Scientific workflows for accelerated computational materials discovery

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Abstract

With the prospect of an increase in global warming, clean energy materials helping to reduce emissions are needed more than ever. One of the cornerstones of accelerating the discovery of new materials with improved properties is the access to large amounts of high quality data obtained from systematic high-throughput simulations and experiments. Despite the promises data-driven discovery holds, access to reliable data sets is often limited in the field of materials science.

Scientific workflows in materials science help to create such reliable datasets by combining several subsequent computational tasks, which calculate specific material properties in an automated way. Moreover, they allow for a full provenance tracking and for ensuring reproducibility of the data. In this thesis two scientific workflows are implemented in the framework of Density Functional Theory (DFT) to accelerate the discovery of inorganic nanotubes and battery electrodes. The first workflow calculates stability properties of inorganic Janus nanotubes. Janus nanotubes consist of three asymmetric layers. The different elements inside and outside the tube lead to an embedded strain causing spontaneous self-rolling. Here, it is found that the preferred small radius of the tubes is influenced by the lattice mismatch of the corresponding parent sheets composing the Janus structure as well as a difference in bond-strength between the elements inside and outside the tube. The second workflow identifies ion insertion battery properties including thermodynamic properties, such as stability, volume change, and open-circuit voltages, together with kinetic properties, such as diffusion barriers. The workflow is tested for the specific example of Mg-ion batteries. In addition to a few candidates that have been identified for experimental verification, simple descriptors have been found, which can accelerate the exploration of new ionic conductors by predicting which materials and diffusion paths are worth to be calculated.

While the workflows are able to produce reliable datasets, they have also proven to enable the sharing of data and knowledge in terms of best
practices in between researchers. Through building on top of existing knowledge, it can be expected that the reuse and further extensions of the workflows can greatly improve the speed of computational materials discovery and pave the way for efficient data-driven discovery.
Resumé

Med udsigt til fremtidige temperaturstigninger på grund af global opvarmning, er materialer med anvendelse inden for grønne teknologier mere vigtige end nogensinde. En fundamental forudsætning for at optimere opdagelsen af disse er tilgængeligheden af datasæt af høj kvalitet fra systematiske, automatiserede studier baseret på både eksperimenter og computersimuleringer. Trods de lovende udsigter som opdagelsen af nye materialer baseret på eksisterende data har, er adgangen til sådanne datasæt dog stadig begrænset inden for materialevidenskab.

Videnskabelige workflows kan inden for materialevidenskab bruges til at generere datasæt af høj kvalitet ved at automatisere processen med at forudsige bestemte egenskaber for materialer, som ellers ville ske i flere trin. Ydermere gør denne systematisering det nemmere at gemme hvert skridt i udregningerne hvilket sikrer reproducerbarhed. I denne afhandling beskrives implementeringen af to videnskabelige workflows baseret på tæthedsfunktionaler, som bruges til henholdsvis at accelerere opdagelsen af inorganiske nanorør samt materialer til anvendelse inden for batterielektroder. Det første workflow udregner stabiliteten af inorganiske Janus nanorør. Disse består af tre asymmetriske lag. De forskellige grundstoffer på inder- og ydersiden af røret giver anledning til at disse spontant ruller sig sammen. Baseret på resultaterne fra workflowet konkluderes det her, at den foretrukne radius for sådanne nanorør er bestemt af forskellen i gitterkonstanter mellem de to oprindelige 2D lag, som Janus strukturen er dannet ud fra samt forskellen i bindingsstyrken mellem grundstofferne på inder- og ydersiden af nanorøret. I det andet workflow udregnes egenskaber forbundet med indsætning af ioner i batteri-materialer, herunder termodynamiske egenskaber som stabilitet, volumenændringer og spændingskurver samt kinetiske egenskaber som difussionsbarrierer. Workflowet testes her for batterier baseret på Mg-ioner. Resultaterne fra dette workflow er ud over opdagelsen af enkelte materialerkandidater der kræver videre eksperimentel udforskning også et sæt af simple deskriptorer der i
fremtiden kan bruges til at accelerere opdagelsen af nye batterimaterialer ved at kunne bruges til hurtigt at forudsige hvilke materialer og diffusionssretninger der er værd at bruge computerressourcer på.

Udover at være i stand til at generere datasæt af høj kvalitet, har workflowene også vist sig at facilitere data- og vidensdeling mellem forskere. Ved således at bygge ovenpå den nuværende viden, kan det vise sig at genbrug og optimering af disse workflows kan bane vejen for at accelerere opdagelsen af materialer til bestemte anvendelser.
Preface

This thesis is submitted in candidacy for a Doctor of Philosophy (PhD) degree from the Technical University of Denmark (DTU). The work has been carried out between February 2018 and January 2021 at the Section for Atomic Scale Materials Modelling (ASM) at the Department of Energy Conversion and Storage. The studies have been supervised by Tejs Vegge, Ivano Eligio Castelli and Kristian Sommer Thygesen. Part of the work was carried out during a three month research stay at the Theory and Simulation of Materials (THEOS) group at the École Polytechnique Fédérale de Lausanne (EPFL) hosted by professor Nicola Marzari. The project was partially funded by the Special Competence Initiative ”Autonomous Materials Discovery (AiMade)” from the Department of Energy Conversion and Storage, DTU.

Kongens Lyngby, January 2021

Felix Tim Bölle
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I would also like to express my gratitude to all my colleagues at ASM. A special thanks goes to Juan Maria Garcia Lastra for his many insights on modeling battery materials and the countless discussions on helping me to understand things. My sincere thanks to the colleague that started the journey with me and surely brightened up my days in the office - August Mikkelsen. I also thank Steen Lysgaard, Alexander Tygesen, Arghya Bhowmik, Heine Hansen, Karina Frederiksen, Katrine Svane, Jens Kildgaard, Jin Chang, Martin Uhrin, Nicolai Mathiesen, Pernille Pedersen, Peter Jørgensen, Piotr da Silva, Piotr Jankowski, Rune Christensen, Smobin Vincent, Tiantian Wu, Tipaporn Patniboon for their support and the many discussions.

I cannot express enough thanks to my parents, for always supporting me and my decisions, and my partner Emma, for your love, support and understanding - not only while we were apart during my time in Switzerland but also when we were sharing a home office for the last year. This would have simply not been possible without you!
List of Publications

Publications included in this thesis

Paper I
Structural and chemical mechanisms governing stability of inorganic Janus nanotubes
Felix Tim Bölle, August E. G. Mikkelsen, Kristian S. Thygesen, Tejs Vegge and Ivano E. Castelli
(Accepted in) npj Computational Materials

Paper II
Band structure of MoSTe Janus nanotubes
August E. G. Mikkelsen, Felix Tim Bölle, Kristian S. Thygesen, Tejs Vegge and Ivano E. Castelli

Paper III
Autonomous discovery of materials for intercalation electrodes
Felix Tim Bölle, Nicolai Rask Mathiesen, Alexander Juul Nielsen, Tejs Vegge, Juan Maria García Lastra and Ivano E. Castelli

Paper IV
Topological descriptors for predicting kinetic barriers in magnesium cathode materials
Felix Tim Bölle, Tejs Vegge, Juan Maria García Lastra and Ivano E. Castelli
To be submitted
Publication not included in this thesis

Book chapter I
Generation of Computational Data Sets for Machine Learning Applied to Battery Materials
Arghya Bhowmik, Felix Tim Bölle, Ivano E. Castelli, Jin Hyun Chang, Juan Maria García Lastra, Nicolai Rask Mathiesen, Alexander Sougaard Tygesen and Tejs Vegge
Atomic-Scale Modelling of Electrochemical Systems, edited by Marko Melander, Tomi Laurila, Kari Laasonen, ISBN 9781119605614, Copyright John Wiley and Sons Ltd. (IN PRESS)
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Anthropogenic emissions of green house gases are known to be the driving cause for climate change.[1] The Intergovernmental Panel on Climate Change (IPCC) found human activities to be responsible for increasing global warming by approximately 1.0 °C above pre-industrial levels.[2] Due to a likely expected increase of 1.5 °C between 2030 and 2052 dramatic consequences are expected including:[1]

- Sea level rise posing an imminent threat to coastal regions,
- hot extremes causing droughts and water scarcity impacting food security,
- heavy precipitation and the associated prospect of flooding even at altitudes above sea level,
- uninhabitable environments leading to social impacts like poverty and ultimately force people to flee.[3]

Common strategies to combat climate change are usually divided into mitigation, e.g. the use of biomass to produce energy [4], and adaption, e.g. improved soil organic carbon management or flood control.[5] While adaptive strategies usually only delay the negative impacts of global warming, mitigation of emitting greenhouse gases is key to keeping global warming to a limit. In order to find effective methods to mitigate emissions, it is necessary to consider the main reasons for it.

Rapid global economic growth is sometimes believed to be the main reason for global warming.[6, 7, 8] Assuming that striving for economical growth will not stop any time soon, a plausible solution is to shift towards an emission free economy.[9] This can for example be achieved through climate friendly policies, such as putting a price on carbon-dioxide emissions.[10] While such policies and climate agreements are inevitable,
appropriate technology and innovations are needed to achieve the reduction in emissions that these agreements aim for.[11] Technological progress has already made solar powered energy in combination with battery storage systems a viable economic alternative to fossil fuels.[12] An important aspect of technological innovation is to find solutions that are cheap and sustainable. Most of the clean energy devices found in for example solar cells, batteries or catalysts consist of specific materials. Therefore, finding new materials with (1) improved properties while (2) reducing costs and being (3) more sustainable than competing materials are cornerstones to reduce emissions.[13]

A specific example of a class of clean energy devices, where materials discovery is expected to play an important future role, are batteries. Indeed, improvements in energy densities of batteries have already been mainly achieved through improved materials in combination with being able to combine existing materials into more efficient battery cells.[14] While the latter one will always be limited by the materials available, the possible pool of materials, i.e. the amount of possible chemical structures, is in theory staggeringly large.[15] In practice, a conservative lower bound on the amount of possible and synthesizable structures for solely organic molecules is as large as $10^{60}$.[16] Similarly, it is believed that only a small fraction of inorganic compounds have been explored.[13] Therefore, recent scientific efforts in the field of materials science focus strongly on how to accelerate the materials discovery.[13, 17]

1.1 Accelerated materials discovery

Accelerated materials discovery comprises the search for unknown materials, but also determining properties of interests for already known compounds. While some of the problems are the same for experimental and computational studies, in the following it will only be focused on the computational part. In order to better understand what exactly should be accelerated, a simplified materials discovery process is sketched in Figure 1.1.

At the beginning of any materials discovery process there is usually the requirement to find a material with specific properties. For instance,
this could be finding cathode battery materials with an improved energy density. Subsequently, a subset of structures is chosen from the shear infinitely large material compound space (material selection). The amount of chosen structures in the subset directly correlates to the computational cost of the chosen methods. These materials are then studied in terms of the wanted property and the most suitable candidates are chosen. Accelerating the computational materials discovery process focuses on speeding up the “property prediction” step which includes: (1) An \textit{increase in computational power} directly leads to faster calculations and allows to study more materials in less time. (2) \textit{Improvements of existing simulation methods} help to accelerate the process. For instance, DFT machine learning (ML) force-fields have gained a lot of attention recently which allow to study larger systems and longer time scales with improved chemical accuracy.\cite{18, 19} (3) \textit{Automating computational tasks} allows to study material properties with minimum manual user interference. Recent developments in software engineering including the use of version control tools have made it possible to write complex workflows in a collaborative environment (e.g. \cite{20}). (4) Ultimately, all of the three aforementioned steps enable \textit{data-driven discovery of new materials}, if all of the generated
data is made available. This not only allows to navigate more efficiently through chemical space, but also reduces the property prediction of already calculated materials to a simple database query.

If now the property prediction for materials is always consistent, it is reasonable to assume that at one point in the future enough data is available to choose the best candidate for a specific task without running calculations, *i.e.* data-driven discovery. Nevertheless, materials science researchers realized that several obstacles need to be overcome before achieving this, since there is rarely "one" way of determining a specific material property.[21]

Three main problems for not being able to learn from previously conducted material studies have been identified:[21]

1. Decentralization of materials data leading to smaller databases without central access. The diversity of materials data (*e.g.* different dimensionalities etc.) is often mentioned as the main cause.[22]

2. The access to structured data that can be easily downloaded is limited.

3. Missing data standards make it impossible to compare results in between experiments and calculations.

The computational materials science community started efforts to tackle the above mentioned problems which resulted in data sharing platforms like the materialsproject [23] or materialscloud [24]. Already now they allow researchers to download bulk data of material properties without having to run the calculations themselves. One of the reasons for the success of these databases is also thanks to the high fidelity of the materials property data. In terms of computational materials science, this means that any property prediction can in principle be reproduced since all input and output files of the simulation are stored including all steps carried out in between. Combining several subsequent tasks required to predict a material property is also often referred to as a scientific workflow. In contrast to manually executing each individual task, scientific workflows directly include the logic in between tasks through dependencies. This allows calculations to be called reproducible, since for deterministic workflows the same input always leads to the same results. Additionally, researchers can
1.2 Inorganic nanotubes

Inorganic nanotubes have been studied extensively throughout the last decades and possible applications focus among others on catalysis, solid lubricants and photovoltaic cells. Nevertheless, advancements have been hampered by the difficulties in synthesizing nanotubes of similar size and shape in large quantities. To overcome this issue, here we conduct a computational high-throughput screening study of so called Janus nanotubes. Janus nanotubes have an intrinsic tendency to form tubular shapes making them a particularly interesting class of inorganic nanotubes exhibiting well-defined shapes and sizes. Previous computational studies have shown the theoretical existence of these tubes, but are limited to only a few materials.

The computational workflow presented in this work calculates the stability of nanotubes at different tube sizes. While the workflow itself has
only a few dependencies and is therefore low in complexity, the difficulty arises from studying hypothetical and often unstable structures shifting the focus towards the *material selection* step of the discovery process.

### 1.3 Ion insertion batteries

![Diagram of Mg battery](image)

**Figure 1.2:** Schematic sketch of discharging a Mg battery using a pure metal anode, an electrolyte and an ion-insertion cathode.

Figure 1.2 shows a simplified sketch of the working principle of rechargeable ion insertion batteries. During the discharge phase, ions migrate from the anode through the electrolyte. Subsequently, the ions get inserted and reduced in the cathode host structure. Upon charging, the cathode retains its crystal structure while ions are migrating back to the anode. From a practical point of view, it is valuable to know how fast ions are transported within the cathode. It directly impacts how fast the battery can be charged and poses a major challenge especially for multivalent ions like magnesium.[35] Consequently, the workflow developed in this work
includes the calculation of kinetic barriers. Calculating barriers computationally usually involves several manual steps by the user which slows down the materials discovery process and often limits theoretical studies to only a few hand-picked materials. The goal of the workflow is to overcome these limitations through automating the tasks and being able to study a larger variety of possible candidates. While in this workflow the material selection is restricted to known and synthesizable materials, the workflow itself contains more dependencies and creating unique starting structures automatically becomes more difficult.


1.4 Outline of the thesis

This thesis includes all findings from paper I-IV. In addition to focusing on the individual outcomes of the different papers, this thesis puts everything into the broader context of developing scientific workflows for creating reproducible datasets. It is structured into the following chapters:

- **Chapter 1 - Introduction**
  Starting with the importance of accelerated materials discovery to combat climate change, this chapter introduces the role of scientific workflows in computational materials discovery helping in this context. The two main scientific topics of inorganic nanotubes and insertion batteries are introduced.

- **Chapter 2 - Methods**
  A brief overview of Density Functional Theory (DFT) and the Nudged Elastic Band (NEB) method is presented. Tools used to develop the scientific workflows are discussed.

- **Chapter 3 - Workflow for creating an inorganic nanotube database**
  A screening study of 135 materials forming so called Janus nanotubes is presented. The properties of interest focus on the stability of these tubes. Simple descriptors describing the stability are identified.

- **Chapter 4 - Workflow for calculating ion insertion battery properties**
  An automated workflow is presented which calculates stability properties, open circuit voltages (OCVs) and kinetic barriers using the NEB-method. The workflow is tested studying magnesium cathode materials and the data is analyzed in order to get a better understanding on how different chemical structures affect ion diffusivity.

- **Chapter 5 - Conclusion**
  Main conclusions from chapter 3+4 are presented.

- **Chapter 6 - Discussion and Outlook**
  Scientific workflows and their use in this work are discussed.
A brief introduction to Density-functional theory (DFT) is provided with a focus on the applied methods in this work. More details on DFT can be found in literature.\cite{36} The Nudged Elastic Band method is discussed outlining its basic principles as well as the extension of considering reflection symmetries for accelerated calculations. Since a substantial part of this work focuses on scientific workflows in materials science, the last part of this section introduces the used tools and the motivation for using workflows.

## 2.1 Density Functional Theory

Understanding and developing new materials has been influenced by the use of computational simulation methods. The simulation methods are usually distinguished through the time and length scales that can be simulated. Continuum models usually attempt to simulate materials on the millimeter scale being on the upper end of what sizes of materials are feasible to study. DFT acts on the nanometer scale, since larger simulations are computationally infeasible. Treating electrons explicitly, it has the advantage of being able to study for instance chemical reactions. Moreover, the method is derived \textit{ab-initio} meaning it is based on first-principles rather than on fitted empirical parameters.

### 2.1.1 The Schrödinger Equation

DFT is derived directly from the Schrödinger Equation. Therefore, calculations using DFT are said to be from first principles or \textit{ab-initio}. Following the Born-Oppenheimer approximation, nuclei can be treated stationary when solving the wave functions for the electrons.\cite{37} The time-
independent Schrödinger equation for the electronic degrees of freedom then reads [38]

$$\hat{H}\psi(r) = E\psi(r),$$

(2.1)

where $\psi$ is the wave function and $E$ is the total energy. The Hamiltonian $\hat{H}$ can be written as

$$\hat{H} = \sum_i -\frac{\hbar^2 \nabla_i^2}{2m} + \frac{1}{2} \sum_{i<i'} \frac{q_i^2}{|r_i - r_{i'}|} - \frac{1}{2} \sum_{i<j} \frac{Q_j g}{|r_i - R_j|},$$

(2.2)

where $\hat{T}_e$ is the electronic kinetic operator, $\hat{V}_{e-e}$ is the electron-electron interaction and $\hat{V}_{e-n}$ is the interactions between electrons at $r_i$ with nuclei at position $R_j$. The operators $\hat{V}_{e-n}$ and $\hat{V}_{e-e}$ require to calculate the interaction of an electron with all electrons and nuclei in the system making it a complex many-body problem. Solving Schrödinger’s equation for the wave function enables to calculate, besides other observables, the particle density of the system

$$n(r) = N \int d^3r_2 \int d^3r_3 \ldots \int d^3r_N \psi^*(r, r_2, \ldots, r_N)\psi(r, r_2, \ldots, r_N),$$

(2.3)

where $N$ is the number of electrons.

### 2.1.2 The Hohenberg-Kohn theorems

While solving the many-body problem in equation 2.1 is practically infeasible, DFT shifts the problem of solving it from looking at the wave function as the fundamental variable to the electronic density. The underlying theorems provided by Hohenberg and Kohn are:[39]

**Theorem 1**: The external potential, and hence the energy, of a system is uniquely determined by the electron density $n(r)$.

**Theorem 2**: The exact ground-state density gives the minimum total energy of a system and can be obtained variationally.

This means that the ground-state wave function $\psi_0$ can be derived from a given a ground-state density $n_0(r)$. It also implies that $\psi_0$ becomes a
2.1 Density Functional Theory

functional of $n_0(r)$ and both functions contain equivalent information:

$$\psi_0(r_1, r_2, ..., r_N) = \psi[n_0(r)].$$

(2.4)

2.1.3 The Kohn-Sham equations

One observable that can be directly calculated is the total ground-state energy

$$E_{v,0} = E_v[n_0] = \langle \psi[n_0] | \hat{H} | \psi[n_0] \rangle,$$

(2.5)

where $E_{v,0}$ is the ground-state energy in a potential $v$ and $\hat{H}$ has the variational property

$$E_v[n_0] \leq E_v[n'].$$  

(2.6)

Since it is a variational property, any density different from the ground-state density will lead to larger energies than $E_{v,0}$.

For the Kohn-Sham scheme, the idea is to find a system of non-interacting electrons which generate the same ground state density as the interacting many-body system. The non-interacting (or single-particle with subscript $s$) part of the kinetic energy can then be expressed for this density by introducing single-particle orbitals (antisymmetric wave function of the Slater determinant type) as a sum over all particles by

$$T_s[n] = -\frac{\hbar^2}{2m} \sum_i^N \int d^3 r \phi_i^*(r) \nabla^2 \phi_i(r).$$

(2.7)

All remaining interactions that are not considered by using the non-interacting system are added through additional terms. The total energy functional then becomes

$$E[n] = T_s[\phi_i[n]] + V_H[n] + E_{xc}[n] + V_{ext}[n],$$

(2.8)

where $V_H$ is the Hartree energy. The difference between the fully interacting system comes now from the the differences in $T - T_s$ and $V - V_H$. These differences are incorporated in the exchange-correlation functional $E_{xc}$ making the formulation exact for describing an interacting system. The energy term from electron-nuclei interactions is included in $V_{ext}[n]$. The Kohn-Sham equations are solved for a noninteracting system in a potential

$$v_s(r) = v_{ext}(r) + v_{xc}(r) + v_H(r)$$

(2.9)
where
\[
-\frac{\hbar^2 \nabla^2}{2m} + v_s(r) \phi_i(r) = \epsilon_i \phi_i(r),
\] (2.10)
and the orbitals of the noninteracting system yields the density of the system as
\[
n(r) = \sum_i N f_i |\phi_i(r)|^2,
\] (2.11)
with \( f_i \) being the occupation number of the respective orbital. The equations are then solved by guessing \( n(r) \) and using it in equation 2.10. Subsequently, the new density is obtained using equation 2.11. This process continues iteratively until a converged solution is found. Although equation 2.8 formally provides the exact total energy, a practical expression for \( E_{xc} \) is not known.

### 2.1.4 Exchange-Correlation Functionals

A main concern before doing the calculation includes choosing an appropriate Exchange-Correlation functional. The different functionals differ in terms of accuracy, i.e., how close they can approximate the true underlying value for \( E_{xc} \), as well as in terms of the ability to predict specific structure properties. The local density approximation (LDA) \([40]\) was derived from the homogeneous electron gas. Assuming the system to be locally homogeneous, it was possible to get a direct expression for the exchange-correlation energy as
\[
E_{xc}^{LDA}[n] = \int n(r) \epsilon_{xc}^{LDA}[n(r)] dr,
\] (2.12)
where \( \epsilon_{xc}^{LDA} \) is the exchange-correlation functional based on the homogeneous electron gas. LDA is successfully applied for systems with a uniform electron density, like bulk metals, but tends to overestimate energies for more complicated systems or highly localized electrons.\([41]\)

While the LDA approximation only considers knowledge of the density at point \( r \), a natural extension is used in the so called ‘generalized-gradient approximations’ (GGAs). GGAs consider in addition to the density, also the gradient of the density at point \( r \), accounting better for the spatially varying density \( n(r) \) found in an electronic system. One of the most popular GGAs is the Perdue-Burke-Ernzerhof (PBE) functional, which is
applied extensively throughout this work.[42] While PBE usually gives a
good agreement with experiments over a wide range of properties, revi-
sions of the original functional have led to the PBEsol functional. PBEsol
has proven to give improved lattice constant predictions over PBE when
compared with experimental values, making it especially valuable for es-
timating intercalation and diffusion properties in batteries calculated in
this work.[43]

Self-interaction error and the Hubbard-U correction
DFT describes electrons as electron densities making it difficult to pre-
cisely determine which density belongs to a single electron. Consequently,
the Coulomb energy of an electron (Hartree term) includes the interac-
tion with its own electron-density which is known as the self-interaction
error in DFT calculations.[44] This error has a particular strong impact
on highly localized electrons, like d-electrons in transition metals which
tend to delocalize under the influence of strong self-interaction. While so
called hybrid functionals aim at reducing the self-interaction error [45],
it comes at the cost of significantly higher computational times which is
usually infeasible for high-throughput screening studies.

In order to correct for the strong electrostatic interaction found in the
d-electrons in transition metals while keeping computational costs modest,
a Hubbard-U correction can be applied.[46, 47] The strength of the U
correction is decided by the value of the parameter U itself and is usually
chosen through fitting procedures to match a desired property like the
band gap of a material. In this thesis, the U value aims at describing phase
stability properties of transition metal-oxide systems more accurately.

2.2 Nudged Elastic Band calculations

Different structural configurations of the same chemical system lie on dif-
f erent points on the potential energy surface (PES) under investigation.
If one is interested in how much energy is associated with changing its
configuration from the initial to the final structure, the minimum energy
path (MEP) on the PES can be investigated. The MEP includes all low
lying energy configurations connecting initial and final structures. The
associated energy barrier is determined by the structure with the largest
energy along the MEP, which is also know as the transition state. The nudged elastic band (NEB) method optimizes an initial path guess towards the MEP. The initialization between initial and final state is often obtained through linear interpolation between the two structures. The interpolated structures in between are called images denoted by \([R_0, R_1, R_2, \ldots, R_N]\), where \(N\) is the total amount of structures along the path. These images are connected through elastic springs. The ‘nudging’ of the images is related to the projection of the force acting on an image defined as \([48, 49]\)

\[
F_{\text{NEB}}^i = F_{i}^{s,\|} + F_{i}^{\perp},
\]

(2.13)

where \(i\) indicates a single image, and \(s\) is the spring force. The projected force consists of two components. The perpendicular component of the true force moves the image towards low lying energy configurations and is given by

\[
F_{i}^{\perp} = F_{i} - F_{i} \cdot \hat{\tau}_i,
\]

(2.14)

where \(\hat{\tau}_i\) is the normalized local tangent at image \(i\). That means that the force components parallel to the tangent are projected out. The parallel component of the spring force is given by

\[
F_{i}^{s,\|} = s(| R_{i+1} - R_i | - | R_i - R_{i-1} |) \hat{\tau}_i
\]

(2.15)

and ensures that the images are equidistantly spaced in order to prevent images from sliding down towards other low lying structures on the PES. The NEB method optimizes the forces acting on each image until it reaches a defined convergence criterion. In order to get a better estimate of the exact shape of the MEP at the transition state, the climbing image NEB (CI-NEB) method has been introduced.\([50]\) The transition state is a saddle point on the MEP. In the CI-NEB method the spring forces on the maximum energy image are removed and the forces along the tangent are reversed, so that the image can freely climb up the potential energy surface along the elastic band.

