to thermodynamics, bond strength, and charge distribution to make predictions, consistent with our physical and chemical intuition, as well as empirical observations. The model predicted 111 new MAX phases and 18 new single M MXenes to be synthesizable. We also identified the 20 most promising MAX phases that can also be chemically etched into new MXenes with high probability. We discussed the synthesis, structure, and stability of disordered Mo<sub>4</sub>VAlC<sub>4</sub> MAX and Mo<sub>4</sub>VC<sub>4</sub> MXene, the first MXene with five atomic layers of transition metal, and our predictions that many other M'<sub>4</sub>M''AlC<sub>4</sub> solid solution phases are synthetically accessible. With the aim of bringing new functionality to 2D materials, we presented detailed studies of electronic structure in Ti-based MXenes and direct comparison to experimental band structure and x-ray absorption measurements. This work further bridges the gap between theoretical materials design and experimental realization of novel 2D materials.

# Chapter 3 Rational design of 2D magnetic materials

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H. Kumar, N. C. Frey, L. Dong, B. Anasori, Y. Gogotsi, and V. B. Shenoy, ACS Nano 11, 7648 (2017),

N. C. Frey, H. Kumar, B. Anasori, Y. Gogotsi, and V. B. Shenoy, ACS Nano 12, 6319 (2018), and

N. C. Frey, A. Bandyopadhyay, H. Kumar, B. Anasori, Y. Gogotsi, and V. B. Shenoy, ACS Nano 13, 2831 (2019).

# **3.1 Introduction**

Magnetism in the monolayer limit has become a vibrant playground for exploring condensed matter physics phenomena, following the experimental realization of long-range magnetic order in monolayer chromium triiodide [56], atomic layers of  $Cr_2Ge_2Te_6$  [8], and  $VSe_2$  on van der Waals substrates [57]. In this chapter we introduce models to describe magnetic behavior in 2D and exploit this understanding to rationally design 2D magnetic materials with tunable, externally addressable spin states. We explore magnetic ordering in transition metal nitride MXenes and show how the chemical degrees of freedom in these systems allow for tunable magnetic anisotropy and spin symmetries. A strategy for reversibly switching 2D magnetic order with applied electric fields is proposed and rationalized with a simple macroscopic strain-response model.

## **3.2 Methods**

## **3.2.1 Crystal field theory**

Group theory is a powerful formalism used in condensed matter physics to describe physical systems based purely on symmetry considerations. For magnetic materials with strongly correlated electrons in localized d and f orbitals, group theory governs how the degeneracies of these orbitals split due to the presence of the external potential in a crystal lattice. The resulting crystal field, determined by the coordination environment of an atom in a crystal, gives states and degeneracies that are labeled by the irreducible representations of the symmetry group of Schrödinger's equation. The exact energy splittings due to a crystal field must be calculated (usually by a first-principles method), but the energy level degeneracies are specified exactly by the point group symmetry of the atom in the crystal field [58]. Physically, we interpret the degeneracy breaking as a consequence of orbitals overlap between d orbitals and the resulting repulsion, which raises the energy of orbitals closer to neighboring ligand atoms.

Most commonly, metal ions are coordinated in an octahedral environment, surrounded by six ligand atoms that form an octahedron. The  $O_h$  point group symmetry breaks the *d*-orbital degeneracy into low-lying  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$  orbitals labeled  $t_{2g}$  and higher energy  $d_z^2$  and  $d_x^2$ - $y^2$  orbitals labeled  $e_g$ . Depending on the competition between the crystal field energy splitting,  $\Delta_{cf}$ , and the Coulomb repulsion, the system will settle into either a high- or low-spin configuration. If  $\Delta_{cf}$  is large, electrons will pair in the low-lying orbitals and there will be a reduced net magnetic moment (low-spin configuration). Likewise, if the energy cost of  $\Delta_{cf}$  is small compared to the cost of doubly occupying an orbital, a high-spin complex is formed. This simple picture gives an intuitive understanding of electronic structure in magnetic materials, although the details of the energetics that precisely determine magnetic behavior are materials-specific.

#### 3.2.2 Hubbard model and spin-orbit coupling

Magnetism arises from correlations between electrons in materials, and so the singleparticle picture of Kohn-Sham DFT breaks down when dealing with magnetic materials. The simplest description of interacting fermions in a lattice is the Hubbard model:

$$H = -t \sum_{i,\sigma} \left( c_{i,\sigma}^* c_{i+1,\sigma} + c_{i+1,\sigma}^* c_{i,\sigma} \right) + U \sum_i n_{i\downarrow} n_{i\uparrow}$$
(3.1)

where t is the hopping parameter,  $c_{i,\sigma}^*$  and  $c_{i,\sigma}$  are the creation and annihilation operators for the *i*-th site and spin  $\sigma$ , U is the on-site interaction, and  $n_{i\sigma} = c_{i,\sigma}^* c_{i,\sigma}$ . The first term is a kinetic energy term that accounts for electron hopping between lattice sites, while the second is a potential term that represents Coulomb repulsion. The Hubbard model is an extension of the tight-binding model (discussed in detail in section 5.2.1 of this thesis) and so the same approximations and limitations are relevant. Importantly, the on-site term introduces repulsive Coulomb interactions between particles of opposite spin on lattice sites. Taking limits, if  $U/t \gg 1$ , the model describes isolated magnetic moments, while if  $U \rightarrow 0$ , we recover the tight-binding model. The Hubbard model is incorporated in DFT following Dudarev's approach [59] in which an effective  $U_{eff} = U - J$  parameter is introduced to account for on-site Coulombic (U) and on-site exchange (J) interactions. The DFT+U method modifies the DFT total energy with the term

$$\sum_{\alpha} \frac{U_{eff}}{2} Tr(\rho^{\alpha} - \rho^{\alpha} \rho^{\alpha})$$
(3.2)

where  $\rho^{\alpha}$  is the atomic orbital occupation matrix. This is a sort of penalty term that enforces on-site occupation. Practically,  $U_{eff}$  is a tunable, materials- and orbital-specific parameter that localizes *d*- and *f*-orbital electrons with increasing magnitude.

The essential ingredient for describing magnetism in 2D materials is spin-orbit coupling (SOC). SOC is a relativistic interaction between electron spin and the electrostatic field of the nucleus. In the frame of the electron, there is an effective magnetic field, B, that gives rise to an energy splitting given by

$$\Delta H = -\boldsymbol{\mu} \cdot \boldsymbol{B} \tag{3.3}$$

where  $\boldsymbol{\mu} = -g_S \mu_B \boldsymbol{S}/\hbar$  is the spin magnetic moment of the electron with  $g_S$ ,  $\mu_B$ , and  $\hbar$  the g-factor, the Bohr magneton, and Planck's constant, respectively. The  $\boldsymbol{B}$  field can be expressed in terms of a central potential U(r), such that  $\boldsymbol{B} \sim \frac{1}{r} \frac{\partial U(r)}{\partial r} \boldsymbol{L}$ , where  $\boldsymbol{L}$  is the angular momentum of the electron. The total spin-orbit energy shift is reduced by half due to Thomas precession, but the important result is that  $\Delta H \sim \frac{1}{r} \frac{\partial U(r)}{\partial r} \boldsymbol{L} \cdot \boldsymbol{S}$ . This splitting, although usually on the order of meV in most crystals, results in important symmetry breaking in orbital energy levels. For example, materials with both SOC and broken inversion symmetry  $\mathcal{P}$  experience a momentum-dependent Rashba or Dresselhaus splitting of the spin bands (which can be naively understood as electron spins interacting with an effective field resulting from inversion symmetry breaking).

In magnetic crystals, the orbital motion of electrons couples to the crystal field and gives rise to SOC-induced anisotropy. This results in preferential directions (so-called "easy axes" or "easy planes") for magnetic moments to orient along. In two dimensions, this anisotropy enables spontaneous magnetization to occur, lifting the restrictions imposed by the well-known Mermin-Wagner theorem [60], which states that continuous symmetries cannot be spontaneously broken at finite temperatures in dimension  $d \le 2$  in the presence of short-range interactions. In such systems, long-wavelength fluctuations destroy long-range ordering. In spin systems, these fluctuations are gapless Goldstone modes called magnons (spin waves) – collective excitations of the spin lattice. However, SOC introduces a spin wave gap in 2D systems that allows for long-range magnetic order.

## 3.2.3 Heisenberg model and Monte Carlo

The usual model for systems of localized spins is the Heisenberg Hamiltonian [61]:

$$H = -\frac{1}{2} \sum_{i \neq j} S_i^{\alpha} J_{ij}^{\alpha\beta} S_j^{\beta} - \sum_i \gamma_i (S_i^z)^2 - \frac{1}{2} \sum_{i \neq j} B_{ij} S_i^z S_j^z$$
(3.4)

where  $J_{ij}^{\alpha\beta}$  is a second rank tensor that parameterizes the exchange coupling between sites *i* and *j*, *S*<sub>i</sub> is the spin operator on site *i*,  $\gamma_i$  is the single-ion anisotropy parameter, and  $B_{ij}$  is an anisotropic exchange coupling.  $J_{ij}^{\alpha\beta}$  is a 3 x 3 tensor with diagonal terms giving the isotropic exchange coupling between sites, an anti-symmetric part giving the Dzyaloshinkii–Moriya interaction (DMI), and symmetric off-diagonal Kitaev interactions. For simplicity, Eq. 3.4 assumes that anisotropic exchange occurs between spins oriented in the *z*-direction and isotropic in-plane interactions. Because the DMI and Kitaev interactions are usually dominated by the exchange and anisotropy terms, they are typically neglected in determining macroscopic quantities like Curie ( $T_c$ ) and Néel ( $T_N$ ) transition temperatures, such that the exchange tensor reduces to a scalar coupling  $J_{ij}$ . Similarly, in the classical Heisenberg model the spin operator is approximated as a classical vector spin. The parameters in Eq. 3.4 are then obtained by mapping the model to different magnetic orderings and calculating their energies *via* first-principles methods.

To determine the critical temperature of the phase transition to a paramagnetic state, Monte Carlo simulations are performed. A lattice with periodic boundary conditions is initialized in some spin configuration. At each temperature T, spins are randomly flipped with probability  $P \sim \exp\left(-\frac{\Delta E}{k_BT}\right)$ , where  $\Delta E$  is the difference in energy after the move, according to the Heisenberg Hamiltonian. Many Monte Carlo moves are performed at each temperature to equilibrate the system, then more moves are performed to sample the ensemble properties of the system at that temperature.

For certain classes of systems, expressions exist for the transition temperature that are fit from Monte Carlo results and (in the case of 2D ferromagnets) renormalized spin wave theory [62]. Starting from the mean field expression  $T_C = S^2 J T_C^{Ising} / k_B$ , where  $T_C^{Ising}$  is the Curie temperature of the corresponding 2D Ising system (1.52, 2.27, and 3.64 for the honeycomb, square, and triangular lattices, respectively), the expression is modified by a fitted function that depends on the spin wave gap  $\Delta = A(2S - 1) + BSN$ . N is the number of nearest neighbors and  $\Delta$  can be interpreted as the minimum energy required to excite a magnon. A finite spin wave gap (finite magnetic anisotropy) is then a requirement to obtain out-of-plane magnetization in 2D. Note that in the factor (2S - 1), the -1 is a quantum correction in the *renormalized* spin wave theory which guarantees that anisotropic exchange is required to gap the spin wave spectrum for S = 1/2.

## 3.2.4 Strain-response model for 2D magnets under applied electric field

In Ref. [63] we developed a simple macroscopic model to describe how quasi-2D magnetic materials respond under an applied electric field,  $\boldsymbol{E}$ . Consider a monolayer with some finite out-of-plane extent and broken inversion symmetry, such that there exists a dipole moment,  $\boldsymbol{p}$ . Under small applied fields (< 1 V/nm), as the field strength increases from zero, strain is induced, and the out-of-plane bonds will stretch or compress. There is a dipole potential energy  $\beta \boldsymbol{p} \cdot \boldsymbol{E}$  and a corresponding induced strain energy  $\frac{1}{2}\mu\varepsilon^2$ , where  $\beta$  and  $\mu$  are constants and  $\varepsilon$  is the strain. In the regime of small fields, the dipole moment increases linearly with strain and the dipole potential energy can be expressed as  $\boldsymbol{p} \cdot \boldsymbol{E} = (p_0 + \chi\varepsilon)E$ , where  $p_0$  is the magnitude of the zero-field dipole moment and  $\chi$  is a

constant. Equating the two energies and ignoring trivial constants gives the simple expression

$$\varepsilon = \frac{2\chi\beta}{\mu}E\tag{3.5}$$

So it is clear that under small applied fields, there is a linear relationship between the field magnitude and the induced strain in  $\mathcal{P}$ -broken monolayers. This relationship can be exploited to control the structural degrees of freedom in these monolayers and tune the exchange and superexchange interactions that govern magnetic behavior, as will be seen in the discussion below.

# **3.3 Results**

## **3.3.1 Simple model for magnetism**

Briefly, we will discuss the application of crystal field theory to predict and rationalize magnetic behavior in 2D transition metal nitride MXenes. The goals are to present a general picture of the physics of magnetism in MXenes and to use that understanding to identify and engineer MXenes with intrinsic, tunable, and robust ferromagnetic (FM) and antiferromagnetic (AFM) ground states. Although magnetism has been predicted in many MXene systems [64], we focus on nitride MXenes of the form  $M_2NT_x$  (M = Ti, V, Cr, Mn; T = F, OH, O) in particular because the extra electron compared to the carbides leads to favorable magnetic properties. By considering Ti, V, Cr, and Mn, we cover the full range of accessible electronic configurations.



**Figure 3.1** Top view of an octahedrally coordinated transition metal atom in a MXene (left) and electron configuration of  $Cr_2NF_2$  (right). Dashed arrow indicates electron may be localized on top or bottom Cr atom. Reproduced with permission from [65].

The nonbonding *d*-orbitals involved in localized magnetic moments lie between the bonding and anti-bonding M-X and M-T bonds. For simplicity, we assume that all atoms are in their nominal oxidation states (C<sup>4-</sup>, N<sup>3-</sup>, O<sup>2-</sup>, F<sup>-</sup>, and OH<sup>-</sup>), such that bonding states are filled and anti-bonding states are unfilled. M atom *d*-orbitals are split into  $t_{2g}$  and  $e_g$  manifolds by the octahedral crystal field from neighboring N and T atoms. Figure 3.1 shows the octahedral coordination and the resulting electron configuration in one example MXene, Cr<sub>2</sub>NF<sub>2</sub>. The two Cr atoms are left in Cr<sup>3+</sup> and Cr<sup>2+</sup> oxidation states, such that in a high-spin configuration there is a net magnetic moment of 7  $\mu_B$ /formula unit. Different electron configurations can be achieved by modulating the M and T atoms, with the largest net moment (9  $\mu_B$ /formula unit) due to Mn<sub>2</sub>NF<sub>2</sub>. DFT calculations confirm that this simple crystal field model and electron counting approach yields accurate predictions of the magnetic moment in FM systems. We identify five MXenes with robust FM ground states: Mn<sub>2</sub>NF<sub>2</sub>, Mn<sub>2</sub>NO<sub>2</sub>, Mn<sub>2</sub>N(OH)<sub>2</sub>, Ti<sub>2</sub>NO<sub>2</sub>, and Cr<sub>2</sub>NO<sub>2</sub>. Interestingly, due to the minority spins being tightly bound in the Mn<sub>2</sub>NT<sub>x</sub> systems, each of these exhibits strong FM half-metallicity with wide minority spin gaps (up to 3 eV).

The other considered MXenes exhibit either intralayer or interlayer AFM ordering, due to stronger contributions from AFM superexchange interactions. In the MXenes, double exchange mechanisms mediated along 90° M-T-M bonds promote delocalized FM moments to lower the kinetic energy, while virtual excitations of anti-parallel spins coupled across M-N-M bonds promote AFM ordering. Stronger AFM coupling is seen in materials with smaller, more localized moments (M = Ti, V, Cr; T = OH, F) while stronger FM coupling is generally seen in materials with larger, more delocalized moments (M = Mn, T = O).

## **3.3.2 Magnetic anisotropy**

With a basic understanding of ground state magnetic ordering in MXenes, we next turn a deeper exploration of the fundamental spin interactions in the FM nitrides. Due to the many degrees of freedom in choice of transition metal, layer thickness, and surface functionalization, it is possible to fine-tune desirable magnetic properties and anisotropy in 2D magnetic MXenes. In particular, spin-orbit coupling (SOC) mediated by the transition metal atom and electron localization via surface functionalization can be exploited to tune the spin symmetry and magnetic anisotropy energy (MAE) [66].



**Figure 3.2** Schematic of  $M_2NT_x$  MXenes with high-symmetry axes highlighted. (a) Top view including in-plane high-symmetry axes. (b) Side view including out-of-plane highsymmetry axes. Reproduced with permission from [66].

The MAE is defined as the energy difference between the system with spins aligned to the magnetic easy axis (lowest energy orientation) and a spin quantization axis  $\hat{s}(\phi, \theta)$ , where  $\phi$  is the azimuthal angle and  $\theta$  is the polar angle. For systems with hexagonal symmetry, the uniaxial anisotropy evolves according to the equation

$$\frac{E}{V} = K_1 \sin^2 \phi + K_2 \sin^4 \phi \tag{3.6}$$

where  $K_1$  and  $K_2$  are material-specific anisotropy constants and only even orders of the expansion survive due to rotational invariance. Positive values of the coefficients indicate Ising-like ferromagnetism and an out-of-plane easy axis. In general,  $\frac{K_1}{K_2} \gg 1$  and higherorder terms can be neglected. Figure 3.3a shows the evolution of MAE as \$ rotates from 40

the easy axis (001), through the *ac* plane, to (100) in the Ising ferromagnet Mn<sub>2</sub>NO<sub>2</sub>. The MAE is fit to Eq. 3.6, confirming the Ising-like spin symmetry. The entire energetic landscape of the magnetization orientation was determined by computing the energy for finely discretized values of  $\hat{s}$  (Figure 3.3b), thereby identifying the out-of-plane easy axis. The MAE exhibits a strong dependence on  $\phi$  and is nearly isotropic with respect to  $\theta$ . The MAE reaches a maximum value of 63  $\mu$  eV/atom in the *ab* plane. With OH functionalization, the MAE decreases to 1.3  $\mu$ eV/atom and the polar dependence reflecting the 3-fold rotational symmetry is much more apparent. Cr<sub>2</sub>NO<sub>2</sub> exhibits similar Ising-like qualities, with an MAE of 22  $\mu$ eV/atom.



**Figure 3.3** Magnetic anisotropy in the Ising ferromagnet  $Mn_2NO_2$ . (a) MAE energy as a function of azimuthal angle in the *ac* plane. (b) Spherical plot indicating higher MAE (lighter coloration and greater radial distance) as the spin quantization axis rotates away from the easy axis. (c) Electron localization function with isosurface value 0.05. Reproduced with permission from [66].

To further quantify the magnetic anisotropy, we define the dimensionless parameter

$$\gamma = \frac{E_{\parallel} - E_{\perp}}{3(J_1 + 2J_2)}$$
(3.7)

where  $E_{\parallel}$ ,  $E_{\perp}$ ,  $J_1$ , and  $J_2$  are the energies with  $\hat{s}$  aligned parallel or perpendicular to the plane of the monolayer, and the interlayer (next nearest-neighbor) and intralayer (nearest-neighbor) exchange couplings, respectively. With this parameter, we estimate the critical temperatures using a simplified anisotropic Heisenberg Hamiltonian

$$H = -J \sum_{\langle ij \rangle} \left[ (1 - \gamma) \left( S_i^x S_j^x + S_i^y S_j^y \right) + S_i^z S_j^z \right].$$
(3.8)

This model neglects single-ion anisotropy, but has been fit to Monte Carlo simulations of 2D systems [67] to enable a simple estimation of  $T_c$  and it has been shown that for small values  $10^{-3} < \gamma < 10^{-1}$ , the  $T_c$  values are comparable regardless of whether anisotropy is incorporated *via* single-ion or exchange mechanisms. We also find through DFT calculations that, due to the octahedral symmetry, the orbital moments are nearly completed quenched in all MXenes, so exchange anisotropy dominates any contribution from single-ion anisotropy. The MAEs, anisotropy constants, anisotropy parameters, and estimated  $T_c$  values are given in Table 3.1.