Optimizing the path requires heavy calculations and is usually unfeasible to do in a high-throughput manner. Several methods to speed up the NEB calculations have been discussed in literature like approximating the potential energy surface (PES) along the MEP instead of explicitly calculating it \([51, 52]\) or improving the initial path guess in comparison
2.2 Nudged Elastic Band calculations

One option discussed in detail in this work, is to make use of symmetry considerations of the PES along the path by using the recently implemented Reflective Nudged Elastic Band method (R-NEB).

2.2.1 Reflective nudged elastic band method

In a conventional NEB calculation, every image along the path is evaluated through DFT calculations in order to obtain the forces needed in equation (2.13). The R-NEB method exploits, if present, reflection symmetry along the MEP path. Reflection symmetries in a three-dimensional structure can be present either along a plane, line or point. These three reflection matrices need to be orthogonal and involutory, while the latter condition implies that the matrix is also its own inverse. For instance, the initial $i_0$ and final state $i_{N+1}$ can now be related through

$$i_0 = T U \underbrace{S}_{S} i_{N+1},$$

(2.16)

where $N$ is the total amount of images and $S$ is the symmetry operation including a translation $T$ and a rotation $U$. While this condition can be used to, for instance, create final images from an initial image, it also has to be ensured that the full path conserves the reflection symmetry. Only if the full path is reflective, the PES possesses the same symmetry. In this way only half of the images of the path including the middle image have to be calculated using DFT leading to a reduction in the required computational time.

Combining the R-NEB method with a linear interpolation of the path consisting of equidistantly spaced images conserves the reflection symmetries. Extensions beyond linear interpolations can be made by ensuring that the path is characterized by the same reflection operation. Further details of the R-NEB method can be found in Ref.[54].
2.3 Automated workflows

Why

The increased use of computational tools for materials discovery has resulted in a stark increase in publications of computational papers. While this resulted in accelerating the material discovery it also raised concerns about the reliability (fidelity) of the published data. A Nature survey conducted in 2016 with more than 1500 researchers revealed that only 3% do not think that there is a reproducibility crisis.[55] More than 70% of the researchers have tried and failed to reproduce their own or other peoples’ experiments. Although for computational work it is obviously easier to achieve reproducible results, there is no requirement that computational researchers should be able to reproduce their results a second time after publication. The lack of fidelity in computational data has been extensively discussed and resulted in several efforts to increase the reproducibility of published computational databases.[56] One of the large efforts towards this goal includes the NOMAD Center of Excellence trying to achieve the so called FAIR data principles (F- Findable, A- Accessible, I- Interoperable and R- Reproducible).

While it becomes obvious that big-data driven analysis can only be achieved through reliable datasets, no requirements exist in the DFT community on when a calculation is marked reproducible. This has a direct consequence for machine learning tools that rely heavily on consistent input parameters. Another aspect in DFT are the plethora of different codes. Lejaeghere et al. subjected DFT data produced by different codes to critical scrutiny and found that the precision of the calculation is also influenced by the choice of the underlying DFT code. In other words, the same input parameters for two different DFT-codes for a given structure will not lead to exactly the same results. At the time of writing, it is the researcher conducting computational studies that has to define what reproducibility effectively is in the respective project. In the following, existing tools supporting researchers with this task are presented with a focus on putting the used tools in this work into context.
2.3 Automated workflows

How

Workflow systems allow the researcher to combine different computational steps needed to calculate specific properties that usually require several subsequent and parallel jobs being submitted to a supercomputer. These workflow systems are usually very domain specific, as the needs in different research fields vary drastically.[57] What sets scientific workflow systems in computational materials science apart from other workflow schemes in different disciplines like biology (e.g. Kepler [58] or Galaxy [59]), is the ability of creating dynamic workflows, i.e. the change of the workflow structure during runtime. This means that the workflow graph is not limited to being a strictly directed acyclic graph (DAG). This feature arose due to the large error rate DFT calculations encounter and the need for resubmitting failed calculations. Within the scope of DFT-based computational materials science, two established workflow management systems exist. (1) The automated interactive infrastructure and database for computational science (AiiDA) was designed for providing the researcher with a tool, that stores detailed information on every single computational step involved in the calculation of properties. Any user input or used software is stored in a graph, that can be traversed through to get a full computational fingerprint of the calculation.[60] (2) Fireworks [61] is a workflow management system that builds on top of pymatgen (manipulate structures and create input data) [62] and custodian (error handling software). The user is free to combine the tools to build workflows and some of them have been collected in the atomate package.[25]

In this work, an in-house workflow scheduling system called myqueue [63] in combination with the atomic simulation environment (ASE [26] - manipulate structures, create inputs and submit calculations) is used. Myqueue is a simple, yet powerful front-end for the scheduling system Slurm, that lets the researcher combine sequential calculations to complex workflows. Since the error-handling of a workflow has turned out to be crucial to any successful workflow, a new tool has been implemented in this work. The need for a new error-handling tool stems from the fact, that interoperability between the two discussed tools AiiDA and Fireworks together with ASE is not given. A more detailed explanation on the developed error-handler is provided in section 2.3.1.

Figure 2.1 depicts all three examples of tools used in the materials
### 2.3 Automated workflows

<table>
<thead>
<tr>
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<th>AiiDA</th>
<th>Fireworks</th>
<th>Myqueue</th>
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<tbody>
<tr>
<td>structure manipulation</td>
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<td>pymatgen</td>
<td>ASE</td>
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<td>calculation input</td>
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<td>error handling</td>
<td>AiiDA</td>
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<td>workflow system</td>
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<td>Atomate</td>
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<td>finished workflow</td>
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Figure 2.1: Common software tool combinations used to build scientific workflows in materials science.

Science community to build scientific workflows. One crucial difference between the overall design of the three examples, lies in AiiDA being an "all-in-one" solution, while Fireworks and the tools used in this work (labeled Myqueue in the graph) are a more modular approach. While modularity makes it easier for the user to get started, AiiDA has all tools at the same place.

Choosing the right tools heavily depends on the need of the user as well as on the knowledge already existing in the group. All solutions will lead to workflows that can be run on demand without expert knowledge. Nevertheless, all tools require a strong interest in programming combined with a few months of familiarization with the software.

In this work the solution of choosing the workflow system myqueue was chosen. This decision is mainly based on the pre-existing knowledge inside the group as well as the need for a flexible tool, that easily allows to implement new features. Additionally, the modular approach of codebases
in contrast to an "all-in-one" solution keeps the infrastructure nimble to possible changes. Throughout the thesis it will be commented on advantages and also disadvantages of the chosen tools providing guidance for possible future work on this topic.

2.3.1 Implementing workflows in this work

Having the tools in place, the next step is to write workflow software. While the step leaves the developer maximum freedom, in this work the two investigated workflows (inorganic nanotubes and insertion batteries) follow the same logic. The main idea behind the software design is to structure every step in the workflow as a separate task, representing one specific class. These task classes are structured consistently, i.e. containing consistent functions that retrieve information or get the calculator input. This helps creating workflows that can more easily be taken apart piece-wise in order to serve as an input for new workflows, just like putting together lego bricks. Another main advantage has turned out to be testing the software following the simple principle of creating one class for each task of the workflow.

The workflows developed in this work are structured into three layers (Figure 2.2). (1) The bottom layer contains the interfaces to different tools responsible for the calculation input as well as interfaces to the calculation codes. Given the flexibility of ASE, different DFT-codes (e.g. GPAW [64, 65] or VASP [66, 67]) are straightforward to implement with minimal changes to the overall structure of the workflow. Although being least generic, the bottom layer allows for storage of useful functions, e.g. finding symmetry equivalent sites, that might be useful in other projects. Eventually these tools can be provided to the community through implementing them in large collaborative projects like ASE. (2) The workflow layer contains the above mentioned tasks. Optimization tasks relax a structure, usually including a DFT calculation. Decision tasks analyze the produced data and interrupt or continue a current workflow based on user defined threshold values. The prepare tasks include steps which decide on how many subsequent tasks might be needed, since this is often not known upfront. As an example, the number of symmetry inequivalent elements can increase upon optimization. (3) The top layer includes the workflow management system which sets up the dependencies (the logic)
2.3 Automated workflows

Figure 2.2: Different layers of the workflows used in this thesis. Figure adapted and reprinted with permission from paper III. Copyright Wiley-VCH GmbH.

In between the task. Additionally, all the data produced is collected using a data collection script.

**Automatic Error Handler**

An automatic error-handler for the DFT-code VASP has been implemented in this work which is compatible with ASE. It is inspired by the error-handler implemented in the CUSTODIAN package.\cite{62} The tool is flexible enough to be used in any ASE based workflow and has been successfully used throughout this work.

As an input it takes the ASE-atoms object, containing information about the chemical structure, as well as the calculator object, containing all information on the chosen DFT code and its input parameters. The tool proceeds then by scanning the output files in the current working directory and handles by default the following errors in hierarchical order (Figure 2.3): (1) A calculation reached the wall-time limit on the cluster and needs to be restarted, (2) not enough memory required for the task and (3) VASP specific errors.
Figure 2.3: Basic idea behind the error handler enabling automated scientific workflows. The purple fields represent the two ASE objects atoms (containing structural information) and calculator (containing information on the calculator and its input parameters). If the error handler does not find any errors, the tool stops the workflow.

VASP specific errors are detected and the input parameters of the calculation adjusted accordingly. For instance, this could mean choosing a tighter convergence value for the break condition during the electronic self-consistent loop. These VASP errors and the according adjustments can be altered or transferred in between new and existing workflows by the user, leaving enough flexibility to which extent errors are handled automatically. Additionally, further decision blocks (yellow diamonds in Figure 2.3) can be included if necessary.
CHAPTER 3

Workflow for creating an inorganic nanotube database

This chapter presents paper I with the title “Structural and chemical mechanisms governing stability of inorganic Janus nanotubes” in its complete form. The paper is also included in this thesis together with the supplemental information. The text is directly taken from the paper, while the chapters are restructured for the purpose of this thesis. In addition to the paper, a discussion of the workflow has been added at the end of this chapter including extensions that have led to paper II with the title “Band structure of MoSTe Janus nanotubes” which is also included in this thesis.

3.1 Introduction

In the last decades miniaturization of devices has been a main trend driving the electronics industry. In addition to reducing the usage of raw materials, nanomaterials often show improved properties compared to their larger counterparts. Among these nanomaterials are two-dimensional (2D) sheets, one-dimensional (1D) structures such as nanotubes and nanoribbons, and zero-dimensional (0D) nanoparticles.

Since their discovery, nanotubes have shown promise for a wide range of applications including gas separation and capture, catalysis, solid lubrication and controlled drug delivery.[32] In addition to the well-known carbon nanotubes [68] numerous inorganic nanotubes have been synthesized .[69, 70] Although the first successful synthesis of single-wall MoS$_2$
nanotubes has been reported [5], such structures usually appear together with numerous multi-wall tubes showing a distribution of radii and wall thicknesses.[71] These multi-wall structures alleviate the built-in strain energy through van der Waals interactions in between the layers leading to an increase in stability.[32] Overall, this has made it difficult to establish an experimental synthesis pathway to produce single-wall tubes with a specific radius and controllable physio-chemical properties.

A possible solution to this problem is the approach of considering asymmetric sheets, which can naturally wrap and form nanotubes with a well-defined size. Due to the asymmetry, the unsupported sheet is expected to be unstable compared to other curled shapes, such as tubes or scrolls. Pauling, already in the 1930s, mentioned that the driving force of sheets to curve is related to the lattice-mismatch between the two inner and outer atomic layers.[72] Single-wall inorganic nanotubes with well-defined diameters hold promise for technological applications, not only because of their reduced dimensionality, but also for their unique properties, often inherently different from the ones of the corresponding asymmetric sheets. An example of a small-radius, single-wall nanotube formed from an asymmetric sheet is imogolite \((\text{Al}_2\text{Si}_3\text{O}_10(\text{OH})_4)\) which was first discovered in volcanic ash soil [73] and later synthesized.[74, 75] Other tubular minerals include chrysotile \((\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4)\) and halloysite \((\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4)\) that however occur as multi-wall tubes.[76, 77] Besides naturally occurring nanotubes, ”misfit-layer” compounds, composed of two separate sheets, make use of the lattice mismatch between the two sheets to induce a natural driving force to form a tube.[78]

One of the possible classes of materials forming asymmetric 2D monolayers are Janus sheets, like MoS\(_2\)Se [79] or BiTeI [80], which can be wrapped to form 1D tubes.[33, 34] A recent work[33] has shown that radii well below 35 Å are needed to create single-wall Janus transition metal dichalcogenide (TMD) tubes, which have significantly different (electronic) properties from the corresponding asymmetric sheet. Although facile synthesis routes for the production of single-wall inorganic nanotubes has long been actively researched, not much attention has been paid to the question of which materials would be able to make such a structure avoiding the creation of multi-wall tubes. Consequently, a high throughput study on the stability of a wide range of Janus-based nanotubes, would provide valuable information for guiding future synthesis of small-radius single-wall nanotubes.
In this work we present a comprehensive screening study in the framework of Density Functional Theory (DFT) on the stability of 135 different inorganic nanotubes generated from the rolling of asymmetric 2D Janus sheets along both the armchair and zigzag directions. The calculations focus on the stability and strain energy of the chosen nanotubes. We show that for pure chalcogen or halogen tubes (isovalent anions), the wrapping mechanism is mostly governed by the lattice-mismatch between the two inner and outer atomic layers, while for mixing anions (non-isovalent anions) this is dominated by the difference in valency between the X/Y elements. These findings provide a physical foundation for designing Janus nanotubes with optimal (small) radii.

3.2 Workflow and computational details

The first step to create our library of nanotubes is to relax the 2D Janus sheets, taken from the Computational 2D Materials Database (c2db).[20] If a 2D Janus sheet is not present in the database, the 2D Janus sheet is created by averaging the lattice constants from its constituent MX$_2$ and MY$_2$ parent sheets. Subsequently, tubes are generated by repeating and wrapping the 2D sheets both along the armchair and zigzag wrapping directions, thereby obtaining tubes with various radii (similar to what is shown in Figure 3.1). In details, the initial number of unit cell repetitions is $n = (6, 8, 10, 12, 14)$ for the armchair and $n = (10, 13, 16, 19, 22)$ for the zigzag wrapping direction, which correspond to tubes with a radius smaller than 20 Å. We apply a set of filters to decide whether or not the relaxed structure is accepted for further investigation. These filters include assuring that a tube retained its circular shape and that no unwanted changes into different prototypes occurred during the relaxation. The filters discard $\sim 40\%$ of the data generated. A detailed discussion on how the data is filtered prior to visualization can be found in the SI for paper I. For consistent and reproducible calculations, we implement a workflow combining the Atomic Simulation Environment (ASE) [26] and the workflow scheduling system MyQueue [63]. Inspired by the CUSTODIAN package [62], we establish an ”ASE error handler” to handle
common DFT errors thus limiting the need for user intervention. A similar approach has been recently implemented to autonomously discover battery electrodes.[81] The workflow is continuously developed and may be accessed at https://gitlab.com/ivca/Nanotubes.

All calculations are carried out with the Vienna ab initio Simulation Package (VASP) using a plane-wave basis set with an energy cutoff of 550 eV.[66, 67, 82] In order to approximate the exchange-correlation effects the Perdew-Burke-Ernzerhof (PBE) form generalized gradient approximation (GGA) is used.[42] A k-point density $> 4.7 /\text{Å}^{-1}$ is used to sample the Brillouin zone. All forces are converged to less than 0.01 eV/Å. The structures are relaxed in a non-magnetic configuration, i.e. without applying initial magnetic moments on the elements. A minimum vacuum in between repeating images of 16 Å is ensured. Dipole corrections are applied along the non-periodic direction for materials with an out-of-plane dipole moment. To assess the stability versus 3D phases, we use a convex hull analysis, where the reference structures are the ones defining the convex hull in the Materials Project database.[23] These structures are then relaxed with the matching input parameters used in this work, [62] while the reference energy of oxygen is obtained by calculating the difference in energy between water and hydrogen in the gas phase, including the zero point energy (ZPE) corrections.[83] For the calculation of the stiffness tensor we use the workflow described by Haastrup et al. in Ref. [20]. Here, the k-point density applied for calculating elastic constants is $> 12.0 /\text{Å}^{-1}$ together with an applied strain of $\pm 1\%$. 
Figure 3.1: The symmetric MY\textsubscript{2} and MX\textsubscript{2} are the parent sheets for the asymmetric 2D Janus MXY sheet, which can be wrapped up to form a 1D Janus nanotube. In this case M = Bi (light purple), X = Te (dark yellow) and Y = I (dark purple).

The nanotubes considered in this study consist of three layers (MXY, as illustrated in Figure 3.1) composed of different mid-layer elements (M = \{Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Fe, Ge, Sn, As, Sb, Bi\}) decorated with inner X and outer Y chalcogen and halogen atoms (X,Y = \{O, S, Se, Te, Cl, Br, I\}). Here we denote all group 16 elements including oxygen as chalcogens. For the three pnictogens (As, Sb and Bi) having 3+ as one of their possible oxidation states, we mix chalcogens and halogens in the structures. For the remaining 12 elements, the inner X and outer Y elements are either chalcogens or halogens. The idea of mixing chalcogens and halogens to form 2D MXY Janus sheets was recently explored in Ref. [84], but has so far not been pursued in the context of nanotubes. We construct the tubes by rolling up 2D layers in both the T- and H-phase.
crystal structures, corresponding to the crystal structures found for the experimentally synthesized MoSSe [79] and BiTeI [80] 2D sheets, along both the armchair and zigzag directions.

**Nanotube strain energy**

Two main quantities that are needed to characterize an asymmetric nanotube are the optimal radius, which defines the most stable nanotube size, and the strain energy, which defines the energy associated with the wrapping of a 2D sheet into a nanotube (negative strain energies indicate a spontaneous wrapping).

The strain energy is defined as the difference between the energy of the nanotube and the corresponding 2D sheet.[85] In formula:

\[
E_{\text{strain}}(R) = \frac{E_{\text{tube}}}{N_{\text{tube}}} - \frac{E_{\text{MXY}}}{N_{\text{MXY}}} \tag{3.1}
\]

where \(E_{\text{tube}}\) is the energy of a nanotube with \(N_{\text{tube}}\) atoms and \(E_{\text{MXY}}\) is the energy of the corresponding 2D Janus sheet with \(N_{\text{MXY}}\) atoms in the unit cell. In the infinite limit \(R \to \infty\), the strain energy is zero, since the energy per atom of a tube is equal to the energy per atom of an infinite 2D Janus sheet.

It has been shown that for symmetric tubes (carbon, for example) the nanotube strain energy follows a \(1/R^2\) dependence.[86, 87] This relationship does not hold for asymmetric tubes in which the strain energy curve exhibits a minimum.[88, 89, 90, 91] Instead, it can be more accurately described using the equation:[88]

\[
E_{\text{strain}}(R) = \frac{a}{R^2} + \frac{b}{R} \tag{3.2}
\]

Extrapolating the function using the obtained DFT data and evaluating the function at the minimum strain energy \(E_{\text{strain-min}}\) leads to the optimal tube radius \(R_{\text{opt}}\) (see also Figure 3.2). We note that, although Eq. 3.2 fits well in the region around the optimal tube radius, large strain energies can lead to a deviation.[92] We take this into consideration during the screening using Bayesian statistics (details in the SI for paper I) which helps to identify cases where the function chosen does not capture the observed data points well across all tube radii.
Figure 3.2: Strain energy as a function of the radius for the symmetric MoS$_2$ nanotube and the two asymmetric NbSSe and BiSI nanotubes. The label in brackets indicates the prototype (H-/T-phase) and the wrapping direction (a/z indicating armchair/zigzag).

As an example, Figure 3.2 shows the strain energy as a function of the tube radius for three different materials, comparing a symmetric MoS$_2$ tube with the two studied asymmetric tubes NbSSe and BiSI. The symmetric MoS$_2$ tube shows a $1/R^2$ dependence of the strain energy over the tube radius indicating the single-wall nanotube is less stable than the infinite sheet. This is not the case for the asymmetric NbSSe and BiSI tubes, where the strain curve exhibits a minimum. The strain energy curve for BiSI shows a strain energy minimum of -31 meV/atom at the optimal radius of $\sim$ 10 Å while the strain energy curve for NbSSe is instead very shallow (minimum at -1.1 meV/atom at 85 Å) due to the minor lattice-mismatch of 0.96 between the two parent sheets NbS$_2$ and NbSe$_2$. Such a shallow strain energy curve makes it difficult to establish an optimal radius.
3.3 Results and data analysis

3.3.1 Stability and optimal radius

Figure 3.3 shows the optimal tube radii for all studied materials and its associated uncertainty. For around 20 structures the uncertainty on the radius is estimated to be larger than 30 Å (blue shaded triangles in upper right corner in Figure 3.3). We employ Bayesian regression (details in the SI for paper I) to automatically assess the uncertainty associated with fitting the obtained DFT data to equation 3.2. This makes it possible to spot data points during the screening study that might require a more detailed investigation, while the data points that fit the underlying fitting function show reduced uncertainties. We have identified three situations where the uncertainties are large: (1) The model is not able to fully capture the variation of strain energies across different tube radii. Only few structures, such as SbTeBr, do not fit the proposed model (similar to imogolite, Figure 2 in the SI for paper I), leading to large uncertainties in the prediction. (2) The strain energy curves are rather flat due to a less pronounced energy minimum making it difficult to estimate a precise optimal tube radius. This is, for example, the case for NbSSe, TiSSe or VSSe. (3) Only three data points are available, as it happens for BiSI, BiSBr and BiSCl. Nevertheless, in these cases three data points are sufficient to identify the mid-point as the minimum and adding additional data points is not necessary. However, the limited amount of data points lead to an extended uncertainty interval using Bayesian regression. In general the values for the optimal tube radii are similar to what has been found in literature for a much smaller set of TMD Janus nanotubes.[34]

Figure 3.4 shows the minimum strain energies corresponding to a tube at the optimal tube radius as shown in Figure 3.3. The stability of a phase can be estimated through constructing a phase stability diagram, from which we can extract the so-called convex hull. The convex hull defines the stability frontier of a given combination at 0K, i.e. which phase(s) are the most stable at a given stoichiometry. It is constructed by using the DFT total energies of all the known phases of a given chemical space and identifying all the thermodynamically stable phases and all two-phase equilibria between them. In this work these phases are extracted from the Materials Project database.[62] The convex hull is then obtained by connecting the stable phases with tie-lines.
Figure 3.3: Overview of the 135 investigated materials and their extrapolated optimal radius according to equation 3.2. It is ensured that at least three data points after filtering according to the criteria described in the SI for paper I exist (otherwise marked with a hatched box). The asterisk indicates that the difference in energy between the H-/T- phase is less than 10 meV/atom and that the smaller optimal tube radius is chosen given the extrapolated optimal radius from both prototypes. The lowercase letters a/z indicate which wrapping direction (armchair/zigzag) is preferred.
Figure 3.4: The heatmap shows convex hull and tube strain energies at the optimal tube radius. Blue and bright colors indicate good stability, while a red color indicates poor stability. Values exceeding the metastability criterion of 0.2 eV/atom are shown in black.
If the novel candidate material has an energy below the hull, it is considered stable and the convex hull is updated to include this new point. On the other hand, if its energy is above the hull, the material is unstable or metastable. A more detailed explanation of the construct of the convex hull used here can be found in the literature. To compare the energy of the tube to its most stable 3D bulk structures, we also calculate the convex hull energy of the tube $E_{CH}$ at its optimal radius ($E_{CH-min}$).

The calculated values for the convex hull energy of the infinite 2D Janus monolayers are in good agreement with published literature. Except for Fe, all studied nanotubes show good stability against the decomposition into competing bulk structures (taken from the Materials Project database) for at least one of the calculated combinations (here we define a combination stable when the energy of the candidate compound is within 0.2 eV/atom above the convex hull to account for a possible metastability). This is in good agreement with published studies on the stability of 2D Janus monolayers. Given the mid-layer element is in its preferred oxidation state, the resulting tube shows higher stability compared to the case of an unfavored oxidation state as expected. Ge, for example, generates more stable tubes when combined with two halogens (Ge$^{2+}$) than with two chalcogens (which would need a Ge$^{4+}$, instead). We do not find stable nanotubes for 23 combinations (hatched boxes in Figure 3.4). 18 of these materials can be attributed to the transition metal in its unfavored 2+ oxidation state, when paired with two halogens. The remaining 5 materials contain either Fe, Sn or Ge which form in general less stable nanotubes for most of the studied combinations (i.e. more than 0.1 eV/atom above the convex hull). Because of their stability in the 3D form, oxygen containing tubes are in general more prone to decompose compared to the pure chalcogenide ones.

For almost 90 % of the materials, the energy difference between the armchair and zigzag wrapping direction is below 10 meV/atom, which indicates that there is only a weak driving force causing wrapping up around a specific direction. Although the armchair and zigzag wrapping directions only have a minor impact on the stability of the tube, it can be expected that the wrapping direction has a larger impact on the electronic properties due to the difference in bond distances in these tube configurations. We have recently demonstrated this for MoSTe, but a more comprehensive study focusing specifically on the electronic properties would be needed.
to establish general design rules. (Ref. [96] - also attached as paper II in this thesis)

The combination of the three metals As, Sb and Bi mixed together with a chalcogen sitting inside and a halogen element sitting outside of the structure generates stable and small-radius nanotubes with a rather small strain energy associated with its optimal radius. For instance, AsSI has a minimum strain energy of -80 meV/atom which is ~ 40 meV smaller than that of the experimentally observed imogolite nanotube when compared to computational reference data found in literature.[97] The MXY nanotubes share with imogolite, which is known to exist as a single-wall nanotube, the shape of the strain energy curve (see BiSI in SI for paper I Figure 2).