MXene	MAE [µeV]	Κ1 [μeV]	Κ2 [μeV]	gamma	$T_{\rm C}$ [K]
$Mn_2NO_2$	63	63	0.004	$2 \times 10^{-3}$	67
$Mn_2N(OH)_2$	1.3	1.7	-0.05	$6 \times 10^{-5}$	N/A
$Mn_2NF_2$	2.0	2.9	-1.4	$8 \times 10^{-5}$	1148*
$Cr_2NO_2$	22	23	-0.05	$1 \times 10^{-3}$	53
Ti <sub>2</sub> NO <sub>2</sub>	0.78	0.09	-0.03	N/A	N/A

**Table 3.1** Magnetic anisotropy energies, magnetic anisotropy parameters, and estimated Curie temperatures from anisotropic Heisenberg model and \*XY model. Reproduced with permission from [66].

In agreement with previous studies, even small finite amounts of anisotropy are sufficient to stabilize Ising-like ferromagnetism and yield a finite  $T_c$ .  $\gamma \sim O(10^{-3})$  gives nonzero Curie temperatures, while smaller values (e.g. for Mn<sub>2</sub>N(OH)<sub>2</sub>) are insufficient to stabilize long-range order against thermal fluctuations. Importantly, these estimates neglect the longer-range FM exchange couplings in the MXenes and the higher coordination number in the bilayer-triangular lattice, so these values are underestimated. However, these order-of-magnitude estimates establish two promising Ising-like 2D ferromagnets in Mn<sub>2</sub>NO<sub>2</sub> and Cr<sub>2</sub>NO<sub>2</sub>.



**Figure 3.4** Magnetic anisotropy in the XY ferromagnet  $Mn_2NF_2$ . (a) MAE energy as a function of azimuthal angle in the *ac* plane. (b) Contour plot indicating higher MAE (lighter coloration) as the spin quantization axis rotates away from the easy plane. (c) Electron localization function with isosurface value 0.05. Reproduced with permission from [66].

Motivated by this successful identification, we consider the Mn<sub>2</sub>N system and modify the surface functionalization to reduce the anisotropy and modify the spin structure. We find that F-functionalized Mn<sub>2</sub>N exhibits an easy plane with no energetic barrier to rotating spins within the plane, while there is an MAE barrier (2  $\mu$ eV/atom) to rotating spins perpendicular to the plane. The MAE as a function of rotation  $\phi$  and the heatmap in Figure 3.4 show the characteristic energetics of an XY ferromagnet with a continuous O(2) spin symmetry in the plane. According to the Mermin-Wagner theorem, this prohibits true long-range FM ordering, but instead we expect a Berezinskii–Kosterlitz–Thouless (BKT) transition to a quasi-long-range ordered phase [68,69].



**Figure 3.5** Magnetic anisotropy in the Heisenberg ferromagnet Ti<sub>2</sub>NO<sub>2</sub>. Reproduced with permission from [66].

Next, we consider the half-metallic ferromagnet with the lightest transition metal atom and therefore, the weakest SOC: Ti<sub>2</sub>NO<sub>2</sub>. Indeed, the plot of MAE in Figure 3.5 (which is reminiscent of a  $p_z$  orbital) reveals that the MAE < 1  $\mu$ eV/atom for all rotations. Collinear AFM spin states are unstable in Ti<sub>2</sub>NO<sub>2</sub>, so it is not possible to estimate the anisotropy parameter, but the anisotropy constants are extremely low. Hence, we conclude that Ti<sub>2</sub>NO<sub>2</sub> is a Heisenberg ferromagnet with a continuous O(3) spin symmetry. An applied magnetic field can be used to easily rotate the magnetic moments and open a spinwave excitation gap to produce a nonzero transition temperature, as demonstrated in atomically-thin layers of Cr<sub>2</sub>Ge<sub>2</sub>Te<sub>6</sub> [8].

Appealing to a simple physical model, we rationalize the diversity of spin structures predicted in the FM MXenes. To understand the trends in magnetic anisotropy, we consider the strength of the spin-orbit interaction and the degree of electron localization modulated by the surface terminations. The SOC strength evolves as  $Z^4$ , where Z is the atomic number of the M atom. In the M = Ti, Cr, Mn series (Z = 22, 24, 25) we estimate that the SOC strength increases by roughly 42% from Ti to Cr and by 18% from Cr to Mn. SOC-induced contributions are expected to dominate the anisotropy. However, further anisotropy-tuning is possible due to the three most common surface terminations in

MXenes (in order of increasing electronegativity): O, OH, and F. O terminations form highly directional, anisotropic covalent bonds (seen in the electron localization function plotted in Figure 3.3c), while OH and F bonds form isotropic, ionic bonds (Figure 3.4c). This is seen both in the electron localization function (ELF) and in the site-projected DOS, in which there is substantial overlap between *p* orbitals from the O atoms and *d* orbitals in the Ising-like  $Mn_2NO_2$  and  $Cr_2NO_2$  systems, while the more isotropic systems have little contribution from ligand *p* orbitals near the Fermi level.



**Figure 3.6** Phase diagram of spin symmetries in the ferromagnetic MXenes as a function of spin-orbit interactions and electron localization. Reproduced with permission from [66].

Indeed, the phase diagram in Figure 3.6 shows exactly the trend of increasing SOC and decreasing electron localization leading to stronger magnetic anisotropy. These two axes: SOC (mediated by transition metal atom) and electron localization (mediated by surface functionalization) provide controllable chemical degrees of freedom to tune the magnetic anisotropy and achieve any spin symmetry. We further examine the effects of electron localization by varying the Hubbard U parameter from 0 to 7 eV in Mn<sub>2</sub>NO<sub>2</sub>. As

*U* increases, the spins on the Mn atoms are increasingly localized and the magnetic moment per atom increases monotonically from 2.4 to 4.2  $\mu_B$ . The system remains a strong Ising-like ferromagnet over the full range of reasonable *U* values.



Figure 3.7 Electronic band structure with SOC showing the appearance of Dirac-like dispersion near the Fermi level in  $Mn_2NF_2$ . Reproduced with permission from [66].

We also investigate the appearance of Dirac-like dispersion in the band structure of these ferromagnets. There have been predictions of Dirac points and potential nontrivial band topology in MXenes [70–73], although these predictions are still awaiting experimental verification. It is expected that Dirac points may appear at high-symmetry points and accidental points in the hexagonal Brillouin zone [74]. Essential Dirac points do indeed appear at the *K* point along the  $\Gamma - M - K - \Gamma$  path for Cr<sub>2</sub>NO<sub>2</sub>, Mn<sub>2</sub>N(OH)<sub>2</sub>, and Mn<sub>2</sub>NF<sub>2</sub> (Figure 3.7). Further study is required of these and other magnetic nitride MXenes to explore the possibility of 2D magnetic topological phases in these materials. Surface termination effects, varying the monolayer thickness, doping, and applied electric fields may allow for tuning the linear dispersion in these systems.

## 3.3.3 Magnetism with inversion symmetry breaking

These findings naturally raise questions about the effects of more realistic (disordered) surface chemistries and symmetry breaking on the magnetic properties of MXenes. For that reason, we next turn to exploring so-called "Janus" MXenes with asymmetric surface functionalization. We propose a general strategy for exploiting disordered surface chemistries to enable electrical switching of magnetic order and enhanced magnetic anisotropy [63]. The term "Janus" MXene refers generally to materials with some compositional and/or structural asymmetry between the top and bottom faces of the monolayer. The local disorder spontaneously breaks inversion symmetry in the monolayer, inducing charge distribution asymmetries that allow for coupling to external electric fields.



**Figure 3.8** Models of Janus functionalization and collinear magnetic ordering in  $M_2XO_xF_{2-x}$  MXenes. (a) Side, top, and bottom views of the supercell with the four termination sites labeled. (b) Side views of the x = 1.0, 0.5, and 1.5 models. The space groups and termination species compositions are labeled in each model. (c) Collinear ferromagnetic (FM), intralayer antiferromagnetic (AFM1), and interlayer antiferromagnetic (AFM2) ordering configurations are shown with spin up (spin down) in yellow (blue). Reproduced with permission from [63].

We first construct five different models of asymmetric surface functionalization to span the entire range of surface termination compositions and structures in the  $M_2XT_xT'_{2-x}$ MXene. We consider the most common terminations, O and F, neglecting OH which is isoelectronic to F and has been shown to display similar magnetic behavior [65,75]. With a 2 x 1 x 1 supercell, compositions of x = 0.5, 1.0, and 1.5 were sampled. There are four possible termination sites, yielding three unique orderings when x = 1.0. For this reason, the models are labeled by the composition with a superscript indicating the symmetry. For example, in the OF<sup>(3)</sup> model, the top surface is O-functionalized and the bottom surface is F functionalized, so x = 1.0 and the 3-fold rotation symmetry is preserved. The structural models with their compositions and symmetries are shown in Figure 3.8. We also consider the typical collinear magnetic orderings: FM, intralayer AFM (AFM1), and interlayer AFM (AFM2). Considering larger supercells would allow for a more thorough exploration of composition space, but as we will show, the main drivers of magnetic behavior are the crystal field (determined by the symmetry) and the transition metal oxidation state (determined by the termination composition), and both factors are well-sampled by the five models introduced here.

Two MXene systems with previously predicted robust magnetic order are considered ( $Mn_2N$  and  $Cr_2C$ ) [65,76], as well as MXenes that can be synthesized and are therefore of immediate interest ( $Ti_2C$  and  $V_2C$ ) [34]. Exhaustive first-principles calculations were performed for each MXene system with each of the five surface termination models. Rather than destroying the magnetic ordering seen in the pristine systems (as is predicted for many magnetic MXenes after surface functionalization) [77], the FM ordering remains robust for  $Mn_2N$  regardless of the surface structure. Large energy splittings between the FM and AFM orders (up to 1291 meV) are calculated.



**Figure 3.9** Magnetic and electronic structure in Janus  $M_2X$  systems. (a)  $Mn_2N$  remains strongly FM regardless of disordered functionalization, as predicted by the arrangement of electrons on the Mn atoms in the top and bottom layers. Semitransparent, dotted arrows indicate half-integer spin up electrons. (b, c) Nonmagnetic, pure O-terminated Ti<sub>2</sub>C and weakly AFM V<sub>2</sub>C become robustly AFM under all considered mixtures of O and F termination. Band structures of semiconducting, (d) FM  $Mn_2NOF^{(3)}$ , (e) AFM Ti<sub>2</sub>COF<sup>(3)</sup>, and (f) V<sub>2</sub>COF<sup>(3)</sup>. Reproduced with permission from [63].

Despite the distortions in the octahedral crystal field due to the disordered surfaces, the crystal field model successfully predicts the ground state magnetic ordering in the Janus MXenes. The  $t_{2g}$  and  $e_g$  orbital manifolds are present, and the net magnetic moments from first-principles calculations agree with the simplified crystal field model to within 0.1  $\mu_B$ /atom. Representative examples are shown for Mn<sub>2</sub>NOF<sup>(3)</sup>in Figure 3.9a. In the unit cell, the top layer Mn atoms are bonded to three N and three O atoms. The Mn donates 2/3 of an electron to each O atom and 1/2 of an electron to each N atom. Three electrons occupy the t<sub>2g</sub> orbitals, while any remaining electrons are forced into the e<sub>g</sub> manifold. On the bottom layer, each Mn is bonded to three N and three F atoms. The Mn donates 1/2 of an
electron to each N atom and 1/3 of an electron to each F. Between both Mn atoms in the unit cell, six electrons in total are donated, resulting in either two Mn<sup>3+</sup> oxidation states or an Mn<sup>4+</sup>/Mn<sup>2+</sup> pair if one of the unpaired electrons preferentially localizes on one of the Mn atoms. In the former case, the e<sub>g</sub> level is partially filled in both layers, and there is an average local magnetic moment of 4  $\mu_B$  per Mn atom. The partial filling promotes hopping of the majority spins and favors FM ordering, which is consistent with the DFT calculations. The crystal field model predicts partial filling in the e<sub>g</sub> band of both layers regardless of surface termination, and the same reasoning can be applied to see that all the systems remains FM, regardless of the surface termination.

The calculated intralayer and interlayer exchange parameters are FM in nature, ranging from 2 to 6 eV, indicating strong couplings. However, the mean field transition temperature estimates are significantly suppressed compared to the structures with pristine terminations. Although more careful studies of the transition temperatures including the spin-wave gap are needed, these crude estimates suggest that the mixed termination (which are unavoidable in experiments) may suppress critical temperatures and affect experimental measurements of magnetic MXenes [78].

The calculated magnetic ground states for all carbide MXene mixed-termination models have AFM ordering. This effect can be explained by the presence of carbon instead of nitrogen and the AFM superexchange between interlayer transition metal atoms, mediated by carbon. Generally, FM ordering is more robust in the nitrides because of the extra electron introduced by nitrogen compared to carbon, which leads to higher magnetic moments [65]. Moreover, there is a strong AFM superexchange interaction between interlayer transition metal atoms mediated through the C atom. We probe the strength of this interaction by inducing artificial strain in the out-of-plane direction in  $Cr_2C$  to strain the Cr-C-Cr bond and reduce the AFM superexchange [79]. At a critical value of strain (14%), the Cr layers decouple, and the expected FM ground state is recovered. Due to the mixed oxidation states from the asymmetric functionalization, some materials with AFM spin configurations may be weakly ferrimagnetic (FiM). For example,  $Cr_2CO_{1.5}F_{0.5}$  has an AFM1 spin configuration, but the unequal O and F compositions result in a net

magnetization of 0.12  $\mu_B$ /atom. We note that Ti<sub>2</sub>C and V<sub>2</sub>C, while predicted to be nonmagnetic when functionalized [80,81], recover their magnetic nature under Janus functionalization, which introduces free unpaired electrons.



**Figure 3.10** Scatter plot of transport (semiconducting (SC), half-metallic (HM), and metallic (M)) and magnetic behavior available in Janus MXenes. The density of states of a representative half-metallic antiferromagnet is shown in the inset. Reproduced with permission from [63].

Asymmetric surface functionalization also results in a variety of interesting transport behavior. As in Mn<sub>2</sub>N with pure termination, the minority spin channel is gapped and the Janus Mn<sub>2</sub>N structures exhibit robust half-metallic FM states. In the carbides, we find that the mixed termination causes a symmetry breaking, resulting in two distinct sublattices and an exchange splitting between the spin channels. This yields elusive half-metallic AFM states, which are difficult to construct but highly desirable for spintronic devices that require spin-polarized currents without stray magnetic fields [82]. We also

find other rare combinations of transport and magnetic behavior, like semiconducting ferromagnets. The range and diversity of accessible properties in the Janus MXenes are shown in Figure 3.10.

#### 3.3.4 Electro-mechanical coupling

The tendency towards AFM ordering and the suppression of magnetic interactions under disordered surface termination seems to suggest that achieving intrinsic magnetism in MXenes (without dopants) will require careful control of surface chemistry, which has proven to be immensely challenging. High-temperature annealing is routinely used to cause desorption of OH and F, but currently there are no available methods for creating pristine MXene surfaces with a single surface termination or avoiding surface termination altogether. This motivates the search for a different method, one that takes advantage of local disorder, requiring only the degree of control of surface termination that can be achieved with annealing. One such avenue is highlighted by the fact that out-of-plane stress reduces AFM superexchange and promotes FM ordering, as discussed above. Although mechanically induced out-of-plane strain may be difficult to apply experimentally, its theoretical utility in switching nanoscale magnetic states encourages us to pursue analogous means of external magnetic control.

In the Janus systems there is a surface dipole moment induced by the charge asymmetry and finite separation of the M atom layers. To achieve an out-of-plane strain effect, we couple the surface dipole to an external electric field, which causes charge redistribution and changes bond lengths, effectively tuning the strength of the magnetic exchange interactions in the system. We relax each structure and compute the changes in bond lengths and energy for each magnetic phase while applying small fields between 0.1 and 1.0 V/nm. Calculating the zone-centered ( $\Gamma$ -point) phonon frequencies as a function of electric field for Mn<sub>2</sub>NOF<sup>(3)</sup> and Cr<sub>2</sub>CO<sub>1.5</sub>F<sub>0.5</sub>, we find no negative frequencies, confirming the dynamical stability of the structures under an applied field. In the simplest case, applying a small electric field of the order 1.0 V/nm to Janus Mn<sub>2</sub>N further destabilizes the

AFM phases and increases the exchange splitting, commensurate with the asymmetry present in the system. These results indicate that robust FM states can be achieved in Mn<sub>2</sub>N via applied electric fields without requiring pristinely terminated surfaces.

Beyond stabilizing 2D magnetic ordering, electric fields can be used to rapidly switch between magnetic states. There has been recent success in using applied electric fields for magnetic switching of bilayer CrI<sub>3</sub>, which is AFM in bilayer form [83], back to the FM state observed in the monolayer [84]. In an analogous manner to the electrostatic gating that induces FM coupling in bilayer CrI<sub>3</sub>, small electric fields enable magnetic switching of AFM  $Cr_2CO_xF_{2-x}$ . Extremely small fields, below 1.0 V/nm, were sufficient to induce an FM ground state by altering the 180° Cr–C–Cr bonds and reducing the AFM superexchange (Figure 3.11a).



**Figure 3.11** Electrical control of magnetic ordering in  $Cr_2CO_{1.5}F_{0.5}$ . (a) Applied electric field increases the Cr–C–Cr bond length, b, reduces AFM superexchange, and causes a transition from AFM to FM phase. The out-of-plane deformation is exaggerated for visual clarity to emphasize the structural change. (b) Linear relationship between strain and dipole moment (eÅ) and electric field (V/nm). (c) PDOS before (left) and after (right) application of an electric field. Reproduced with permission from [63].

As the field strength is increased, we compute the change in the M–X–M bond length(strain) and the corresponding change in the dipole moment. Figure 3.11b shows the relationship between induced strain and dipole moment as a function of applied electric field in  $Cr_2CO_{1.5}F_{0.5}$ . Over the whole range of applied electric fields, between 0.1 and 1.0 V/nm, the structure transitions from an AFM ground state to FM. The strain is measured compared to the zero-field relaxed ground state, and the surface dipole moment is estimated by multiplying the interlayer separation by the interlayer charge difference (obtained from Bader charge analysis). In the  $O_{1.5}F_{0.5}$  structure there is significant charge separation because of the mixed average oxidation states in the upper layer ( $Cr^{3.5+}$ ) and the bottom layer ( $Cr^{4+}$ ), and the commensurate strain-electric field coupling is strong. The linear relationship is explained *via* the model developed in section 3.2.4 of this chapter.

The macroscopic picture describes the induced strain under applied fields, and fitting the DFT data to this model (blue dashed line in Figure 3.11b) gives  $\alpha = 1.12 \text{ nm/V}$  for Cr<sub>2</sub>CO<sub>1.5</sub>F<sub>0.5</sub>. The magnitude of  $\alpha$  quantifies the degree of asymmetry in a system as a function of the electric field response. Additionally, plotting the dipole moment as a function of applied field (red triangles in Figure 3.11b) for the O<sub>1.5</sub>F<sub>0.5</sub> configuration reaffirms that the assumption of linear behavior is valid for the small field strengths considered.

Examining the electronic structure evolution with applied fields provides a deeper, microscopic understanding of the magnetic state switching. Because of the broken inversion symmetry and intrinsic charge asymmetry in the Janus MXenes, the out-of-plane external field causes further charge redistribution, raising the energy of the  $d_z^2$  orbitals and weakening the bonds. The applied potentials on both sides of the monolayer tune the energy of the highly localized d states and the resulting bond elongation weakens AFM superexchange, driving the AFM to FM transition. Just as in the intrinsically FM MXenes, the induced FM transition leads to a strong magnetic exchange field that promotes exchange splitting between the majority and minority bands and half-metallic transport. The shift in the *d* state energies and the resultant half-metallicity can be seen in the partial density of states (PDOS) before (Figure 3.11c, left) and after (Figure 3.11c, right) application of an electric field. Because of the generality of this result, we expect this strategy can be used for electrical control of magnetism in any asymmetric magnetic MXene. Further, electric fields can be combined with in-plane stress [85,86] to achieve even finer control of magnetic ordering and to enhance local magnetic moments.

Practical electrical control of magnetic ordering is not the only advantage inherent to magnetic Janus MXenes. We discussed above that tuning electron localization through pure surface terminations in Mn<sub>2</sub>N can promote robust Ising ferromagnetism or introduce a noncollinear XY spin structure [66]. Since the SOC and electron localization that govern noncollinear magnetism can be controlled to produce strong magnetic anisotropy in pristine MXene systems, it is of great interest to consider the effects of asymmetric functionalization on the anisotropy, which enables long-range magnetic ordering at finite temperatures in 2D. In pristine Mn<sub>2</sub>NO<sub>2</sub>, the magnetic anisotropy energy (MAE) is greater than 60 µeV/atom, while pristine Mn<sub>2</sub>NF<sub>2</sub> has MAE less than 2 µeV/atom and no in-plane MAE, resulting in a continuous XY spin symmetry and no out-of-plane Ising ferromagnetism. In a realistic experimental setting then, the mixture of F and O surface functionalization might be expected to destroy long- range order. However, there is also structural symmetry breaking that may contribute to anisotropy.