Figure 3.5 reports the correlation between various quantities, namely the extrapolated optimal radius $R_{opt}$ versus the lattice-mismatch $a_{MX_2}/a_{MY_2}$ (a), which is the important parameter in Pauling’s mechanism, the minimum strain energy $E_{strain-min}$ (b) and the ratio of the Mulliken electronegativities of the X/Y elements (c). Figure 3.5 (d) shows the ratio in layer thickness $t_{M-X}/t_{M-Y}$ versus the lattice-mismatch $a_{MX_2}/a_{MY_2}$, where the thickness is measured as the M-X and M-Y element distance along the vacuum direction in the 2D Janus sheet (inter-layer distance). A similar plot showing the optimal radius versus the convex hull energies can be found in the SI for paper I in Figure 3. Figure 3.5 (b) indicates that very low strain energies are not necessary to obtain small-radius nanotubes. Nanotubes with a diameter smaller than 15 Å are predicted to be found in a range of strain energy minima from -15 meV/atom (BiSeBr) to -280 meV/atom (TaOTe, which has the most negative strain energy in our dataset). The optimal radius increases sharply when approaching the limit of no lattice-mismatch between the MX$_2$ and MY$_2$ parent sheets (i.e. lattice-mismatch $a_{MX_2}/a_{MY_2} = 1$, see Figure 3.5 (a) - blue dashed curve). Additionally, the lattice-mismatch is correlated with the ratio of ionic radii when mixing two chalcogens (Janus-Cal-Cal class following trend OTe > OSe > OS > STe > SeTe > SSe) or two halogens (Janus-Hal-Hal class following ClI > BrI > ClBr) with each other.
Figure 3.5: $R_{\text{opt}}$ versus the lattice mismatch of the corresponding parent sheets (lattice mismatch $X/Y$ calculated as $a_{MX_2}/a_{MY_2}$ with $a$ being the lattice constant) (a), the minimum strain energy at the optimal radius (b) and the Mulliken ratio of the corresponding Mulliken electronegativities of outer and inner elements (Mulliken ratio $X/Y$) (c) are shown. Figure (d) shows the ratio in layer thicknesses in the 2D Janus sheet versus the lattice-mismatch. The different colors represent the three classes of pairing the mid-layer with either two chalcogens (Janus-Cal-Cal, $\{\text{O, S, Se, Te}\}$, green) , two halogens (Janus-Hal-Hal, $\{\text{Br, I, Cl}\}$, red) or a mix of chalcogens inside and halogens outside (Janus-Cal-Hal, yellow).
The lattice-mismatch between the two parent sheets can give an estimate on the optimal tube radius in the case of isovalent anions, while it fails for mixing halogens with chalcogens (Janus Cal-Hal class). Here, it would predict the halogen to sit inside of the tube, instead of on the outside, as several of the materials show a lattice mismatch \( a_{MX_2}/a_{MY_2} \) larger than 1 (Figure 3.5 (a), yellow dashed line). For instance, the MoO\textsubscript{Te} parent sheets (H-phase) have a lattice mismatch of 0.79 \( (a_{\text{MoO}_2} = 2.82 \text{ Å}, a_{\text{MoTe}_2} = 3.55 \text{ Å}) \) leading to the small radius of 7.2 Å. Conversely, the BiTeCl parent sheets (T-phase) have a lattice mismatch of 1.06 since the parent structure BiCl\textsubscript{2} \( (a = 3.68 \text{ Å}) \) has a smaller lattice constant than BiTe\textsubscript{2} \( (a = 3.9 \text{ Å}) \). Based on the lattice mismatch, the tube should wrap in a way that the Chlorine atoms are inside of the tube. The three different classes appear well-separated when the radius is plotted versus the ratio of the Mulliken electronegativities of the X and Y element (Figure 3.5 (c)). Having more electronegative elements sitting on the inside of the tube does not seem to be a necessary criterion for forming small-radius nanotubes (Janus-Cal-Hal, yellow).

A possible explanation on the reason why the chalcogen is sitting inside of the non-isovalent tube can be made by investigating the bond lengths in the non-isovalent structures closer. Shevelkov et al. [98] studied the experimental 3D-bulk crystal structure of layered BiTeI and find the Bi-X bond distance in these structures to be significantly longer (ionic) than the ones found in bismuth trihalides. Additionally, the geometry of the \((\text{BiTe})\) layer is shown to be comparable to the one found in Bi-bulk metal and the bond-distance of Bi-Te in the BiTeI layer is similar to the one found in bismuth tellurides. [98]

To illustrate this, we take the BiSI structure in Figure 3.6 and assume the Bi-I \( (d_{M-Y}) \), Bi-Bi \( (d_{M-M}) \) and Bi-S \( (d_{M-X}) \) bond distances to not vary significantly when the 2D Janus sheet is being wrapped up into a tube. By looking at the sheet from the side, the layer thicknesses of both inner and outer layer are \( t_{M-X} \) and \( t_{M-Y} \), respectively (Figure 3.6 mid column). Larger bond-distances now also lead to thicker layers. This means that the M-Y layer is considerably thicker, owed to the ionic like bond between the M-layer element and the halogen. Larger thicknesses of the M-Y layer impose a constraint resulting in M-X bonds taking less space inside the tube and therefore leading to less steric effects as opposed to having M-Y bonds on the inside of the tube (Figure 3.5 (d)). Additionally, we
Figure 3.6: Side (or cross-section) view for the energetically favored armchair BiSI nanotube, the infinite 2D Janus layer and the unstable inverse wrapped BiIS nanotube. Measures are given in Å.

Observe for the non-isovalent structures a shortening in M-X bond lengths upon wrapping the infinite 2D Janus sheet into a nanotube leading to the effective thickness of the MX layer in a tube being even thinner than in the sheet.

In order to further clarify this point we compare the stable BiSI tube and the energetically unstable inverse wrapped counterpart BiIS in Figure 3.6 on the right. In the inverse wrapped case steric effects in between I-I elements even lead to a bond expansion of the Bi-Bi bond, $d_{M-M}$, from 4.2 Å to 4.6 Å. Given both tube configurations differ by 0.14 eV/atom in energy in favor of the tube in which the chalcogen element sits inside, the importance of the (BiTe) layer for the stability is underlined. Plotting the stability difference in between the stable (chalcogen inside) and the inverse wrapped tube (chalcogen outside) for nine selected non-isovalent tubes we find the points to follow a positive linear correlation with the ratio in thickness $r = t_{M-X}/t_{M-Y}$ (Figure 4 in the SI for paper I). We conclude that the steric effects caused by a difference in layer thickness significantly influences the stability of the tubes. Steric effects can also explain the reduced minimum strain energy for BiXI < BiXBr < BiXCl structures, as well as the reduced optimal radius for BiSY < BiSeY <
BiTeY structures. In these cases, the element forming stronger bonds determines the wrapping direction.

### 3.3.2 Optimal radius descriptors

As we have reported above, to estimate the optimal radius, we need to calculate the tubes at different sizes. These calculations are approximately three orders of magnitude more computationally demanding than to simulate the corresponding infinite Janus sheets. Identifying descriptors to predict the optimal radius based exclusively on the 2D Janus sheet is a valuable pathway to faster navigate through the studied phase space and discover small-radius nanotubes.

All studied tubes are more stable if the chalcogen element is placed inside. In fact, for some of the studied non-isovalent nanotubes the optimal tube radius is independent of the halogen sitting on the outside of the tube (e.g. SbSCl, SbSBr and SbSI). Thus, only considering MX$_2$ and MY$_2$ parent structures provides an inaccurate picture when studying non-isovalent nanotubes. Additionally, the parent structures of non-isovalent tubes will each have a M-element oxidation state different from the 2D Janus sheet (e.g. BiI$_2$, BiS$_2$ and BiSI). Two models from literature use the parent structure lattice constants as descriptors for predicting the optimal tube radius of isovalent nanotubes. The first approach is based on the plate theory as described by Timoshenko [99, 100], while the second approach makes use of the Poisson ratios of the parent sheets (Poisson model) [33]. Both models require the calculation of the stiffness tensors of the parent structures. Our approach, which we refer to as Inner-bond model, is instead based on solely geometrical parameters, which can be readily obtained from existing 2D databases (e.g. [20]). By circumventing the time consuming calculation of the stiffness tensor, we are able to calculate these descriptors at least one order of magnitude faster. The Inner-bond model uses the lattice constants of the 2D MXY Janus and MX$_2$ parent sheets as well as the 2D Janus $t_{M-X}$ layer thickness, as discussed above. It is initially assumed that the optimal tube radius is determined by the the lattice mismatch between the MXY Janus sheet and the corresponding MX$_2$ parent sheet. The derivation of the Inner-bond model and the used formulas for the two reference models are provided in the SI for paper I.
Figure 3.7: (a) Optimal tube radius using the three models based on the Timoshenko plate theory [99], considering the Poisson ratios (Poisson) [33] and using lattice mismatches between Janus MXY and MY₂ parent sheets (Inner-bond model). The optimal radius based on DFT calculations $R_{opt}$ is also shown which has been obtained extrapolating the function given in equation 3.2. The asterisk indicates that due to prototype changes when straining the SbBr₂ sheet, it was not possible to get the elastic tensor required for the Timoshenko and Poisson model. (b) The radius plotted against the lattice mismatch $MX₂/MXY$. 
All three models capture the rolling mechanism for isovalent anions for a selected set of materials (with discrepancies up to 30% compared to the calculated DFT radius - Figure 3.7 (a)), while only the Inner-bond model predicts the optimal radii of non-isovalent nanotubes to be small. Nevertheless, it fails to capture that the optimal DFT radius for some tubes, in which a chalcogen sits inside the tube, is almost independent of the chosen halogen element sitting outside of the tube (see orange bars for SbSCl, SbSBr and SbSI in Figure 3.7 (a)). Here, the layer thickness $t_{M-X}$ is so thin, that the steric effects of the halogen atoms at small radii do not decisively impact the stability of the tube.

In this picture, the wrapping mechanism is solely governed by the steric effects of the chalcogen elements. Controversely, the 2D Janus sheet lattice constants increases for SbSCl < SbSBr < SbSI due to the size difference of the halogen atoms, leading to a mismatch in predicted values for the Inner-bond model.

One feature all the studied materials share is that the lattice mismatch between the parent MX$_2$ and the Janus MXY sheets is always smaller than 1 (Figure 3.7 (b)). This is different from the idea of comparing MX$_2$ and MY$_2$ lattice constants, for which, in the case of mixing chalcogen and halogen X/Y elements, the lattice mismatch exceeds 1 (Figure 3.5 (a)). Although only giving quantitative predictions, the Inner-bond model shows that the bond distances of the elements in the inner MX$_2$ sheet together with the MXY lattice constant are good descriptors for predicting the optimal radius within the studied compound space. In the case of isovalent anions the lattice-mismatch of the parent structures can also be used as a descriptor.

### 3.3.3 Strain energy descriptors

The Janus sheets show an asymmetry between the two sides of the layer. We can make a sheet where the mirror symmetry along the mid-layer (M-layer) is restored through rearranging the X/Y elements into alternating X/Y rows (as shown in Figure 3.8). The graph in Figure 3.8 shows the energy difference between the alternating and the Janus sheet ($E_{2D-\text{alt}} - E_{2D-\text{Janus}}$) as a descriptor for the strain energy minimum ($E_{\text{strain-min}}$). Few outliers ($> 50$ meV/atom error in prediction) correspond to structures with a low convex hull stability, i.e. $E_{CH} > 0.2$ eV/atom.
Figure 3.8: Comparing the energy of the tube at its optimal radius versus the energy of a sheet consisting of alternating anion rows (2D-alternating rows prototype structure or 2D-alt). The mean average error for the different combinations are 22.9 meV/atom (Janus-Cal-Cal), 14.4 meV/atom (Janus-Cal-Hal) and 3.1 meV/atom (Janus-Hal-Hal).

For instance, this descriptor, which does not require the calculation of the tubes, could be used to indicate if a sheet exfoliated onto a host structure might undergo spontaneous curling. The strain energy would need to be larger than the adsorption energy of the sheet on the host structure, which is for example not the case for the experimentally exfoliated BiTeI sheet. Whether a large strain energy is needed to form single-wall nanotubes (in favor of multi-wall nanotubes or other forms of rolled structures) requires a deeper experimental investigation, or, at least, to consider growing and other experimental conditions which might impact the formation mechanism.

Different synthesis procedures can be imagined leading to the synthesis of the Janus nanotubes suggested here. Besides the exfoliation of a monolayer onto a host structure and its subsequent spontaneous wrapping, which might need lithography techniques to cut the monolayer into the required dimensions, the intercalation of ions into Janus multilayered materials, combined with ball-milling, can be a viable experimental
synthesis path allowing to produce larger quantities. A common issue with these methods would be preventing unwanted reactions occurring at unsaturated bonds. A possible alternative synthesis pathway could be to use Atomic Layer Deposition combined with lithography to cut the 2D layer into a desired shape before it spontaneously wraps. Regardless the synthesis procedure, the intrinsic driving force of the 2D Janus sheets to form 1D tubes (or alternatively other curled shapes) should be large enough to be observed.

A promising starting material to experimentally verify our predictions is the layered BiTeI 3D bulk crystal structure for which experimental synthesis routes have been established. Other interesting candidates include tubes based on Vanadium or Titanium, which, by displaying a variety of oxidation states, are suitable for electrochemical applications. Curled multiwall VO$_x$ structures with much larger inner radii than the tubes predicted here have already been reported. Other non-isovalent anion based tubes, such as BiSI, might be feasible. However, the weaker ionic halogen bonds might drive reconstructions, in contrast to less reactive covalent bonds.

3.4 Conclusion

In this work, we investigated the formation mechanism of nanotubes by studying their stability and optimal nanotube radius. 135 different Janus nanotubes have been calculated using a structure prototype approach (T-/H-phase). Each three-layered material consisted of one of 15 different cation mid-layer elements in combination with inner and outer atomic layers being occupied by either chalcogens, halogens or their mixture as anions. For isovalent anions, the wrapping mechanism could be explained by the lattice-mismatch between the two inner and outer atomic layers, while for non-isovalent anions steric effects caused through short pnictogen-chalcogen inside and longer pnictogen-halogen bonds outside of the material drive the stability. These effects are beneficial to the formation of some of the smallest identified nanotubes showing optimal radii below 10 Å. We noted that in general a large minimum strain energy is not needed to find tubes with an optimal radius smaller than 35 Å. Additionally, the minimum strain energy was reasonably well estimated
using the energy difference between a 2D Janus and alternating sheet as a descriptor. We employed Bayesian statistics to assess the quality of our fitting in order to identify uncertainties in our predictions of the optimal radius due, for example, to a misfit between the obtained data and the underlying strain energy curve function.

Nanotubes based on BiTeI and related compositions appear to be a particular interesting starting point for experimental verification due to their synthesizability in a 3D structure and exfoliability into 2D layers, as well as their predicted stability in 1D form. Following the interest in Vanadium- and Titanium-based nanotubes for electrochemical applications, we suggest that the metastable combinations of these metals paired with either OTe, OSe, or OS can be additional interesting candidates.

The findings reported here, shed light on the mechanism behind the curling of 2D Janus sheets and define a new path for the synthesis of nanotubes with small radii, for which the lattice mismatch and the bonding character of the anions play a fundamental role.

3.5 Workflow discussion and Outlook

This discussion focuses specifically on the workflow including the advantages, difficulties as well as possible extensions.

**Advantages**

More than 4500 DFT calculations have been carried out with automated error handling leading to a high fidelity data set. Consequently, subsequent post-processing of the data due to consistent output was straightforward. Additionally, the code was improved along the way through collaborative workflow development.

**Difficulties**

The main difficulties during the development of the workflow arose from the fact, that many of the structures are meta- or even unstable. This is reflected in almost 40% of the data being discarded upon post-processing. A main take-away is, that prior to running a lot of heavy calculations on different prototypes, a way of determining the most stable and likely prototypes should be investigated.
Extensions and Improvements
As mentioned, a viable way of determining the stable prototypes in the present nanotube project, is to calculate each material in the 2D unit cell containing only three atoms. The energy difference between the prototypes can give a good estimate on, whether or not the tubes will be stable. Using this approach, it is possible to determine whether or not it is reasonable to simulate certain prototypes based on the stability.
Extensions of the workflow already include calculating the band structure as presented in paper II on the specific example of MoSTe that can be found in this thesis. It is planned to further investigate electronic and catalytic properties and therefore possible applications of the nanotubes.

Code availability
The workflow is continuously developed and may be accessed at https://gitlab.com/asc-dtu/workflows/nanotubes/
CHAPTER 4
Workflow for calculating ion insertion battery properties

This chapter combines paper III - "Autonomous Discovery of Materials for Intercalation Electrodes" - and paper IV - "Topological descriptors for predicting kinetic barriers in magnesium cathode materials". Excerpts from paper III introduce the workflow and the general motivation for looking at the specific example of Magnesium-cathode batteries. The text is mainly from the chapter "1 Introduction" and chapter "2 Workflow Overview" from paper III. Minor adjustments have been made to the text in order to better combine paper III+IV into one chapter. For a more detailed discussion and visualization of the different battery properties calculated by the workflow, readers of this thesis are referred to reading chapter "3 Results and Discussion" from paper III.

The Results and data analysis part is based on paper IV which naturally builds on top of paper III and focuses on how the output of the workflow can be used for a more general descriptor search. The text is taken from the chapter "2 Methods and Theory" and chapter "3 Results and Discussion" from paper IV, again with minor adjustments for the sake of the flow of this chapter. The chapter "1 Introduction" from paper IV is not included in this thesis, to which the reader of this thesis is referred to for a more general context of descriptor search for battery cathode mate-
4.1 Introduction

The prospects of substantial global warming calls for a transition towards a more sustainable energy infrastructure, based on the production of energy from renewable sources. Energy storage devices, e.g. rechargeable batteries, play a fundamental role in the transition from fossil fuels to renewable energy sources, as highlighted from the recent (2019) Nobel price in Chemistry awarded to Yoshino, Whittingham, and Goodenough.

Nowadays, Li-ion is the prevalent technology in electric vehicles and even used for stationary storage applications. While the concomitant development of portable electronics and that of the Li-ion technology are apparent, the ability of battery technologies to meet the necessary requirements cannot be taken for granted in other areas. Aside concerns on availability and cost of lithium and other critical raw materials (CRM), some general arguments could be raised against a potential generalized implementation of lithium based technology at large scale. Amongst the most promising alternative to Li-chemistries are the Na-ion batteries and analogous technologies based on multivalent cations like Mg$^{2+}$, Ca$^{2+}$, Zn$^{2+}$ and Al$^{3+}$.[105] The main drawback in Mg, Ca, Zn and Al batteries is related to the slow diffusion of multivalent elements, which drastically reduces the power performance. The foremost benefit is that for achieving a given capacity, the number of ions needed are reduced by a factor equal to the ion valence. This turns out in less stressed electrode materials and seemingly less degradation upon cycling. Multivalent electropositive metals include aluminum, zinc, calcium and magnesium. Aluminum, in spite of limited potential (2 V) and capacity (70 mAh/g) values.[106] Regarding calcium, initial studies show fast rate capability.[107] Arguably, the most interesting multivalent ion is magnesium, where significant progresses in performance has been achieved.[105] The state-of-the-art cathode in commercial prototype Mg batteries is the Mo$_6$S$_8$ Chevrel phase, which is a covalent host where Coulombic interactions are reduced, favoring Mg ion diffusion.[108] However, the potential achievable from this cathode is rather
low ($\approx 1$ V vs Mg/Mg$^{2+}$). The discovery of novel cathode materials which can display higher potentials keeping, or even better improving, the ion diffusivity, is necessary to boost the Mg-ion technology.

Following an Edisionian "trial and error" approach to search for new materials is extremely time consuming and inefficient. During the last decades, quantum mechanical calculations, mostly within the framework of Density Functional Theory (DFT), have been efficiently used to predict properties and design novel materials for multiple applications. Recently, to accelerate the materials discovery, autonomous workflow schemes have been implemented,[28, 109, 20, 110, 111] and more specifically for the discovery of battery materials, where a special focus was put on the kinetic properties, i.e. cation diffusivity.[112, 113] Including the kinetic aspect in an autonomous workflow is rather expensive and, in most cases, some approximations need to be done to compromise between accuracy and computational cost, e.g. pinball model[114] or bond-valence calculations.[113]

These workflows are usually based on generic tools that in addition to enable the complex inter-dependencies of the workflow steps allow for an easier reproducibility and provenance of the data [60, 61]. On one side, this helps researchers to share knowledge and expertise in the form of workflows, which can be reused by others as well as extended to include more features, and from the other they solve many issues[115] related with consistency and reproducibility of the data. Workflows, in fact, enable the creation of consistent data sets by setting all the parameters at the beginning of the project and being consistent with them.

Most of the design for new materials proceeds through a 'funnel/sieve scheme', where at each steps materials, which do not fulfill the desired properties, are discarded. In addition, the complexity of the calculations and their simulation cost increases at each step. Examples of funnel schemes and workflows for, e.g., visible solar light ferroelectric devices can be found in the literature.[116] In these cases, materials are selected for their stability, light harvesting properties, and interfaces. The discovery of battery materials is not dissimilar from these examples.

In this work, we establish an autonomous workflow to identify intercalation electrodes in batteries. Although we specifically search for novel cathodes for Mg batteries, the workflow is general enough to allow for the discovery of both cathode and anode electrodes for other battery technologies. In detail, the workflow is based on descriptors calculated at the DFT level, such as volume change upon charge/discharge, which gives in-
formation on the stability of the cathode, Mg adsorption energy, which indicates the open circuit voltage (OCV), and diffusion barriers, which is a descriptor for the ion mobility at different charge states. For the first time in a workflow, the kinetic aspects are kept at the DFT level of accuracy.

4.2 Workflow and computational details

Figure 4.1 gives a schematic view of the seven main components of the workflow. The input from the user consists of choosing input parameters as well as providing a list of materials, i.e. compositions and structures, that will be investigated. Additionally, a database containing reference structures for the evaluation of the stability of an input structure on the convex hull is needed. The reference structures workflow is separated from the general workflow for finding ion-insertion cathode electrodes but ensures a consistent choice of input parameters for the reference calculations. Subsequently, the workflow autonomously takes care of generating and relaxing all needed structures necessary to determine crucial battery material properties. The three properties currently calculated are the stability (volume change upon charging/discharging and the thermodynamic stability), the electrode potential (Mg-adsorption energy) and the ion diffusivity (Mg-diffusion barriers). The two latter properties are evaluated both at a low and high state of charge (SOC). With respect to other work recently published [54], this workflow accelerates the calculations of the ion diffusivity by making use of symmetry considerations. In the following, the steps of the workflow are discussed in more detail. The workflow is interfaced with the Atomic Simulation Environment (ASE).[26] Moreover, it is intended to work with the VASP DFT code [66, 67, 82], as well as with the workflow management system MyQueue.[117] Efforts have been made to keep the workflow as general as possible in order to use the flexibility of ASE, which allows an interface with other DFT codes.
Figure 4.1: Structure of the workflow to identify suitable materials to be used as ion-insertion cathode electrodes in batteries. Figure adapted from paper III. Copyright Wiley-VCH GmbH. Reproduced with permission.
4.2 Workflow and computational details

4.2.1 User input

In addition to the list of materials to investigate, the user needs to define 4 parameters:

- **Ion**: The ion that will be studied which typically is an alkali or alkali-earth ion (i.e. Li, Na, K, Mg, or Ca).

- **Material ID**: A unique identifier for each structure that is used to avoid duplicate calculations.

- **Magnetic state**: The magnetic state parameter allows to study different magnetic starting configurations. This magnetic state is used for all structures throughout the workflow. The two options are the "non-magnetic" initialization or to initialize all ions "ferromagnetically". The ferromagnetic initialization is carried out by initializing magnetic ions in a high spin state.

- **Nudged Elastic Band (NEB) path length**: The NEB path length determines the maximum linear distance between the initial and final site of the ion diffusing along the path. Paths that exceed this maximum length are neglected.

Three decision blocks are directly incorporated in the workflow scheme to decide whether to discard the candidate material or proceed with the calculations. The threshold values are given by the user deciding whether a material is suitable for further investigation or not, e.g. full computational OCV curve [118] or experimental validation. These thresholds are the **Potential threshold**, which sets a requirement on the minimum average OCV, and the **Diffusivity threshold**, which favors the search for materials exhibiting low diffusion barriers (Figure 4.1). A **Stability threshold** can be given optionally by setting constraints on the maximum volume change upon discharging or the energy above the convex hull for the fully charged/discharged structures.

4.2.2 Calculation steps

The potential materials investigated in the screening presented here are obtained from computational and experimental databases, such as the Materials Project,[23] the Open Quantum Materials Database (OQMD),[119]
and Inorganic Crystal Structure Database (ICSD).[120] All these materials have in common that the charge carrier (from now on, we explicitly write the charge carrier as Mg, although the workflow is not limited to identify cathode materials for Mg batteries) is present in the structure. Therefore, the starting structure of the workflow is always a fully discharged cathode material, from which we are going to remove magnesium. The workflow presented here is, however, more general and it could also be used to discover cathodes where the charge carriers are not present and intercalate in the interstitial sites.

4.2.2.1 Structure optimization

The first step is to relax the input structure (with all Mg-ions, fully discharged state); the calculation details are discussed in Section ???. In parallel, we calculate the same structure where we have removed all Mg-ions (deionized unit cell, optimized charged unit cell), as indicated in Figure 4.2. Both relaxations are carried out by the cell shape, volume and the atomic positions. From these two relaxations, it is possible to calculate the volume change in the charged and discharged states, which gives an indication on the mechanical stability of the battery. In addition, we relax a charged unit cell constraining its cell shape and volume. This is done by removing all Mg ions from the optimized discharged unit cell and scaling all atomic positions and the cell according to the ratio between the volume of the optimized charged unit cell and the optimized discharged unit cell, $r = \frac{V_{\text{charged}}}{V_{\text{discharged}}}$. Subsequently, all atomic positions are relaxed while keeping the cell shape and volume fixed. This structure, referred to as discharged-constraint unit cell, is used for the calculation of the OCV at a high SOC as it is explained in more detail in Section 4.2.2.5.

4.2.2.2 Decision point 1 - Stability

The volume change is calculated as

$$\Delta V = \frac{V_{\text{charged}} - V_{\text{discharged}}}{V_{\text{discharged}}}$$  \hspace{1cm} (4.1)
4.2 Workflow and computational details

Figure 4.2: Structure creation throughout the workflow shown for the Chevrel Phase. The different labels on the arrows indicate how the resulting structure is obtained, i.e. optimize: Optimization of the cell shape, volume and atomic positions; optimize + constrain: Optimization of the atomic positions while keeping volume and cell shape unchanged; optimize + constrain + scale: Optimization of the atomic positions while re-scaling the volume according to the ratio $r = \frac{V_{\text{charged}}}{V_{\text{discharged}}}$ and keeping the cell shape fixed; repeat: solely repeating the cell; NEB: linear interpolation in between the initial and final site and subsequent optimization of the atomic positions while keeping cell shape and volume unchanged. Color coding: dark green (Magnesium), yellow (Sulfur), light blue (Molybdenum). Figure taken from paper III. Copyright Wiley-VCH GmbH. Reproduced with permission.

where $V_{\text{charged, discharged}}$ are the volumes of the unit cell with/without Mg-ions, respectively. The energy above the convex hull $E_{\text{hull}}$ is evaluated for both structures giving an indication on the thermodynamic stability of the fully charged and discharged structures. Large energies above the hull
will have implications on the structures cyclability and synthesizability and might lead to unwanted conversion reactions.[35] On the other hand, due to kinetic stabilization metastable structures can still lead to the discovery of viable electrodes which makes it difficult to define a threshold value upfront.[121, 94]

4.2.2.3 Preparation of the structures with Mg-vacancies

To limit possible errors associated with defect-defect interactions, we need to create a supercell, which is obtained by repeating the relaxed unit cell from 4.2.2.1 until it satisfies the condition that the spacing between two vacancies is at least twice the NEB path length, defined in the user input. To ensure relatively fast calculations, we have added an additional requirement on the number of atoms in the supercell, which should not exceed 200 atoms. If this limit is reached, the workflow will automatically reduce the NEB path length (vacancy spacing) parameter to ensure that the maximum number of atoms in the supercell is not exceeded. To save computational time and retain symmetries, we assume that the supercell is fully relaxed after its creation. Subsequently, each of the symmetry-in-equivalent Mg ions is removed one-by-one from the supercell structure. The newly created defected structures, with one Mg vacancy, are analyzed by the Symmetry Equivalence Check tool, as implemented in ASE. The tool is based on the recipe as explained in Ref. [122]. Symmetry in-equivalent sites are checked for percolating paths. Possible diffusion paths are only accepted if intermediate images obtained through linear initialization between initial and final images do not get closer than 1 Å to any atoms in the host structure. If combining all possible diffusion paths does not lead to percolating paths, i.e. the ion cannot traverse through the full structure, the selected ion occupying the site is non-conductive. In such cases the structure is discarded.

Once that the symmetry in-equivalent sites have been identified, a similar procedure is used to determine the symmetry in-equivalent NEB paths by removing the initial and final Mg site of the path from the structure. Checking for symmetry in-equivalent vacancy defect pairs (possible NEB paths) at this point of the workflow allows us to rank the materials according to the number of NEB calculations which need to be run. The
Symmetry Equivalence Check tool identifies all the in-equivalent NEB paths that can be drawn between two Mg ions, which are spatially apart by less than the NEB path length value.

The output of this step of the workflow therefore consists not only of the supercell, but also of the information on the symmetry of the structure with respect to Mg-vacancies, which practically is a list of which Mg (or vacancy defect pairs) are symmetrically equivalent. Before continuing with the (heavy) optimization of the supercell, it is therefore possible to get a rough estimate of the number of NEB calculations that need to be performed to evaluate the size of the diffusion barrier. The NEB paths are also checked for reflection symmetry at this point. Reflection symmetry will result in a less computationally expensive NEB calculation as will be explained in 4.2.2.6.

One problem that is frequently encountered is the correct labelling of defect sites. Indices of structures change as soon as vacancy defects are created. In order to work around this issue we tried to work with scaled positions of defects instead of specific indices whenever possible. If indices for specific sites were used (i.e. initial and final site in the NEB paths) they always match the indices in the created supercell.

### 4.2.2.4 Optimization of the vacancy defect structures

The optimization of the vacancy defect structures is carried out for the dilute vacancy limit (low SOC) as well as for the high vacancy limit (high SOC). For the dilute vacancy limit, a single Mg-vacancy is created by removing only the symmetry in-equivalent ions from the supercell. In this case, the cell shape and volume is kept fixed during the relaxation and only the atomic positions are optimized. In the limit of high vacancy concentration, only a single symmetry in-equivalent Mg is left in the supercell and the supercell is scaled according to the ratio between the volume of the optimized charged unit cell and the optimized discharged unit cell, \( r = V_{\text{charged}}/V_{\text{discharged}} \) (see also Figure 4.2). Therefore, in the limit of high vacancy concentration, the shape and the volume of the supercell is fixed during relaxation and all atomic positions as well as lattice parameters are scaled. By keeping the cell shape fixed, the symmetries from the dilute vacancy limit case are preserved and the reflection symmetries have
not changed. This enables to use the advantage of a reflection symmetry (reflective NEB) during the computationally expensive NEB calculations, as explained in 4.2.2.6. The assumption of a fixed cell shape even for the low Mg concentration limit will not hold in situations where a rather drastic change in cell shape upon charging occurs. On the other side, such materials would most likely break all contacts in a real battery and it should probably be discarded [123], irrespective. This could be checked already during step 4.2.2.1.

### 4.2.2.5 Decision point 2 - Minimum voltage

The calculations performed so far allow us to calculate the potential at different SOCs, which is a descriptor for the minimum voltage of the cathode electrode. The different charge states include the low SOC (removing a single Mg from the supercell), calculated as

\[
V_{\text{low-SOC}} = \frac{(\text{E}_{\text{low-SOC}} + \text{E}_{\text{bulk-Mg}}) - \text{E}_{\text{discharged}}}{z} \quad (4.2)
\]

where \( E_{\text{discharged}} \) is the DFT energy of the relaxed unit cell, \( E_{\text{low-SOC}} \) is the DFT energy of the supercell in the dilute vacancy limit, \( E_{\text{bulk-Mg}} \) is the DFT energy of a single Mg atom in its most stable bulk structure and \( z \) is the amount of electrons transferred (in the case of Mg, \( z = 2 \)), the high SOC (removing all but one ion from the supercell) calculated as

\[
V_{\text{high-SOC}} = \frac{(\text{E}_{\text{charged-constrained}} + \text{E}_{\text{bulk-Mg}}) - \text{E}_{\text{high-SOC}}}{z} \quad (4.3)
\]

where \( E_{\text{high-SOC}} \) is the DFT energy of the supercell in the high vacancy limit and \( E_{\text{charged-constrained}} \) is the DFT energy of the deionized unit cell with the same cell shape as the supercell in the high vacancy limit but with a scaled volume. The last charge state considered is the average OCV calculated as

\[
V_{\text{average}} = \frac{(\text{E}_{\text{charged}} + n \cdot \text{E}_{\text{bulk-Mg}}) - \text{E}_{\text{discharged}}}{n \cdot z} \quad (4.4)
\]
where $E_{\text{charged}}$ is the DFT energy of the deionized unit cell and $n$ is the amount of Mg ions in the discharged supercell.\(^1\)

### 4.2.2.6 Preparation of NEB paths and calculation of diffusion barriers

Methodologies to accelerate NEB calculations have been discussed in the literature. For instance, Rong et al. \([124]\) make use of an improved initial path guess over the usual linear initialization scheme and subsequently perform single point calculations on the images. They predict diffusion barriers that are within 20 meV compared to DFT calculations for Li systems. A different approach probes the potential energy surface (PES) using a gaussian process regression model to find the minimum energy path \([52, 51]\). In this work, we investigate the possibility of using the recently implemented Reflective - Nudged Elastic Band Method (R-NEB) for accelerating NEB calculations (see \([54]\) for details about the implementation). In contrast to the two other methods, this does not approximate the PES but rather accelerates NEB calculations by considering symmetry operations to reduce the images to calculate.

The logic behind the preparation of the NEB path, in fact, decides which kind of NEB calculation to perform, as schematized in Figure 4.3. All NEBs are run with ASEs internal NEB optimizer. We initialize the magnetic moments of all images using the information from the previously relaxed initial and final images. The total magnetic moment is forced to be the same in the initial and intermediate images. If no convergence is observed we remove the constraint of a fixed total magnetic moment and carefully inspect the structure visually after the workflow finishes for consistent magnetic moments.

The step 4.2.2.3 provides the necessary information about all the defect structures and their symmetries. A NEB path can be drawn by taking two of these structures, which are indicated as initial and final image. In case of the path not being reflective or the initial and final image not being symmetry equivalent, a conventional NEB is performed. We define a conventional NEB calculation as the process of setting up the initial and

\(^1\)Note: These expressions are valid only if the energies are expressed in eV.
Figure 4.3: NEB workflow logic for the preparation of in-equivalent NEB paths by including reflection symmetry considerations, with the goal of reducing the computational time needed to find the transition state. Figure taken from paper III. Copyright Wiley-VCH GmbH. Reproduced with permission.

final structures followed by two separate relaxations of the initial and final image. After this, intermediate images, built through an interpolation of the initial and final relaxed structures, are added to the full path length (Figure 4.4 (a)).

If the initial and final image are symmetry equivalent the NEB path is tested for reflection symmetry. In three dimensions, the reflection symmetries can be reflective with respect to a plane (reflecting on one mirror plane), line (reflecting on two mirror planes), or point (reflecting on three mirror planes). If at least one reflection symmetry is found, we can perform a reflective-middle-image NEB (RMI-NEB) calculation. The RMI-NEB (sketched in Figure 4.4 (c)) is closely related to the Reflective NEB (R-NEB) method (sketched in Figure 4.4 (b)), which is also explained in ref. [54]. In contrast to a conventional NEB where initial and final image are supplied, RMI-NEB needs only the initial image, as the final image can be created through symmetry operations from the initial image.
4.2 Workflow and computational details

Figure 4.4: The four figures sketch the principles of the different ways of running a NEB calculation including a conventional NEB (a), reflective NEB or R-NEB (b), reflective-middle image NEB or RMI-NEB (c) and the climbing image reflective NEB or CI-RNEB (d). The images that lay in the grey shaded area indicate that these images are not calculated explicitly but are created by using symmetry operations. This is done by running a recent implementation of the NEB method. The two colored lines show an example of a truly bell-shaped energy barrier (black solid line) as well as an energy barrier with two maxima (red solid line). Figure taken from paper III. Copyright Wiley-VCH GmbH. Reproduced with permission.

This is schematically shown in Figure 4.4 (c) where the final image lies in the grey shaded area (dashed circle) indicating that the image has been created by symmetry operations rather than from a full DFT relaxation. Only one single image (middle image) needs to be calculated now. With respect to a conventional NEB run with a single middle image, this improvement and speed-up here is that the relaxation of the final image is
not needed. This speed-up is even more if several images are used for the NEB path. Consider a NEB path with five intermediate images (Figure 4.4 (a)). The reflective NEB (Figure 4.4 (b)) only considers three images including two intermediate images as well as the middle image. The two remaining intermediate images are then created by symmetry operations. Using the approach of a single middle image, we always find an energy barrier that is smaller or equal to the energy of the transition state. For instance, it finds the correct transition state energy in case of a truly bell-shaped barrier (Figure 4.4 (c) solid black line) but it does not return the true height of the energy barrier in case of an energy barrier that has two maxima. Figure 4.4 (c) shows the true energy barrier curve with two maxima (grey line) as well as the found energy barrier curve with the RMI-NEB method in red that overlaps with the truly bellshaped energy barrier. An energy barrier with two maxima is rather common and can for example be found for the diffusion of Mg in Spinel structures [125], where the middle image corresponds to a configuration of the Mg ion in an octahedral site. In order to find the global maximum and the true height of the energy barrier in such example cases, we can subsequently run a climbing image reflective NEB (CI-RNEB), if the barrier is not already above the diffusion threshold value. Reflection symmetry is again applied by mirroring half of the intermediate images. The climbing image now finds the exact energy of the transition state for a barrier shape with two maxima (Figure 4.4 (d) solid red line). We stop the CI-RNEB in case we find all intermediate images to lie below the extracted maximum energy from the RMI-NEB, because this indicates that the maximum energy barrier has already been found (black line, Figure 4.4 (d)).

We note that the initialization of the NEB paths is done by linear interpolation of two images. However, it is possible to follow different path initialization schemes, which might be preferred, especially when running a conventional NEB. For instance, the image dependent pair potential method providing an improved initial guess for the NEB path is already implemented in ASE requiring minimal changes in the code. In case of the reflective NEB paths, the user would have to make sure that the initialized path preserves the reflection symmetry which is not implemented in the presented workflow.
4.2.2.7 Decision point 3 - ion diffusivity and data collection

The final step of the workflow is to calculate the Mg diffusivity, which can be estimated from the Mg diffusion barriers obtained from the NEB method.

At the end, all the structures, calculations, and estimated properties are collected and stored in a database.

4.2.3 Computational Details

The computational details refer to the data described here in section 4.3, and can easily be modified. All calculations have been performed using the Vienna Ab-initio Simulation Package (VASP) using a plane-wave basis set.[66, 67, 82] The exchange and correlation effects are approximated using the Perdew-Burke-Ernzerhof revised for solids (PBEsol) functional.[126] An energy cut-off of 520 eV was applied to describe the valence electrons. Sampling the Brillouin zone is done using a k-point density > 4.7^{-1}. As a required convergence criterion all forces on the movable nuclei had to be less than 0.03 eV/Å. To account for the self interaction error in the d orbitals of the transition metal oxides a +U correction is applied with the values taken from the Material Project database, i.e. \( U_V = 3.25 \text{ eV}, \ U_{Co} = 3.32 \text{ eV}, \ U_{Cr} = 3.7 \text{ eV}, \ U_{Mn} = 3.9 \text{ eV}, \ U_{Mo} = 4.38 \text{ eV}, \ U_{Fe} = 5.3 \text{ eV}, \ U_{Ni} = 6.2 \text{ eV}.[23, 127] \) In the calculation for the convex hull, the reference for oxygen in the gas phase is approximated using the approach suggested by Rossmeisl et al.,[83] where the energy of oxygen at 0K is calculated as the difference in energy of water and hydrogen molecules in gas phase, including the zero point energy (ZPE) corrections.

All NEB simulations[50] have been calculated using the GGA-PBEsol functional. The R-NEB method was applied[54] as implemented in the Atomic Simulation Environment package (ASE)[26], whenever reflection symmetry in the path is observed. As a required convergence criterion all forces had to be less than 0.05 eV/Å. The +U correction penalizes the energy of the transition state since it is a less localized state than the initial and final state. Thus, we do not apply a +U correction to the NEB calculation as also discussed in Ref. [125]. The distance between repeating defects in the super cells is always larger than 8 Å to avoid defect-defect
interaction errors.

4.3 Results and data analysis

The following text is directly taken from the chapters "2 Methods and Theory" and "3 Results and Discussion" from paper IV. The paper analyzes the data produced using the workflow on the example of Mg-batteries, while the workflow is also applicable to other battery chemistries. In this chapter the focus lies on predicting the kinetic properties, since this is the most expensive part of the workflow.

4.3.1 Initial pool of materials

Initially we consider all ICSD [120] structures as found in the materialsproject database [23] containing at least three different elements including (1) a metal \( M = \{ \text{Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Mo, Sn, Sb, Pb, Nb, Zr} \} \), (2) an anion \( A = \{ \text{O, N, S, Se, Te, Cl} \} \) as well as (3) either Mg or Zn. Zn containing structures are included due to the similar valence and ionic radius of \( \text{Zn}^{2+} \) and \( \text{Mg}^{2+} \). These criteria lead to 304 initial structures out of which 105 contain Mg and 199 contain Zn. Ensuring that at least one percolating path for the Mg ion exists \( (i.e. \) ion is not trapped inside the structure) as well as only considering structures in which the metal atom does not exceed its maximum oxidation state upon fully charging the electrode, reduces the amount of possible structures to 105. We denote a structure a duplicate, if upon exchanging Zn with Mg in the Zn-containing structures, the chemical composition as well as spacegroup match. A NEB path connects the two structures with the moving ion residing in the initial and final site, respectively. Geometric interpolation in between the initial and final configuration leads to intermediate images along the diffusion path. A path is marked as non-percolating if upon linear interpolation in between the initial and final configuration any of the images contain atom-atom distances below 1 Å. This leaves us with a total of 77 structures serving as an input for the workflow described in section 4.2.
Upon initial relaxation of the unit cell with the chosen input parameters, 18 more structures are discarded due to the convex hull threshold of 0.5 eV/atom being exceeded by the fully charged unit cell. Additionally, some of the structures are marked as non-percolating since the relaxation of atomic positions leads to structural changes.

Figure 4.5: Comparison of the number of total paths with the number of paths that are reflective within each individual structure.

Carrying out a symmetry analysis on the remaining 59 structures reveals that in total 238 symmetry inequivalent possible diffusion paths exist (see also Figure 4.5). More than half of the paths are reflective, making the R-NEB method especially useful to fully characterize more paths while using less computational resources.

Even though the R-NEB method improves the speed of relaxing the NEB-paths, 238 paths are still extremely computationally expensive. Additionally, we do not consider structures with partial occupancies easily leading to more than the maximum number of symmetry inequivalent paths found in the more symmetric materials in this study. Here, we use
4.3 Results and data analysis

a subset of the structures which have at most four symmetry inequivalent paths and at least one percolating path consisting of solely reflective paths. In this way, it is possible to characterize as many different crystal structures in terms of their ionic diffusivity while obtaining a diverse dataset. Due to stability reasons, we further disregard structures containing Nitrogen as an anion. In more detail, we relax 40 symmetry inequivalent reflective NEB-paths obtained from 16 different materials ranging over 10 different spacegroups. We further classify the different materials into structure groups including: spinel (8 structures), garnet (3), layered (2, Mg$_3$Nb$_6$O$_{11}$ and MgMn$_3$O$_7$), chevrel (1), $P4_2/mbc$ (1, Mg(SbO$_2$)$_2$) and $Pnma$ (1, MgSb$_2$Cl$_2$O$_3$).

4.3.2 Structural descriptors

Structural and chemical descriptors describing the ion mobility in bulk structures have been discussed extensively in literature.[128, 129, 130, 131, 132] Three main contributions to the barrier obtained from DFT calculations have been identified to be electrostatic interactions as well as electronic and ionic relaxation effects.[133, 134, 135] Relaxed NEB-paths allow to study the effect of electronic and ionic relaxations in the structure. Additionally, the transition state can be investigated structurally which is not possible when only considering electrostatic interactions in an immobile host framework.[131] In this work we investigate simple descriptors that correlate with the NEB-barrier and therefore also with the structure of the transition state. It is highly desirable to find descriptors that can be directly derived from the relaxed supercell, since this is the least expensive calculation of the workflow. Rough estimates on whether or not the barrier might be below a certain threshold are acceptable in a screening study, as long as the needed descriptors are fast to calculate. In order to describe the transition state before relaxing the NEB path, we introduce a path finder tool that predicts a transition state geometry given the stable insertion sites ($E_s$) of initial and final position of the moving ion in the path as an input. It is based on the observation made in literature, that often the critical radius, corresponding to the largest free sphere radius possible along the path is crucial (see also red circle in Figure 4.6 (a)).[131, 132] Following the ideas of connecting initial and final site through Voronoi node and edges, the path finder tool proceeds
as follows:

(1) Start from the initial position;

(2) Find possible unoccupied ion sites (possible intermediate sites $E_i$) using a Voronoi tesselation of the structure as implemented in pymatgen [62] including clustering and removing collisions of Voronoi nodes with a tolerance of 1 Å;

(3) Identify all nearest neighbors of the ion at the current position using O’Keeffe’s method to obtain the Coordination number (CNN) defined as:[136]

$$CNN = \sum \frac{\sigma}{\sigma_{\text{max}}},$$

where $\sigma$ is the solid angle and $\sigma_{\text{max}}$ defines the neighboring atom whose polyhedron site subtends the largest solid angle. Following the recent findings on benchmarking nearest neighbors algorithms by Pan et. al., we consider an atom a neighbor if the solid angle is larger than 50% of the maximum solid angle, i.e. $\sigma > 0.5 \times \sigma_{\text{max}}$.[137];

(4) Create faces enclosing the current position;

(5) Investigate each face found in step (4) and find the center ($E_a$). In order to account for possible unequal ionic radii on the edges of the face, we define the center as the Chebyshev center of the face, which is the largest inscribed circle within a polygon (see Figure 4.6 (a)). For creating the polygon for which the Chebyshev center is calculated, all vertices of the face are considered. From each vertex, a line is drawn from the center of the atom site with an angle $\theta/2$ that interesects with the circle representing the atomic radius (orange crosses). $\theta$ is the angle spanned by the two edges intersecting at the vertex. The tangent on the ion going through the orange crosses makes up the edges of the inner polygon for which the Chebyshev center is calculated;

(6) Investigate each edge of the face at the center in between the two vertices again considering ionic radii. Find the CNN at this ”bridge site” according to the definition in step (3) (see also image on top in Figure 4.6 (b)). If the CNN is larger than the CNN at the Chebyshev center, choose the bridge position;
(7) Consider all valid bridge and Chebyshev center and choose the position that minimizes the distance to the final position;

(8) Consider the next position, being either an accessible unoccupied site $E_i$ or the final position. If an unoccupied site is accessible, repeat steps (3) - (8) until final position is reached.

Figure 4.6: (a) Estimation of the critical radius using the Chebyshev center in a three-coordinated face consisting of atoms with the two different radii $r_A$ and $r_B$. (b) Motivation for including bridge sites when finding transition state geometries. Given four atoms arranged in a rhombus like shape, the consideration of only Voronoi vertices leads to identifying three nearest neighbors while including the bridge site leads to four nearest neighbors.

The critical radius along the path is then defined as the minimum radius of a sphere in all possible bridge and face positions along the path. Moreover, this position is then denoted as possible transition state configuration. Considering the bridge site is motivated through the example shown in Figure 4.6 (b). The atom sites are arranged in a rhombus. The Voronoi tessellation identifies the Voronoi vertex as a possible transition state of the face under investigation (grey shaded triangle). A secondary Voronoi tessellation around this vertex results in three nearest neighbors. Applying the Voronoi tessellation around the bridge site at the center of...
the rhombus (Figure 4.6 (b) case ”(2) include bridge site”) leads to four nearest neighbors being identified. While this case only shows a simplified example in 2D, the approach directly translates into three-dimensional spaces. For instance, we find that the transition state configuration for the Chevrel phase can be best described through a bridge site.

4.3.3 Results

The path finder tool is able to give a good estimate of the unrelaxed transition state geometry based on solely the relaxed supercell. This is important, since it allows to study features of the unrelaxed initial and transition state of the NEB path. For instance, for the case of the spinel structure, the path finder tool takes as an input the initial and final positions of the Magnesium ion residing in a tetrahedral coordination. As a result, it predicts the path to traverse through a triangular face, into an octahedral unoccupied site. From this intermediate state it subsequently traverses through a second triangular face to the final position of the NEB path. The critical radius is predicted to be found at the triangular faces in agreement with literature.[125, 129]

The considered activation barriers obtained from the CI-NEB calculations for the 40 paths range from 0.23 eV up to 1.42 eV. The lowest barrier is obtained for one of the symmetry inequivalent paths of the Chevrel phase, which is known to be a working cathode with reasonably fast magnesium-ion diffusion rates.[138] Interestingly, the path finder tool finds for the Chevrel phase, that the transition state is located at a bridge site (see Figure 4.6 (b)). While the face is three fold coordinated, investigating the bridge site leads to four nearest sulfur neighbors being accessible. The fourth nearest neighbor is in fact a coordinating atom of the final site. We note that while this is the only material in the dataset that exhibits this geometrical feature, it coincides with the smallest barrier observed. It is therefore a specific geometrical characteristic that can be exploited automatically through using the presented tool.

Using DFT-NEB calculations allows us to study electronic and ionic relaxation effects on the transition state, which have been found to impact the barrier.[133, 135] This information is not accessible when using methods that assume the host structure to be immobile (i.e. Bond Valence
4.3 Results and data analysis

Site Energy methods [131]). As a possible descriptor for studying these effects we use the root mean square deviation (RMSD) in between the first-shell nearest neighbor anionic positions (anion$_{NN}$ according to equation 4.5) of the initial and relaxed supercell structure upon vacancy defect creation. The mobility of nearby anions is expected to directly influence their ability to stabilize the transition state. This feature still circumvents relaxing the full NEB-path.

In order to study the statistical relationship of the structural distortions of the coordinating anions on the barrier, Pearson correlation coefficients are calculated. Separating the spinel structure group (accounting for 24/40 data points) from the remaining five groups leads to a medium correlation with a Pearson coefficient of +0.37. Magnesium can attract anions more easily in the dilute vacancy case leading to a stronger distortion. At the same time, the decreased volume upon removing all remaining magnesium ions increases the kinetic barrier for spinel structures. Conversely, the Pearson correlation coefficient for the remaining five groups when plotted against the barrier is -0.24. This trend can be explained by taking for instance the garnet structures, for which the increased ion mobility at the charged states leads to a stabilization of the transition state and therefore lower barriers. In the case of the garnet structures in the charged state, the increased anion mobility can also be directly related to the weak stability, i.e. the convex hull energies are above 0.35 eV/atom. When choosing to correlate all barrier values obtained in this work, the Pearson coefficient suggests only a very weak correlation of -0.07 (see Table 4.1 - feature 7). In addition to the dataset being rather limited in terms of data points, this clearly indicates that it would be beneficial to group the symmetry inequivalent NEB paths in order to find relations to similar path geometries and structure groups.

One approach to visualize possible clusters of similar NEB-paths can be obtained through a Principal Component Analysis (PCA). PCA is a technique to find a lower-dimensional representation of a high-dimensional dataset while maximizing the variance captured by the different descriptors in the dataset. Here, we try to use a minimal set of descriptors given the limited amount of data points. Geometric descriptors have been found to be most relevant for finding fast lithium-ion conductors.[139] The barrier is calculated as the total energy difference between the initial
4.3 Results and data analysis

<table>
<thead>
<tr>
<th>Feature</th>
<th>Pearson correlation coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Minimum ion-anion$_{NN}$ separation distance initial configuration</td>
<td>-0.09</td>
</tr>
<tr>
<td>2 Maximum ion-anion$_{NN}$ separation distance initial configuration</td>
<td>+0.02</td>
</tr>
<tr>
<td>3 Minimum ion-anion$_{NN}$ separation distance transition state</td>
<td>-0.25</td>
</tr>
<tr>
<td>4 Maximum ion-anion$_{NN}$ separation distance transition state</td>
<td>-0.38</td>
</tr>
<tr>
<td>5 Minimum ion-atom$_{host}$ separation distance transition state</td>
<td>-0.31</td>
</tr>
<tr>
<td>6 Change of CNN between initial and transition state</td>
<td>+0.31</td>
</tr>
<tr>
<td>7 Distortion of anion$_{NN}$ atoms upon vacancy creation</td>
<td>-0.07</td>
</tr>
</tbody>
</table>

Table 4.1: Pearson Correlation coefficients for seven different features measuring the correlation with the kinetic barrier obtained through the NEB-calculations. The anion$_{NN}$ contain all first-shell anionic nearest neighbors obtained using equation 4.5. Features 1 - 6 are considered for the Principal Component Analysis.

and transition state configuration. If a path is symmetry inequivalent, at least one of these configurations is most likely structurally unique. Using the unrelaxed transition state configuration $E_a$ obtained from the path finder tool as well as the initial unrelaxed configuration $E_s$ we extract for both configurations a total of six geometrical descriptors given in Table 4.1 (features 1 - 6). While searching for nearest neighbors using a Voronoi tesselation finds all atoms in the first neighbor shell, it does not contain information on possible interactions with elements in the second nearest neighbor shell. Therefore, we also include the minimum ion-atom$_{host}$ separation distance where the atom$_{host}$ structure comprises all elements that are not an anion$_{NN}$ or the moving species. Finally, the change of coordination number in between the initial and transition configuration is included which has been found to be correlated to the barrier.[140] In general, we find a better correlation between the barrier and the local geometry for the transition state (Features 4+5 < -0.3) than the initial state (Features 1+2) underlining the importance of describing the transition configuration when trying to estimate the associated kinetic barrier of the path.
All six features are readily available and only require the relaxation of the supercell.