**Figure 3.12** MAE ( $\mu$ eV/atom) as a function of in-plane angle  $\phi$  (deg) for mixed termination models of Mn<sub>2</sub>N. Reproduced with permission from [63].

Surprisingly, we find that for all mixed termination models, Mn<sub>2</sub>N remains a strong Ising ferromagnet with an out-of-plane easy axis, robust to both thermal and chemical disorder. We performed DFT calculations with SOC to calculate the total energies for each structure with the spin quantization axis along the high symmetry directions: out-of-plane (001), in-plane (100), (110), and (010), and canted out-of-plane (111). After confirming that the (001) direction is the easy axis for all structures, we then calculated the MAE between the (001) direction and in-plane directions, sampling the entire *xy* plane from 0° to 360° at intervals of 12°. The MAE between the (001) direction and an in-plane orientation (xy0) at an angle  $\phi$  is given by E( $S_{xy}$ ) – E( $S_{001}$ ). The MAE as a function of  $\phi$ is plotted for each Mn<sub>2</sub>N model in Figure 3.12.

Starting from the  $O_{1.5}F_{0.5}$  configuration, which has 75% O and 25% F termination (yellow points), we see that the MAE is in fact not at all reduced by the presence of F termination. It remains above 60  $\mu$ eV/atom, as in the case of pure O termination, suggesting

that the structural asymmetry compensates for the increased electron localization (isotropic bonding) from the F termination. When the compositions are switched to 25% O and 75% F as in the  $O_{0.5}F_{1.5}$  model (purple points), the MAE is reduced to between 20 and 40 µeV/atom, but the presence of O ensures that the MAE is still an order of magnitude larger than that of pristine F terminated  $Mn_2N$ . The substantial  $\phi$  dependence of the MAE can be understood by recognizing that the peaks occur at 30° and 210° (identical due to 2-fold rotation symmetry), the orientations that align spins with the highly directional, covalent Mn–O bond. The  $\phi$  dependence is similarly pronounced in structures with significant asymmetry in the xy plane, e.g.,  $OF^{(2)}$ . At intermediary composition (50% O and 50% F) in models  $OF^{(3)}$  and  $OF^{(2)}$  (blue and red points), the MAE is between that of  $O_{0.5}F_{1.5}$  and O<sub>1.5</sub>F<sub>0.5</sub> and shows little to no angular dependence because of the in-plane symmetry of these structures. The  $OF^{(2_1)}$  model, despite having the same 1:1 composition, exhibits stronger anisotropy than even the pure O-terminated structure. It reaches values above 100  $\mu$ eV/atom, and the 2-fold rotation symmetry is strongly apparent in the angular variation of the MAE. This is because the OF(21) configuration uniquely breaks the structural symmetry, distorting the Mn–N–Mn bond angle, introducing significant anisotropy. Two powerful conclusions can be drawn from these results: (1) Ising ferromagnetism persists with surface impurities, such that observable 2D magnetism is robust to both thermal and chemical disorder, and (2) rather than undermining the magnetic ordering, local disorder and induced structural symmetry breaking can be used to enhance the magnetic anisotropy.

### **3.4 Conclusions**

In this chapter we developed models for understanding magnetic ground states, noncollinear ordering and relativistic effects, and electrical switching of magnetism in 2D transition metal carbides and nitrides. We used these models to inform a rational-design strategy and identified functionalized MXenes with robust Ising-like, XY, and Heisenberg spin symmetries. Mn<sub>2</sub>NO<sub>2</sub>, Mn<sub>2</sub>N(OH)<sub>2</sub>, and Cr<sub>2</sub>NO<sub>2</sub> are 2D Ising ferromagnets, due to the interplay of sufficiently strong SOC and bond anisotropy. Ti<sub>2</sub>NO<sub>2</sub> was predicted to be a 2D

isotropic Heisenberg magnet with continuous O(3) spin symmetry, with magnetic anisotropy less than 1 µeV/TM for all spin orientations. F-functionalized Mn<sub>2</sub>N has no inplane anisotropy, but does possess appreciable out-of-plane anisotropy, yielding an XY system expected to have a BKT transition to a quasi-long-range ordered configuration. We showed how the chemical and structural degrees of freedom in these systems could be exploited to tune the spin states and control the magnetic anisotropy that enables longrange magnetic ordering in two dimensions. Ground-state FM ordering is preserved in Janus Mn<sub>2</sub>N for all models of mixed termination, and Janus Cr<sub>2</sub>C, V<sub>2</sub>C, and Ti<sub>2</sub>C were found to be robustly AFM. Surprisingly, asymmetric surface functionalization also induces or stabilizes magnetic ground states in systems that are predicted to be nonmagnetic or weakly magnetic in their pristine states. Janus MXenes exhibit a diverse range of magnetic and transport behavior, including semiconducting ferromagnets and half-metallic antiferromagnets. Beyond their interesting intrinsic behavior, the structural, chemical, and charge asymmetries in Janus MXenes enable external control of their magnetic states. Small applied electric fields tune the magnetic exchange parameters and enable switching from AFM to FM states. This work provides insight into tuning magnetic anisotropy in 2D systems for practical device applications and obtaining robust, electrically controllable nanoscale magnetism in MXenes with realistic surface functionalization.

## Chapter 4 High-throughput discovery of quantum materials

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## 4.1 Introduction

The discovery of intrinsic magnetic topological order in MnBi<sub>2</sub>Te<sub>4</sub> [87,88] has invigorated the search for materials with coexisting magnetic and topological phases. These multiorder quantum materials are expected to exhibit new topological phases that can be tuned with magnetic fields, but the search for such materials is stymied by difficulties in predicting magnetic structure and stability. In this chapter we detail automated workflows developed to determine exchange parameters, critical temperatures, and topological invariants in magnetic materials. We apply these workflows to a subset of over 3,000 transition metal oxides to determine their magnetic ground states and identify 18 candidate magnetic topological semimetals and insulators.

## 4.2 Methods

#### 4.2.1 Automated first-principles calculation workflows

High-throughput workflows for materials science calculations are enabled by state-of-theart open-source libraries: *pymatgen* [89], *custodian*, *FireWorks* [90], and *atomate* [91]. Together, these codes provide a framework for setting up and analyzing first-principles calculations in an automated fashion. They provide a dynamic workflow system and flexible job management for complex, interdependent calculations and automated error correction. We make use of a recently developed workflow for the high-throughput determination of collinear magnetic ground states [92]. The workflow proceeds by enumerating potential collinear orderings, starting from the most symmetric (ferromagnetic (FM)) ordering and proceeding to antiferromagnetic (AFM) orderings sorted by symmetry. Constraints are imposed by restricting the maximum allowable supercell size and setting a "soft" cutoff of eight allowed orderings. If multiple AFM orderings with equal symmetry are found, the cutoff is extended to 16 orderings. Previous applications of this workflow found that the true, experimentally determined ground state is typically found within the first two or three enumerated orderings, although a long tail exists in the distribution of orderings.

To extend the magnetic ordering workflow, we developed a follow-on "Exchange Workflow" that takes a set of low-energy magnetic orderings and fits them to a classical Heisenberg Hamiltonian to calculate the exchange parameters and critical temperatures. The underlying physics of this procedure is discussed above, in section 3.2.3. The automated Hamiltonian fitting is performed by representing magnetic structures as graphs with the *NetworkX* package [93], where magnetic ions are nodes and exchange interactions are edges in the graph. Using the calculated exchange parameters, Monte Carlo calculations of the critical temperature are automated using the VAMPIRE atomistic simulations package [94]. It should be noted that this method is only applicable for systems that are well described by the classical Heisenberg model, that is, systems with localized magnetic moments and reasonably high Curie or Néel temperatures ( $T_{C/N} > 30$  K), such that quantum effects can be neglected.

#### **4.2.2** Topological invariant calculation in magnetic systems

We further developed a framework for high-throughput band topology analysis called *Python Topological Materials (pytopomat)* [95]. The package implements several methods for analyzing band topology and calculating topological invariants, as well as high-throughput workflows to enable calculations at scale. Topological invariants are determined using the *vasp2trace* [96] and *irvsp* [97] codes to compute irreducible representations of electronic states, as well as the hybrid Wannier function method in *Z2Pack* [98].

The goal is to identify materials with "nontrivial" band topology. A simple way to think about band topology is to imagine the trivial "atomic limit" of insulators. If an insulator can be pulled apart into a collection of isolated atoms without closing its bandgap, then the material is topologically trivial. More formally, we can smoothly deform the valence bands of the material to that of a Hamiltonian with no *k*-dependence. For these trivial insulators, localized Wannier functions exists that respect the crystal symmetry. Topological phases cannot be smoothly deformed to the atomic limit without closing the gap. A brute-force method for diagnosing topological phases is then to enumerate all possible atomic limits by their symmetry eigenvalues at the high-symmetry points in the Brillouin zone. If a material's band structure symmetry eigenvalues do not match one of the atomic limits, it must be topological. The band structure is completely specified by the material space group, the site symmetries and arrangement of atoms within that space group (Wyckoff positions), and the subset of atomic orbitals that make up the valence bands. The irreducible representations (irreps) of symmetries that leave high-symmetry *k* points invariant can be deduced from group theory, but their orderings in energy are unspecified without a Hamiltonian. By considering only orbitals that are irreps and maximal site symmetry groups (the highest symmetry sites in a lattice), there are found to be 10,403 *elementary band representations* (EBRs) [99], a large but finite space of atomic limits. Because smooth deformations cannot change *k* point symmetry labels, topological bands are those that are not a simple sum of EBRs [100]. This orbital + site symmetry description of band topology is called "topological quantum chemistry" [101].

In this chapter we are interested in materials with broken time-reversal symmetry,  $\Theta$ . To simplify the high-throughput evaluation of band topology, we restrict our search to ferromagnets that are invariant under inversion,  $\mathcal{I}$ , and antiferromagnets that are invariant under  $\mathcal{S} = \Theta T_{1/2}$ , where  $T_{1/2}$  is a primitive-lattice translational symmetry. For centrosymmetric ferromagnets, their band topology is determined by the parity eigenvalues of occupied bands at the eight time-reversal invariant momenta (TRIM) in the BZ. For 3D antiferromagnets with  $\mathcal{S}$  symmetry [102], we can define a set of indices

$$\mathbb{Z}_2 = (v; v_x v_y v_z), \qquad 4.1a$$

$$v = \Delta(k_i = 0) + \Delta(k_i = 1/2) \mod 2,$$
 4.1b

$$v_i = \Delta(k_i = 1/2), \qquad 4.1c$$

where  $\Delta(k_i)$  is the 2D topological invariant on the time-reversal invariant (TRI) plane  $k_i$ in the BZ and  $k_i$  is in reduced coordinates. v is the strong topological index, such that v =1 indicates a strong antiferromagnetic topological insulator (AFTI), while v = 0 and  $v_i =$ 1 for any  $v_i$  is a weak topological insulator [98,103]. For ferromagnets with  $\mathcal{I}$  symmetry, we define the strong topological index  $\mathbb{Z}_4$  [104,105] in terms of parity eigenvalues as

$$\mathbb{Z}_{4} = \sum_{\alpha=1}^{8} \sum_{n=1}^{n_{occ}} \frac{1 + \xi_{n}(\Lambda_{\alpha})}{2} \mod 4.$$
 4.2

The eight TRIM points are  $\Lambda_{\alpha}$ , *n* is the band index,  $n_{occ}$  is the number of occupied bands, and  $\xi_n(\Lambda_{\alpha})$  is the parity eigenvalue (±1) of the *n*-th band at  $\Lambda_{\alpha}$ .  $\mathbb{Z}_4 = 1, 3$  indicates a Weyl semimetal phase (WSM) with an odd number of Weyl points in half the BZ.  $\mathbb{Z}_4 = 2$ indicates either an axion insulator phase, a WSM phase with an even number of Weyl points in half the BZ, or a 3D Chern insulator phase [106].  $\mathbb{Z}_4 = 0$  corresponds to a topologically trivial phase.

With these definitions in place, the problem of diagnosing band topology in magnetic materials is reduced to calculating parity eigenvalues at TRIM points and 2D topological invariants on TRI planes in the BZ. The parity eigenvalues are straightforward to determine by calculating the wavefunction *via* first principles. For atomic orbitals the parity is simply  $(-1)^l$  where *l* is the angular momentum. Thus, parity is odd for *p* and *f* orbitals where l = 1, 3 and even for *s* and *d* orbitals where l = 0, 2. For materials with  $\mathcal{I}$  symmetry and non-interacting fermions that are well-described by band structures, we calculate the parity eigenvalue, *c*, as  $\mathcal{I}|\psi_{nk}\rangle = c|\psi_{nk}\rangle$  for the Bloch function  $|\psi_{nk}\rangle$  with band index *n* and momentum **k**.

The hybrid Wannier function (HWF) method is more complex and more generally applicable. HWFs are localized in one direction and delocalized in the others. The main signature of nontrivial topology in this formalism is the flow of HWF charge centers, which determines the Chern number. Wannier functions [107] are a non-unique localized basis obtained from delocalized Bloch functions through a Fourier transform. Likewise, HWFs can be thought of as a 1D Wannier function [108] in  $k_x$  coupled to external parameters  $k_y$ and  $k_z$ . The Wannier charge center (WCC) is simply the average position of charge of a Wannier function in the unit cell; similarly, the hybrid WCC is the WCC of a 1D system coupled to external parameters. To calculate  $\mathbb{Z}_2$  phases [109] with the HWF method, 2D invariants are calculated by tracking the evolution of hybrid WCCs on TRI planes.

## 4.3 Results

#### 4.3.1 Magnetic topological material discovery workflow

The workflow presented here is graphically summarized in Figure 4.1. For any candidate magnetic material, the method previously developed by some of the coauthors [92] is used to generate likely collinear magnetic configurations based on symmetry considerations. The method proceeds by generating up to eight candidate magnetic orderings and sorting them by symmetry (with ferromagnetic being the most symmetric). If multiple orderings are found with equal symmetry at the eighth index, then the cutoff is increased and up to 16 orderings are considered. The exact number of orderings considered depends on the size of the unit cell, the number of unique magnetic sublattices, and the number of different species of magnetic ions. Exhaustive DFT calculations are performed to compute the energies of each magnetic ordering and determine the ground state. Alternatively, the machine learning classifier discussed below can be used to predict the ground state ordering based solely on structural and elemental data to accelerate the ground state classification. The low energy orderings are then mapped to the Heisenberg model for classical spins.



**Figure 4.1** Workflow diagram for high-throughput computation of magnetic ordering, exchange parameters, and topological invariants. Reproduced with permission from [110].

Solving the resulting system of equations yields the exchange parameters. The computed exchange parameters and magnetic moments provide all the necessary inputs to obtain the critical temperature through Monte Carlo simulations. The crystal is represented as a structure graph where nodes represent atoms and edges represent exchange interactions. Monte Carlo calculations are enabled in the workflow by interfacing with the VAMPIRE atomistic simulations package [94]. It should be noted that this method is only applicable for systems that are well described by the classical Heisenberg model, that is,

systems with *localized magnetic moments* and reasonably high Curie or Néel temperatures, such that quantum effects can be neglected.

The second branch of the workflow diagnoses band topology. Topological invariants are determined using the *vasp2trace* [96] and *irvsp* [97] codes to compute irreducible representations of electronic states, as well as the hybrid Wannier function method in *Z2Pack* [98]. Automated workflows to calculate topological invariants are implemented in the *Python Topological Materials (pytopomat)* code [95]. By coordinating workflows, we are able to discover materials with coexisting quantum orders, like magnetic topological insulators, in a high-throughput context. The schematic in Figure 4.1 shows one such example: a magnetic system exhibiting the quantum anomalous Hall effect.

#### **4.3.2** Transition metal oxide database construction

We restrict our search to the family of transition metal oxides (TMOs), which has the advantages of encompassing thousands of candidate magnetic materials and having standardized Hubbard U values based on experimental enthalpies of formation [111]. A subset of 3,153 TMOs were considered, encompassing over 27,000 computed magnetic orderings, with any combination of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, O, and any other non fblock elements. Because we have considered only oxides with magnetic ions and Hubbard U interactions that favor localized magnetic moments, most of the materials in the TMO data set will exhibit magnetic ordering at 0 K. However, it is possible that some systems are nonmagnetic or weakly magnetic. Importantly, only stable and metastable phases within 200 meV of the convex hull are included in our database. For each TMO, up to 16 likely magnetic orderings were generated, yielding a total of 923 ferromagnetic (FM) and 2,230 antiferromagnetic (AFM) ground states. Seven structures relaxed into nonmagnetic ground states and were discarded. For simplicity, ferrimagnetic (FiM) ground states were called AFM if they have an anti-parallel spin configuration with a net magnetic moment less than 0.1  $\mu_B$ /cell, and FM if the net magnetic moment in the system is greater than 0.1  $\mu_B$ /cell. Our results on predicting AFM vs FM ground states are not sensitive to the choice

of cutoff, as increasing the cutoff by an order of magnitude (to 1.0  $\mu_B$ /cell) yields only 25 additional materials labeled AFM rather than FM.



**Figure 4.2** Survey of magnetic transition metal oxides in the database. (A) Histogram of crystal systems. (B) Maximum magnetic moment per atom in each system. Clustering is observed around integer values. (C) Average nearest neighbor distance between magnetic ions. (D) Occurrence of 3*d* block transition metal atoms across FM and AFM systems. Reproduced with permission from [110].

A statistical summary of the data set is presented in Figure 4.2. Figure 4.2A is a histogram of the crystal systems contained in the data. All seven crystal systems are represented, with monoclinic being the most prevalent and hexagonal the least. Similarly, there are a variety of space groups, compositions, and symmetries present in the materials considered. There are compounds with one, two, three, or more magnetic sublattices. As expected for TMOs, most compounds have an average coordination number of four or six. Considering the computed ground states, there is a large range of maximum magnetic moments per atom, with clustering observed around the integer values of 1, 2, 3, and 4  $\mu_B$ /atom (Figure 4.2B). This plot shows the maximum moment present in a unit cell, rather than the net magnetic moment per cell, which is simply zero for AFM materials. The histogram of average nearest neighbor distance between two TM atoms in a compound is shown in Figure 4.2C. There is again a large range of values, from 2 to 6 Å, with a peak around 3 Å. We also show the relative occurrence of 3*d* block transition metal species across FM and AFM compounds in Figure 4.2D. Mn is the most common transition metal,

occurring in 1016 compounds in the database, while Cu is the least prevalent, occurring in fewer than 100 compounds.



**Figure 4.3** Low-energy ordering and effective exchange interactions. (A) Energy splitting be-tween ground state and first excited state. (B)  $J_{eff}$  versus maximum magnetic moment in the unit cell. Reproduced with permission from [110].

A wealth of information is available in the computed higher energy orderings as well. We define the energy gap,  $\Delta E = E_0 - E_1$ , where  $E_0$  is the ground state energy and  $E_1$  is the energy of the first excited state. When the low-energy orderings are successfully found,  $\Delta E$  quantifies the robustness of the ground state ordering. The plot of  $\Delta E$  in Figure 4.3A shows the heavy-tailed distribution of the energy gaps. Over 600 compounds exhibit  $\Delta E < 0.5$  meV/unit cell and may have correspondingly small J and  $T_{C/N}$  values. An effective J parameter can be estimated from the energy gap as  $J_{eff} = \frac{\Delta E}{NS^2}$ , where N is the number of magnetic atoms in the unit cell and S is the magnitude of the average magnetic moment. From this crude estimate, the transition temperature is given in the mean field approximation as  $T_{C/N}^{MFT} = \frac{2J_{eff}}{3k_B}$ , where  $k_B$  is Boltzmann's constant. The plot in Figure 4.3B shows the  $J_{eff}$  values, more or less clustered by the integer values of the maximum magnetic moment (indicated by the light red ovals) in each material. One representative high  $J_{eff}$  material is  $La_2NiO_4$  (41.7 meV), which has an AFM ground state and an estimated  $T_N$  of 323 K (measured value of 335 K [112]). The mean field critical temperature estimates may be useful as an additional screening criterion for identifying materials that warrant further investigation, but they are not accurate enough to provide quantitative agreement with experiment.