Figure 4.7: PCA analysis of the six descriptors based on the unrelaxed initial and transition state configuration. The grey square indicates the structure $\delta$-$V_2O_5$, which has been discarded during the screening process before estimating kinetic barriers.

Figure 4.7 shows the PCA analysis using the six discussed descriptors for the symmetry inequivalent NEB paths. The two first components of the PCA carry $\sim 94\%$ of the variance in the data meaning it is reasonable to visually inspect the data projected on only two dimensions. The different crystal groups spinel, chevrel, layered and garnet appear well separated. Additionally, the two symmetry inequivalent paths found in the Chevrel structure appear separated. Especially the smallest barrier found in the dataset for the path in the dilute vacancy limit for the Chevrel structure can be distinguished from paths with larger barriers (blue point)
in group marked as "Chevrel" in Figure 4.7). The separation of data points for the Spinel group can be mainly attributed to the different anions O, S, Se and Te. All spinel compounds containing oxygen are lumped together on the left hand side due to the short bond length distances Mg-O. For spinel compounds, larger anions (S, Se and Te) lead to improved ion diffusivity due to an increased critical radius.[141] All barriers for the NEB paths in the Spinel group are found to be 0.8 eV at most, while all 24 paths only differ by 0.47 eV. Thus, adding additional data points from other Spinel compounds falling in the same area will only add minor information.

An example of how to use this approach to more efficiently find new structures that have not been explored is to look at areas, where data points are sparse or the barrier values vary in between data points close by. The latter indicates that the given descriptors do not capture all information necessary to determine the barrier which will be the topic of a subsequent study. For instance, NEB barriers of the five paths of the group of layered materials differ by 1.0 eV. Nevertheless, we find the material Mg$_3$Nb$_6$O$_{11}$ to have percolating paths with low barriers. In the dilute vacancy limit (discharged) the NEB barrier is 0.42 eV, while at the high vacancy limit (charged) it is 0.53 eV. To fully characterize this structure and its ionic conductivity, all non-reflective percolating paths need to be investigated which is beyond the scope of this study.

In order to test that the approach also works beyond the structures in the dataset, we include the $\delta$-phase of the known cathode material V$_2$O$_5$ [142, 143] in the PCA analysis. Initially, this structure was removed during the screening process, since upon linear initialization of the path the moving ion is closer than 1 Å to an anion along the path. The path finder tool finds the transition state configuration at the three-coordinated oxygen face in accordance with literature.[129] Additionally, it finds the intermediate "square pyramid" site as an accessible unoccupied site. Replacing the linear initialization guess with the found intermediate states from the path finder tool can be seen as a viable approach to also find initial curved path guesses for the NEB calculations. The added data point of the $\delta$-V$_2$O$_5$ structure in the PCA analysis (grey square in Figure 4.7) is in close vicinity to Mg(SbO$_2$)$_2$ ($P4_2/mbc$ - 0.81 eV barrier in the discharged state) and MgSb$_2$Cl$_2$O$_3$ ($Pnma$ - 0.88 eV barrier in the discharged state) that both have 1D-like diffusion channels, although $\delta$-V$_2$O$_5$ is a pseudolayered material. Published literature on the NEB-barrier for similar DFT input
parameters (PBE instead of the chosen PBESol functional here) suggests the barrier at the discharged state to be at around $\sim 0.8 \text{ eV}$, which is in good agreement with the points close by. This underlines the importance of being able to group NEB-paths based on unrelaxed structures as it allows to focus on identifying new diffusion topologies (data points in close vicinity to others) or mechanisms enabling fast diffusion in similar topologies (e.g. lowered barrier for the garnet structure in the charged state enabled through high anion mobility).

4.4 Conclusion

We have presented a workflow based on DFT calculations, which automatically identifies candidate materials to be used as intercalation electrodes in batteries. The workflow is composed of different steps, where the volume change and thermodynamic stability upon charging, the OCV at different charge states and the NEB diffusion energy barrier at high and low SOC are calculated. This workflow has been tested to identify possible cathode materials for Mg batteries, which can improve the performance (faster Mg$^{2+}$ diffusion and higher OCVs) of the Chevrel phase; the most common cathode material in Mg batteries.

16 different materials were calculated in terms of the kinetic properties of magnesium diffusion resulting in a dataset containing 40 symmetry inequivalent diffusion paths. The anionic framework of the materials consisted of either O, S, Se, Te or Cl. In order to extract relevant descriptors for the NEB barrier, we introduce a path finder tool that takes as an input only the position of the initial and the final site of the moving ion. The tool is able to estimate a transition state configuration solely based on the relaxed supercell which gives a significant speed-up compared to calculating the relaxed transition state in screening studies. Investigating the relation of the distortion of the anionic framework upon vacancy defect creation to the barrier, reveals the importance of being able to distinguish NEB-paths into sub-groups. While the strong distortion of the anionic framework lowers the NEB barrier for garnet structures, it is non-beneficial to the diffusivity in the case of the spinel structures. Extracting six geometrical descriptors from the initial and transition state configuration a PCA analysis was carried out. We find that PCA can help
to find sub-groups with similar diffusion topologies. In detail, we find that such an approach can support a more efficient screening study through: (1) Identifying points in the reduced-dimensionality space that are in no close vicinity to any other points, indicating a possible new diffusion topology in the dataset; (2) Finding points that are in close vicinity but show significant differences in the observed barriers pointing towards peculiarities in the ion migration. For instance, we find the latter case for the garnet structures. This study paves the way for more efficient screening studies when searching for fast ionic cathode conductors through employing simple but informative descriptors that can lead to a speed-up on the order of three-magnitudes compared to running the full calculations.

4.5 Workflow discussion and Outlook

Advantages
Using the workflow it is possible to calculate kinetic barriers with minimal user input, namely the unit cell of the structure of interest. The results can be compared across structures, allowing to derive descriptors based on statistical analyses.

Difficulties
While the discharged cathode structures presented here have been experimentally synthesized, the stability of the fully charged structures (high vacancy limit) is not known upfront. This, in combination with the vacancy defect creation, led to convergence problems for some structures. Automatic ways of handling such cases is currently under investigation. Additionally, the workflow is not able to find the correct magnetic state ordering for all structures. Initializing all magnetic ions in a high spin state led to satisfactory convergence for the materials shown but also failed to find the correct spin state for specific cases. We are currently working on finding a more automated way to find the correct magnetic ordering leading to the minimum energy configuration.
Extensions and Improvements
As discussed, improvements should focus on improved initial path guesses enabling to study a wider range of materials. The R-NEB method has proven to be a robust tool in screening studies. It should now be quantified in more detail, how much faster it is compared to conventional NEB calculations as well as other accelerated NEB-methods (e.g. surrogate-ML models [51]).

Until now we only removed Mg ions from a structure that had the ion already inserted. It is in principle also possible to include structures where Mg (or any other element) is added into the interstitial sites and feed that structure to the workflow presented here. Voronoi tesselations have already shown to be a viable geometrical approach for identifying possible sites.[132] This would enable us to study a wide range of crystal systems like 2-D layered structures without making changes to the workflow.

Code availability
The workflow is continuously developed and may be accessed at https://gitlab.com/asc-dtu/workflows/ion-insertion-battery-workflow.
In this thesis two scientific workflows based on Density Functional Theory have been presented. The first workflow, discussed in chapter 3, calculated the stability of inorganic Janus nanotubes which led to a 1D-nanotube structure database comprising 135 different materials. Analyzing the data revealed, that the stability of three layered Janus nanotubes is governed by the lattice mismatch between the two layers composing the sheet, as well as the difference in bond strength between inner and outer elements. The second workflow presented in chapter 4 was developed to fully automate the calculation of battery cathode properties including the kinetic barriers, Open circuit voltages, convex hull energies and volume changes. The workflow was tested on different magnesium cathode materials. Through the identification of relevant descriptors including the structure of the transition state, it was possible to sub-group ionic diffusion systematically based on the percolating channel geometry of the respective crystal structure. Using these findings, it was possible to more efficiently explore the chemical space of fast ionic conductors through focusing on unknown or promising channel geometries. Additionally, the automated and reproducible workflow paves the way to extend the existing dataset for future studies which can in turn benefit and learn from the data generated in this work.
Discussion and Outlook

Having conducted two successful studies using scientific workflows, the material selection process at the very beginning of each project turned out to be essential. For instance, only high-symmetry battery cathode materials consisting of reflective diffusion paths were considered. This criterion discards any other promising ion conductor not obeying this filter. It was possible to fully automate the property prediction step within the limitations discussed. These limitations included for instance, keeping cell shapes fixed for the battery material in order to preserve symmetry. Such limitations of scientific workflows appeared hard to foresee. It is therefore highly advisable to first perform all steps of a scientific workflow manually before starting to try and automate subsequent tasks. This will also help to circumvent the biggest disadvantage of scientific workflows: the time it takes to implement automatic and robust workflows.

After having confirmed the feasibility for the two workflows, it was inevitable to have an error handling tool in place. Additionally, it was crucial to build the software on the basis of version control and unit testing. The presented logic of the workflows changed rapidly throughout this project. Without the use of these tools, the development process at one point will stagnate since the complexity of the workflow will become impossible to deal with. Introducing changes and "hoping for the best" can have unwanted side effects. In the worst case this can lead to reproducibility being broken between different versions without even realizing it.

In the Introduction, three problems hampering data-driven materials discovery were mentioned including decentralized databases, unstructured data as well as missing data standards. The scientific workflows are of great help when tackling the problem of missing data standards. Through collaborating on establishing new workflows, researchers can avoid making the same mistakes over and over again. At the same time, best practices are incorporated and help to find a more "standard way" of calculating
specific properties. Currently, both workflows are actively used by people in the group.

6.1 Outlook

The two other problems with materials science data, i.e. decentralized databases and unstructured data, have only been addressed to a minor extent. Currently, the databases are available online but can only be found through the corresponding papers. It is assumed, that both problems can be solved by creating online databases which can easily be accessed and present the data in a visually appealing and structured way. While ”structured data” in DFT is still not defined, sharing the data opens up for discussion on how this can be achieved. Among others, the materialsproject database [23] can be taken as an inspiration for VASP calculations due to its widespread acceptance in the materials science community.

Other than assuring easy access to the data, the next step for both workflows is to be extended or modified. Currently, electronic and catalytic properties are investigated for nanotubes. The battery workflow can and should be improved through finding appropriate NEB initialization schemes going beyond the linear interpolation. Furthermore, accelerated approaches, like the accelerated NEB methods using Gaussian-Process-Regression [52], can be tested on the presented materials. This work proofed the robustness of using the R-NEB method to accelerate the calculations, i.e. the method converges for several different crystal structures. For other methods to be useful in a scientific workflow setting, they need to not only accelerate the discovery, but more importantly they need to be robust across many materials in terms of convergence.

Finally, the found structures should be compared to experimental results. The knowledge gained should also be reflected in the developed workflows through, for instance, choosing appropriate threshold values in the battery workflow.
6.2 Final remarks

This thesis was initially intended to investigate the use of Machine Learning (ML) for accelerated materials discovery. Several unsuccessful attempts in predicting material properties led to the conclusion, that any data-driven model needs reliable datasets. Such datasets did not exist for neither the nanotubes nor the kinetic barriers obtained through NEB calculations. Eventually, this led to the development of the two discussed scientific workflows. I genuinely hope, that for any following ML project researchers will not only be able to predict materials with improved properties using ML, but actually be able to calculate these using scientific workflows and suggest promising materials directly to experimentalists.


[69] R. Tenne et al. “Polyhedral and cylindrical structures of tungsten disulphide.” In: *Nature* 360.6403 (December 1992), pages 444–446. ISSN: 1476-4687. DOI: 10.1038/360444a0. URL: https://doi.org/10.1038/360444a0.


[118] Ying Shirley Meng and M Elena Arroyo-de Dompablo. “First principles computational materials design for energy storage materials in lithium ion batteries.” In: Energy & Environmental Science 2.6 (2009), pages 589–609.


Included publications

Paper I

Structural and chemical mechanisms governing stability of inorganic Janus nanotubes
Felix Tim Bölle, August E. G. Mikkelsen, Kristian S. Thygesen, Tejs Vegge and Ivano E. Castelli
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Structural and chemical mechanisms governing stability of inorganic Janus nanotubes

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Abstract

One-dimensional inorganic nanotubes hold promise for technological applications due to their distinct physical/chemical properties, but so far advancements have been hampered by difficulties in producing single-wall nanotubes with a well-defined radius. In this work we investigate, based on Density Functional Theory (DFT), the formation mechanism of 135 different inorganic nanotubes formed by the intrinsic self-rolling driving force found in asymmetric 2D Janus sheets. We show that for isovalent Janus sheets, the lattice mismatch between inner and outer atomic layers is the driving force behind the nanotube formation, while in the non-isovalent case it is governed by the difference in chemical bond strength of the inner and outer layer leading to steric effects. From our pool of candidate structures we have identified more than 100 tubes with a preferred radius below 35 Å, which we hypothesize can display unique properties compared to their parent 2D monolayers. Simple descriptors have been identified to accelerate the discovery of small-radius tubes and a Bayesian regression approach has been implemented to assess the uncertainty in our predictions on the radius.

Key Words

single-wall nanotubes, High-Throughput screening, density functional theory, Janus monolayers, stability

Introduction

In the last decades miniaturization of devices has been a main trend driving the electronics industry. In addition to reducing the usage of raw materials, nanomaterials often show improved properties compared to their larger counterparts. Among these nanomaterials are two-dimensional (2D) sheets, one-dimensional (1D) structures such as nanotubes and nanoribbons, and zero-dimensional (0D) nanoparticles.

Since their discovery, nanotubes have shown promise for a wide range of applications including gas separation and capture, catalysis, solid lubrication and controlled drug delivery.[1] In addition to the well-known carbon nanotubes [2] numerous inorganic nanotubes have been
synthesized. [3, 4] Although the first successful synthesis of single-wall MoS$_2$ nanotubes has been reported [5], such structures usually appear together with numerous multi-wall tubes showing a distribution of radii and wall thicknesses. [5] These multi-wall structures alleviate the built-in strain energy through van der Waals interactions in between the layers leading to an increase in stability. [1] Overall, this has made it difficult to establish an experimental synthesis pathway to produce single-wall tubes with a specific radius and controllable physio-chemical properties.

A possible solution to this problem is the approach of considering asymmetric sheets, which can naturally wrap and form nanotubes with a well defined size. Due to the asymmetry, the unsupported sheet is expected to be unstable compared to other curled shapes, such as tubes or scrolls. Pauling, already in the 1930s, mentioned that the driving force of sheets to curve is related to the lattice-mismatch between the two inner and outer atomic layers. [6] Single-wall inorganic nanotubes with well-defined diameters hold promise for technological applications, not only because of their reduced dimensionality, but also for their unique properties, often inherently different from the ones of the corresponding asymmetric sheets. An example of a small-radius, single-wall nanotube formed from an asymmetric sheet is imogolite (Al$_2$SiO$_4$(OH)$_4$) which was first discovered in volcanic ash soil [7] and later synthesized. [8, 9] Other tubular minerals include chrysotile (Mg$_3$Si$_2$O$_5$(OH)$_4$) and halloysite (Al$_2$Si$_2$O$_5$(OH)$_4$) that however occur as multi-wall tubes. [10, 11] Besides naturally occurring nanotubes, ”misfit-layer” compounds, composed of two separate sheets, make use of the lattice mismatch between the two sheets to induce a natural driving force to form a tube. [12]

One of the possible classes of materials forming asymmetric 2D monolayers are Janus sheets, like MoSSe [14] or BiTeI [15], which can be wrapped to form 1D tubes. [16, 17] A recent work [16] has shown that radii well below 35 Å are needed to create single-wall Janus transition metal dichalcogenide (TMD) tubes, which have significantly different (electronic) properties from the corresponding asymmetric sheet. Although facile synthesis routes for
the production of single-wall inorganic nanotubes has long been actively researched, not much attention has been paid to the question of which materials would be able to make such a structure avoiding the creation of multi-wall tubes. Consequently, a high throughput study on the stability of a wide range of Janus-based nanotubes, would provide valuable information for guiding future synthesis of small-radius single-wall nanotubes.

In this work, we present a comprehensive screening study in the framework of Density Functional Theory (DFT) on the stability of 135 different inorganic nanotubes generated from the rolling of asymmetric 2D Janus sheets along both the armchair and zigzag directions. The calculations focus on the stability and strain energy of the chosen nanotubes. The total number of DFT relaxations performed in this work amounts to approximately 4500. We show that for pure chalcogen or halogen tubes (isovalent anions), the wrapping mechanism is mostly governed by the lattice-mismatch between the two inner and outer atomic layers, while for mixing anions (non-isovalent anions) this is dominated by the difference in valency between the X/Y elements. These findings provide a physical foundation for designing Janus nanotubes with optimal (small) radii.

Results

The nanotubes considered in this study consist of three layers (MXY, as illustrated in Figure 1) composed of different mid-layer elements (M = \{Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Fe, Ge, Sn, As, Sb, Bi\}) decorated with inner X and outer Y chalcogen and halogen atoms (X,Y = \{O, S, Se, Te, Cl, Br, I\}). Here we denote all group 16 elements including oxygen as chalcogens. For the three pnictogens (As, Sb and Bi) having 3+ as one of their possible oxidation states, we mix chalcogens and halogens in the structures. For the remaining 12 elements, the inner X and outer Y elements are either chalcogens or halogens. The idea of mixing chalcogens and halogens to form 2D MXY Janus sheets was recently explored in Ref. [18], but has so far not been pursued in the context of nanotubes. We construct the tubes
Figure 1: The symmetric MY$_2$ and MX$_2$ are the parent sheets for the asymmetric 2D Janus MXY sheet, which can be wrapped up to form a 1D Janus nanotube. In this case M = Bi (light purple), X = Te (dark yellow) and Y = I (dark purple).

by rolling up 2D layers in both the T- and H-phase crystal structures, corresponding to the crystal structures found for the experimentally synthesized MoSSe [14] and BiTeI [15] 2D sheets, along both the armchair and zigzag directions.

**Nanotube strain energy**

Two main quantities that are needed to characterize an asymmetric nanotube are the optimal radius, which defines the most stable nanotube size, and the strain energy, which defines the energy associated with the wrapping of a 2D sheet into a nanotube (negative strain energies indicate a spontaneous wrapping).

The strain energy is defined as the difference between the energy of the nanotube and...
the corresponding 2D sheet.\[19\] In formula:

\[
E_{\text{strain}}(R) = \frac{E_{\text{tube}}}{N_{\text{tube}}} - \frac{E_{\text{MXY}}}{N_{\text{MXY}}}
\]  

(1)

where \(E_{\text{tube}}\) is the energy of a nanotube with \(N_{\text{tube}}\) atoms and \(E_{\text{MXY}}\) is the energy of the corresponding 2D Janus sheet with \(N_{\text{MXY}}\) atoms in the unit cell. In the infinite limit \(R \to \infty\), the strain energy is zero, since the energy per atom of a tube is equal to the energy per atom of an infinite 2D Janus sheet.

It has been shown that for symmetric tubes (carbon, for example) the nanotube strain energy follows a \(1/R^2\) dependence.\[20, 21\] This relationship does not hold for asymmetric tubes in which the strain energy curve exhibits a minimum.\[22, 23, 24, 25\] Instead, it can be more accurately described using the equation:\[22\]

\[
E_{\text{strain}}(R) = \frac{a}{R^2} + \frac{b}{R}.
\]  

(2)

Extrapolating the function using the obtained DFT data and evaluating the function at the minimum strain energy \(E_{\text{strain-min}}\) leads to the optimal tube radius \(R_{\text{opt}}\) (see also Figure 2). We note that, although Eq. 2 fits well in the region around the optimal tube radius, large strain energies can lead to a deviation.\[26\] We take this into consideration during the screening using Bayesian statistics (details in the SI) which helps to identify cases where the function chosen does not capture the observed data points well across all tube radii.

As an example, Figure 2 shows the strain energy as a function of the tube radius for three different materials, comparing a symmetric MoS\(_2\) tube with the two studied asymmetric tubes NbSSe and BiSI. The symmetric MoS\(_2\) tube shows a \(1/R^2\) dependence of the strain energy over the tube radius indicating the single-wall nanotube is less stable than the infinite sheet. This is not the case for the asymmetric NbSSe and BiSI tubes, where the strain curve exhibits a minimum. The strain energy curve for BiSI shows a strain energy minimum of ~31 meV/atom at the optimal radius of \(\sim 10 \text{ Å}\) while the strain energy curve for NbSSe is instead
very shallow (minimum at -1.1 meV/atom at 85 Å) due to the minor lattice-mismatch of 0.96 between the two parent sheets NbS$_2$ and NbSe$_2$. Such a shallow strain energy curve makes it difficult to establish an optimal radius.

**Stability and optimal radius**

Figure 3 shows the optimal tube radii for all studied materials and its associated uncertainty. For around 20 structures the uncertainty on the radius is estimated to be larger than 30 Å (blue shaded triangles in upper right corner in Figure 3). We employ Bayesian regression (details in the SI) to automatically assess the uncertainty associated with fitting the obtained DFT data to equation 2. This makes it possible to spot data points during the screening study that might require a more detailed investigation, while the data points that fit the underlying fitting function show reduced uncertainties. We have identified three situations where the uncertainties are large: (1) The model is not able to fully capture the variation of
Figure 3: Overview of the 135 investigated materials and their extrapolated optimal radius according to equation 2. It is ensured that at least three data points after filtering according to the criteria described in the SI exist (otherwise marked with a hatched box). The asterisk indicates that the difference in energy between the H-/T- phase is less than 10 meV/atom and that the smaller optimal tube radius is chosen given the extrapolated optimal radius from both prototypes. The lowercase letters a/z indicate which wrapping direction (armchair/zigzag) is preferred.

strain energies across different tube radii. Only few structures, such as SbTeBr, do not fit the proposed model (similar to imogolite, Figure 2 in the SI), leading to large uncertainties in the prediction. (2) The strain energy curves are rather flat due to a less pronounced energy minimum making it difficult to estimate a precise optimal tube radius. This is, for example, the case for NbSSe, TiSSe or VSSe. (3) Only three data points are available, as it happens for BiSI, BiSBr and BiSCI. Nevertheless, in these cases three data points are sufficient to identify the mid-point as the minimum and adding additional data points is not necessary. However, the limited amount of data points lead to an extended uncertainty...
interval using Bayesian regression. In general the values for the optimal tube radii are similar to what has been found in literature for a much smaller set of TMD Janus nanotubes. [17]

Figure 4: The heatmap shows convex hull and tube strain energies at the optimal tube radius. Blue and bright colors indicate good stability, while a red color indicates poor stability. Values exceeding the metastability criterion of 0.2 eV/atom are shown in black.

Figure 4 shows the minimum strain energies corresponding to a tube at the optimal tube radius as shown in Figure 3. The stability of a phase can be estimated through constructing a phase stability diagram, from which we can extract the so-called convex hull. The convex hull defines the stability frontier of a given combination at 0K, i.e. which phase(s) are the most stable at a given stoichiometry. It is constructed by using the DFT total energies of all the known phases of a given chemical space and identifying all the thermodynamically stable
phases and all two-phase equilibria between them. In this work these phases are extracted
from the Materials Project database. The convex hull is then obtained by connecting
the stable phases with tie-lines. If the novel candidate material has an energy below the
hull, it is considered stable and the convex hull is updated to include this new point. On
the other hand, if its energy is above the hull, the material is unstable or metastable. A
more detailed explanation of the construct of the convex hull used here can be found in the
literature. To compare the energy of the tube to its most stable 3D bulk structures, we
calculate the convex hull energy of the tube $E_{CH}$ at its optimal radius ($E_{CH-min}$).
The calculated values for the convex hull energy of the infinite 2D Janus monolayers are
in good agreement with published literature. Except for Fe, all studied nanotubes
show good stability against the decomposition into competing bulk structures (taken from
the Materials Project database) for at least one of the calculated combinations (here
we define a combination stable when the energy of the candidate compound is within 0.2
eV/atom above the convex hull to account for a possible metastability). Given the
mid-layer element is in its preferred oxidation state, the resulting tube shows higher stability
compared to the case of an unfavored oxidation state as expected. Ge, for example, generates
more stable tubes when combined with two halogens (Ge$^{2+}$) than with two chalcogens (which
would need a Ge$^{4+}$, instead). We do not find stable nanotubes for 23 combinations (hatched
boxes in Figure 4). 18 of these materials can be attributed to the transition metal in its
unfavored 2+ oxidation state, when paired with two halogens. The remaining 5 materials
contain either Fe, Sn or Ge which form in general less stable nanotubes for most of the
studied combinations (i.e. more than 0.1 eV/atom above the convex hull). Because of their
stability in the 3D form, oxygen containing tubes are in general more prone to decompose
compared to the pure chalcogenide ones.

For almost 90 % of the materials, the energy difference between the armchair and zigzag
wrapping direction is below 10 meV/atom, which indicates that there is only a weak driving
force causing wrapping up around a specific direction. Although the armchair and zigzag
wrapping directions only have a minor impact on the stability of the tube, it can be expected that the wrapping direction has a larger impact on the electronic properties due to the difference in bond distances in these tube configurations. We have recently demonstrated this for MoSTe, but a more comprehensive study focusing specifically on the electronic properties would be needed to establish general design rules. [13]

The combination of the three metals As, Sb and Bi mixed together with a chalcogen sitting inside and a halogen element sitting outside of the structure generates stable and small-radius nanotubes with a rather small strain energy associated with its optimal radius. For instance, AsSI has a minimum strain energy of -80 meV/atom which is ~ 40 meV smaller than that of the experimentally observed imogolite nanotube when compared to computational reference data found in literature. [31] The MXY nanotubes share with imogolite, which is known to exist as a single-wall nanotube, the shape of the strain energy curve (see BiSI in SI Figure 2).

Figure 5 reports the correlation between various quantities, namely the extrapolated optimal radius $R_{opt}$ versus the lattice-mismatch $a_{MX_2}/a_{MY_2}$ (a), which is the important parameter in Pauling’s mechanism, the minimum strain energy $E_{strain-min}$ (b) and the ratio of the Mulliken electronegativities of the X/Y elements (c). Figure 5 (d) shows the ratio in layer thickness $t_{M-X}/t_{M-Y}$ versus the lattice-mismatch $a_{MX_2}/a_{MY_2}$, where the thickness is measured as the M-X and M-Y element distance along the vacuum direction in the 2D Janus sheet (inter-layer distance). A similar plot showing the optimal radius versus the convex hull energies can be found in the SI in Figure 3. Figure 5 (b) indicates that very low strain energies are not necessary to obtain small-radius nanotubes. Nanotubes with a diameter smaller than 15 Å are predicted to be found in a range of strain energy minima from -15 meV/atom (BiSeBr) to -280 meV/atom (TaOTe, which has the most negative strain energy in our dataset). The optimal radius increases sharply when approaching the limit of no lattice-mismatch between the MX$_2$ and MY$_2$ parent sheets (i.e. lattice-mismatch $a_{MX_2}/a_{MY_2} = 1$, see Figure 5 (a) - blue dashed curve). Additionally, the lattice-mismatch
Figure 5: $R_{\text{opt}}$ versus the lattice mismatch of the corresponding parent sheets (lattice mismatch calculated as $a_{MX}/a_{MY}$ with a being the lattice constant) (a), the minimum strain energy at the optimal radius (b) and the Mulliken ratio of the corresponding Mulliken electronegativities of outer and inner elements (Mulliken ratio $X/Y$) (c) are shown. Figure (d) shows the ratio in layer thicknesses in the 2D Janus sheet versus the lattice-mismatch. The different colors represent the three classes of pairing the mid-layer with either two chalcogens (Janus-Cal-Cal, \{O, S, Se, Te\}, green), two halogens (Janus-Hal-Hal, \{Br, I, Cl\}, red) or a mix of chalcogens inside and halogens outside (Janus-Cal-Hal, yellow).

is correlated with the ratio of ionic radii when mixing two chalcogens (Janus-Cal-Cal class following trend OTe > OSe > OS > STe > SeTe > SSe) or two halogens (Janus-Hal-Hal class following ClI > BrI > ClBr) with each other.

The lattice-mismatch between the two parent sheets can give an estimate on the optimal tube radius in the case of isovalent anions, while it fails for mixing halogens with chalcogens (Janus Cal-Hal class). Here, it would predict the halogen to sit inside of the tube, instead of on the outside, as several of the materials show a lattice mismatch $a_{MX}/a_{MY}$ larger than 1 (Figure 5 (a), yellow dashed line). For instance, the MoOTe parent sheets
(H-phase) have a lattice mismatch of 0.79 ($a_{MoO_2} = 2.82$ Å, $a_{MoTe_2} = 3.55$ Å) leading to the small radius of 7.2 Å. Conversely, the BiTeCl parent sheets (T-phase) have a lattice mismatch of 1.06 since the parent structure BiCl$_2$ ($a = 3.68$ Å) has a smaller lattice constant than BiTe$_2$ ($a = 3.9$ Å). Based on the lattice mismatch, the tube should wrap in a way that the Chlorine atoms are inside of the tube. The three different classes appear well-separated when the radius is plotted versus the ratio of the Mulliken electronegativities of the X and Y element (Figure 5 (c)). Having more electronegative elements sitting on the inside of the tube does not seem to be a necessary criterion for forming small-radius nanotubes (Janus-Cal-Hal, yellow).

A possible explanation on the reason why the chalcogen is sitting inside of the non-isovalent tube can be made by investigating the bond lengths in the non-isovalent structures closer. Shevelkov et al. [32] studied the experimental 3D-bulk crystal structure of layered BiTeI and find the Bi-X bond distance in these structures to be significantly longer (ionic) than the ones found in bismuth trihalides. Additionally, the geometry of the (BiTe) layer is

![Figure 6](image-url)

**Figure 6:** Side (or cross-section) view for the energetically favored armchair BiSI nanotube, the infinite 2D Janus layer and the unstable inverse wrapped BiIS nanotube. Measures are given in Å.
shown to be comparable to the one found in Bi-bulk metal and the bond-distance of Bi-Te in the BiTeI layer is similar to the one found in bismuth tellurides. [32]

To illustrate this, we take the BiSI structure in Figure 6 and assume the Bi-I (d_{M-Y}), Bi-Bi (d_{M-M}) and Bi-S (d_{M-X}) bond distances to not vary significantly when the 2D Janus sheet is being wrapped up into a tube. By looking at the sheet from the side, the layer thicknesses of both inner and outer layer are t_{M-X} and t_{M-Y}, respectively (Figure 6 mid column). Larger bond-distances now also lead to thicker layers. This means that the M-Y layer is considerably thicker, owed to the ionic like bond between the M-layer element and the halogen. Larger thicknesses of the M-Y layer impose a constraint resulting in M-X bonds taking less space inside the tube and therefore leading to less steric effects as opposed to having M-Y bonds on the inside of the tube (Figure 5 (d)). Additionally, we observe for the non-isovalent structures a shortening in M-X bond lengths upon wrapping the infinite 2D Janus sheet into a nanotube leading to the effective thickness of the MX layer in a tube being even thinner than in the sheet.

In order to further clarify this point we compare the stable BiSI tube and the energetically unstable inverse wrapped counterpart BiIS in Figure 6 on the right. In the inverse wrapped case steric effects in between I-I elements even lead to a bond expansion of the Bi-Bi bond, d_{M-M}, from 4.2 Å to 4.6 Å. Given both tube configurations differ by 0.14 eV/atom in energy in favor of the tube in which the chalcogen element sits inside, the importance of the (BiTe) layer for the stability is underlined. Plotting the stability difference in between the stable (chalcogen inside) and the inverse wrapped tube (chalcogen outisde) for nine selected non-isovalent tubes we find the points to follow a positive linear correlation with the ratio in thickness r = t_{M-X}/t_{M-Y} (Figure 4 in the SI). We conclude that the steric effects caused by a difference in layer thickness significantly influences the stability of the tubes. Steric effects can also explain the reduced minimum strain energy for BiXI < BiXBr < BiXCl structures, as well as the reduced optimal radius for BiSY < BiSeY < BiTeY structures. In these cases, the element forming stronger bonds determines the wrapping direction.
**Optimal radius descriptors**

As we have reported above, to estimate the optimal radius, we need to calculate the tubes at different sizes. These calculations are approximately three orders of magnitude more computationally demanding than to simulate the corresponding infinite Janus sheets. Identifying descriptors to predict the optimal radius based exclusively on the 2D Janus sheet is a valuable pathway to faster navigate through the studied phase space and discover small-radius nanotubes.

All studied tubes are more stable if the chalcogen element is placed inside. In fact, for some of the studied non-isovalent nanotubes the optimal tube radius is independent of the halogen sitting on the outside of the tube (e.g. SbCl, SbBr and SbI). Thus, only considering MX$_2$ and MY$_2$ parent structures provides an inaccurate picture when studying non-isovalent nanotubes. Additionally, the parent structures of non-isovalent tubes will each have a M-element oxidation state different from the 2D Janus sheet (e.g. BiI$_2$, BiS$_2$ and BiI). Two models from literature use the parent structure lattice constants as descriptors for predicting the optimal tube radius of isovalent nanotubes. The first approach is based on the plate theory as described by Timoshenko [33, 34], while the second approach makes use of the Poisson ratios of the parent sheets (Poisson model) [16]. Both models require the calculation of the stiffness tensors of the parent structures. Our approach, which we refer to as Inner-bond model, is instead based on solely geometrical parameters, which can be readily obtained from existing 2D databases (e.g. [35]). By circumventing the time consuming calculation of the stiffness tensor, we are able to calculate these descriptors at least one order of magnitude faster. The Inner-bond model uses the lattice constants of the 2D Mxy Janus and MX$_2$ parent sheets as well as the 2D Janus $t_{M-X}$ layer thickness, as discussed above. It is initially assumed that the optimal tube radius is determined by the the lattice mismatch between the MXY Janus sheet and the corresponding MX$_2$ parent sheet. The derivation of the Inner-bond model and the used formulas for the two reference models are provided in the SI.
Figure 7: (a) Optimal tube radius using the three models based on the Timoshenko plate theory [33], considering the Poisson ratios (Poisson) [16] and using lattice mismatches between Janus MXY and MY$_2$ parent sheets (Inner-bond model). The optimal radius based on DFT calculations R$_{opt}$ is also shown which has been obtained extrapolating the function given in equation 2. The asterisk indicates that due to prototype changes when straining the SbBr$_2$ sheet, it was not possible to get the elastic tensor required for the Timoshenko and Poisson model. (b) The radius plotted against the lattice mismatch MX$_2$/MXY.

All three models capture the rolling mechanism for isovalent anions for a selected set of materials (with discrepancies up to 30 % compared to the calculated DFT radius - Figure 7 (a)), while only the Inner-bond model predicts the optimal radii of non-isovalent nanotubes to be small. Nevertheless, it fails to capture that the optimal DFT radius for some tubes, in which a chalcogen sits inside the tube, is almost independent of the chosen halogen element sitting outside of the tube (see orange bars for SbSCl, SbSBr and SbSI in Figure 7 (a)). Here, the layer thickness t$_{M-X}$ is so thin, that the steric effects of the halogen atoms at small radii do not decisively impact the stability of the tube. In this picture, the wrapping mechanism is solely governed by the steric effects of the chalcogen elements. Controversely, the 2D Janus sheet lattice constants increases for SbSCl < SbSBr < SbSI due to the size difference of the halogen atoms, leading to a mismatch in predicted values for the Inner-bond model.

One feature all the studied materials share is that the lattice mismatch between the
parent MX\textsubscript{2} and the Janus MXY sheets is always smaller than 1 (Figure 7 (b)). This is different from the idea of comparing MX\textsubscript{2} and MY\textsubscript{2} lattice constants, for which, in the case of mixing chalcogen and halogen X/Y elements, the lattice mismatch exceeds 1 (Figure 5 (a)). Although only giving quantitative predictions, the Inner-bond model shows that the bond distances of the elements in the inner MX\textsubscript{2} sheet together with the MXY lattice constant are good descriptors for predicting the optimal radius within the studied compound space. In the case of isovalent anions the lattice-mismatch of the parent structures can also be used as a descriptor.

### Strain energy descriptors

![Figure 8: Comparing the energy of the tube at its optimal radius versus the energy of a sheet consisting of alternating anion rows (2D-alternating rows prototype structure or 2D-alt). The mean average error for the different combinations are 22.9 meV/atom (Janus-Cal-Cal), 14.4 meV/atom (Janus-Cal-Hal) and 3.1 meV/atom (Janus-Hal-Hal).](image)

The Janus sheets show an asymmetry between the two sides of the layer. We can make a sheet where the mirror symmetry along the mid-layer (M-layer) is restored through rear-
ranging the X/Y elements into alternating X/Y rows (as shown in Figure 8). The graph in Figure 8 shows the energy difference between the alternating and the Janus sheet \( (E_{2D-\text{alt}} - E_{2D-\text{Janus}}) \) as a descriptor for the strain energy minimum \( (E_{\text{strain-min}}) \). Few outliers (\( > 50 \text{meV/atom error in prediction} \)) correspond to structures with a low convex hull stability, \( i.e. E_{CH} > 0.2 \text{eV/atom} \).

For instance, this descriptor, which does not require the calculation of the tubes, could be used to indicate if a sheet exfoliated onto a host structure might undergo spontaneous curling. The strain energy would need to be larger than the adsorption energy of the sheet on the host structure, which is for example not the case for the experimentally exfoliated BiTeI sheet [15]. Whether a large strain energy is needed to form single-wall nanotubes (in favor of multi-wall nanotubes or other forms of rolled structures) requires a deeper experimental investigation, or, at least, to consider growing and other experimental conditions which might impact the formation mechanism.[36]

Different synthesis procedures can be imagined leading to the synthesis of the Janus nanotubes suggested here. Besides the exfoliation of a monolayer onto a host structure and its subsequent spontaneous wrapping, which might need lithography techniques to cut the monolayer into the required dimensions, the intercalation of ions into Janus multilayered materials, combined with ball-milling, [37] can be a viable experimental synthesis path allowing to produce larger quantities. A common issue with these methods would be preventing unwanted reactions occurring at unsaturated bonds. A possible alternative synthesis pathway could be to use Atomic Layer Deposition combined with lithography to cut the 2D layer into a desired shape before it spontaneously wraps. Regardless the synthesis procedure, the intrinsic driving force of the 2D Janus sheets to form 1D tubes (or alternatively other curled shapes) should be large enough to be observed.

A promising starting material to experimentally verify our predictions is the layered BiTeI 3D bulk crystal structure for which experimental synthesis routes have been established.[32] Other interesting candidates include tubes based on Vanadium or Titanium, which, by dis-
playing a variety of oxidation states, are suitable for electrochemical applications.[38, 39] Curled multiwall VO$_x$ structures with much larger inner radii than the tubes predicted here have already been reported.[39] Other non-isovalent anion based tubes, such as BiSI, might be feasible. However, the weaker ionic halogen bonds might drive reconstructions, in contrast to less reactive covalent bonds.

**Discussion**

In this work, we investigated the formation mechanism of nanotubes by studying their stability and optimal nanotube radius. 135 different Janus nanotubes have been calculated using a structure prototype approach (T-/H-phase). Each three-layered material consisted of one of 15 different cation mid-layer elements in combination with inner and outer atomic layers being occupied by either chalcogens, halogens or their mixture as anions. For isovalent anions, the wrapping mechanism could be explained by the lattice-mismatch between the two inner and outer atomic layers, while for non-isovalent anions steric effects caused through short pnictogen-chalcogen inside and longer pnictogen-halogen bonds outside of the material drive the stability. These effects are beneficial to the formation of some of the smallest identified nanotubes showing optimal radii below 10 Å. We noted that in general a large minimum strain energy is not needed to find tubes with an optimal radius smaller than 35 Å. Additionally, the minimum strain energy was reasonably well estimated using the energy difference between a 2D Janus and alternating sheet as a descriptor. We employed Bayesian statistics to assess the quality of our fitting in order to identify uncertainties in our predictions of the optimal radius due, for example, to a misfit between the obtained data and the underlying strain energy curve function.

Nanotubes based on BiTeI and related compositions appear to be a particular interesting starting point for experimental verification due to their synthesizability in a 3D structure and exfoliability into 2D layers, as well as their predicted stability in 1D form. Following
the interest in Vanadium- and Titanium-based nanotubes for electrochemical applications, we suggest that the metastable combinations of these metals paired with either OTe, OSe, or OS can be additional interesting candidates.

The findings reported here, shed light on the mechanism behind the curling of 2D Janus sheets and define a new path for the synthesis of nanotubes with small radii, for which the lattice mismatch and the bonding character of the anions play a fundamental role.

**Methods**

The first step to create our library of nanotubes is to relax the 2D Janus sheets, taken from the Computational 2D Materials Database (c2db).[35] If a 2D Janus sheet is not present in the database, the 2D Janus sheet is created by averaging the lattice constants from its constituent MX$_2$ and MY$_2$ parent sheets. Subsequently, tubes are generated by repeating and wrapping the 2D sheets both along the armchair and zigzag wrapping directions, thereby obtaining tubes with various radii (similar to what is shown in Figure 1). In details, the initial number of unit cell repetitions is $n = (6, 8, 10, 12, 14)$ for the armchair and $n = (10, 13, 16, 19, 22)$ for the zigzag wrapping direction, which correspond to tubes with a radius smaller than 20 Å. We apply a set of filters to decide whether or not the relaxed structure is accepted for further investigation. These filters include assuring that a tube retained its circular shape and that no unwanted changes into different prototypes occurred during the relaxation. The filters discard $\sim 40\%$ of the data generated. A detailed discussion on how the data is filtered prior to visualization can be found in the SI. For consistent and reproducible calculations, we implement a workflow combining the Atomic Simulation Environment (ASE) [40] and the workflow scheduling system MyQueue [41]. Inspired by the CUSTODIAN package [27], we establish an "ASE error handler" to handle common DFT errors thus limiting the need for user intervention. A similar approach has been recently implemented to autonomously discover battery electrodes.[42]
All calculations are carried out with the Vienna ab initio Simulation Package (VASP) using a plane-wave basis set with an energy cutoff of 550 eV. In order to approximate the exchange-correlation effects the Perdew-Burke-Ernzerhof (PBE) form generalized gradient approximation (GGA) is used. A k-point density $> 4.7 \text{ Å}^{-1}$ is used to sample the Brillouin zone. All forces are converged to less than 0.01 eV/Å. The structures are relaxed in a non-magnetic configuration, i.e. without applying initial magnetic moments on the elements. A minimum vacuum in between repeating images of 16 Å is ensured. Dipole corrections are applied along the non-periodic direction for materials with an out-of-plane dipole moment. To assess the stability versus 3D phases, we use a convex hull analysis, where the reference structures are the ones defining the convex hull in the Materials Project database. These structures are then relaxed with the matching input parameters used in this work, while the reference energy of oxygen is obtained by calculating the difference in energy between water and hydrogen in the gas phase, including the zero point energy (ZPE) corrections. For the calculation of the stiffness tensor we use the workflow described by Haastrup et al. in Ref. Here, the k-point density applied for calculating elastic constants is $> 12.0 \text{ Å}^{-1}$ together with an applied strain of ± 1%.

**Code availability**

The workflow is continuously developed and may be accessed at https://gitlab.com/asc-dtu/workflows/nanotubes/.

**Data availability**

The structures presented in this work are available on DTU DATA with the identifier "doi.org/10.11583/DTU.13153355".
References


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Supplementary Information

Filtering of the database, formulas used to predict the optimal radius, graphs include a comparison of BiSI nanotubes to experimental reference tubes, the optimal radius versus the


convex hull stability and a comparison of tube energies versus layer thicknesses

Author contributions

F.T.B. wrote all scripts for the analysis of the data and the draft of the manuscript. F.T.B and A.E.G.M. implemented the workflow and performed the calculations. T.V. and I.E.C. designed the project. All authors contributed to discussing the results as well as writing and revising of the manuscript.

Competing interests

The authors declare no competing interests.
Supplementary Information for paper I
Structural and chemical mechanisms governing stability of inorganic Janus nanotubes

Supplementary Information

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Filtering the database

We simulate smaller tube radii if the first data points indicate the tube minimum lies below the simulated data. In contrast to that, due to computational reasons, we do not simulate larger nanotubes in case the predicted minimum tube radius is larger than the largest simulated tube. Only a few tubes were selected to study larger tube radii. Subsequent filtering of the database includes:

- Did a change of prototype occur? For several tubes we observe a change in between the different prototypes (H-/T- phase) during relaxation in favor of its energetically favored prototype. All janus sheets, even in the minimum tube energy configuration, underlie a certain strain energy. This strain energy can cause changes of prototypes as kinetic barriers associated with it can be overcome. We use similarity measures between the corresponding infinite janus sheet and the nanotube in order to ensure the prototype is consistent.

- Did the tube elongate or contract along the tube axis? Some of the nanotubes reach lower energy minima through elongating its lattice constant along the tube axis. As they can not be compared to the corresponding janus sheet, these tubes are disregarded.

- Is the tube still circular? It is ensured that the tube does not segregate during relaxation by checking that all atoms still form a circular tube shape. Additionally we exclude tubes that form fragments. For instance, we observe that some tubes change its prototype to the 1T’ distorted type, which is not part of the study.

- Calculation finished without errors? This also includes marking calculations that did not finish within a reasonable amount of time as "timed out".
Formulas used to predict the optimal radius

*Timoschenko plate theory model*

The formula used to predict nanotubes was taken from Ref. ¹

\[ \frac{1}{R} = \frac{6(E_{MY_2} \epsilon_m t_{MY_2})}{E_{MX_2} t^2} \gamma \]  
\[ \gamma = \frac{(1 + \beta)^3}{1 + 4\alpha \beta + 6\alpha \beta^2 + 4\alpha \beta^3 + \alpha^2 + \beta^4} \]  
\[ \alpha = \frac{E_{MY_2}}{E_{MX_2}} \]  
\[ \beta = \frac{t_{M-Y}}{t_{M-X}} \]  
\[ t = t_{M-Y} + t_{M-X} \]  
\[ \epsilon_m = \frac{a_{MX_2} - a_{MY_2}}{a_{MY_2}} \]  

where \( E \) is the bulk modulus, \( t \) is the sheet thickness and \( a \) is the lattice constant.

*Poisson model*

For a 2D material disregarding shear stresses, the stress tensor can be written as

\[
\begin{bmatrix}
\sigma_{xx} \\
\sigma_{yy}
\end{bmatrix} =
\begin{bmatrix}
c_{11} & c_{12} \\
c_{21} & c_{22}
\end{bmatrix}
\begin{bmatrix}
\epsilon_{xx} \\
\epsilon_{yy}
\end{bmatrix}
\]

Assuming for a nanotube that a stress is applied along the x-direction, the forces along the y-direction are 0 and therefore

\[ \sigma_{yy} = 0 = c_{12} \epsilon_{xx} + c_{22} \epsilon_{yy} \]  
\[ \frac{\epsilon_{yy}}{\epsilon_{xx}} = -\frac{c_{12}}{c_{22}} \]
For a 2D material poisson’s ratio can then be described as

\[ \nu = -\frac{\epsilon_{yy}}{\epsilon_{xx}} = \frac{c_{12}}{c_{22}} \]  

(9)

which is readily available from the c2db database. We use the c2db workflow to get results for sheets that do not exist in the database, ensuring consistency in between the calculated mechanical properties.

The final formula is taken from Ref.\(^2\)

\[ R_0 = \frac{a'_Y h_Y + a'_X h_X}{2(a'_Y - a'_X)} \]  

(10)

where

\[ a'_i = -\nu_i a_H + a_i(1 + \nu_i) = a_i + \nu_i(a_i - a_H) \]  

(11)

Inner-bond model

![Diagram of Inner-bond model](image)

Figure 1: Isosceles triangle showing the bond distances used for the Inner-bond model.
Given the hexagonal unit cell, the lattice constant of the MX$_2$ sheet corresponds to the X-X bond distance (Figure 1). It follows from the equality of the isosceles triangle in Figure 1:

\[ 2 \arcsin \left( \frac{a_{MX_2}}{2(R - t_{M-X})} \right) = \theta = 2 \arcsin \left( \frac{a_{MXY}}{2R} \right) , \]  
\[ (12) \]

and we obtain the optimal tube radius, R, as

\[ R = \frac{t_{M-X}}{1 - \frac{a_{MX_2}}{a_{MXY}}} \]
\[ (13) \]

where $a_{MXY}$ is the lattice constant of the 2D Janus nanosheet (or M-M bond distance), $t_{M-X}$ is the thickness of the MX layer and $a_{MX_2}$ is the lattice constant of the 2D parent MX$_2$ sheet (or X-X bond distance).

**Bayesian regression**

For sampling of the uncertainty of the predicted radius $R_{DFT}$ we use the underlying function

\[ E_{str}(R) = \frac{a}{R^2} + \frac{b}{R} \]  
\[ (14) \]

Strain energies are now sampled from

\[ y \sim \mathcal{N}(\beta^TX, \sigma^2I) \]  
\[ (15) \]

The observations consist of at least 3 data points, corresponding to a specific tube radius and its associated strain energy. The coefficients are sampled, using least-square prior information, from

\[ a \sim \mathcal{N}(a_{LS}, \sigma^2) \quad b \sim \mathcal{N}(b_{LS}, \sigma^2) \quad \sigma \sim \mathcal{N}(0, 1). \]  
\[ (16) \]
Using the obtained coefficient distributions, the minimum radius is sampled from the sampled 
(a, b) coefficient pairs by using that the minimum radius is

\[ R_{DFT} = \frac{-2a}{b}. \]  

We take the 95\% confidence interval to estimate the uncertainty. The NUTS sampler is used to draw samples with 2000 burnin steps and 2000 posterior samples while running a total of 4 chains. All calculations have been carried out using the PyMC3 v3.8 python package.\textsuperscript{3}

Figure 2: The three experimentally observed nanotubes and a theoretically predicted BiSI nanotube. The 2D Janus sheets 1T-lizardite (ICSD 202358 - Mg\textsubscript{3}Si\textsubscript{2}O\textsubscript{5}(OH)\textsubscript{4}) kaolinite (ICSD 63192 - Al\textsubscript{2}Si\textsubscript{2}O\textsubscript{5}(OH)\textsubscript{4}) are taken as starting structures for the chrysotile and the halloysite nanotube, respectively. The imogolite ((HO)\textsubscript{3}Al\textsubscript{2}O\textsubscript{3}SiOH) structure is the Z8-Si’ImoHB’ nanotube taken from Ref.\textsuperscript{4} a/z indicates an armchair/zigzag wrapping direction.
Figure 3: Optimal tube radius versus the convex hull energy.

Figure 4: Energy difference of a stable tube compared to its inverse wrapped counterpart versus the thickness ratio of outer and inner atomic layer in the Janus sheet.
References


Band structure of MoSTe Janus nanotubes

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Band structure of MoSTe Janus nanotubes

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Nanotubes generated by rolling up transition metal dichalcogenide Janus monolayers are a new class of low-dimensional materials, which are expected to display unique electronic properties compared to their parent two- and three-dimensional structures. Here, we investigate the band structure of 1H-MoSTe Janus armchair and zigzag nanotubes, which were recently hypothesized to be stable as single-walled structures with radii of only a few nanometers. We first investigate the most stable nanotube sizes and assess the influence of quantum confinement and curvature on the band structures, showing that these are heavily modified by curvature while confinement effects are negligible. The curvature dependence is then further studied by analyzing the band gap dependence on the nanotube radius, where band gap changes as large as 0.5 eV are observed. By investigating the band edge positions and orbital projected density of states for different tube sizes, we find that this high sensitivity is mainly attributed to the Mo d states in the conduction band.

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I. INTRODUCTION

During the past decades, the study and characterization of low-dimensional materials has been one of the most active fields in materials science. The immense scientific interest is fueled by the expectation that low-dimensional materials will have novel applications within a broad range of research areas, from batteries and electrocatalysis, to electronics and photonics [1–3]. On the experimental side this has resulted in numerous reports of novel two- and one-dimensional (2D and 1D) structures [4–9], and on the computational side several databases have emerged containing thousands of hypothetical materials with remarkably different properties compared to their parent 3D structures [10–12].