We briefly highlight some promising material candidates that may be reduced into a two-dimensional (2D) form [29] with possible access to intriguing low-dimensional magnetic properties [113,114], and materials with strong spin-orbit coupling (SOC). We apply the method from Ref. [115] to identify potentially layered TMOs, which yields 105 candidates. There are also 66 TMOs that contain either Bi or Hg and are therefore expected to exhibit strong SOC. At the intersection, we find three Bi-containing layered magnetic materials,  $Ba_2Mn_2Bi_2O$ ,  $CoBiO_3$ , and  $CrBiO_4$ . It should be noted that in monolayers, the magnetic behavior and critical temperature is strongly dependent on magnetic anisotropy [66,116]. Therefore, the estimated exchange parameters and critical temperatures for the bulk phases will not correspond to the 2D limit.

#### 4.3.3 Machine learning classifier for magnetic ordering

The primary computational burden in generating this data set is calculating the relaxed geometries and energies of all likely magnetic orderings, as we have no *a priori* way of determining the magnetic ground states. Further, it is useful to compute the spectrum of low-energy magnetic orderings to estimate the strength of exchange couplings, thereby determining the nature of magnetic interactions and critical temperatures. For simple compounds with small unit cells and a single type of magnetic ion, it is relatively

easy to determine the ground state and only a few (< 4) orderings need to be computed. However, there is a long tail to the number of orderings required for complex structures that may have many highly symmetric AFM orderings [92]. For the TMO data set, nine orderings per compound are required, on average, to find the ground state. Due to the computational cost, we are limited to collinear magnetic orderings in this combinatorial approach. Considering noncollinear ordering with SOC often increases the computation time by 1-2 orders of magnitude, due to the inclusion of the full spin-density matrix and the reduced symmetry [92]. For this reason, a full noncollinear screening of the TMO database is not currently feasible (although all band topology calculations include SOC). Collinearity is a reasonable assumption, as many materials exhibit collinear magnetic ordering, although this assumption breaks down for triangular and Kagome lattices with frustrated antiferromagnetism and in systems with lanthanides and actinides [117]. However, this work is an important and necessary first step towards determining possible noncollinear orderings. It is highly desirable to augment these laborious DFT calculations with computationally inexpensive, physics-informed models that can predict magnetic behavior.

The size of the TMO data set and the number of easily available, physically relevant descriptors suggests that a physics-informed machine learning classifier may be able to predict magnetic ground states. Our goal is to use features based purely on structural and compositional information, *without any DFT calculations*, to predict magnetic orderings and prioritize calculations. With the *matminer* [118] package, we have access to thousands of descriptors that are potentially correlated with magnetic ordering. Drawing on physical and chemical intuition, this list was reduced to ~100 descriptors that are likely indicators of magnetic ordering, e.g. elemental *d* orbital filling, electronegativity, and tabulated atomic magnetic moments. We note that to explore the possible magnetic and topological ordering of a material, a composition and crystal structure is required. Crystal structures are already available in the Materials Project database and are used for generating features. The DFT geometry relaxations that yield reasonable crystal structures are not sufficient to determine magnetic and topological order. Our goal is to use these already available crystal

structures and compositions to generate descriptors and predict magnetic properties. We use relaxed structures already available in the Materials Project database to generate additional features more specific to magnetic compounds, including the average nearest neighbor distance between TM atoms, TM-O-TM bond angle information, TM atom coordination number, and the number of magnetic sublattices. We have implemented these features in the 'magnetism' module of *pymatgen*.

Unsurprisingly, no features have Pearson correlation coefficients larger than 0.3 with respect to ground state ordering. There are no features with strong enough linear correlation to reliably predict magnetic behavior. To further reduce the feature space, we train a minimal model and discard features with extremely low impurity importance and then perform hierarchical clustering [119] of the features based on the Spearman rank correlation, removing a feature from each cluster. Hierarchical clustering with Spearman rank correlation is a standard method of feature selection for eliminating redundant features based on the dependence between the rankings of features, rather than their linear correlation. This kind of feature reduction is useful to simplify the inputs to the model and remove redundancies in the feature set.



**Figure 4.4** Random forest classifiers for magnetic ground state prediction. (A) An example of a "leaf" in the decision tree. (B) Graphic representation of a decision tree in the random forest. Reproduced with permission from [110].

Next, using the reduced feature set of 14 features, we construct an ensemble of machine learning classifiers to predict the magnetic behavior. For simplicity and interpretability, a random forest classifier was used, although other techniques like

Adaptive Boosting and Extra Trees perform similarly. The random forest achieves superior performance compared to other models considered through AutoML in Automatminer [120]. Automatminer compares model performance between many standard classifiers, including random forest, logistic regression, and support vector classification, to determine the optimal classifier. The random forest is an ensemble of decision trees made up of "leaves" like the one shown schematically in Figure 4.4A. For each feature, the tree splits the data set to enable classification. In the illustration in Figure 4.4A, the simplified split illustrates that samples with more than one magnetic sublattice are more likely to be AFM than FM. To capture the complexity of the data, a full decision tree is more fleshed out, like the one shown in Figure 4.4B. The random forest is an ensemble of many such trees, where the predictions of uncorrelated trees are averaged over to reduce overfitting. 10% of the data was held as a test set, hyperparameters were tuned through a grid search, and five-fold cross-validation was used for validation, following the conventions in *Matbench* and *Automatminer* [120].

Because of the class imbalance between FM and AFM ground states (30% of compounds are FM), the FM compounds are synthetically oversampled using SMOTE [121]. SMOTE generates synthetic data from the minority class (ferromagnets) by randomly choosing a sample and one of its nearest neighbors (in feature space), taking the feature vector between the two and multiplying it by a random number between 0 and 1. In this way, synthetic data that resembles data in the minority class is generated without simply duplicating samples. Rather than using accuracy (number of correct predictions divided by the total number of predictions), which can be artificially inflated in imbalanced learning problems by always guessing the majority class, we use three more robust classification metrics to evaluate our models: F1 score, receiver operating characteristic (ROC) area under the curve (AUC) and precision-recall (PR) AUC. The classifier exhibits good and consistent performance in five-fold cross-validation, as seen in the mean and median F1 scores of 0.85 for both FM and AFM classes. The trained model achieved an F1 score of 0.85 (0.59) for AFM (FM) compounds on the test set, suggesting that the synthetic oversampling results in difficulties generalizing to new FM compounds, while

AFM systems are well characterized. However, the classifier performs much better than either random guessing or naively always choosing the majority class. The F1 scores, ROC, and PR curves all show that the classifier outperforms random and majority class guessing. For the test set of 315 samples (236 AFM and 79 FM), 198 AFM samples are correctly classified, and 50 FM samples are correctly classified.

The success of the classifier allows us to reexamine the input features and use the model feature importances to identify nontrivial predictors of magnetic behavior. Whereas the Gini impurity-based feature importance somewhat misleadingly shows equal contributions from many features, here we use the permutation importance, which avoids bias towards numerical and high cardinality features. By far the most important descriptor is the number of magnetic sublattices. Other features relate to space group symmetry, delectron counts, coordination number, and distances between TM atoms; features we expect to describe magnetism. Another important descriptor is the sine Coulomb matrix, which is a vectorized representation of the crystal structure that has been introduced and used in previous studies to predict formation energies of crystals [122]. Finally, the structural complexity is observed to be 47% higher on average for AFM compounds than FM. The AFM systems exhibit an average structural complexity that is 17 bits/unit cell higher than the FM systems. This simple metric might indicate that more structurally complex materials are more likely to favor the more complex AFM orderings, rather than simple FM configurations. This could be related to the most important descriptor, which is also a metric of magnetic lattice complexity. Surprisingly, these complexity metrics along with simple TM-TM atom distances and the sine Coulomb matrix are much better predictors of magnetic ordering than bond angle information, as might be expected from the Goodenough-Kanamori rules. It is possible that more sophisticated features may do a better job at capturing the superexchange mechanisms that govern the magnetic behavior. We note that high model performance, measured by ROC area under the curve, was achieved for magnetic material classification in Ref. [123] using similar features, including *d*-orbital chemical descriptors.

It is clear that models like the one presented here are not guaranteed to generalize beyond the material types that comprise the training data. However, we expect that the physical insights related to feature engineering, as well as the tested methods, will be of use in future studies. The developed models are particularly useful in the context of highthroughput virtual screening, where tens of thousands of materials are potentially of interest and it is highly desirable to quickly predict target properties to prioritize calculations. Even for smaller data sets of 100 - 1,000 materials, models for property prediction can be used in active learning [124] to efficiently identify materials with desired properties. Further difficulties will be encountered when constructing machine learning models for critical temperature prediction, which is inherently a problem of outlier-detection. Fortunately, this work provides both a set of promising materials to consider for further study and the framework to automate evaluation of exchange parameters and critical temperatures.

#### 4.3.4 Topological material discovery



**Figure 4.5** Magnetic topological materials. (A) Time-reversal invariant momenta (TRIM) in the Brillouin zone. (B) Schematic of parity eigenvalues of occupied bands at TRIM points. (C) The candidate ferromagnetic topological semimetal, spinel CuCr<sub>2</sub>O<sub>4</sub>. (D) Schematic of a Dirac cone in an antiferromagnetic topological insulator with *S* symmetry. (E) Schematic of Weyl cones in a ferromagnetic topological semimetal without time-reversal and with inversion symmetry. (F) The candidate ferromagnetic axion insulator, spinel CdNi<sub>2</sub>O<sub>4</sub>. Reproduced with permission from [110].

Finally, we discuss the search for nontrivial band topology in the magnetic TMOs. The zoo of available topological order is ever expanding. Here, we simplify our search by considering classes of centrosymmetric magnetic topological materials that can be readily classified with high-throughput calculations of topological indices, where band topology can be determined by the parity eigenvalues of occupied bands at the eight time-reversal invariant momenta (TRIM) in the Brillouin zone (BZ) (Figure 4.5, A and B). We consider antiferromagnetic topological insulators (AFTIs), ferromagnetic topological semimetals

(FMTSMs), and ferromagnetic axion insulators. In the first case, we consider materials that exhibit an AFM ground state that breaks both time-reversal ( $\Theta$ ) and a primitive-lattice translational symmetry  $T_{1/2}$ , but is invariant under the combination  $S = \Theta T_{1/2}$ . The preserved S symmetry (Figure 4.5D) allows for the definition of a  $\mathbb{Z}_2$  topological invariant [102] that lends itself to high-throughput evaluation. For ferromagnets, we consider FM ground states that break  $\Theta$  symmetry but preserve inversion symmetry ( $\mathcal{I}$ ). Specifically, we restrict our search to ferromagnets with centrosymmetric tetragonal structures, where ideal Weyl semimetal (WSM) features (Figure 4.5E) may appear and where the magnetization direction can tune the band topology [125]. These filters greatly simplify the screening, but recent work suggests that over 30% of non-magnetic [96,126] and magnetic [105] materials exhibit nontrivial topology, so there are almost certainly many more interesting MTQMs to uncover in the TMO data set than we have considered here.

**Table 4.1** Candidate tetragonal ferromagnetic topological semimetals and axion insulators.

 Theoretical materials that have not yet been experimentally synthesized are labeled with a

 †.

Material	Space	Materials	Energy	$\mathbb{Z}_4$
	group	Project	above	
		ID	hull	
			(meV/atom)	
$CuFe_2O_4$	$I4_1/amd$	N/A	N/A	1
$CrO_2$	$P4_2/mnm$	mp-19177	63	3
$Sr_3CaFe_4O_{12}^{\dagger}$	P4/mmm	mp-1076424	14	3
$Mn_3O_4F_2^{\dagger}$	$P4_2/mnm$	mp-780777	76	2
$\mathrm{Sr}_{2}\mathrm{La}_{2}\mathrm{Mn}_{4}\mathrm{O}_{11}$	I4/mmm	mp-1218776	65	2
$Mn_2PO_5^{\dagger}$	$I4_1/amd$	mp-754106	27	1
$\mathrm{Sr}_5\mathrm{Mn}_5\mathrm{O}_{13}$	P4/m	mp-603888	2	2
$CaV_2O_4^{\dagger}$	$I4_1/amd$	mvc-10887	31	2
$CdNi_2O_4^{\dagger}$	$I4_1/amd$	mp-756341	0	2
$Cr_2 TeO_6$	$P4_2/mnm$	mp-21355	0	2
$\mathrm{CuCr}_2\mathrm{O}_4$	$I4_1/amd$	mp-1103973	13	1
$\text{LiNiO}_2^{\dagger}$	$I4_1/amd$	mp-770635	17	2
$\rm VMg_2O_4^\dagger$	$I4_1/amd$	N/A	N/A	2

The TMO database was screened for materials with FM ground states, a tetragonal crystal structure, and inversion symmetry, resulting in 27 candidates. By computing the  $\mathbb{Z}_4$  indices for these materials, we identify eight materials with  $\mathbb{Z}_4 = 2$ , indicating either a WSM phase with an even number of Weyl points in half of the BZ, or an axion insulator phase. Recent work has shown  $\mathbb{Z}_4 = 2$  can also indicate a 3D Chern insulator phase [106]. Five materials have an odd number of Weyl points in half of the BZ, with  $\mathbb{Z}_4 = 1,3$ . The candidate FMTSMs and axion insulators and their respective  $\mathbb{Z}_4$  indices are listed in Table 4.1. We also give the unique identifiers for the Materials Project database entries and the calculated energy above the convex hull. Here, we highlight the candidate FMTSM CuCr<sub>2</sub>O<sub>4</sub> (Figure 4.5C). CuCr<sub>2</sub>O<sub>4</sub> has an FM ground state and  $\mathbb{Z}_4 = 1$ . CuCr<sub>2</sub>O<sub>4</sub> is a hausmannite-like spinel structure with the tetragonal I4<sub>1</sub>/*amd* space group. Cr atoms bond with O atoms to form CrO<sub>6</sub> octahedra that share corners with CuO<sub>4</sub> tetrahedra. Cr<sup>3+</sup> atoms occupy Wyckoff position 8*d*, Cu<sup>2+</sup> occupy Wyckoff 4*a*, and O<sup>2-</sup> occupy Wyckoff 16*h*. We also draw special attention to the spinel CdNi<sub>2</sub>O<sub>4</sub> (Figure 4.5F), which is predicted to be an FM axion insulator with  $\mathbb{Z}_4 = 2$  and a bandgap  $E_{bg} = 0.125$  eV. This material has not yet

been successfully synthesized and represents one of many promising opportunities to grow new magnetic oxides and investigate their topology.

Material	Space	Materials	Energy	$\mathbb{Z}_2$
	group	Project	above	
		ID	hull	
			(meV/atom)	
${\rm FeMoClO_4}$	P4/nmm	mp-23123	6	(1;100)
$MnMoO_4$	P2/c	mp-19455	5	(1;001)
$Ca_2MnO_3^{\dagger}$	I4/mmm	mp-1227324	27	(1;000)
$SrV_3O_7$	Pmmn	mp-510725	3	(1;010)
$Li_2TiVO_4^{\dagger}$	P2/m	N/A	N/A	(1;001)

**Table 4.2** Candidate antiferromagnetic topological insulators. Theoretical materials that

 have not yet been experimentally synthesized are labeled with a <sup>†</sup>.



**Figure 4.6** The candidate antiferromagnetic topological insulator,  $Ca_2MnO_3$ . (A) Crystal structure of  $Ca_2MnO_3$  in the tetragonal *I4/mmm* phase. (B) Phase diagram of bandgap versus the Hubbard *U* value for Mn showing the dependence of the band topology on the strength of Hubbard interactions. Reproduced with permission from [110].

Potential AFTIs were identified by screening the TMO database for AFM ground states with S symmetry, yielding 298 candidate materials. Of these, 46 are predicted to be layered antiferromagnets by at least one of the methods available in pymatgen. These layered systems are of special interest due to their unique and tunable topological and magnetic properties [113,127]. Eight additional antiferromagnets with S symmetry exhibit small bandgaps (< 0.5 eV) and are therefore likely candidates to exhibit band inversion. For each of these 54 materials, the  $\mathbb{Z}_2$  invariant is calculated using the hybrid Wannier function method in Z2Pack. Four layered AFTIs were identified: FeMoClO<sub>4</sub>, MnMoO<sub>4</sub>, Ca<sub>2</sub>MnO<sub>3</sub>, and SrV<sub>3</sub>O<sub>7</sub>. One small bandgap AFTI was also discovered: Li<sub>2</sub>TiVO<sub>4</sub> in a P2/m phase. These systems and their  $\mathbb{Z}_2$  indices are listed in Table 4.2. We highlight the tetragonal I4/mmm phase of Ca<sub>2</sub>MnO<sub>3</sub> (Figure 4.6A), which has a nontrivial  $\mathbb{Z}_2 = (1;000)$ . It is a caswellsilverite-like structure in which  $Ca^{2+}$  ions are bonded with O atoms to form CaO<sub>6</sub> octahedra and Mn<sup>2+</sup> ions bond to form MnO<sub>6</sub> octahedra. In the primitive cell, Ca atoms occupy Wyckoff position 4e, Mn occupies Wyckoff 2a, and the O atoms occupy Wyckoff 2b and 4e. Because the topology of the AFTI phase is sensitive to the nature of the bandgap and the strength of electron correlations, we plot a phase diagram (Figure 4.6B) for Ca<sub>2</sub>MnO<sub>3</sub> indicating the regions where the system is a strong AFTI or a trivial insulator. We find that the material is a strong AFTI under a wide range of Hubbard Uvalues, although it is predicted to be topologically trivial at U = 4 eV and for U > 6 eV. Future work will identify the origin of this correlation-dependent change in topological order.

Importantly, none of the identified candidate MTQMs were considered in previous efforts to screen the Materials Project for topological materials [96], because the correct magnetic orderings were not available [92]. We have also highlighted theoretical materials, unique to the Materials Project database, that have not yet been experimentally synthesized and do not have experimental structures reported in the ICSD. Theoretical materials are labeled with a † in Table 4.1 and Table 4.2. Three materials (CuFe<sub>2</sub>O<sub>4</sub>, VMg<sub>2</sub>O<sub>4</sub>, and Li<sub>2</sub>TiVO<sub>4</sub>) relaxed into new phases not previously included in the Materials Project database after determining the magnetic ground states. Notably, all MTQM candidates are

within 100 meV per atom of the convex hull, indicating that all candidate materials are thermodynamically stable or metastable and may be synthesizable [20].

#### 4.3.5 Machine learning magnetic topological phases

We have extended the machine learning approach discussed above to classify magnetic topological materials from a recently published data set [105] of 403 magnetic structures containing 130 magnetic topological materials. Calculations were performed with U values of 0, 2, 4, and 6 eV for each material and the 130 predicted magnetic topological materials are magnetic enforced semimetals or topological insulators for at least one tested value of the Hubbard U parameter. Using only structural and chemical information, we trained a machine learning classifier to identify magnetic materials that are topologically nontrivial for at least one U value, versus materials that are trivial for all U values. The random forest model achieves a 0.74 F1 score on topological material classification in five-fold cross-validation, using 13 primarily symmetry- and orbital-based descriptors, requiring no calculations. The F1 scores, ROC, and PR curves indicate that the classifier does much better than random guessing and majority class guessing.

Due to the modularity and interoperability of the workflows developed and applied here, it is straightforward to extend the search to other types of quantum orders. Here, we have provided a high-throughput, relatively coarse-grained method to identify promising MTQMs. The topological structure can be sensitive to the Hubbard U parameter value, noncollinear magnetic order and the resulting magnetic space group (MSG) determination, and how the strength of SOC compares to the bandgap. Future work will involve detailed studies of candidate materials with the recently introduced Magnetic Topological Quantum Chemistry (MTQC) [105,128] formalism, better exchange-correlation functionals to more accurately compute bandgaps, applying the workflow to non-centrosymmetric materials, and careful determination of U values with the linear response approach.

## **4.4 Conclusions**

In this chapter, we have developed and applied a high-throughput computational workflow to determine magnetic exchange couplings, critical temperatures, and topological invariants of electronic band structures in magnetic materials. By studying over 3,000 transition metal oxides spanning all crystal systems, nearly all space groups, and a wide range of compositions, we have produced a data set of materials rich in magnetic and topological physics. This enabled the training of a machine learning classifier to predict magnetic ground states and give insight into structural and chemical factors that contribute to magnetic ordering. We extended this machine learning approach to classify topological order in magnetic materials from a recently published data set using only symmetry- and orbital-based descriptors. We identified five promising candidate antiferromagnetic topological insulators (*e.g.* tetragonal  $Ca_2MnO_3$ ), including four layered materials, as well as 13 candidate ferromagnetic topological semimetals (spinel  $CuCr_2O_4$ ) and axion insulators (spinel CdNi<sub>2</sub>O<sub>4</sub>).