A particular class of low-dimensional materials, which have been studied intensely, are 2D monolayers based on transition metal dichalcogenides (TMDs). TMD monolayers have the chemical formula MX$_2$, where M is a transition metal atom and X is a chalcogen atom, and include examples such as MoS$_2$, MoTe$_2$, and WS$_2$, all of which have been synthesized experimentally [6,13,14]. Furthermore, several TMDs have also been synthesized in a one-dimensional form as multiwalled nanotubes with diameters of several nanometers [8,9]. Such tubular structures are expected to have promising applications within a broad range of scientific areas such as, e.g., gas separation and capture, catalysis, solid lubrication, and controlled drug delivery [15], but so far advancements have been hampered by difficulties in producing single-wall nanotubes with a well-defined radius.

A less known class of 2D structures are the so-called TMD Janus monolayers with the chemical formula MXY [16]. Such layers can, at least in principle, be obtained by substitution of the chalcogen atoms on one side of a regular MX$_2$ monolayer, and examples include MoSSe, MoSTe, and WSSe, among which MoSSe was recently synthesized [17]. TMD Janus monolayers are particularly interesting because their asymmetry gives rise to an intrinsic strain, which makes self-rolling into the nanotube structure energetically favorable [18,19]. In contrast to the multiwalled nanotubes mentioned above, such nanotubes are expected to be stable as single-walled structures with diameters of only a few nanometers. At such small radii the finite size and curvature will subject the atoms to significant distortion, and these nanotubes are thus expected to display unique and tunable electronic properties compared to their parent monolayers [20–22].

We have recently conducted a comprehensive study on the thermodynamic stability of a wide range of inorganic nanotubes obtained from the wrapping of Janus monolayers [23]. As part of this effort, the present paper is devoted to a more detailed study on the electronic properties of nanotubes made from monolayer MoSTe in the 1H phase, which was recently proposed as a promising candidate material for piezoelectric applications [24].

A sketch of how the relevant MoSTe nanotubes are constructed is shown in Fig. 1(a): Starting from a 1H monolayer of MoSTe described by the hexagonal unit cell vectors $\mathbf{a}_1$, $\mathbf{a}_2$, a change of basis to the symmetrically equivalent rectangular basis described by the vectors $\mathbf{a}_1'$, $\mathbf{a}_2'$ is first performed. Armchair and zigzag MoSTe nanotubes of different sizes are then obtained by wrapping up nanoribbons corresponding to different numbers of unit cell repetitions along either $\mathbf{a}_1'$ (zigzag) or $\mathbf{a}_2'$ (armchair). In the screening study of Ref. [23], both armchair and zigzag type nanotubes were investigated (chiral nanotubes were not considered), and both types were found to
show promising signs of thermodynamic stability compared to both their bulk constituents as well as their parent 2D monolayer. The latter is demonstrated in Fig. 1(c), which displays the nanotube strain energy, defined as the energy difference with respect to the parent monolayer, as a function of the radius. Evidently both armchair and zigzag MoSTe nanotubes are stable with respect to their parent 2D layer with a peak in stability at a radius of only $\sim 18$ Å. Combining this with the fact that the dynamical stability of both 1H-MoSTe monolayers and MoSTe nanotubes has been confirmed through phonon calculations [19,24], makes these structures particularly well suited for a more detailed investigation focusing on the electronic properties.

The paper is structured as follows: Starting from the most stable MoSTe zigzag and armchair configurations shown in Fig. 1(c), we first analyze the band structures and how they differ from their parent monolayer as well as the symmetric MoS$_2$ and MoTe$_2$ structures. We then proceed to perform a more systematic investigation of how the band structure, and in particular the band gap, depends on the size of the simulated nanotubes, and how the behavior may be qualitatively understood from the orbital projected density of states (PDOS) around the Fermi level. Our study demonstrates how 1D Janus TMD tubes can display remarkably different electronic properties compared to their 2D and 3D counterparts, thus showing that targeted screening of such nanotubes for specific applications such as catalysis and thermoelectrics might be of future interest.

II. COMPUTATIONAL METHODOLOGY

All calculations are carried out using the Perdew-Burke-Ernzerhof (PBE) functional [25] as implemented in the Vienna ab initio simulation package [26]. We employ a plane-wave basis set with an energy cutoff of 550 eV. The construction and relaxation of the nanotubes is performed using the atomistic simulation environment (ASE) [27] and follows the procedure outlined in Ref. [23], where a $k$-point density $> 4.7$ per Å$^{-1}$ is used to sample the Brillouin zone and the forces on the atoms are converged to less than 0.02 eV/Å. To obtain well-converged band structures and band gaps we perform self-consistent calculations for the relaxed structures using a gamma-centered uniform $k$ mesh with a density greater than 15.0 per Å$^{-1}$. We use a dipole correction for all structures with an out-of-plane dipole moment such as the nanoribbons described in Sec. III. For the band structure, band edge, and projected density of states results presented in Figs. 2 and 3 we have used the vacuum level energy defined by the asymptotic value of the Hartree potential as our reference. For a nanotube we obtain this by averaging the Hartree potential on a radial grid centered on each nanotube. For the asymmetric nanoribbons, where a dipole correction is applied, we use the asymptotic value of the planar averaged Hartree potential on the side of the structure, which would make up the outer side of the corresponding nanotube. All the calculations were performed with a computational workflow, which is described in detail in Ref. [23], and may be accessed via

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FIG. 1. (a) Sketch of how armchair and zigzag nanotubes are constructed by rolling up a 2D MoSTe monolayer along different directions. The different unit cells involved are indicated and their relation in reciprocal space is displayed in the top right. (b) Band structure of a 2D MoSTe monolayer with the band gap indicated. (c) Calculated strain energies of armchair and zigzag MoSTe nanotubes for different radii. A minimum strain energy is attained at $r_{\text{min}}$ which is the most stable nanotube radius.
FIG. 2. Band structures of armchair and zigzag MoS$_2$, MoSTe and MoTe$_2$ nanotubes (solid black lines) along with the corresponding curvatureless band structures (opaque red lines). The band gap transitions are indicated by blue arrows. (a) MoS$_2$ armchair nanotube with a radius of $\sim$16 Å. (b) MoSTe armchair nanotube with a radius of $\sim$18.5 Å. (c) Armchair MoTe$_2$ nanotube with a radius of $\sim$18 Å. (d) Zigzag MoS$_2$ nanotube with a radius of $\sim$15 Å. (e) Zigzag MoSTe nanotube with a radius of $\sim$16 Å. (f) Zigzag MoTe$_2$ nanotube with a radius of $\sim$15 Å.

Ref. [28]. The relaxed 2D sheets and nanotube structures are furthermore stored in a database in the DTU Data Repository [29].

III. RESULTS AND DISCUSSION

Figure 2 displays the band structure for selected armchair [Figs. 2(a)–2(c)] and zigzag [Figs. 2(d)–2(f)] MoS$_2$, MoSTe, and MoTe$_2$ nanotubes. The nanotubes have been selected to correspond to the most stable radii for the MoSTe armchair and zigzag configurations as shown in Fig. 1(c). Consequently, the MoSTe armchair nanotube was chosen to have a radius of $\sim$18.4 Å and 120 atoms in the unit cell, while for the zigzag nanotube a radius of $\sim$18.1 Å and 204 atoms in the unit cell was used. The sizes of the symmetric MoS$_2$ and MoTe$_2$ nanotubes were chosen to be consistent with these numbers, i.e., with 120 and 204 atoms in the unit cell for the armchair and zigzag, respectively. We emphasize that these nanotubes, in contrast to MoSTe, are not formed from a Janus structure and are therefore likely to be unstable with respect to their planar counterpart.

To understand the general features of the nanotube band structures in Fig. 2, we first note that these are influenced by two separate structural effects: (i) The effect of quantum confinement arising from the finite extent of a nanotube along its wrapping axis. This is manifested by periodicity of the electronic Bloch states along its circumference as discussed below. (ii) The effect of curvature arising from the bending of the parent nanoribbon into the nanotube form.

In order to separate the effects described in (i) and (ii) we have included in Fig. 2 a set of band structures, which neglect the effect of the nanotube curvature. These are obtained from the 2D band structure of the parent MoSTe monolayer [see Fig. 2(b)] following the procedure described in Ref. [30], where the $k$ points inside the Brillouin zone allowed by (i) are selected and used to generate the corresponding 1D band structure. An example of how this is done, we consider generating the curvatureless band structure equivalent of a nanotube corresponding to $N$ repetitions along the armchair direction as shown in Fig. 1(a). In this case, periodicity of the electronic states along the wrapping direction combined with Bloch’s theorem yields $\psi(R) = \psi(R + N \cdot a'_z) \Rightarrow \psi(R) = \psi(R)e^{iNk \cdot a'_z}$, which leads to the following quantization condition for the allowed values of $k$:

$$k \cdot a'_z = 2\pi \frac{m}{N}, \quad m = 0, 1, \ldots, N - 1. \quad (1)$$

The result is a discrete set of allowed $k$ points along the $a'_z$ direction, which, as shown in Fig. 1(a), is along the $\Gamma$-$M'$ path in reciprocal space. The band structure is then obtained from the 2D band structure of MoSTe by plotting its value for each discrete $k$ value in Eq. (1) in the direction perpendicular to $\Gamma$-$M'$ as shown by the blue lines in Fig. 1(a). A similar analysis for the zigzag direction leads to a discrete set of $k$ values along the $\Gamma$-$K$ path and in this case the band structure is obtained by plotting the values of the 2D band structure along the path marked by the red lines of Fig. 1(a). As shown in Fig. 1(a), we label the boundary of the rectangular Brillouin zone as $Z$ in both the armchair and zigzag directions to be consistent with the labeling of the $Z$ point in the nanotube band structures of Fig. 2.
Comparing the band structures of Fig. 2, we can make several qualitative observations. First of all, the band structures of the Janus MoSTe nanotubes appear significantly different from those of the symmetric MoS₂ and MoTe₂ nanotubes. Second, we observe that while the nanotube and nanoribbon band structures share the same overall features, the nanotube band gaps are heavily modified by curvature. Indeed, by comparing Figs. 2(b) and 2(e) with the band structure of 2D MoSTe shown in Fig. 1(b), we can see that the nanotube band gaps are significantly different from the band gap of 2D MoSTe, while the nanoribbon band gaps practically coincide with the latter. This shows that quantization has a very minor influence on the size of the band gap. To understand this we first note that the band gap of 2D MoSTe corresponds to an indirect $\Gamma$-$K$ transition. Since $k = 0$ is included in the discrete set of $k$ values in Eq. (1) for all values of $N$, the $\Gamma$ point will likewise be included when generating the nanotube band structure for a nanotube of any size. Any dependence of the band gap must thus be attributed to whether or not the discrete set of $k$ points of Eq. (1) includes the $K$ point. For armchair nanotubes, this will always be included since the discretization is along $\Gamma$-$M'$. Consequently, their band gap cannot be influenced by confinement effects. For zigzag nanotubes this is a possibility, but for the typical tube sizes simulated, the $k$ mesh in Eq. (1) will be practically dense and any dependence is extremely minor. We thus conclude that the band gap changes observed in Fig. 2 are purely an effect of the curvature induced by the bending of the atoms in the nanotube form.

To explore further the effect of curvature on the band gap, we have calculated the band gap for MoSTe armchair and zigzag nanotubes of different radii as displayed in Figs. 3(a) and 3(d). From this we can see that the band gap depends strongly on the radius of the simulated nanotubes and is seen to increase from a value below the band gap of 2D MoSTe to a value above, followed by a slow decay towards this limiting value. This behavior, which is in agreement with the results reported in Ref. [19], may be qualitatively understood from Figs. 3(b) and 3(e), which display the position of the valence and conduction band edge as a function of the radius of the simulated nanotubes. Evidently, the size dependence of the band gap is mainly attributed to the position of the conduction band edge, which, compared to the valence band edge, increases sharply as a function of the radius. Based on this, it is therefore natural to investigate the PDOS around the conduction band edge to determine what states are mainly responsible for the observed band gap sensitivity. The PDOS for selected armchair and zigzag nanotubes is shown in Figs. 3(c) and 3(f), and from these plots we see that the lower part of the conduction band is mainly composed of states with Mo $d$ character. We therefore conjecture that these states are particularly sensitive to the nanotube curvature, and a natural starting point for future work would therefore be to try and understand the origin of this sensitivity and whether or not
similar trends will be observed for Janus nanotubes based on other elements.

Another natural question to ask is whether the conclusions reported here hold when employing higher-level electronic structure methods and/or when including spin-orbit coupling. The latter is in fact known to heavily modify the electronic structure of many TMD monolayers [24,31] and is therefore particularly relevant. While not reported here, we have in fact performed band structure calculations for selected nanotube sizes with spin-orbit coupling included and found that while it does indeed lead to a modest change in the band gap of ~50 meV, this acts mostly as a constant shift across different nanotube radii. The conclusions reported in Fig. 3 are thus unchanged by the inclusion of spin-orbit coupling.

IV. CONCLUSION

We have investigated the band structure of armchair and zigzag 1H-MoSTe Janus nanotubes with special emphasis on understanding how these differ from that of their parent monolayer. By comparing the band structures of the most stable MoSTe tube size with those of the symmetric MoS2 and MoTe2 nanotubes and nanoribbons, we were able to separate the effects of quantum confinement and curvature, and we found that confinement effects were modest while curvature led to large changes in the band gap. We further analyzed the band gap changes by studying its dependence of the nanotube radius and found variations in the band gap of up to 0.5 eV with values both above and below that of 2D monolayer MoSTe. By investigating the position of the band edges and PDOS for different tube sizes, we found that these large variations are mainly attributed to the Mo conduction band d states.

Our study demonstrates that Janus TMD nanotubes can display remarkably different and tunable electronic properties compared to their parent 2D monolayers, which make them an interesting platform for computational materials screening targeting specific applications within materials science.

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Autonomous discovery of materials for intercalation electrodes
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Autonomous Discovery of Materials for Intercalation Electrodes**


The development of automated computational tools is required to accelerate the discovery of novel battery materials. In this work, we design and implement a workflow, in the framework of Density Functional Theory, which autonomously identifies materials to be used as intercalation electrodes in batteries, based on descriptors like adsorption energies and diffusion barriers. A substantial acceleration for the calculations of the kinetic properties is obtained due to a recent implementation of the Nudged Elastic Bands (NEB) method, which takes into consideration the symmetries of the system to reduce the number of images to calculate. We have applied this workflow to discover new cathode materials for Mg batteries, where two of these materials display a threefold increase in the potential of the Chevrel phase, the state-of-the-art cathode in commercial prototype Mg batteries.

1. Introduction

The prospects of substantial global warming calls for a transition towards a more sustainable energy infrastructure, based on the production of energy from renewable sources. Energy storage devices, e.g. rechargeable batteries, play a fundamental role in the transition from fossil fuels to renewable energy sources, as highlighted from the recent (2019) Nobel price in Chemistry awarded to Yoshino, Whittingham, and Goodenough.

Nowadays, Li-ion is the prevalent technology in electric vehicles and even used for stationary storage applications. While the concomitant development of portable electronics and that of the Li-ion technology are apparent, the ability of battery technologies to meet the necessary requirements cannot be taken for granted in other areas. Aside concerns on availability and cost of lithium and other critical raw materials (CRM), some general arguments could be raised against a potential generalized implementation of lithium based technology at large scale. Amongst the most promising alternative to Li-chemistries are the Na-ion batteries and analogous technologies based on multivalent cations like Mg²⁺, Ca²⁺, Zn²⁺ and Al³⁺.[1] The main drawback in Mg, Ca, Zn and Al batteries is related to the slow diffusion of multivalent elements, which drastically reduces the power performance. The foremost benefit is that for achieving a given capacity, the number of ions needed are reduced by a factor equal to the ion valence. This turns out in less stressed electrode materials and seemingly less degradation upon cycling. Multivalent electropositive metals include aluminum, zinc, calcium and magnesium. Aluminum, in spite of limited potential (2 V) and capacity (70 mAh/g) values,[2] Regarding calcium, initial studies show fast rate capability.[3] Arguably, the most interesting multivalent ion is magnesium, where significant progresses in performance has been achieved.[1] The state-of-the-art cathode in commercial prototype Mg batteries is the MoS₂ Chevrel phase, which is a covalent host where Coulombic interactions are reduced, favoring Mg ion diffusion.[4] However, the potential achievable from this cathode is rather low (≈ 1 V vs Mg/Mg²⁺). The discovery of novel cathode materials which can display higher potentials keeping, or even better improving, the ion diffusivity, is necessary to boost the Mg-ion technology.

Following an Edisonian “trial and error” approach to search for new materials is extremely time consuming and inefficient. During the last decades, quantum mechanical calculations, mostly within the framework of Density Functional Theory (DFT), have been efficiently used to predict properties and design novel materials for multiple applications. Recently, to accelerate the materials discovery, autonomous workflow schemes have been implemented[5–9] and more specifically for the discovery of battery materials, where a special focus was put on the kinetic properties, i.e. cation diffusivity.[10,11] Including the kinetic aspect in an autonomous workflow is rather expensive and, in most cases, some approximations need to be done to compromise between accuracy and computational cost, e.g. pinball model[12] or bond-valence calculations.[11]

These workflows are usually based on generic tools that in addition to enable the complex inter-dependencies of the workflow steps allow for an easier reproducibility and provenance of the data.[13,14] On one side, this helps researchers to share knowledge and expertise in the form of workflows, which
can be reused by others as well as extended to include more features, and from the other they solve many issues related with consistency and reproducibility of the data. Workflows, in fact, enable the creation of consistent data sets by setting all the parameters at the beginning of the project and being consistent with them.

Most of the design for new materials proceeds through a ‘funnel/sieve scheme’, where at each steps materials, which do not fulfill the desired properties, are discarded. In addition, the complexity of the calculations and their simulation cost increases at each step. Examples of funnel schemes and workflows for, e.g., visible solar light ferroelectric devices can be found in the literature. In these cases, materials are selected for their stability, light harvesting properties, and interfaces. The discovery of battery materials is not dissimilar from these examples.

In this work, we establish an autonomous workflow to identify intercalation electrodes in batteries. Although we specifically search for novel cathodes for Mg batteries, the workflow is general enough to allow for the discovery of both cathode and anode electrodes for other battery technologies. In detail, the workflow is based on descriptors calculated at the DFT level, such as volume change upon charge/discharge, which gives information on the stability of the cathode, Mg adsorption energy, which indicates the open circuit voltage (OCV), and diffusion barriers, which is a descriptor for the ion mobility at different charge states. For the first time in a workflow, the kinetic aspects are kept at the DFT level of accuracy.

2. Workflow Overview

Figure 1 gives a schematic view of the seven main components of the workflow. The input from the user consists of choosing input parameters as well as providing a list of materials, i.e. compositions and structures, that will be investigated. Additionally, a database containing reference structures for the evaluation of the stability of an input structure on the convex hull is needed. The reference structures workflow is separated from the general workflow for finding ion-insertion cathode electrodes but ensures a consistent choice of input parameters for the reference calculations. Subsequently, the workflow autonomously takes care of generating and relaxing all needed structures necessary to determine crucial battery material properties. The three properties currently calculated are the stability (volume change upon charging/discharging and the thermodynamic stability), the electrode potential (Mg-adsorption energy) and the ion diffusivity (Mg-diffusion barriers). The two latter properties are evaluated both at a low and high state of charge (SOC). With respect to other work recently published [15], this workflow accelerates the calculations of the ion diffusivity by making use of symmetry considerations. In the following, the steps of the workflow are discussed in more detail. The workflow is interfaced with the Atomic Simulation Environment (ASE). Moreover, it is intended to work with the VASP DFT code [16–20] as well as with the workflow management system MyQueue [21]. Efforts have been made to keep the workflow as general as possible in order to use the flexibility of ASE, which allows an interface with other DFT codes.

Figure 1. Structure of the workflow to identify suitable materials to be used as ion-insertion cathode electrodes in batteries. The workflow is divided into eight steps (middle row – General workflow). The steps prepare an optimization calculation (steps 3 and 6), optimize a structure (steps 1, 4 and 7) or check candidate materials for certain threshold values (steps 2, 5 and 8). The top row shows all the crystal structures created during the workflow given a reference unit cell, while the bottom row gives an overview of the output generated. Once that the initial input is given (crystal structure and composition) and the parameters are set up, the workflow autonomously proceeds through all the steps.
2.1. User Input

In addition to the list of materials to investigate, the user needs to define 4 parameters:

- **Ion**: The ion that will be studied which typically is an alkali or alkali-earth ion (i.e., Li, Na, K, Mg, or Ca).
- **Material ID**: A unique identifier for each structure that is used to avoid duplicate calculations.
- **Magnetic state**: The magnetic state parameter allows to study different magnetic starting configurations. This magnetic state is used for all structures throughout the workflow. The two options are the “non-magnetic” initialization or to initialize all ions “ferromagnetically”. The ferromagnetic initialization is carried out by initializing magnetic ions in a high spin state.
- **Nudged Elastic Band (NEB) path length**: The NEB path length determines the maximum linear distance between the initial and final site of the ion diffusing along the path. Paths that exceed this maximum length are neglected.

Three decision blocks are directly incorporated in the workflow scheme to decide whether to discard the candidate material or proceed with the calculations. The threshold values are given by the user deciding whether a material is suitable for further investigation or not, e.g., full computational OCV curve or experimental validation. These thresholds are the Potential threshold, which sets a requirement on the minimum average OCV, and the Diffusivity threshold, which favors the search for materials exhibiting low diffusion barriers (Figure 1). A Stability threshold can be given optionally by setting constraints on the maximum volume change upon discharging or the energy above the convex hull for the fully charged/discharged structures.

2.2. Calculations Steps

The potential materials investigated in the screening presented here are obtained from computational and experimental databases, such as the Materials Project, 

The Open Quantum Materials Database (OQMD), and Inorganic Crystal Structure Database (ICSD). All these materials have in common that the charge carrier (from now on, we explicitly write the charge carrier as Mg, although the workflow is not limited to identify cathode materials for Mg batteries) is present in the structure.

Therefore, the starting structure of the workflow is always a fully discharged cathode material, from which we are going to remove magnesium. The workflow presented here is, however, more general and it could also be used to discover cathodes where the charge carriers are not present and intercalate in the interstitial sites.

2.2.1. Structure Optimization

The first step is to relax the input structure (with all Mg-ions, fully discharged state); the calculation details are discussed in Section 5. In parallel, we calculate the same structure where we have removed all Mg-ions (deionized unit cell, optimized charged unit cell), as indicated in Figure 2. Both relaxations are carried out by the cell shape, volume and the atomic positions. From these two relaxations, it is possible to calculate the volume change in the charged and discharged states, which gives an indication on the mechanical stability of the battery. In addition, we relax a charged unit cell constraining its cell shape and volume. This is done by removing all Mg ions from the optimized discharged unit cell and scaling all atomic positions and the cell according to the ratio between the volume of the optimized charged unit cell and the optimized discharged unit cell, \( r = V_{\text{charged}} / V_{\text{discharged}} \). Subsequently, all atomic positions are relaxed while keeping the cell shape and volume fixed. This structure, referred to as discharged-constraint unit cell, is used for the calculation of the OCV at a high SOC as it is explained in more detail in Section 2.2.5.

2.2.2. Decision Point 1 - Stability

The volume change is calculated as [Eq. (1)]

\[
\Delta V = \frac{V_{\text{charged}} - V_{\text{discharged}}}{V_{\text{discharged}}}
\]

where \( V_{\text{charged}}, \, V_{\text{discharged}} \) are the volumes of the unit cell with/without Mg-ions, respectively. The energy above the convex hull \( E_{\text{hull}} \) is evaluated for both structures giving an indication on the thermodynamic stability of the fully charged and discharged structures. Large energies above the hull will have implications on the structures cyclability and synthesizability and might lead to unwanted conversion reactions. On the other hand, due to kinetic stabilization metastable structures can still lead to the discovery of viable electrodes which makes it difficult to define a threshold value upfront.

2.2.3. Preparation of the Structures with Mg-Vacancies

To limit possible errors associated with defect-defect interactions, we need to create a supercell, which is obtained by repeating the relaxed unit cell from 2.2.1 until it satisfies the condition that the spacing between two vacancies is at least twice the NEB path length, defined in the user input. To ensure relatively fast calculations, we have added an additional requirement on the number of atoms in the supercell, which should not exceed 200 atoms. If this limit is reached, the workflow will automatically reduce the NEB path length (vacancy spacing) parameter to ensure that the maximum number of atoms in the supercell is not exceeded. To save computational time and retain symmetries, we assume that the supercell is fully relaxed after its creation. Subsequently, each of the symmetry-in-equivalent Mg ions is removed one-by-one from the supercell structure. The newly created defective structures, with one Mg vacancy, are analyzed by the Symmetry Equivalence Check tool, as implemented in ASE. The tool is based on the recipe as explained in Ref. [30]. Symmetry in-
equivalent sites are checked for percolating paths. Possible diffusion paths are only accepted if intermediate images obtained through linear initialization between initial and final images do not get closer than 1 Å to any atoms in the host structure. If combining all possible diffusion paths does not lead to percolating paths, i.e. the ion cannot traverse through the full structure, the selected ion occupying the site is non-conductive. In such cases the structure is discarded.

Once that the symmetry in-equivalent sites have been identified, a similar procedure is used to determine the symmetry in-equivalent NEB paths by removing the initial and final Mg site of the path from the structure. Checking for symmetry in-equivalent vacancy defect pairs (possible NEB paths) at this point of the workflow allows us to rank the materials according to the number of NEB calculations which need to be performed to evaluate the size of the diffusion barrier. The NEB paths are also checked for reflection symmetry at this point. Reflection symmetry will result in a less computationally expensive NEB calculation as will be explained in 2.2.6.

One problem that is frequently encountered is the correct labelling of defect sites. Indices of structures change as soon as vacancy defects are created. In order to work around this issue we tried to work with scaled positions of defects instead of specific indices whenever possible. If indices for specific sites were used (i.e. initial and final site in the NEB paths) they always match the indices in the created supercell.