# Chapter 5 Engineering quantum confinement and point defects for information processing

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\* Equal contribution

## **5.1 Introduction**

Achieving robust, localized quantum states in two-dimensional (2D) materials like graphene is desirable for optoelectronics, solid-state devices [129,130], and quantum information [131] yet challenging due to the difficulties in constructing and controlling these localized states. In this chapter, we design and optimize 2D heterostructures and point defects in monolayers to engineer individual quantum states. We propose nanoscale monolayer transition-metal dichalcogenide (TMD) heterostructures to natively host massive Dirac fermion bound states. We introduce an integrated multiscale approach to translate first-principles electronic structure to higher length scales, where we apply a continuum model to consider arbitrary 2D quantum dot geometries and sizes. We further develop an approach based on deep transfer learning, machine learning, and first-principles calculations to rapidly predict key properties of point defects in 2D materials. Physicsinformed featurization is used to generate a minimal description of defect structures and present a general picture of defects across materials systems. We identify over one hundred promising, unexplored dopant defect structures in layered metal chalcogenides, hexagonal nitrides, and metal halides. These defects are prime candidates for quantum emission, resistive switching, and neuromorphic computing.

### **5.2 Methods**

## 5.2.1 Low-energy Dirac fermion description with tight binding and the k·p method

The computational workflow for describing 2D quantum dots is shown in Figure 5.1a. For any two TMDs,  $MX_2$  and  $M'X_2$ , with direct band gaps at the high symmetry *K* point, the band structures are calculated *via* DFT. The chalcogen X atom is chosen to be the same in both TMDs to minimize lattice mismatch and ensure that the band gaps remain

direct [132,133]. The valence and conduction bands are fit around the K point to obtain the parameters for a two-band  $\mathbf{k} \cdot \mathbf{p}$  model, which captures the relevant physics of the conduction and valence bands in the K valley [134].



Figure 5.1 Schematic of the continuum approach to describing planar quantum dot electronic structure. (a) Parameters from density functional theory are used as inputs to a  $\mathbf{k} \cdot \mathbf{p}$  model that is solved for device geometries with the finite element method. (b) Triangular and hexagonal regions of MX<sub>2</sub> in an M'X<sub>2</sub> matrix form 2D quantum dots. (c) The band offsets between MX<sub>2</sub> and M'X<sub>2</sub> create quantum wells for confining electrons and holes. Reproduced with permission from [135].

The two-band  $\mathbf{k} \cdot \mathbf{p}$  model to first order in  $\mathbf{k}$  corresponds to a massive Dirac Hamiltonian, H, which captures the salient structure of the K valley in MoS<sub>2</sub> [136], while
the second order contribution describes the anisotropic dispersion and electron-hole asymmetry, and including the third order contribution completely recovers the DFT band structure [134,137,138]. We ignore the spin degree of freedom (reducing H to a 2 x 2 matrix) and spin-orbit coupling and include contributions up to second order in k, such that the model is given by [134]:

$$H_{kp}^{1}(\boldsymbol{k}) = \begin{bmatrix} \frac{\Delta}{2} & at(k_{x} - ik_{y}) \\ at(k_{x} + ik_{y}) & -\frac{\Delta}{2} \end{bmatrix}$$
 5.1

$$H_{kp}^{2}(\mathbf{k}) = a^{2} \begin{bmatrix} \gamma_{1}k^{2} & \gamma_{3}(k_{x} + ik_{y})^{2} \\ \gamma_{3}(k_{x} - ik_{y})^{2} & \gamma_{2}k^{2} \end{bmatrix}$$
 5.2

where  $\Delta$  is the direct band gap, *a* is the lattice constant, *t* is the hopping parameter,  $\gamma_1 - \gamma_3$  are energy parameters, and  $k^2 = k_x^2 + k_y^2$ . With the Fermi level in the middle of the gap set to zero, the valence band maximum and conduction band minimum of MX<sub>2</sub> are  $-\Delta/2$  and  $\Delta/2$ , respectively, where the band gap of the MX<sub>2</sub> quantum dot is  $\Delta$ . The top (or bottom) of the potential well is then  $\Delta/2 + V_e$  or  $-\Delta/2 - V_h$  for electrons or holes, respectively.

Figure 5.1b shows an atomistic model of the physical realization of a laterally confined TMD quantum dot system. A TMD with the formula unit MX<sub>2</sub> forms a nanoscale regular triangle or hexagon [139] within an M'X<sub>2</sub> matrix. The spatial extent of a quantum dot is defined by  $R_{\blacktriangle}$  and  $R_{\bullet}$ , which gives the corner-to-corner distance of the minority material region. The band offsets between the two TMDs create the quantum confinement depicted in Figure 5.1c. To describe the spatially dependent band gap variation, we introduce an external finite potential term  $V(\mathbf{x})$  given by

$$V(\mathbf{x}) = \begin{bmatrix} V_e(\mathbf{x}) & 0\\ 0 & V_h(\mathbf{x}) \end{bmatrix}$$
 5.3

where  $V_e$  is the conduction band offset and  $V_h$  is the valence band offset. V(x) is zero inside the quantum dot and nonzero in the M'X<sub>2</sub> matrix. The magnitudes  $|V_e|$  and  $|V_h|$ 

control the strength of the confining potentials. If  $V_e$  is positive, there is a confining electron potential well in the quantum dot. Likewise, if  $V_h$  is negative, there is a confining hole potential well in the dot. The model  $H_{kp}(\mathbf{k}, \mathbf{x}) = H_{kp}^1(\mathbf{k}) + H_{kp}^2(\mathbf{k}) + V(\mathbf{x})$  can then be numerically solved in the COMSOL MULTIPHYSICS package for any device geometry or material combination, given the appropriate parameters [140]. The computed eigenvalues and eigenvectors correspond to the bound state energies and wavefunctions of the quantum dot system.

The tight-binding model was constructed by considering nearest-neighbor hopping between Mo  $d_z^2$ ,  $d_{xy}$ , and  $d_{x^2-y^2}$  orbitals [134]. The tight-binding Hamiltonian for the finite triangular quantum dot includes diagonal submatrices that account for the on-site energies, spin-orbit coupling, and an external scalar potential V(x), and off-diagonal submatrices that describe the directional hopping between Mo *d* orbitals [141]. The external potential was adjusted on the outermost edge of atoms to model the band offset between Mo and W.

# 5.2.2 Toy model: 2D massive Dirac Hamiltonian in a radial finite potential well

Our investigation into the existence of bound states in the MoS<sub>2</sub>/WS<sub>2</sub> heterostructure begins with a simple toy model that emphasizes the unusual behavior of the massive Dirac fermions. It is well known that for a particle in a finite potential well described by the Schrodinger equation, the ground state is bound for any arbitrarily shallow or narrow well in one or two dimensions. [142] On the contrary, due to particle-antiparticle conversion, bound state existence is not guaranteed for Dirac fermions and depends explicitly on the form of the potential and the effective fermion mass. There is evidence that the existence of a bound ground state in 2D is uncertain even for simple radially symmetric potential wells. [143,144]

We construct a toy model of the MoS<sub>2</sub>/WS<sub>2</sub> system by approximating the MoS<sub>2</sub> quantum dot as a circular region in a radially symmetric finite potential. Following DiVincenzo and Mele, [145] we solve the massive Dirac Hamiltonian for a finite potential to develop straightforward existence criteria for bound states in the MoS<sub>2</sub>/WS<sub>2</sub> quantum disk system. For simplicity, we consider the simplified Hamiltonian  $H(\mathbf{k}, \mathbf{r}) = H_{kp}^1(\mathbf{k}) + V(\mathbf{r})$  and set the finite band offset  $V_e = V_h = V_0$ , such that  $V(r < r_0) = 0$  and  $V(r > r_0) = V_0$ , where  $r_0$  is the radius of the MoS<sub>2</sub> dot and r is the radial coordinate. Since we are interested in potential well dimensions that support at least one bound state, we restrict the solution space to the ground state, where the angular quantum number m = 0. We apply continuity boundary conditions to the wavefunction at the well edge  $r = r_0$  and look for bound state solutions with energy E in the range  $\frac{\Delta}{2} < E < \frac{\Delta}{2} + V_0$ . To exclude quasibound states, we only allow terms in the wavefunction which exponentially decay as  $r \to \infty$ . [146] This leads to a transcendental equation for the bound state which must satisfy:

$$\frac{Re[Y_0(-r_0\alpha_V)]}{J_0(r_0\alpha_W)} = \frac{i\alpha_V}{\alpha_W} \frac{E + \frac{\Delta}{2}}{V_0 - E - \frac{\Delta}{2}} \frac{Im[Y_1(-r_0\alpha_V)]}{J_1(r_0\alpha_W)}$$
5.4

where

$$\alpha_W = \frac{\sqrt{E^2 - \left(\frac{\Delta}{2}\right)^2}}{at}, \, \alpha_V = \frac{\sqrt{E^2 - \left(\frac{\Delta}{2}\right)^2 - 2EV_0 + V_0^2}}{at}$$

Here  $J_n$  and  $Y_n$  are the Bessel functions of the first and second kind, and  $\Delta$ , a, and t are material parameters corresponding to the bandgap, lattice constant, and hopping energy taken from  $H_{kp}^1(\mathbf{k})$ . We numerically solve for the roots of Equation 5.4 and plot (Figure 5.2) the lowest bound state energy as a function of the dimensionless quantities  $\frac{V_0}{\Delta}$  and  $\frac{at}{\Delta r_0}$ . The phase map provides a completely general estimate of the ground state energy for any material parameters, with darker contours representing ground states closer to the bottom of the potential well and lighter contours approaching the top of the well.



Figure 5.2 (a) Phase diagram for bound state existence as a function of heterostructure parameters  $\Delta$  (band gap),  $V_0$  (confining potential magnitude), a (lattice constant), t (k.p hopping energy), and  $r_0$  (dot radius), for the toy model circular finite well. The inset shows comparison with bound state existence boundary taken from numerical solutions for triangular wells. (b) Evolution of the ground state probability density showing decreasing localization with increased number of vertices for dots with equivalent corner-to-corner length. (c) Ground state energy relative to the continuum band edge corresponding to the dot geometries in (b). Reproduced with permission from [135].

#### 5.2.3 Deep transfer learning for 2D material property prediction

Graph-based deep learning methods that account for lattice periodicity in crystals have shown promise in mapping bulk crystal structures directly to target properties when large data sets are available [147–149]. Due to the smaller number of available 2D materials compared to bulk crystals and the resulting lack of data, there have been few studies of machine learning applied to 2D systems [29,150–152]. Additional difficulties arise when trying to apply ML to predict quantum properties, which may arise from strong correlations between electrons that are difficult to capture with first-principles methods.

As the first step in designing ideal defect structures, we apply deep learning as a framework for 2D material property prediction and identify optimal host 2D materials. The Computational 2D Materials Database (C2DB) [42] contains nearly 4,000 2D materials and it would be highly desirable to leverage this data to produce powerful, general models that can predict properties of arbitrary 2D materials. However, even 4,000 materials are not sufficient to train data hungry deep neural networks (DNNs). To address the lack of data on 2D materials, transfer learning [153,154] is used for property prediction by starting from networks trained on large data sets of bulk crystals. Here, we make use of graph networks [155] (a generalization of graph-based neural networks) as implemented in MatErials Graph Network (MEGNet) [148] models. Any material, e.g. h-BN and MoS<sub>2</sub> (shown in Fig. 1a), can be mapped to a graph representation characterized by the atomic numbers of the constituent elements and the spatial distance (bond lengths) between atoms. The graph network maps input graphs to outputs by "learning" the relationship between material structure and some target property. We use three MEGNet models constructed to predict formation energy, band-gap, and Fermi energy, and one that classifies metals versus nonmetals. These models were trained on between  $10^4 - 10^5$  crystal structures from the Materials Project database [156] and as such, the model weights are already tuned to capture material properties. Furthermore, they contain elemental embeddings (vector representations of elements) from the formation energy model using the largest data set (133,000+ materials) to encode chemical trends. Starting from these pretrained models, we

fine-tune the model weights by training on the much smaller data set of 2D materials  $(\sim 10^3)$ .

#### 5.2.4 Minimal model of point defects in 2D wide band gap materials

Even greater challenges are involved in studying defects due to the exploding combinatorics in the defect search space, but this also provides opportunity to increase the amount of data available by orders of magnitude and use ML [157–159] to obtain insight into the many outstanding questions about how imperfections affect material behavior [157,160–164]. An understanding of defects across materials systems is necessary not only for engineering artificial atoms to enable new technologies, but also because defects are inextricably linked to material properties and performance.

We describe the defect state by a simple model Hamiltonian

$$H_{defect} = H_0 + H_{sb} + H_{shift}.$$
 5.5

 $H_0$  includes a minimal description of the electrically neutral defect, namely the formation energy (Figure 5.3a) and the position of defect levels relative to the conduction and valence bands (Figure 5.3c).  $H_{sb}$  contains symmetry breaking terms (crystal field splitting, spinorbit coupling, Jahn-Teller distortion, uniaxial strain, *etc.*) that split degenerate levels.  $H_{shif}$  includes terms that preserve the crystal symmetry (biaxial strain, small applied fields, doping) but tune the energy levels and charge states of defect levels in the gap (Figure 5.3d). All the host structures considered in this work have either  $D_{3h}$  (h-BN, AlN),  $D_{3d}$  (MgI<sub>2</sub>), or  $C_{3v}$  (GeS) point group symmetry (neglecting large structural distortions). The point group symmetry immediately gives a first-order description of the defect energy level splitting due to the crystal field.





permission from [165].

The process of taking a proposed deep center defect and engineering an ideal twolevel system is shown in Figure 5.3d. For example, dopants or vacancies with  $C_{3v}$  symmetry have levels split into three irreducible representations denoted  $a_1$ ,  $a_2$ , and e. These levels are further split by other symmetry breaking effects like SOC and external stimuli like applied strain, which generates a two-level system with an optically accessible transition. Applied fields and doping will then tune the position of the levels within the gap and the Fermi level. Complexing the dopants with vacancies is one particularly robust strategy to engineer isolated two-level systems [161,166]. In this work, we focus on characterizing  $H_0$ to obtain statistics, trends, and understanding of point defects across many materials systems with machine learning and without prohibitively expensive hybrid functional calculations. The most promising candidates can then be further studied with higher levels of theory to determine and design the perturbative effects of the symmetry breaking and energy shifting terms [161,166–168].

### **5.3 Results**

#### **5.3.1** Van der Waals heterostructure quantum dot architecture

First, we discuss the application of the tight binding and  $\mathbf{k} \cdot \mathbf{p}$  models to TMD heterostructure design for ideal quantum confinement. We consider two model systems for lateral quantum confinement: an MoS<sub>2</sub> dot in a WS<sub>2</sub> matrix (MoS<sub>2</sub>/WS<sub>2</sub>), and a WS<sub>2</sub> dot in an MoS<sub>2</sub> matrix (WS<sub>2</sub>/MoS<sub>2</sub>). The band offsets between these TMDs result in Type 2 band alignment [169]; for MoS<sub>2</sub>/WS<sub>2</sub>,  $V_e = 0.31$  eV, and for WS<sub>2</sub>/MoS<sub>2</sub>,  $V_h = -0.36$  eV [170].

Thus, the first configuration yields an electron potential well, while the second forms a hole potential well.

In our model system of an  $MoS_2$  dot in a  $WS_2$  matrix, we find that minimum values of  $r_0$  and  $V_0$  define a phase boundary beyond which no bound states are supported. This behavior is particular to massive Dirac fermions in 2D. In contrast with a 2D Schrodinger quantum dot where confinement effectively disappears beyond some *maximum* diameter, in the Dirac quantum disk there is additionally a *minimum* critical size beyond which there is no confinement due to the Klein effect. This condition can also be achieved by taking  $\Delta$ to 0 at finite  $V_0$  and fixed size  $r_0$ , which recovers the massless graphene case. For the toy model MoS<sub>2</sub>/WS<sub>2</sub> system with a conduction band offset  $V_0 = V_e = 0.31$  eV, we find that the circular well has a critical radius of 2.6 Å, which is less than one unit cell. However, for more realistic quantum dot geometries that are not radially symmetric, the critical radius will be larger. In the limit of small  $r_0$ , breaking the radial symmetry of the quantum disk and introducing a three-fold rotational symmetry shifts the critical bound state phase boundary in a non-trivial way, increasing the minimum critical size for the  $MoS_2/WS_2$ system from 0.5 nm to 1.5 nm (Figure 5.2a, inset). These critical sizes are highly dependent on the band offset, and the criteria are more restrictive for confining wells with smaller band offsets. Having shown the existence of bound states for massive fermions in TMD heterostructures, we next turn to exploring the effects of realistic quantum dot geometries on confinement.

Several different quantum dot geometries are accessible based on the crystal symmetry of the component TMD materials and synthesis conditions [139]. We compute the ground state using the continuum method for a circular quantum dot, finding quantitative agreement with the toy model results ( $E_{analytic} - E_{continuum} = 0.5$  meV, which equals the  $E(H_{kp}^2)$  correction absent from the toy model), and then repeat the process for hexagonal, square, and triangular geometries. Figure 5.2b shows the evolution of the ground state wavefunction as the number of vertices in the dot geometry increases from three (triangle) to infinity (circle), with the vertex-vertex distance fixed at 10 nm (significantly above the bound state existence boundary). At this size, at least one bound

state is present for the MoS<sub>2</sub>/WS<sub>2</sub> system in all geometries, but as shown in Figure 5.2c, the energy of this state relative to the band offset varies considerably. This is primarily explained by the fact that the dot area is minimized for a given vertex-vertex length in the triangle, and this reduction in area manifests as an effective geometric confinement. The sensitivity of the ground state energy to this geometrical effect is an important consideration for device design, as the transition from a hexagonal dot to a triangular dot (two common geometries in TMD flake systems) [171,172] in the model system increases the ground state energy by a factor of almost three (30 meV vs 80 meV). Therefore, the triangular system is better for engineering confinement at larger dot sizes, which may be advantageous for experimental observations.

#### 5.3.2 Energy scaling relations

Since triangular and hexagonal shapes are most commonly observed for TMD monolayers due to the hexagonal unit cell, we focus on these geometries to investigate the evolution of the electron and hole ground states with system size. To engineer quantum confinement, we determine the maximum and optimal dot sizes for hosting bound states. We systematically vary  $R_{\blacktriangle}$  and  $R_{\bullet}$  and compute the ground state energies for each geometry. The electron (Figure 5.4a) and hole (Figure 5.4b) ground state energies are plotted versus inverse side length for triangular (green points) and hexagonal (blue points) geometries to show the characteristic scaling. The corresponding  $R_{\blacktriangle}$  and  $R_{\bullet}$  values are given on the upper x-axis for convenience. Rescaling the energies such that  $\frac{\Delta}{2}$  (the bottom of the well) corresponds to 0, we see a monotonic decrease in the electron ground state with increasing dot size. For small dots ( $R_{\blacktriangle} < 5$  nm), the ground state energy is close to the top of the electron well. The quantum confinement persists for large dots ( $R_{\perp} > 20$ nm), as the ground state approaches the bottom of the potential well. This confinement predicted for large nanoscale geometries is a consequence of the ideal confinement in the out-of-plane direction in these 2D structures, despite the finite nature of the potential barrier and relativistic properties of the carriers.



**Figure 5.4** Scaling of the electron and hole ground states with inverse side length. (a) Electron and (b) hole ground state energies for triangular (green) and hexagonal (blue) quantum dots show a characteristic dependence on quantum dot size. (c) Electron and (d) hole ground state wavefunctions delocalize with increasing quantum dot size. Reproduced with permission from [135].

The ground state energy dependence on quantum dot size follows the simple relation

$$E_{qs}(R) = \alpha R^{-2} + \beta R^{-1} + c$$
 5.6

where *R* is length,  $\alpha$  and  $\beta$  are materials-dependent constants, and *c* is a constant specified to set the bottom of the potential well equal to zero. This scaling with inverse length and inverse length squared follows immediately from the expansion in *k* (which has units of inverse length) in the  $k \cdot p$  model. The ground state energy for any geometry is then totally specified by the  $\alpha$  and  $\beta$  coefficients for a given MX<sub>2</sub>/M'X<sub>2</sub> pair. The same characteristic scaling behavior is seen for holes in WS<sub>2</sub>/MoS<sub>2</sub> (Figure 5.4b).

Visualizing the ground state wavefunctions provides a qualitative picture of the extent of quantum confinement. Figure 5.4c shows the electron ground state wavefunction in hexagonal MoS<sub>2</sub> quantum dots with  $R_{\bullet} = 10$ , 20, and 30 nm. At  $R_{\bullet} = 10$  nm, the wavefunction is strongly localized. The amplitude is large at the center of the dot and

radially decays, as expected. As the area of the hexagon increases, the wavefunction becomes increasingly delocalized until confinement is no longer apparent. At this point, the ground state of the system is indistinguishable from the infinite periodic band structure, and the finite dot region is no longer discretely quantized. The same wavefunction delocalization is observed for hole ground states in triangular WS<sub>2</sub> dots with increasing area (Figure 5.4d).



**Figure 5.5** Tight-binding model results for finite size scaling of electron and hole ground state energies in a triangular quantum dot. (a) Schematic of workflow for obtaining electronic structure of quantum dot from tight-binding. (b) Electron (top) and hole (bottom) ground state energy in a triangular quantum dot as a function of side length. (c) Ground and excited state wave functions from tight-binding. Reproduced with permission from [135].

To verify the validity (and limitations) of the continuum approach, we repeat the analysis at small dot sizes using a three-band tight-binding model [134] of a triangular MoS<sub>2</sub> quantum dot [141] with an outer edge of WS<sub>2</sub> atoms that forms the finite electron

confining well. We recover the same characteristic ground state energy scaling described by Equation 5.5 in the tight binding model results (Figure 5.5b). The computed wavefunctions (Figure 5.5c) agree with those from the continuum model, although the inclusion of an additional d band and spin-orbit coupling in the tight-binding model leads to degeneracy breaking in the excited states. Importantly, while  $\mathbf{k} \cdot \mathbf{p}$  is a long wavelength theory that is expected to break down at small length scales, the tight-binding approach describes the quantum dot system at these length scales. The continuum approach is wellsuited for device-relevant length scales, so there seem to be no apparent gaps in our multiscale approach. Independently, we verify the validity of the truncation of the kexpansion to second order by measuring the magnitude of the correction introduced by  $H_{kp}^{2}(\mathbf{k})$  as a function of dot size. As expected, the higher order terms are more important for smaller dot sizes, and for a 4 nm MoS<sub>2</sub>/WS<sub>2</sub> triangular dot, the second order correction reaches a maximum of 8.5 meV, which is well within the perturbative regime. At small dot sizes in the tight-binding regime, the higher order terms in the continuum model will affect the quantitative energy values, but overall trends such as the geometry-critical size relationships are minimally impacted.

#### 5.3.3 Layered hosts for quantum point defects

Next, we turn to a different paradigm for achieving local control of quantum states for information processing. We synthesize recent advances in deep learning, machine learning, materials informatics, and *ab initio* materials design to systematically investigate hundreds of 2D materials (both van der Waals and non-van der Waals) [173,174] and quickly identify the most promising defect structures for quantum sensing and neuromorphic computing.



**Figure 5.6** Deep learning property prediction for 2D materials. (a) 2D structures are mapped to structure graphs. (b) Graph network models are pretrained on large data sets of bulk crystals. Transfer learning is used to fine-tune model weights for predicting formation energies, band-gaps, and Fermi energies of 2D materials. (c) Parity plot of DFT calculated 2D material formation energies *versus* formation energies predicted with deep transfer learning for a test set of 381 materials. R<sup>2</sup> value and mean absolute error (MAE) are given. (d) Schematic of the entire workflow. Deep transfer learning is used to predict 2D host material properties and identify promising hosts, a random forest machine learning model

is trained to predict defect structure properties, and finally ideal candidate defects are predicted. Reproduced with permission from [165].

The transfer learning procedure (Figure 5.6b) enables rapid model training and accurate property prediction for 2D materials, simply by exploiting the learning process for the much larger data set of bulk crystal structures. The purpose of the 2D material property prediction models is to efficiently identify promising host materials, without requiring DFT calculations, whether they are present in a database or not. Not all 2D materials are suitable for quantum emission and resistive switching, so it is important to easily be able to screen candidate host materials for these applications. Predicted quantities like the host band-gap and formation energy are also important for ML predictions of defect properties. Figure 5.6c shows the parity plot for the test data of formation energy calculated by density functional theory (DFT) *versus* formation energy predicted by the graph network. The formation energy per atom of a material is given by

$$E_f^{mat} = \frac{E_{total} - \sum_i n_i \mu_i}{n},$$
5.7

where  $E_{total}$  is the total energy of a unit cell, *n* is the total number of atoms in a unit cell, and  $n_i$  and  $\mu_i$  are the number and chemical potential (referenced to the most stable bulk unary phase) of the *i*th atomic species, respectively.  $E_f^{mat} > 0$  eV/atom indicates that the material is thermodynamically unstable or metastable.

The model achieves an impressive  $R^2$  score of 0.98 and a mean absolute error (MAE) of 0.06 eV/atom on the test data. The metal *versus* nonmetal classifier has a test set accuracy of 0.84 and an F<sub>1</sub> score of 0.88 (0.73) for metals (nonmetals). The band-gap model

performs more poorly ( $R^2 = 0.73$ ) than the others, while still achieving an MAE (0.36 eV) similar to that of the band-gap model trained on the bulk nonmetals (0.33 eV) [148]. This is expected because the set of 2D nonmetals comprises only 28% (1067 of 3810 2D materials have non-zero calculated band-gaps) of the total data set. We note that it would be highly desirable to construct a single "multi-task" model with multiple outputs. In this work, we were limited by the availability of models pre-trained on bulk crystal structures, and by significant differences in the training datasets. For example, the band-gap regressor datasets for bulk and 2D crystals are smaller than the formation energy dataset, because they include only nonmetals. These models enable rapid and accurate prediction of 2D material properties with deep learning, requiring no feature engineering or ML experience.

The entire workflow is summarized in Figure 5.6d: deep transfer learning enables efficient prediction of critical host material properties (particularly band-gap and formation energy) to identify promising hosts, a random forest machine learning model is trained to predict defect structure properties that are referenced to first-principles calculations, and finally ideal candidate defects are predicted.

#### 5.3.4 Engineered defects workflow

We narrow our focus to only those 2D materials that will make optimal hosts for engineered point defects. A good host material should have a wide band-gap allowing for isolated deep defect levels and small spin-orbit coupling (SOC) [175]. These conditions are satisfied by screening for nonmagnetic materials with band-gaps greater than 2 eV

calculated with the GW approximation. This yields 158 potential WBG materials. We further screen out compounds with heavy elements as needed to reduce the effects of SOC. To identify promising defects in these systems, we establish some screening criteria and specify which are amenable to a high-throughput, machine learning-driven approach, and which require more individual study. By analogy to the NV<sup>-</sup> center in diamond, a deep defect center should have a paramagnetic qubit state with an energy splitting between two spin sublevels that is isolated from the bulk and other bound states [175]. Further details involving the magnitude of the two-level splitting and transitions between ground and important for assessing whether the state is excited states are optically addressable [166,175]. For resistive memory applications, the defect state should be reversible, long-lived, and controllable with experimentally feasible switching voltages [176,177]. By estimating the neutral defect formation energy and the position of defect states relative to the band edges, we evaluate hundreds of defects with machine learning and treat the other criteria as engineerable perturbations. This method has been validated by previous studies [158,159] on point defects in bulk crystals.

We generated over 10,000 defects in the WBG materials by considering all possible vacancies, divacancies, antisites, and common dopants. Of these, we computed relaxed defect geometries and band structures for over 1,000 quantum point defects (QPDs) and for 140 substitutional metal defects in the atomically-thin resistive memory materials  $MX_2$  (M = Mo, W; X = S, Se, Te) and h-BN. Figure 5.3b shows a schematic of the process: the candidate defects are funneled into a subset for electronic structure calculations, which are

then used to test ML models for defect property prediction, and finally to predict ideal defect structures.



**Figure 5.7** Machine learning model prediction of defect properties. (a) Host material and defect properties that are easily available from online databases or deep transfer learning model predictions are used as inputs to a random forest model. Decision trees in the random forest make predictions that are averaged to generate final predictions. (b) Deep defect center classifier predicts whether defect levels are energetically separated from the valence and conduction bands by at least  $k_BT \approx 25$  meV. (c) Distribution of computed defect formation energies. Reproduced with permission from [165].

#### 5.3.5 Machine learning models of defect parameters

Because detailed defect calculations at a high level of theory are computationally expensive and necessarily low-throughput, here we develop an ML approach to predict defect formation energy and energy-level position without requiring any DFT calculations. Fig. 3 shows the ML workflow developed in this paper. For any WBG material, first the host material parameters are obtained (Figure 5.7a). The host material is well-described by automatically generated structural and chemical descriptors [118,120,178] and calculated electronic properties like the band-gaps at the Perdew-Burke-Ernzerhof (PBE) [15], Heyd-Scuseria-Ernzerhof (HSE) [179], and GW approximation [180] levels of theory, which are available in the C2DB. Because of the scarcity of defect data and the large differences in target properties and defect structure graphs compared to pristine host materials, the graphbased approach used above is not tractable here. Instead, defects are described by structural and chemical properties and by percent changes in properties compared to the pristine bulk. For example, one feature may be the mean atomic radius in the structure,  $\bar{r}_d$ , where the d subscript denotes a defect structure. The defect is described both by  $\bar{r}_d$  and by  $\Delta \bar{r} = \frac{\bar{r}_d - \bar{r}_b}{\bar{r}_b}$ , where  $\bar{r}_b$  is the mean atomic radius in the pristine 2D material. For an Sn<sub>Se</sub> substitution (Sn occupying an Se site),  $\Delta \bar{r} > 0$ , while  $\Delta \bar{\chi} < 0$  for mean electronegativity. Using percent differences as features, rather than absolute values, facilitates comparing defect structures across material systems that may have significantly different values. This is a form of feature normalization, which is standard in machine learning applications [120], although it is not strictly necessary for random forest models [181]. There are also features that are not averaged over the entire supercell and only relate to local differences at the defect site.

This is a simple representation for defect structures that is easily interpretable, well-suited as input to ML models, and requires no first-principles calculations.

The ML approach is broken up into two models: a classifier to predict the existence of deep center defects and a regressor to predict defect formation energies. The existence of deep centers is determined by computing the energy differences between the defect level and the valence band maximum and conduction band minimum, denoted  $\Delta VB$  and  $\Delta CB$ (Figure 5.7b), respectively. For simplicity, a defect is labeled a deep level if  $\Delta CB > k_BT$ and  $\Delta VB > k_BT$  at room temperature ( $k_BT \approx 25$  meV). Otherwise, it is a shallow level which is either susceptible to thermal excitations or resonant with the bulk bands. Using this  $k_BT$  threshold, 442 (roughly 35%) of the computed QPDs exhibit deep centers. Figure 5.7c shows the histogram of defect formation energy,  $E_f$ , values for the QPDs. These computed band structures and  $E_f$  values determine the targets for ML prediction, but no first-principles defect calculation data is used as input features.



**Figure 5.8** Physical mechanisms underlying defect energetics, model featurization, and model performance. (a) Schematic of a dopant, M, inducing strain and electrostatic interactions that govern formation energy. (b) Parity plot of DFT computed defect formation energy *versus* predicted formation energy with R<sup>2</sup> value and mean absolute error (MAE). (c) Permutation feature importances in formation energy model. An asterisk (\*) denotes the feature is derived from the pristine or defect structure. All other features are computed as differences in values between the defect and pristine structures. Reproduced with permission from [165].

Before discussing the particulars of the ML model performance, we briefly review the mechanisms at work in the defect that determine the energetics. Understanding the physics of defect formation will inform the feature generation and model training during the ML process. Figure 5.8a is a schematic that shows the interactions between some dopant atom, M, and four atoms (blue spheres) it is bonded to. On the left side, there are the strain-dependent terms that include an elastic dipole contribution that is linear in the strain,  $\epsilon$ , and a strain energy that goes as  $\epsilon^2$ . The strain is spontaneously induced to relax the geometry and lower the energy. On the right side, there are terms arising from electronelectron interactions like Coulomb repulsion and charge transfer that account for the breaking and reforming of bonds, which raises the energy. This simple picture suggests that a minimal description of defects is realized by accounting for local relaxation (strain) and electronegativity (electrostatics) [182].

By constructing feature vectors for defects that encode information about local relaxation and electronic interactions, the ML models are able classify deep centers and predict  $E_f$ . In both cases we use random forest (RF) ensemble models for the benefits in interpretability, performance, and robustness to overfitting [181]. We split 90% of the data into a training set, making use of bootstrapping [27] to generate an out-of-bag (OOB) score for validation, and 10% of the data is held as a test set. The final trained RF model for  $E_f$  prediction has an OOB score of 0.75 and an R<sup>2</sup> of 0.74 on the test set (Figure 5.8b). The MAE on the test set is 0.67 eV, which is small considering the range of computed  $E_f$  values is from 0 to 8 eV. We use the permutation feature importance (Figure 5.8c) to rigorously inspect how the model is working [181]. Looking at only the top ten most important features, there are descriptors clearly related to local relaxation that encode how the defect will induce compression or tension in the lattice, *e.g.* the change in atomic weight of the defect compared to the host atom and the change in van der Waals radius. On the other

hand, the change in mean number of p valence electrons and the change in electronegativity relate to electrostatics and bonding. Finally, amongst the most important features, the chemical potential of the defect species (available from the Materials Project database) [156] is directly related to  $E_f$ .

The model performance is even better for the deep center classifier, with  $F_1 = 0.92$ on the test set for classifying deep level defects. The most important features are more directly related to band structure, with the most important being the lowest unoccupied molecular orbital (LUMO) energy. Other features related to changes in electronegativity and column position (electron count) of constituent elements are also weighted heavily.

Importantly, the linear Pearson correlations of all these individual features with  $E_f$ and the defect energy level position is quite low (< 0.3); in other words, although our physical intuition guides the feature engineering process, it is not possible to construct a simple model to predict defect properties. Linear models like Lasso [183] and Ridge regression [184] fail at predicting  $E_f$ , whereas the nonlinear RF performs much better. Despite the complex, nonlinear nature of the models, we can extract mechanistic insight by considering the permutation feature importance and the mean and median values of the most important features when defects are grouped by formation energy or energy level position. If we classify defects as either high or low formation energy based on whether  $E_f$ is greater than or less than the median formation energy (2.44 eV), it is possible to quantify the contributions from stress-induced and electronic interactions described above. We find that high energy defects have, on average, 23% larger changes in electronegativity compared to low energy defects. High energy defects also have a 7% larger median chemical similarity value compared to low energy defects, indicating that high energy defect structures are associated with larger distortions. Likewise, deep center defects have a median change in the atomic number that is 39% higher than shallow defect states. The interplay between local relaxation and electronic interactions that determines defect energetics is not trivial, but the RF model is able to capture the defect physics we aimed to describe. The model results support our simple picture that structural and electronic distortions induce deep level defects [182,185,186], but large local distortions also raise the formation energy.





Figure 5.9 Engineered defects in atomically thin resistive memory devices. (a) Schematic of a device with a semiconducting  $MoS_2$  layer sandwiched between two metallic electrodes. The  $M_S$  substitutional defect controls the local resistivity. (b) Calculated distances, *z*, between different dopants and the Mo plane in  $MoS_2$  ( $M_S$ ). Colors correspond to magnitude of *z* value. (c) Cross-sections of the charge density in  $MoS_2$  ( $Au_S$ ). The Au dopant atom is circled in gold. (d) Calculated binding energies for dopants in  $MoS_2$  as a function of the dopant chemical potential. Colors correspond to magnitude of maximum  $\mu_M$  value. Reproduced with permission from [165].

Next, we will discuss a subset of engineered defects in TMDs and h-BN that are of importance for their applications in nonvolatile resistance switching (NVRS). These socalled "atomristors" are comprised of a semiconducting monolayer sandwiched between two electrodes. A schematic of this device geometry is shown in **Figure 5.9**a. A voltage is applied across the electrodes to induce a metal atom, M, from the electrode to hop into a naturally occurring vacancy in the semiconductor, *e.g.* a sulfur vacancy in MoS<sub>2</sub>, forming a substitution M<sub>S</sub>. Reversing the voltage causes the vacancy to form again. This gives a voltage-controlled local resistivity that forms a kind of memory in an atomically thin device. The defect geometry can be probed *via* scanning tunneling microscopy (STM) to measure the out-of-plane distance  $z_{TM-M}$  between the defect and the plane of the transition metal (TM) atom in the TMD or the plane in h-BN. We define  $\Delta z = (z_{TM-M} - z_{TM-X})/z_{TM-X}$  as the change in out-of-plane distance relative to the equilibrium distance between the TM plane and the chalcogen plane; this value represents the local strain and bond breaking/formation, although it is not perfectly correlated with the total binding energy. Because the dopants considered here always preserve the point group symmetry of the material (there is no in-plane displacement of the dopant), and because the out-of-plane displacement can be probed with STM [187], we have considered  $\Delta z$  as the primary indicator of local strain. With the M atom electronegativity and atomic orbitals, we know from our ML results above that this information can be used to effectively predict the defect properties. In particular, we will focus on neutral and acceptor defects (chalcogen vacancies) with a metallic cation dopant, where electrically neutral substitutions are of interest.

For this subset of defects, we calculate  $\Delta z$  for every combination of host material and metallic dopant. Among the dopants we also consider C, Si, and Ge, which exist in few-layer semimetallic phases that could be used as electrodes in a completely van der Waals resistive device. The height profiles for all dopants in MoS<sub>2</sub> are given in **Figure 5.9**b, where the dashed red line indicates the equilibrium *z* between the Mo and S planes.  $\Delta z$  increases linearly with the increasing atomic radius of the dopant. We plot crosssections of the calculated charge density at varying distances from the Mo plane to visualize the defect height profile, as shown for Au<sub>S</sub> in MoS<sub>2</sub> in **Figure 5.9**c. As *z* increases, charge density localized on the Au dopant (highlighted with a gold circle in **Figure 5.9**c) remains visible, while the charge density localized on neighboring S atoms decreases.

We define the defect binding energy  $E_{BE}$  of a metallic dopant, M, as

$$E_{BE}(\mu_M) = E_{total} - E_V - \mu_M, \qquad 5.8$$

where  $E_{total}$  is the total energy of the supercell with the dopant,  $E_V$  is the energy of the supercell with the vacancy, and  $\mu_M$  is the chemical potential of the dopant. In experiments, it is difficult to control the dopant chemical potential, so in Figure 5.9d we plot  $E_{BE}(\mu_M)$ for each defect in MoS<sub>2</sub> for the range from  $\mu_M = 0$  to  $\mu_M = \mu_{Ref}$ , where  $\mu_{Ref}$  is the bulk reference value of the most stable unary phase.  $E_{BE} < 0$  indicates that the dopant defect will occur spontaneously in the presence of the vacancy.  $E_{BE}(\mu_M)$  corresponds to the switching voltage (neglecting kinetic barriers) and the plot in Figure 5.9d shows that by varying the M atom species, a wide range of switching voltages and dopant stabilities can be achieved to serve diverse switching applications from information storage to neuromorphic computing. The binding energy is correlated with the dopant species' atomic radius (or equivalently,  $\Delta z$ ), where the  $R^2$  value is 0.51. However, the dopant atomic radius does not completely represent bond breaking and formation, so that the binding energy cannot be directly inferred from the dopant atomic radius. We note that the calculated binding energies for MoS<sub>2</sub> with Au and Ag dopants agree well with experimental measurements [176] of ~1 V switching voltages.

#### 5.3.7 Identifying candidate quantum point defects



**Figure 5.10** Top identified defect candidates. (a) Ten substitutional defects in h-BN, AlN, GeS, and MgI<sub>2</sub> with highest defect scores. (b) Plot of defect scores for top 100 defects. The top ten are highlighted in the inset and color-coded to their corresponding host materials. (c) Highest five and lowest five defects for resistive switching by maximum binding energy. The light purple shaded region indicates high stability defects, while the light yellow shaded region indicates defects with a low switching voltage. Reproduced with permission from [165].

In order to summarize the results of our analysis, we introduce a simple "defect score" metric that succinctly represents a candidate defect's fitness as a potential deep center for quantum emission. The defect score is defined as

$$S = \frac{1}{N} \left( E_{bg}^{GW} + \left( \frac{1}{2} s_d + \frac{1}{2} s_t \right) - A - E_f \right),$$
 5.9

where  $E_{bg}^{GW}$ ,  $s_d$ ,  $s_t$ , A, and  $E_f$  are the GW band-gap, dynamic stability, thermodynamic stability, maximum atomic number in the host (corresponding to SOC), and defect formation energy, respectively. N is an overall normalization factor. Higher scores reflect larger band-gaps, greater stability, smaller defect formation energies, and smaller SOC (smaller maximum atomic number). Although there are not many examples of experimentally verified WBG material quantum emitters, we have compared the average defect scores for three materials (h-BN, h-AlN, and GaN) that have been shown to exhibit quantum emission in either monolayer or crystalline form. We find that the average defect score decreases with reported inverse emission lifetime ( $\tau^{-1}$ ), *i.e.* a higher average defect score corresponds to higher emission lifetime. This could be due to materials with larger band-gaps and low  $E_f$  deep center defects (higher average defect score) having longerlived two-level defect states [188].

The top ten dopant defects are shown in Figure 5.10a. Defects in h-BN score highly, as expected because of its ideal WBG material properties, but we also find optimal defect candidates in AlN, GeS, and MgI<sub>2</sub>. Notably, room temperature quantum emission was recently shown in bulk AlN [189]. The top 100 defect scores are plotted in Figure 5.10b, with the top ten highlighted in the inset. The scores appear Pareto distributed, emphasizing the challenge in identifying promising defect candidates compared to the relatively more abundant, less promising defects. These dopants can be complexed with vacancies to engineer symmetry breaking and construct two-level systems [161,166]. Other than h-BN, these systems are relatively or completely unexplored for quantum emission applications and are prime candidates for further study.

Finally, we highlight the optimal defect candidates for resistive switching. Figure 5.10c shows the highest five and lowest five defects by maximum binding energy,  $E_{BE}(\mu_M = \mu_{Ref})$ . The highest binding energy defects are of interest in memory applications for their assumed stability, while the lower binding energy defects require small switching voltages useful for neuromorphic architectures. We have also listed in the five defect structures with binding energies in an intermediary regime (between 0.60 and 0.49 eV), such that they strike a balance between stability and switching voltage. In general, we find that  $M_X$  defects in TMDs with larger  $\Delta r$  differences in atomic radii between dopant atoms, M, and chalcogen atoms, X, have larger binding energies. TMDs with smaller band-gaps and therefore weaker bonds (larger in-plane lattice constants) have lower binding energies for metallic dopants. This suggests that the unexplored  $MTe_2$  (M = Mo, W) systems are optimal low voltage resistive switching materials, similar to their bulk counterparts [190]. We also find a number of defects with high values of  $E_{bg}/E_{BE}$ , which may form easily and simultaneously offer high ON/OFF current ratios due to the large band-gap [177]. Relatively few experiments [176,177,187,191] have been done on 2D monolayer resistive switching, hence our results here provide ample opportunity to explore more optimal host/dopant architectures that span a large range of accessible switching voltages.

### **5.4 Conclusions**

We have presented and analyzed a lateral TMD heterostructure architecture for ideal quantum confinement. In doing so, we demonstrated a multiscale computational approach for optimizing realistic material and device parameters to achieve robust, coherent single quantum states in ambient conditions. By considering a toy model of a 2D quantum well, we established the criteria for supporting bound states in a TMD heterostructure and clearly emphasized the advantage of intrinsic confinement of massive Dirac fermions, compared to graphene which supports only quasi-bound states under applied fields. With a continuum method for solving a two-band  $\mathbf{k} \cdot \mathbf{p}$  model, geometric effects were shown to play an important role in engineering robust confinement, with triangular 2D quantum dots exhibiting maximal geometric confinement. The ground state energies scale with the system size as  $\alpha R^{-2} + \beta R^{-1}$ , such that the lowest bound state energy can be predicted for any size and shape of quantum dot simply by computing the material dependent coefficients  $\alpha$  and  $\beta$  via fitting to continuum results.

We have systematically investigated and identified optimal point defects in 2D materials using a combination of deep transfer learning, machine learning, and firstprinciples calculations. We have leveraged graph networks trained on tens of thousands of bulk crystal structures to enable deep learning for predicting formation energies, Fermi energies, and band-gaps in 2D materials. Nearly 10,000 defect structures were constructed from over 150 wide band-gap semiconductors and layered metal chalcogenides. Band structures and formation energies were calculated for over 1,000 of these defects and used to test ensemble machine learning models based on physics-informed featurization. The models used easily accessible descriptors, requiring no electronic structure calculations, to encode information about local relaxation and electronic interactions that captures defect physics. The resulting models were able to predict key defect properties including formation energies and the position of defect levels relative to the valence and conduction bands. We identified the 100 most promising deep center defects for quantum emission applications and ten optimal defects for nonvolatile resistive switching in atomically thin memristor devices. Our findings establish straightforward design principles for engineering optimal defects and 2D quantum confinement at room temperature that should be of immediate use in the experimental realization of coherent quantum states.

# **Chapter 6**

# **Conclusions and future directions**

### 6.1 Summary

In the introduction of this thesis, we identified three principal goals: 1) accelerating the synthesis of advanced materials with machine learning; 2) designing materials with novel quantum properties; and 3) engineering materials with controllable local quantum states. These goals were achieved by developing physics-informed, rational design principles and using a suite of multi-scale modeling techniques including machine learning, first-principles calculations, and continuum methods. We designed and investigated platforms for the creation and control of quantum states in layered transition metal nitrides, carbides, dichalcogenides, and oxides. We showed that these synthetically accessible material platforms (**Chapter 2**) host robust and tunable magnetic (**Chapter 3**), multi-order (**Chapter 4**), defect, and bound Dirac fermionic states (**Chapter 5**). New information processing platforms based on coherent quantum states in materials like the model systems investigated in this thesis will have far-reaching impacts across science, technology, and engineering.

## 6.2 Outlook

The future is bright for investigations of emergent phenomena in layered quantum materials. Here, we highlight four particularly interesting directions that build on the work presented in this thesis and work by others in the field.



**Figure 6.1** Future directions for quantum engineering in layered materials. 1) Heterostructure engineering for quantum control. 2) Alloying in 2D materials for property optimization and entropy-stabilized materials [192]. 3) Atomically-thin multiferroic 4-state memories. 4) Moiré spin textures and excitons in heterostructures [193].

First, we make the general observation that constructing designer heterostructures is an active and increasingly vibrant area of research. These heterostructures will couple quantum effects in monolayers; e.g. the magnetic and topological properties of one layer could be used to interact with engineered defect states in an adjacent layer. In the upper left quadrant of Figure 6.1, we show a schematic of three potential quantum systems (all investigated in this thesis) that could be combined to produce emergent, controllable quantum phases. Here, rational design principles should be applied to construct heterostructures of compatible layered materials where interesting physics may emerge at the interface. Interactions between quantum effects, van der Waals coupling, charge transfer, and strain fields induced by lattice mismatch will contribute to emergent behavior in these systems.

Second, alloys and solid solutions in layered materials represent an exciting search space for optimizing properties and engineering composite materials. Just as alloying is a standard method for engineering structural materials and metals, alloying may be a viable path for engineering 2D materials. While 2D materials are certainly an interesting playground for investigating quantum states (as shown in this thesis), there is much work to be done before 2D materials are ready for widespread adoption in devices. Key challenges to overcome include scaling synthesis procedures, controlling sample quality (defects), and engineering properties for iterative improvement. 2D alloys are a promising platform for the next generation of 2D material development.

Third, as an example of a particular synergy between quantum phases, we can imagine achieving intrinsic multiferroic order in a monolayer material. By combining ferroic orders like ferromagnetism and ferroelectricity (which are competing effects) in a single material, we can achieve a sort of "4-state memory", where the ferroic orders can interact and be independently controlled by external fields. There are many examples of quantum orders that arise from competing physical and chemical conditions, so tuning a single material to achieve competing orders represents an interesting scientific and engineering challenge.

Finally, much recent progress in condensed matter physics has been concentrated in twisted graphene systems. Twist angles form Moiré patterns in stacked systems that experience in-plane and out-of-plane relaxation, resulting in correlated phases that are comparatively easy to tune and explore with electrostatic gating. As the field progresses, twisted stacks of magnetic and other quantum 2D materials will lead to even more exotic Moiré physics.

Because of the rich variety of interactions and potential emergent phases, we can easily envision a data-driven approach applied to any of these areas, with machine learning models to predict phases and guide exploration of high-dimensional search spaces. Moreover, models and principles for inverse design may be developed, such that designer layered systems will be proposed to achieve desired quantum phases.

# **Bibliography**

- C. Reimer, S. Sciara, P. Roztocki, M. Islam, L. Romero Cortés, Y. Zhang, B. Fischer, S. Loranger, R. Kashyap, A. Cino, S. T. Chu, B. E. Little, D. J. Moss, L. Caspani, W. J. Munro, J. Azaña, M. Kues, and R. Morandotti, Nat. Phys. 15, 148 (2019).
- [2] S. Lloyd, Science (80-. ). **263**, 695 (1994).
- [3] S. Wang, D. W. Zhang, and P. Zhou, Sci. Bull. 64, 1056 (2019).
- [4] C. Monroe and J. Kim, Science **339**, 1164 (2013).
- [5] A. Stern and N. H. Lindner, Science **339**, 1179 (2013).
- [6] D. D. Awschalom, L. C. Bassett, A. S. Dzurak, E. L. Hu, and J. R. Petta, Science 339, 1174 (2013).
- [7] H. Zhang, ACS Nano 9, 9451 (2015).
- [8] C. Gong, L. Li, Z. Li, H. Ji, A. Stern, Y. Xia, T. Cao, W. Bao, C. Wang, Y. Wang,
   Z. Q. Qiu, R. J. Cava, S. G. Louie, J. Xia, and X. Zhang, Nature 546, 265 (2017).
- Z. Fei, B. Huang, P. Malinowski, W. Wang, T. Song, J. Sanchez, W. Yao, D. Xiao,
   X. Zhu, A. F. May, W. Wu, D. H. Cobden, J. H. Chu, and X. Xu, Nat. Mater. 17, 778 (2018).
- [10] L. Kou, Y. Ma, Z. Sun, T. Heine, and C. Chen, J. Phys. Chem. Lett. 8, 1905 (2017).
- [11] T. T. Tran, K. Bray, M. J. Ford, M. Toth, and I. Aharonovich, Nat. Nanotechnol. 11, 37 (2016).
- [12] G. Burkard, M. J. Gullans, X. Mi, and J. R. Petta, Nat. Rev. Phys. 1 (2020).
- [13] W. Kohn and P. Hohenberg, Phys. Rev. 136, 1912 (1964).
- [14] W. Kohn and L. J. Sham, (n.d.).
- [15] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
- [16] J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou, and K. Burke, Phys. Rev. Lett. 100, 136406 (2008).
- [17] J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. **118**, 8207 (2003).
- [18] J. Paier, M. Marsman, K. Hummer, G. Kresse, I. C. Gerber, and J. G. Angyán, J. Chem. Phys. **124**, 154709 (2006).
- [19] J. Sun, A. Ruzsinszky, and J. Perdew, Phys. Rev. Lett. 115, (2015).
- [20] J. Sun, R. C. Remsing, Y. Zhang, Z. Sun, A. Ruzsinszky, H. Peng, Z. Yang, A. Paul,U. Waghmare, X. Wu, M. L. Klein, and J. P. Perdew, (2016).
- [21] Y. Zhang, J. Sun, J. P. Perdew, and X. Wu, Phys. Rev. B 96, (2017).
- [22] Y. Fu and D. J. Singh, Phys. Rev. B 100, 45126 (2019).
- [23] C. Elkan and K. Noto, in *Proceeding 14th ACM SIGKDD Int. Conf. Knowl. Discov. Data Min. - KDD 08* (2008), p. 213.

- [24] F. Mordelet and J.-P. Vert, Pattern Recognit. Lett. **37**, 201 (2014).
- [25] M. Claesen, F. De Smet, J. A. K. Suykens, and B. De Moor, Neurocomputing 160, 73 (2015).
- [26] G. Niu, M. C. du Plessis, T. Sakai, Y. Ma, and M. Sugiyama, in NIPS'16 Proc. 30th Int. Conf. Neural Inf. Process. Syst. (2016), pp. 1207–1215.
- [27] R. E. Banfield, L. O. Hall, K. W. Bowyer, and W. P. Kegelmeyer, IEEE Trans.Pattern Anal. Mach. Intell. 173 (2007).
- [28] S. B. Kotsiantis, Artif. Intell. Rev. **39**, 261 (2013).
- [29] N. C. Frey, J. Wang, G. I. Vega Bellido, B. Anasori, Y. Gogotsi, and V. B. Shenoy, ACS Nano 13, 3031 (2019).
- [30] S. P. Lloyd, Least Squares Quantization in PCM (1982).
- [31] F. Ducastelle, in (Springer, Berlin, Heidelberg, 1993), pp. 133–142.
- [32] A. van de Walle and G. Ceder, J. Phase Equilibria 23, 348 (2002).
- [33] A. Van de Walle, M. Asta, and G. Ceder, Calphad Comput. Coupling Phase Diagrams Thermochem. 26, 539 (2002).
- [34] B. Anasori, M. R. Lukatskaya, and Y. Gogotsi, Nat. Rev. Mater. 2, 16098 (2017).
- [35] S. Yang, P. Zhang, F. Wang, A. G. Ricciardulli, M. R. Lohe, P. W. M. Blom, and X. Feng, Angew. Chemie - Int. Ed. 57, 15491 (2018).

- [36] M. Naguib, V. N. Mochalin, M. W. Barsoum, and Y. Gogotsi, Adv. Mater. 26, 992 (2014).
- [37] M. Naguib, V. N. Mochalin, M. W. Barsoum, and Y. Gogotsi, Adv. Mater. 26, 992 (2014).
- [38] S. Aryal, R. Sakidja, M. W. Barsoum, and W. Y. Ching, Phys. Status Solidi Basic Res. 251, 1480 (2014).
- [39] M. Ashton, R. G. Hennig, S. R. Broderick, K. Rajan, and S. B. Sinnott, Phys. Rev. B 94, 54116 (2016).
- [40] M. Ashton, K. Mathew, R. G. Hennig, and S. B. Sinnott, J. Phys. Chem. C 120, 3550 (2016).
- [41] G. Deysher, C. E. Shuck, K. Hantanasirisakul, N. C. Frey, A. C. Foucher, K. Maleski, A. Sarycheva, V. B. Shenoy, E. A. Stach, B. Anasori, and Y. Gogotsi, ACS Nano (2019).
- [42] S. Haastrup, M. Strange, M. Pandey, T. Deilmann, P. S. Schmidt, N. F. Hinsche, M. N. Gjerding, D. Torelli, P. M. Larsen, A. C. Riis-Jensen, J. Gath, K. W. Jacobsen, J. J. Mortensen, T. Olsen, and K. S. Thygesen, 2D Mater. 5, 042002 (2018).
- [43] B. Anasori, J. Lu, O. Rivin, M. Dahlqvist, J. Halim, C. Voigt, J. Rosen, L. Hultman,M. W. Barsoum, and E. N. Caspi, Inorg. Chem. 58, 1100 (2019).
- [44] Y. Zhang and C. Ling, Npj Comput. Mater. 4, 25 (2018).

- [45] B. Meredig, E. Antono, C. Church, M. Hutchinson, J. Ling, S. Paradiso, B. Blaiszik,
   I. Foster, B. Gibbons, J. Hattrick-Simpers, A. Mehta, and L. Ward, Mol. Syst. Des.
   Eng. 3, 819 (2018).
- [46] D. S. Bloom and N. J. Grant, JOM **2**, 41 (1950).
- [47] M. N. Abdelmalak, MXenes: A New Family of Two-Dimensional Materials and Its Application as Electrodes for Li-Ion Batteries; PhD Thesis, Drexel University, 2014.
- [48] P. Urbankowski, B. Anasori, T. Makaryan, D. Er, S. Kota, P. L. Walsh, M. Zhao, V.B. Shenoy, M. W. Barsoum, and Y. Gogotsi, Nanoscale 8, 11385 (2016).
- [49] M. Khazaei, A. Ranjbar, K. Esfarjani, D. Bogdanovski, R. Dronskowski, and S. Yunoki, Phys. Chem. Chem. Phys. 20, 8579 (2018).
- [50] Y. Li, H. Shao, Z. Lin, J. Lu, P. O. Å Persson, P. Eklund, L. Hultman, M. Li, K. Chen, X.-H. Zha, S. Du, P. Rozier, Z. Chai, E. Raymundo-Piñero, P.-L. Taberna, P. Simon, and Q. Huang, 1 (n.d.).
- [51] B. Anasori, Y. Xie, M. Beidaghi, J. Lu, B. C. Hosler, L. Hultman, P. R. C. Kent, Y. Gogotsi, and M. W. Barsoum, ACS Nano 9, 9507 (2015).
- [52] M. Dahlqvist, B. Alling, and J. Rosén, Phys. Rev. B 81, 220102 (2010).
- [53] M. Sokol, V. Natu, S. Kota, and M. W. Barsoum, Trends Chem. 1, 210 (2019).
- [54] Y. Yang, K. Hantanasirisakul, N. C. Frey, B. Anasori, R. J. Green, P. C. Rogge, I. Waluyo, A. Hunt, P. Shafer, E. Arenholz, V. B. Shenoy, Y. Gogotsi, and S. J. May,

2D Mater. 7, 025015 (2020).

- [55] T. Schultz, N. C. Frey, K. Hantanasirisakul, S. Park, S. J. May, V. B. Shenoy, Y. Gogotsi, and N. Koch, Chem. Mater. acs. chemmater.9b00414 (2019).
- [56] B. Huang, G. Clark, E. Navarro-Moratalla, D. R. Klein, R. Cheng, K. L. Seyler, D. Zhong, E. Schmidgall, M. A. McGuire, D. H. Cobden, W. Yao, D. Xiao, P. Jarillo-Herrero, and X. Xu, Nature 546, 270 (2017).
- [57] M. Bonilla, S. Kolekar, Y. Ma, H. C. Diaz, V. Kalappattil, R. Das, T. Eggers, H. R. Gutierrez, M.-H. Phan, and M. Batzill, Nat. Nanotechnol. 13, 289 (2018).
- [58] M. S. Dresselhaus, G. Dresselhaus, and A. (Ado) Jorio, Group Theory : Application to the Physics of Condensed Matter (Springer-Verlag, 2008).
- [59] S. Dudarev and G. Botton, Phys. Rev. B Condens. Matter Mater. Phys. 57, 1505 (1998).
- [60] N. D. Mermin and H. Wagner, Phys. Rev. Lett. 17, 1133 (1966).
- [61] D. Torelli, K. S. Thygesen, and T. Olsen, 2D Mater. 6, 045018 (2019).
- [62] D. Torelli and T. Olsen, 2D Mater. 6, (2019).
- [63] N. C. Frey, A. Bandyopadhyay, H. Kumar, B. Anasori, Y. Gogotsi, and V. B. Shenoy, ACS Nano 13, 2831 (2019).
- [64] N. C. Frey, C. C. Price, A. Bandyopadhyay, H. Kumar, and V. B. Shenoy, 2D Met.

Carbides Nitrides 291 (2019).

- [65] H. Kumar, N. C. Frey, L. Dong, B. Anasori, Y. Gogotsi, and V. B. Shenoy, ACS Nano 11, 7648 (2017).
- [66] N. C. Frey, H. Kumar, B. Anasori, Y. Gogotsi, and V. B. Shenoy, ACS Nano 12, 6319 (2018).
- [67] W. Li, L. Sun, J. Qi, P. Jarillo-Herrero, M. Dincă, and J. Li, Chem. Sci. 8, 2859 (2017).
- [68] J. F. Fernández, M. F. Ferreira, and J. Stankiewicz, Phys. Rev. B 34, 292 (1986).
- [69] M. Ashton, D. Gluhovic, S. B. Sinnott, J. Guo, D. A. Stewart, and R. G. Hennig, Nano Lett. 17, 5251 (2017).
- [70] H. Weng, A. Ranjbar, Y. Liang, Z. Song, M. Khazaei, S. Yunoki, M. Arai, Y. Kawazoe, Z. Fang, and X. Dai, Phys. Rev. B 92, 075436 (2015).
- [71] C. Si, K.-H. Jin, J. Zhou, Z. Sun, and F. Liu, Nano Lett. 16, 6584 (2016).
- [72] H. Fashandi, V. Ivády, P. Eklund, A. L. Spetz, M. I. Katsnelson, and I. A. Abrikosov, Phys. Rev. B 92, 155142 (2015).
- [73] Y. Liang, M. Khazaei, A. Ranjbar, M. Arai, S. Yunoki, Y. Kawazoe, H. Weng, and Z. Fang, Phys. Rev. B 96, (2017).
- [74] K. Asano and C. Hotta, Phys. Rev. B 83, 245125 (2011).

- [75] L. Dong, H. Kumar, B. Anasori, Y. Gogotsi, and V. B. Shenoy, J. Phys. Chem. Lett.8, 422 (2017).
- [76] C. Si, J. Zhou, and Z. Sun, ACS Appl. Mater. Interfaces 7, 17510 (2015).
- [77] N. C. Frey, C. C. Price, A. Bandyopadhyay, H. Kumar, and V. B. Shenoy, in 2D Met. Carbides Nitrides (Springer International Publishing, 2019), pp. 291–300.
- [78] K. Hantanasirisakul and Y. Gogotsi, Adv. Mater. 1804779 (2018).
- [79] Y. Xu, X. Liu, and W. Guo, Nanoscale 6, 12929 (2014).
- [80] Y. Xie and P. R. C. Kent, Phys. Rev. B Condens. Matter Mater. Phys. 87, 235441 (2013).
- [81] J. Hu, B. Xu, C. Ouyang, S. A. Yang, and Y. Yao, J. Phys. Chem. C 118, 24274 (2014).
- [82] H. Van Leuken and R. A. De Groot, Phys. Rev. Lett. 74, 1171 (1995).
- [83] N. Sivadas, S. Okamoto, X. Xu, C. J. Fennie, and D. Xiao, Nano Lett. 18, 7658 (2018).
- [84] B. Huang, G. Clark, D. R. Klein, D. MacNeill, E. Navarro-Moratalla, K. L. Seyler,
   N. Wilson, M. A. McGuire, D. H. Cobden, D. Xiao, W. Yao, P. Jarillo-Herrero, and
   X. Xu, Nat. Nanotechnol. 13, 544 (2018).
- [85] G. Gao, G. Ding, J. Li, K. Yao, M. Wu, and M. Qian, Nanoscale 8, 8986 (2016).

- [86] S. Zhao, W. Kang, and J. Xue, Appl. Phys. Lett. 104, (2014).
- [87] J. Li, Y. Li, S. Du, Z. Wang, B. L. Gu, S. C. Zhang, K. He, W. Duan, and Y. Xu, Sci. Adv. 5, eaaw5685 (2019).
- [88] M. M. Otrokov, I. I. Klimovskikh, H. Bentmann, D. Estyunin, A. Zeugner, Z. S. Aliev, S. Gaß, A. U. B. Wolter, A. V. Koroleva, A. M. Shikin, M. Blanco-Rey, M. Hoffmann, I. P. Rusinov, A. Y. Vyazovskaya, S. V. Eremeev, Y. M. Koroteev, V. M. Kuznetsov, F. Freyse, J. Sánchez-Barriga, I. R. Amiraslanov, M. B. Babanly, N. T. Mamedov, N. A. Abdullayev, V. N. Zverev, A. Alfonsov, V. Kataev, B. Büchner, E. F. Schwier, S. Kumar, A. Kimura, L. Petaccia, G. Di Santo, R. C. Vidal, S. Schatz, K. Kißner, M. Ünzelmann, C. H. Min, S. Moser, T. R. F. Peixoto, F. Reinert, A. Ernst, P. M. Echenique, A. Isaeva, and E. V. Chulkov, Nature **576**, 416 (2019).
- [89] S. P. Ong, W. D. Richards, A. Jain, G. Hautier, M. Kocher, S. Cholia, D. Gunter, V.L. Chevrier, K. A. Persson, and G. Ceder, Comput. Mater. Sci. 68, 314 (2013).
- [90] A. Jain, S. P. Ong, W. Chen, B. Medasani, X. Qu, M. Kocher, M. Brafman, G. Petretto, G. M. Rignanese, G. Hautier, D. Gunter, and K. A. Persson, Concurr. Comput. 27, 5037 (2015).
- [91] K. Mathew, J. H. Montoya, A. Faghaninia, S. Dwarakanath, M. Aykol, H. Tang, I. heng Chu, T. Smidt, B. Bocklund, M. Horton, J. Dagdelen, B. Wood, Z. K. Liu, J. Neaton, S. P. Ong, K. Persson, and A. Jain, Comput. Mater. Sci. 139, 140 (2017).
- [92] M. K. Horton, J. H. Montoya, M. Liu, and K. A. Persson, Npj Comput. Mater. 5, 2

(2019).

- [93] A. A. Hagberg, D. A. Schult, and P. J. Swart, in 7th Python Sci. Conf. (SciPy 2008) (2008), pp. 11–15.
- [94] R. F. L. Evans, W. J. Fan, P. Chureemart, T. A. Ostler, M. O. A. Ellis, and R. W. Chantrell, J. Phys. Condens. Matter 26, (2014).
- [95] (n.d.).
- [96] M. G. Vergniory, L. Elcoro, C. Felser, N. Regnault, B. A. Bernevig, and Z. Wang, Nature 566, 480 (2019).
- [97] J. Gao, Q. Wu, C. Persson, and Z. Wang, (2020).
- [98] D. Gresch, G. Autès, O. V. Yazyev, M. Troyer, D. Vanderbilt, B. A. Bernevig, andA. A. Soluyanov, Phys. Rev. B 95, 075146 (2017).
- [99] L. Michel and J. Zak, Phys. Rev. B Condens. Matter Mater. Phys. 59, 5998 (1999).
- [100] J. Kruthoff, J. De Boer, J. Van Wezel, C. L. Kane, and R. J. Slager, Phys. Rev. X 7, (2017).
- [101] B. Bradlyn, L. Elcoro, J. Cano, M. G. Vergniory, Z. Wang, C. Felser, M. I. Aroyo, and B. A. Bernevig, Nature 547, 298 (2017).
- [102] R. S. K. Mong, A. M. Essin, and J. E. Moore, Phys. Rev. B Condens. Matter Mater. Phys. 81, (2010).

- [103] L. Fu, C. L. Kane, and E. J. Mele, Phys. Rev. Lett. 98, (2007).
- [104] H. Watanabe, H. C. Po, and A. Vishwanath, Sci. Adv. 4, eaat8685 (2018).
- [105] Y. Xu, L. Elcoro, Z. Song, B. J. Wieder, M. G. Vergniory, N. Regnault, Y. Chen, C. Felser, and B. A. Bernevig, (2020).
- [106] M. Gu, J. Li, H. Sun, Y. Zhao, C. Liu, J. Liu, and Q. Liu, (2020).
- [107] N. Marzari and D. Vanderbilt, Phys. Rev. B Condens. Matter Mater. Phys. 56, 12847 (1997).
- [108] A. A. Soluyanov and D. Vanderbilt, Phys. Rev. B Condens. Matter Mater. Phys.83, 035108 (2011).
- [109] C. L. Kane and E. J. Mele, Phys. Rev. Lett. 95, 146802 (2005).
- [110] N. C. Frey, M. K. Horton, J. M. Munro, S. M. Griffin, K. A. Persson, and V. B. Shenoy, Sci. Adv. 6, eabd1076 (2020).
- [111] A. Jain, G. Hautier, S. P. Ong, C. J. Moore, C. C. Fischer, K. A. Persson, and G. Ceder, Phys. Rev. B Condens. Matter Mater. Phys. 84, 045115 (2011).
- [112] J. D. Perkins, D. S. Kleinberg, M. A. Kastner, R. J. Birgeneau, Y. Endoh, K. Yamada, and S. Hosoya, Phys. Rev. B 52, (1995).
- [113] K. Kalantar-zadeh, J. Z. Ou, T. Daeneke, A. Mitchell, T. Sasaki, and M. S. Fuhrer, Appl. Mater. Today 5, 73 (2016).

- [114] A. Bandyopadhyay, N. C. Frey, D. Jariwala, and V. B. Shenoy, Nano Lett. 19, 7793 (2019).
- [115] P. Gorai, E. S. Toberer, and V. Stevanović, J. Mater. Chem. A 4, 11110 (2016).
- [116] D. Torelli and T. Olsen, 2D Mater. 6, (2019).
- [117] D. Hobbs, G. Kresse, and J. Hafner, Phys. Rev. B 62, 11556 (2000).
- [118] L. Ward, A. Dunn, A. Faghaninia, N. E. R. Zimmermann, S. Bajaj, Q. Wang, J. Montoya, J. Chen, K. Bystrom, M. Dylla, K. Chard, M. Asta, K. A. Persson, G. J. Snyder, I. Foster, and A. Jain, Comput. Mater. Sci. 152, 60 (2018).
- [119] F. Nielsen, in Undergrad. Top. Comput. Sci. (Springer, Cham, 2016), pp. 195–211.
- [120] A. Dunn, Q. Wang, A. Ganose, D. Dopp, and A. Jain, Npj Comput. Mater. 6, 1 (2020).
- [121] N. V. Chawla, K. W. Bowyer, L. O. Hall, and W. P. Kegelmeyer, J. Artif. Intell. Res. 16, 321 (2002).
- [122] F. Faber, A. Lindmaa, O. A. von Lilienfeld, and R. Armiento, Int. J. Quantum Chem.115, 1094 (2015).
- [123] K. Choudhary, B. Decost, and F. Tavazza, Phys. Rev. Mater. 2, 083801 (2018).
- [124] T. Lookman, P. V. Balachandran, D. Xue, and R. Yuan, Npj Comput. Mater. 5, 1 (2019).

- [125] Y. J. Jin, R. Wang, Z. J. Chen, J. Z. Zhao, Y. J. Zhao, and H. Xu, RAPID Commun.Phys. Rev. B 96, 201102 (2017).
- [126] N. Claussen, B. A. Bernevig, and N. Regnault, Phys. Rev. B 101, (2020).
- [127] Y. Li, Z. Jiang, J. Li, S. Xu, and W. Duan, Phys. Rev. B 100, 134438 (2019).
- [128] L. Elcoro, B. J. Wieder, Z. Song, Y. Xu, B. Bradlyn, and B. A. Bernevig, Magnetic Topological Quantum Chemistry (n.d.).
- [129] D. Jariwala, V. K. Sangwan, L. J. Lauhon, T. J. Marks, and M. C. Hersam, ACS Nano 8, 1102 (2014).
- [130] D. Akinwande, C. Huyghebaert, C. H. Wang, M. I. Serna, S. Goossens, L. J. Li, H.S. P. Wong, and F. H. L. Koppens, Nature 573, 507 (2019).
- [131] M. Atatüre, D. Englund, N. Vamivakas, S. Y. Lee, and J. Wrachtrup, Nat. Rev. Mater. 3, 38 (2018).
- [132] H. Peelaers and C. G. Van de Walle, Phys. Rev. B 86, 241401 (2012).
- [133] W. S. Yun, S. W. Han, S. C. Hong, I. G. Kim, and J. D. Lee, Phys. Rev. B 85, 033305 (2012).
- [134] G. Bin Liu, W. Y. Shan, Y. Yao, W. Yao, and D. Xiao, Phys. Rev. B Condens. Matter Mater. Phys. 88, 85433 (2013).
- [135] C. C. Price, N. C. Frey, D. Jariwala, and V. B. Shenoy, ACS Nano acsnano.9b03716

- [136] D. Xiao, G.-B. Liu, W. Feng, X. Xu, and W. Yao, Phys. Rev. Lett. 108, 196802 (2012).
- [137] H. Rostami, A. G. Moghaddam, and R. Asgari, Phys. Rev. B 88, 85440 (2013).
- [138] A. Kormányos, V. Zólyomi, N. D. Drummond, P. Rakyta, G. Burkard, and V. I.Fal'ko, Phys. Rev. B 88, 45416 (2013).
- [139] H. Ye, J. Zhou, D. Er, C. C. Price, Z. Yu, Y. Liu, J. Lowengrub, J. Lou, Z. Liu, and V. B. Shenoy, ACS Nano 11, 12780 (2017).
- [140] M. Zarenia, A. Chaves, G. A. Farias, and F. M. Peeters, Phys. Rev. B Condens. Matter Mater. Phys. 84, 245403 (2011).
- [141] S. Pavlović and F. M. Peeters, Phys. Rev. B 91, 155410 (2015).
- [142] K. Yang and M. de Llano, Am. J. Phys. 57, 85 (1989).
- [143] H. Huang, X.-Q. Fu, and R.-S. Han, Commun. Theor. Phys. 58, 205 (2012).
- [144] R. D. Benguria, H. Castillo, R. D. Benguria, and M. Loewe, J. Phys. A. Math. Gen.33, 5315 (2000).
- [145] D. P. DiVincenzo and E. J. Mele, Phys. Rev. B 29, 1685 (1984).
- [146] A. Matulis and F. M. Peeters, Phys. Rev. B 77, 115423 (2008).
- [147] T. Xie and J. C. Grossman, Phys. Rev. Lett. 120, (2018).

- [148] C. Chen, W. Ye, Y. Zuo, C. Zheng, and S. P. Ong, Chem. Mater. **31**, 3564 (2019).
- [149] K. T. Schütt, P. Kessel, M. Gastegger, K. A. Nicoli, A. Tkatchenko, and K.-R. Müller, J. Chem. Theory Comput. 15, 448 (2019).
- [150] G. Cheon, E. D. Cubuk, E. R. Antoniuk, L. Blumberg, J. E. Goldberger, and E. J. Reed, J. Phys. Chem. Lett 9, 56 (2018).
- [151] S. Das, H. Pegu, K. K. Sahu, A. K. Nayak, S. Ramakrishna, D. Datta, and S. Swayamjyoti, Synth. Model. Charact. 2D Mater. Their Heterostruct. 445 (2020).
- [152] V. Venturi, H. L. Parks, Z. Ahmad, and V. Viswanathan, Mach. Learn. Sci. Technol. (2020).
- [153] S. J. Pan and Q. Yang, IEEE Trans. Knowl. Data Eng. 22, 1345 (2010).
- [154] D. Jha, K. Choudhary, F. Tavazza, W. keng Liao, A. Choudhary, C. Campbell, and A. Agrawal, Nat. Commun. 10, 5316 (2019).
- [155] P. W. Battaglia, J. B. Hamrick, V. Bapst, A. Sanchez-Gonzalez, V. Zambaldi, M. Malinowski, A. Tacchetti, D. Raposo, A. Santoro, R. Faulkner, C. Gulcehre, F. Song, A. Ballard, J. Gilmer, G. Dahl, A. Vaswani, K. Allen, C. Nash, V. Langston, C. Dyer, N. Heess, D. Wierstra, P. Kohli, M. Botvinick, O. Vinyals, Y. Li, and R. Pascanu, ArXiv, http://arxiv.org/abs/1806.01261 (accessed March 26 (2018).
- [156] A. Jain, S. P. Ong, G. Hautier, W. Chen, W. D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder, and K. A. Persson, APL Mater. 1, 011002 (2013).

- [157] B. Medasani, A. Gamst, H. Ding, W. Chen, K. A. Persson, M. Asta, A. Canning, and M. Haranczyk, Npj Comput. Mater. 2, 1 (2016).
- [158] J. B. Varley, A. Samanta, and V. Lordi, J. Phys. Chem. Lett. 8, 5059 (2017).
- [159] A. Mannodi-Kanakkithodi, M. Y. Toriyama, F. G. Sen, M. J. Davis, R. F. Klie, and M. K. Y. Chan, Npj Comput. Mater. 6, (2020).
- [160] A. Walsh and A. Zunger, Nat. Mater. 16, 964 (2017).
- [161] M. E. Turiansky, A. Alkauskas, L. C. Bassett, and C. G. Van de Walle, Phys. Rev. Lett. 123, 127401 (2019).
- [162] F. Hayee, L. Yu, J. L. Zhang, C. J. Ciccarino, M. Nguyen, A. F. Marshall, I. Aharonovich, J. Vučković, P. Narang, T. F. Heinz, and J. A. Dionne, Nat. Mater. 19, 534 (2020).
- [163] A. Gottscholl, M. Kianinia, V. Soltamov, S. Orlinskii, G. Mamin, C. Bradac, C. Kasper, K. Krambrock, A. Sperlich, M. Toth, I. Aharonovich, and V. Dyakonov, Nat. Mater. 19, 540 (2020).
- [164] A. L. Exarhos, D. A. Hopper, R. R. Grote, A. Alkauskas, and L. C. Bassett, ACS Nano 11, 3328 (2017).
- [165] N. C. Frey, D. Akinwande, D. Jariwala, and V. B. Shenoy, ACS Nano acsnano.0c05267 (2020).
- [166] S. Gupta, J. H. Yang, and B. I. Yakobson, Nano Lett. 19, 408 (2019).

- [167] J. Y. Noh, H. Kim, M. Park, and Y. S. Kim, Phys. Rev. B Condens. Matter Mater.Phys. 92, 115431 (2015).
- [168] A. Singh, A. Manjanath, and A. K. Singh, J. Phys. Chem. C 122, 24475 (2018).
- [169] W. Hu and J. Yang, J. Mater. Chem. C 5, 12289 (2017).
- [170] C. Zhang, C. Gong, Y. Nie, K.-A. Min, C. Liang, Y. J. Oh, H. Zhang, W. Wang, S. Hong, L. Colombo, R. M. Wallace, and K. Cho, 2D Mater. 4, 015026 (2016).
- [171] H. Schmidt, S. Wang, L. Chu, M. Toh, R. Kumar, W. Zhao, A. H. Castro Neto, J. Martin, S. Adam, B. Özyilmaz, and G. Eda, Nano Lett. 14, 1909 (2014).
- [172] Y. Shi, W. Zhou, A.-Y. Lu, W. Fang, Y.-H. Lee, A. L. Hsu, S. M. Kim, K. K. Kim,
  H. Y. Yang, L.-J. Li, J.-C. Idrobo, and J. Kong, Nano Lett. 12, 2784 (2012).
- [173] Z. Du, S. Yang, S. Li, J. Lou, S. Zhang, S. Wang, B. Li, Y. Gong, L. Song, X. Zou, and P. M. Ajayan, Nature 577, 492 (2020).
- [174] A. Puthirath Balan, S. Radhakrishnan, C. F. Woellner, S. K. Sinha, L. Deng, C. D. L. Reyes, B. M. Rao, M. Paulose, R. Neupane, A. Apte, V. Kochat, R. Vajtai, A. R. Harutyunyan, C. W. Chu, G. Costin, D. S. Galvao, A. A. Martí, P. A. Van Aken, O. K. Varghese, C. S. Tiwary, A. Malie Madom Ramaswamy Iyer, and P. M. Ajayan, Nat. Nanotechnol. 13, 602 (2018).
- [175] J. R. Weber, W. F. Koehl, J. B. Varley, A. Janotti, B. B. Buckley, C. G. Van de Walle, and D. D. Awschalom, Proc. Natl. Acad. Sci. U. S. A. 107, 8513 (2010).

- [176] R. Ge, X. Wu, M. Kim, J. Shi, S. Sonde, L. Tao, Y. Zhang, J. C. Lee, and D. Akinwande, Nano Lett. 18, 434 (2018).
- [177] X. Wu, R. Ge, P. Chen, H. Chou, Z. Zhang, Y. Zhang, S. Banerjee, M. Chiang, J. C. Lee, and D. Akinwande, Adv. Mater. 31, 1806790 (2019).
- [178] B. Meredig, A. Agrawal, S. Kirklin, J. E. Saal, J. W. Doak, A. Thompson, K. Zhang,A. Choudhary, and C. Wolverton, Phys. Rev. B 89, 94104 (2014).
- [179] A. V. Krukau, O. A. Vydrov, A. F. Izmaylov, and G. E. Scuseria, J. Chem. Phys. 125, 224106 (2006).
- [180] M. S. Hybertsen and S. G. Louie, Phys. Rev. Lett. 55, 1418 (1985).
- [181] L. Breiman, Mach. Learn. 45, 5 (2001).
- [182] V. Popescu and A. Zunger, Phys. Rev. B 85, 85201 (2012).
- [183] R. Tibshirani, J. R. Stat. Soc. Ser. B 58, 267 (1996).
- [184] A. E. Hoerl and R. W. Kennard, Technometrics 12, 55 (1970).
- [185] P. R. C. Kent and A. Zunger, Phys. Rev. B Condens. Matter Mater. Phys. 64, (2001).
- [186] D. G. Thomas, J. J. Hopfield, and C. J. Frosch, Phys. Rev. Lett. 15, 857 (1965).
- [187] S. M. Hus, R. Ge, P.-A. Chen, M.-H. Chiang, G. E. Donnelly, W. Ko, F. Huang, L. Liang, A.-P. Li, and D. Akinwande, ArXiv, http://arxiv.org/abs/2002.01574

(accesed March 20, (2020).

- [188] B. Lounis and M. Orrit, Reports Prog. Phys. 68, 1129 (2005).
- [189] S. G. Bishop, J. P. Hadden, F. D. Alzahrani, R. Hekmati, D. L. Huffaker, W. W. Langbein, and A. J. Bennett, ACS Photonics 7, 1636 (2020).
- [190] F. Zhang, H. Zhang, S. Krylyuk, C. A. Milligan, Y. Zhu, D. Y. Zemlyanov, L. A. Bendersky, B. P. Burton, A. V. Davydov, and J. Appenzeller, Nat. Mater. 18, 55 (2019).
- [191] M. Kim, R. Ge, X. Wu, X. Lan, J. Tice, J. C. Lee, and D. Akinwande, Nat. Commun.9, 2524 (2018).
- [192] J. Berry, S. Ristić, S. Zhou, J. Park, and D. J. Srolovitz, Nat. Commun. 10, 1 (2019).
- [193] Q. Tong, F. Liu, J. Xiao, and W. Yao, Nano Lett. 18, 7194 (2018).