2.2.4. Optimization of the Vacancy Defect Structures

The optimization of the vacancy defect structures is carried out for the dilute vacancy limit (low SOC) as well as for the high vacancy limit (high SOC). For the dilute vacancy limit, a single Mg-vacancy is created by removing only the symmetry in-equivalent ions from the supercell. In this case, the cell shape and volume is kept fixed during the relaxation and only the atomic positions are optimized. In the limit of high vacancy concentration, only a single symmetry in-equivalent Mg is left in the supercell and the supercell is scaled according to the ratio between the volume of the optimized charged unit cell and the optimized discharged unit cell, $r = \frac{V_{\text{charged}}}{V_{\text{discharged}}}$.
(see also Figure 2). Therefore, in the limit of high vacancy concentration, the shape and the volume of the supercell is fixed during relaxation and all atomic positions as well as lattice parameters are scaled. By keeping the cell shape fixed, the symmetries from the dilute vacancy limit case are preserved and the reflection symmetries have not changed. This enables to use the advantage of a reflection symmetry (reflective NEB) during the computationally expensive NEB calculations, as explained in 2.2.6. The assumption of a fixed cell shape even for the low Mg concentration limit will not hold in situations where a rather drastic change in cell shape upon charging occurs. On the other side, such materials would most likely break all contacts in a real battery and it should probably be discarded, irrespective. This could be checked already during step 2.2.1.

2.2.5. Decision Point 2-Minimum Voltage

The calculations performed so far allow us to calculate the potential at different SOCs, which is a descriptor for the minimum voltage of the cathode electrode. The different charge states include the low SOC (removing a single Mg from the supercell), calculated as [Eq. (2)]

\[ V_{\text{low-SOC}} = \frac{(E_{\text{low-SOC}} + E_{\text{bulk-Mg}}) - E_{\text{discharged}}}{z} \]

(2)

where \( E_{\text{discharged}} \) is the DFT energy of the relaxed unit cell, \( E_{\text{low-SOC}} \) is the DFT energy of the supercell in the dilute vacancy limit, \( E_{\text{bulk-Mg}} \) is the DFT energy of a single Mg atom in its most stable bulk structure and \( z \) is the amount of electrons transferred (in the case of Mg, \( z = 2 \)), the high SOC (removing all but one ion from the supercell) calculated as [Eq. (3)]

\[ V_{\text{high-SOC}} = \frac{(E_{\text{charged-constrained}} + E_{\text{bulk-Mg}}) - E_{\text{high-SOC}}}{z} \]

(3)

where \( E_{\text{high-SOC}} \) is the DFT energy of the supercell in the high vacancy limit and \( E_{\text{charged-constrained}} \) is the DFT energy of the deionized unit cell with the same cell shape as the supercell in the high vacancy limit but with a scaled volume. The last charge state considered is the average OCV calculated as [Eq. (4)]

\[ V_{\text{average}} = \frac{E_{\text{charged}} + n \cdot E_{\text{bulk-Mg}} - E_{\text{discharged}}}{n \cdot z} \]

(4)

where \( E_{\text{charged}} \) is the DFT energy of the deionized unit cell and \( n \) is the amount of Mg ions in the discharged supercell. \(^{1}\)

\(^{1}\)Note: These expressions are valid only if the energies are expressed in eV.

2.2.6. Preparation of NEB Paths and Calculation of Diffusion Barriers

Methodologies to accelerate NEB calculations have been discussed in the literature. For instance, Rong et al.\(^{[12]}\) make use of an improved initial path guess over the usual linear initialization scheme and subsequently perform single point calculations on the images. They predict diffusion barriers that are within 20 meV compared to DFT calculations for Li systems. A different approach probes the potential energy surface (PES) using a gaussian process regression model to find the minimum energy path.\(^{[13,14]}\) In this work, we investigate the possibility of using the recently implemented Reflective-Nudged Elastic Band Method (R-NEB) for accelerating NEB calculations (see [17] for details about the implementation). In contrast to the two other methods, this does not approximate the PES but rather accelerates NEB calculations by considering symmetry operations to reduce the images to calculate.

The logic behind the preparation of the NEB path, in fact, decides which kind of NEB calculation to perform, as schematized in Figure 3 (a). All NEBs are run with ASEs internal NEB optimizer. We initialize the magnetic moments of all images using the information from the previously relaxed initial and final images. The total magnetic moment is forced to be the same in the initial and intermediate images. If no convergence is observed we remove the constraint of a fixed total magnetic moment and carefully inspect the structure visually after the workflow finishes for consistent magnetic moments.

The step 2.2.3 provides the necessary information about all the defect structures and their symmetries. A NEB path can be drawn by taking two of these structures, which are indicated as initial and final image. In case of the path not being reflective or the initial and final image not being symmetry equivalent, a conventional NEB is performed. We define a conventional NEB calculation as the process of setting up the initial and final structures followed by two separate relaxations of the initial and final image. After this, intermediate images, built through an interpolation of the initial and final relaxed structures, are added to the full path length (Figure 3 (b)).

If the initial and final image are symmetry equivalent the NEB path is tested for reflection symmetry. In three dimensions, the reflection symmetries can be reflective with respect to a plane (reflecting on one mirror plane), line (reflecting on two mirror planes), or point (reflecting on three mirror planes). If at least one reflection symmetry is found, we can perform a reflective-middle-image NEB (RMI-NEB) calculation. The RMI-NEB (sketched in Figure 3 (d)) is closely related to the Reflective NEB (R-NEB) method (sketched in Figure 3 (c)), which is also explained in Ref. [17]. In contrast to a conventional NEB where initial and final image are supplied, RMI-NEB needs only the initial image, as the final image can be created through symmetry operations from the initial image. This is schematically shown in Figure 3 (d) where the final image lies in the grey shaded area (dashed circle) indicating that the image has been created by symmetry operations rather than from a full DFT relaxation. Only one single image (middle image) needs to be calculated now. With respect to a conventional NEB run
Figure 3. (a) Logic for the preparation of in-equivalent NEB paths by including reflection symmetry considerations, with the goal of reducing the computational time needed to find the transition state. The four figures to the right sketch the principles of the different ways of running a NEB calculation including a conventional NEB (b), reflective NEB or R-NEB (c), reflective-middle image NEB or RMI-NEB (d) and the climbing image reflective NEB or CI-RNEB (e). The images that lay in the grey shaded area indicate that these images are not calculated explicitly but are created by using symmetry operations. This is done by running a recent implementation of the NEB method [17]. The two colored lines show an example of a truly bellshaped energy barrier (black solid line) as well as an energy barrier with two maxima (red solid line).

2.2.7. Decision Point 3-Ion Diffusivity and Data Collection

The final step of the workflow is to calculate the Mg diffusivity, which can be estimated from the Mg diffusion barriers obtained from the NEB method. At the end, all the structures, calculations, and estimated properties are collected and stored in a database.

2.3. Analysis of the Workflow

The workflow described here can be divided into three different layers, as indicated in Figure 4. The bottom layer contains scripts that directly interact with the calculation engine (VASP in this case) or other tools used to prepare and optimize the structures (ASE). Moreover, this layer includes all parameters used during the calculations, which are strictly connected with the simulation packages used. This layer is the least generic of...
the workflow, because it depends on the choice of code and parameters, decided by the user. This means that the middle layer of the workflow, or workflow layer, which contains the building blocks of the workflow, should allow the user to change any of the blocks of the bottom layer, e.g., the DFT code, without damaging all of the workflow structure. The workflow layer can be structured in three different blocks: a prepare block that prepares the structure to calculate and includes the logic to extract the symmetry equivalent structures; an optimize block that directly accesses the simulation tools and setups to optimize the various structures; and a decision block that acts at the decision points of the workflow and decides whether a material should be considered as a potential candidate for further calculations. The top layer consists of the workflow management system as well as the script to collect the generated data. Various workflow management systems have been implemented to be used in connection with materials science (e.g., AiiDA [13] or Fireworks [14]). In our case, we use an in-house tool called MyQueue, [22] which deals with all the operations to submit (and resubmit failed) calculations as well as setting up the dependencies between the different steps of the workflow. Additionally, we included specific instructions on how to restart automatically failed or timed out calculations throughout the workflow similar to the CUSTODIAN package as implemented in Pymatgen. [36]

3. Practical Application: Cathode Materials for Mg-ion Batteries

We used this workflow to find novel candidate materials to be used as cathodes in Mg-ion batteries. As the aim of this work is to describe the implementation of the workflow, we show, as a proof of concept, only a small subset of the possible materials that can be calculated.

Mo$_3$S$_8$ in the Chevrel phase (MgMo$_3$S$_8$, shown in Figure 5 (a)) is currently the state-of-the-art for commercial prototype Mg cathodes as it can accommodate Mg$^{2+}$-ions for hundreds of cycles at stable potentials and charge capacities. [4] This phase is chosen as the benchmark material and its diffusion and OCV properties provide the necessary input thresholds needed for the workflow.

![Figure 4. Different layers of the workflow.](image1)

![Figure 5. Unit cells of the six candidates investigated. The Mg$^{2+}$ ions are inside the polyhedron to visualize differences in coordination. Shown are the Chevrel Phase, MgMo$_3$S$_8$ (a, Materials Project-ID: mp-677217); Spinel structures, Mg$_8$V$_2$O$_{16}$ with B = [Ti, V, Mn] (b: ICSD-65729, c: ICSD-60412, d:ICSD-290660); and Garnet structures, Mg$_3$B$_2$(SO$_4$)$_3$ with B = [Cr, Mn] (e: ICSD-77432, f:ICSD-27374). The Mg$^{2+}$ ion occupies a tetrahedral site in structures (a-d). In the Garnet structures (e,f) Mg$^{2+}$ has eight closest oxygen neighbors. The structures are visualized using VESTA. [46]](image2)
considered structures comprise three different crystal groups which are shown in Figure 5.

3.2. Results

The discharged structures in this study are known to exist and therefore show energies below 0.1 eV above the hull (Figure 6). For the charged structures especially the silicates exhibit larger energies above the hull of more than 0.4 eV. This might indicate poor stability upon charging the battery using this type of cathode as unwanted conversion reactions might occur. As expected, all materials show the tendency to reduce their volumes upon charging (Mg is removed), as shown in Figure 7 (a). The Manganese Spinel structure (\(\text{Mg}_2\text{Mn}_4\text{O}_8\), Figure 5 (c)) shows the largest distortion among the studied materials. This has been already discussed in literature and has been referred to the filling of higher energy anti-bonding e\(_g\) orbitals for Mn upon reduction as the lower energy t\(_{2g}\) anti-bonding orbitals are fully occupied leading to larger volume changes (this is not the case for other elements, such as Ti, for which free lower energy t\(_{2g}\) orbitals can be occupied).\(^{35,40}\)

The OCVs indicate that all materials have a higher average OCV than the Chevrel phase (Figure 7 (b)). The voltages lie in between a range of 1.3–4.5 V making these materials interesting as Mg cathodes as the OCV is higher than the benchmark material. The only exception is MgTi\(_2\)O\(_4\) (Figure 7 (b)), which has a calculated voltage below the average voltage of the Chevrel phase at a low SOC. Since all materials fulfill the first requirement (average OCV larger than the OCV for the Chevrel phase), we proceed with investigating the Mg-diffusion using NEBs.

The barriers calculated for the benchmark material MgMo\(_3\)S\(_4\) are \(\sim 750\) meV at a low SOC and \(\sim 940\) meV at a high SOC (Figure 8(a) + (b)). They suggest that the multivalent Mg\(_2^+\)-ions are more mobile at a low SOC, i.e. a structure with a high concentration of Mg\(_{2^+}\). The Chevrel phase is the only material that has its transition state barrier at the middle image for the high and low SOC structures. This means that in this case evaluating the barriers using the RMI-NEB method results in the same barriers as obtained using the CI-RNEB method. The Spinel structures (\(\text{MgTM}_2\text{O}_4\), TM = \{Ti, V, Mn\})) show low transition state barriers at the middle images (\(\sim 30–420\) meV). Higher mobility is again observed at a low SOC in agreement with what has been found in recent NEB studies on Spinel structures (e.g. \(\text{MgMn}_2\text{O}_4\) in [35]). Although these barriers are significantly lower than the ones for the benchmark material, the transition state is not found at the middle image which becomes obvious when looking at barriers obtained using a climbing image in Figure 8 (b) (\(\sim 320–660\) meV). NER calculations reported in the literature indicate a barrier shape with two maxima, as can be seen in Ref. [35]. The RMI-NEB method thus fails to find such a global maximum (as described in details above, Figure 3 (d)). The reason behind this shape of the barrier is the diffusion topology, which results in the Mg\(_{2^+}\)-ion diffusing from an initial tetrahedral site through an octahedral intermediate coordination to its final site which is also tetrahedral. In the case of MgTi\(_2\)O\(_4\), the intermediate octahedral
site has a lower energy than the initial and final tetrahedral site. This is indicated by formulas marked with an asterisk (*) indicates that the middle image is lower in energy than the initial and final state.

The two silicate structures (Mg$_3$Si$_2$O$_6$, TM = Cr, Mn)) have low transition state barriers at the middle images for a high SOC (below ~100 meV, where the middle image of Mg$_3$Cr (SiO$_3$)$_2$ is again lower in energy than the initial image). The barriers found using the CI-RNEB are again larger, indicating the transition state does not coincide with the middle image of the path. The diffusion is significantly slower at a low SOC, as shown by the higher transition state energy barrier above 1 eV. This is similar to olivine structures studied in the literature (FePO$_4$) which also show larger diffusion barriers for moving multivalent ions at a low SOC compared to the diffusion barriers at a high SOC. By investigating the middle image from the RMI-NEB calculation and comparing the middle image at a low and high SOC, we note that at a high SOC, less Mg$^{2+}$-ions compete to attract the negatively charged O$^{2-}$-anions. The Mg–O bonds between the diffusing Mg$^{2+}$-ion and its closest oxygen neighbors are approximately 10% shorter for the middle image in the high SOC, compared to the low SOC case, which leads to a more stabilized structure and therefore a lower barrier. The lower transition state barrier might also be a result of the rather unstable charged phase of the silicates (E$_{\text{hull}}$ in Figure 6). A more detailed study on the stability and possible conversion reactions is probably needed.

Within the same crystal symmetries, the materials show similar trends for the height of the diffusion barriers: the Garnet structures show a significantly slower diffusion of Mg$^{2+}$ upon discharging whereas the diffusion barriers of the Spinels are much closer in energy for the high and low SOCs. This indicates that calculating diffusion barriers (and their shapes) for a few representative structures from each crystal group can be a useful approach to accelerate the materials discovery. These trends can be used to select the most promising crystal structures to study using the workflow proposed here. The energy barriers for a single diffusing Mg-ion in the studied oxide systems are thus governed by the diffusion path, which is specific for each crystal symmetry, as already reported in the literature. In contrast, the OCV and volume changes are governed by the Red-Ox properties of the transition metal.

4. Conclusions and Perspective

We have presented a workflow based on DFT calculations, which autonomously identifies candidate materials to be used as intercalation electrodes in batteries. The workflow is composed of different steps, where the volume change and thermodynamic stability upon charging, the OCV at different charge states and the NEB diffusion energy barrier at high and low SOC are calculated. This workflow has been tested to identify possible cathode materials for Mg batteries, which can improve the performance (faster Mg$^{2+}$ diffusion and higher OCVs) of the Chevrel phase; the most common cathode material in Mg batteries. In addition to identifying candidate materials, the workflow can provide quick insights, useful to investigate trends that can even further accelerate the discovery of novel materials. The workflow is continuously developed and may be accessed at https://gitlab.com/asc-dtu/workflows/ion-insertion-battery-workflow. The structures presented in this work are available on FigShare.  

We would like to point out that the workflow is a useful tool for an autonomous screening approach that gives insights in diffusion properties of materials, since calculating diffusivities...
is typically the most expensive part computationally, as well as manually going through and setting up the calculations. The workflow is not a universal tool for studying any cathode material and so far it only works for materials that have the cation inside the structure. We are currently working on extending it to include the following features:

- The workflow is not able to find the correct magnetic state ordering for all structures. Initializing all magnetic ions in a high spin state lead to satisfactory convergence for the materials shown but also failed to find the correct spin state for specific cases. We are currently working on finding a more automated way to find the correct magnetic ordering leading to the minimum energy configuration.
- Until now we only removed Mg ions from a structure that had the ion already inserted. It is in principle also possible to include structures where Mg is added into the interstitial sites and feed that structure to the workflow presented here. This would enable us to study crystal systems like 2-D layered structures without making changes to the workflow.

**Computational Details**

The computational details refer to the example described here in section 3.5, and can easily be modified. All calculations have been performed using the Vienna Ab-initio Simulation Package (VASP) using a plane-wave basis set. The exchange and correlation effects are approximated using the Perdew-Burke-Ernzerhof revised for solids (PBEsol) functional. An energy cut-off of 520 eV was applied to describe the valence electrons. Sampling the Brillouin zone is done using a k-point density \( \approx 4.7 \text{ Å}^{-1} \). As a required convergence criterion all forces on the movable nuclei had to be less than 0.03 eV/Å. To account for the self interaction error in the \( d \) orbitals of the transition metal oxides a +U correction is applied with the values taken from the Material Project database, i.e. \( U_{\text{eff}} = 3.25 \text{ eV}, \text{ } U_{\text{Mg}} = 3.7 \text{ eV}, U_{\text{Mn}} = 3.9 \text{ eV}\). In the calculation for the convex hull, the reference for oxygen in the gas phase is approximated using the approach suggested by Rossmäsl et al., where the energy of oxygen at 0 K is calculated as the difference in energy of water and hydrogen molecules in gas phase, including the zero point energy (ZPE) corrections.

All NEB simulations have been calculated using the GGA-PBEsol functional. The R-NEB method was applied as implemented in the Atomic Simulation Environment package (ASE), whenever reflection symmetry in the path is observed. As a required convergence criterion all forces had to be less than 0.05 eV/Å. The +U correction penalizes the energy of the transition state since it is a less localized state than the initial and final state. Thus, we do not apply a +U correction to the NEB calculation as also discussed in Ref. [35]. The distance between repeating defects in the supercells is always larger than 9 Å to avoid defect-defect interaction errors.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords:** Mg-Batteries - Autonomous discovery - Workflow - Cathodes - Density Functional Theory

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Paper IV

Topological descriptors for predicting kinetic barriers in magnesium cathode materials
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To be submitted
Topological descriptors for predicting kinetic barriers in magnesium cathode materials

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Abstract

Stable and fast ionic conductors for magnesium cathode materials have the prospect of enabling high energy density batteries beyond current Lithium-ion technologies. So far, only a few candidate materials have been identified leading to data only being scarcely available. One of the reasons is the long time it takes to quantify ion conductivity computationally. This limits the development of simple descriptors that can predict ion conductivity. Here, we present a systematic screening study, in the framework of Density Functional Theory, including the estimation of the diffusion barrier for 16 materials through employing Nudged Elastic Band (NEB) calculations. By introducing a path finder tool based on the idea of Voronoi tesselations, we show that an estimate of the transition state configuration can be extracted prior to running NEB-calculations. Using geometrical descriptors in combination with a Principal Component Analysis it is possible to further subdivide the NEB-paths into diffusion topology groups. We show that this approach also extends to materials which...
are not part of the screening study, making it a viable approach to more efficiently explore crystal structures with distinguishable diffusion characteristics.

1 Introduction

Multivalent Magnesium batteries hold great promise through increased energy densities. [1] Finding suitable cathode materials has been difficult since diffusivity is hampered by the increased charge state of magnesium. In terms of stability, the state-of-the-art material is the Mo$_6$S$_8$ Chevrel phase being stable over hundreds of cycles. [2] Since its discovery, high cycling performance has been reported for other cathode materials like the thiospinel Ti$_2$S$_4$ structure. [3] Nevertheless, major drawbacks like the low voltages and weak stability properties remain. [4]

Although rather scarce, screening studies have successfully been conducted using ab-initio molecular dynamics (AIMD) simulations [5] as well as Density-Functional Theory (DFT) based NEB methods [6] to predict the diffusivity in ion insertion materials. One of the main bottlenecks for the screening studies is undoubtedly the computational time it takes to conduct the calculations. In order to more efficiently explore the possible phase space of ionic conductors, one possibility is to find descriptors for NEB-paths being able to quantify and describe the distinct diffusion topology of a unique path.

Previous studies have used few representative structures with distinct diffusion topologies to derive rules for the diffusivity in multivalent magnesium battery materials. [7, 8] Geometrical investigations in combination with cheaper computational methods based on Bond Valence Site energies [9] or DFT calculations on a few selected structures [10] discussed the importance of being able to describe the geometry of the transition state along the diffusion path in order to predict kinetic barriers. One of the advantages of using DFT calculations is to be able to quantify the effect of ionic and electronic relaxations on the migrating ion needed to get a better estimate of the barrier. [11]
A geometric analysis of, e.g. porous materials, can be done through employing a Voronoi tesselation. [12, 13, 14] While Voronoi tesselations find high symmetry points in space, here we show that these points do not necessarily have to coincide with the transition state geometry found in NEB calculations. Therefore, we introduce a path finder tool extending on top of the ideas of Voronoi tesselations. The tool can extract descriptors quantifying the transition state geometry without having to relax the diffusion path. It solely requires a relaxed supercell leading to a speed-up of approximately three orders of magnitude compared to running the full NEB-calculations. Additionally, it can also be used for other techniques than the NEB method. In order to test the tool, we conduct a screening study and determine kinetic barriers for 16 different magnesium cathode material candidates. Using descriptors extracted from the initial and transition state configuration of the path, we discuss how to more efficiently guide screening studies when searching for good ionic conducting cathode materials.

2 Methods and Theory

2.1 Workflow for obtaining NEB-barriers

The workflow for obtaining NEB-barriers has been described in detail in our previous work. [15] Here, we only calculate NEB-paths that posses a reflection symmetry, i.e. all images along the path can be mapped onto a symmetry equivalent image through a reflection operation. Initial Reflective Middle Image-NEB (RMI-NEB) barriers are calculated for all paths, followed by a Climbing Image NEB (CI-NEB) calculation, if the difference in energy between the middle and the initial image is less than 2 eV (for details see Ref. [15]).
2.2 Initial pool of materials

Initially we consider all ICSD [16] structures as found in the materials project database [17] containing at least three different elements including (1) a metal \( M = \{ \text{Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Mo, Sn, Sb, Pb, Nb, Zr} \} \), (2) an anion \( A = \{ \text{O, N, S, Se, Te, Cl} \} \) as well as (3) either Mg or Zn. Zn containing structures are included due to the similar valence and ionic radius of Zn\(^{2+}\) and Mg\(^{2+}\). These criteria lead to 304 initial structures out of which 105 contain Mg and 199 contain Zn. Ensuring that at least one percolating path for the Mg ion exists (i.e. ion is not trapped inside the structure) as well as only considering structures in which the metal atom does not exceed its maximum oxidation state upon fully charging the electrode, reduces the amount of possible structures to 105. We denote a structure a duplicate, if upon exchanging Zn with Mg in the Zn-containing structures, the chemical composition as well as spacegroup match. A NEB path connects the two structures with the moving ion residing in the initial and final site, respectively. Geometric interpolation in between the initial and final configuration leads to intermediate images along the diffusion path. A path is marked as non-percolating if upon linear interpolation in between the initial and final configuration any of the images contain atom-atom distances below 1 Å. This leaves us with a total of 77 structures serving as an input for the workflow described in Ref. [15].

Upon initial relaxation of the unit cell with the chosen input parameters, 18 more structures are discarded due to the convex hull threshold of 0.5 eV/atom being exceeded by the fully charged unit cell. Additionally, some of the structures are marked as non-percolating since the relaxation of atomic positions leads to structural changes.

Carrying out a symmetry analysis on the remaining 59 structures reveals that in total 238 symmetry inequivalent possible diffusion paths exist (see also Figure 1). More than half of the paths are reflective, making the R-NEB method especially useful to fully characterize more paths while using less computational resources.

Even though the R-NEB method improves the speed of relaxing the NEB-paths, 238 paths
are still extremely computationally expensive. Additionally, we do not consider structures with partial occupancies easily leading to more than the maximum number of symmetry inequivalent paths found in the more symmetric materials in this study. Here, we use a subset of the structures which have at most four symmetry inequivalent paths and at least one percolating path consisting of solely reflective paths. In this way, it is possible to characterize as many different crystal structures in terms of their ionic diffusivity while obtaining a diverse dataset. Due to stability reasons, we further disregard structures containing Nitrogen as an anion. In more detail, we relax 40 symmetry inequivalent reflective NEB-paths obtained from 16 different materials ranging over 10 different spacegroups. We further classify the different materials into structure groups including: spinel (8 structures), garnet (3), layered (2, Mg₃Nb₆O₁₁ and MgMn₃O₇), chevrel (1), P₄₂/mnb (1, Mg(SbO₂)₂) and Pnma (1, MgSb₂Cl₂O₃).

Figure 1: Comparison of the number of total paths with the number of paths that are reflective within each individual structure.
2.3 Structural descriptors

Structural and chemical descriptors describing the ion mobility in bulk structures have been discussed extensively in literature. [18, 8, 19, 9, 20] Three main contributions to the barrier obtained from DFT calculations have been identified to be electrostatic interactions as well as electronic and ionic relaxation effects. [21, 11, 22] Relaxed NEB-paths allow to study the effect of electronic and ionic relaxations in the structure. Additionally, the transition state can be investigated structurally which is not possible when only considering electrostatic interactions in an immobile host framework. [9] In this work we investigate simple descriptors that correlate with the NEB-barrier and therefore also with the structure of the transition state. It is highly desirable to find descriptors that can be directly derived from the relaxed supercell, since this is the least expensive calculation of the workflow. Rough estimates on whether or not the barrier might be below a certain threshold are acceptable in a screening study, as long as the needed descriptors are fast to calculate. In order to describe the transition state before relaxing the NEB path, we introduce a path finder tool that predicts a transition state geometry given the stable insertion sites (E$_s$) of initial and final position of the moving ion in the path as an input. It is based on the observation made in literature, that often the critical radius, corresponding to the largest free sphere radius possible along the path is crucial (see also red circle in Figure 2 (a)). [9, 20] Following the ideas of connecting initial and final site through Voronoi node and edges, the path finder tool proceeds as follows:

1. Start from the initial position;

2. Find possible unoccupied ion sites (possible intermediate sites E$_i$) using a Voronoi tesselation of the structure as implemented in pymatgen [23] including clustering and removing collisions of Voronoi nodes with a tolerance of 1 Å;

3. Identify all nearest neighbors of the ion at the current position using O’Keeffe’s method
Figure 2: (a) Estimation of the critical radius using the Chebyshev center in a three-coordinated face consisting of atoms with the two different radii $r_A$ and $r_B$. (b) Motivation for including bridge sites when finding transition state geometries. Given four atoms arranged in a rhombus like shape, the consideration of only Voronoi vertices leads to identifying three nearest neighbors while including the bridge site leads to four nearest neighbors.

To obtain the Coordination number (CNN) defined as: [24]

$$CNN = \sum \frac{\sigma}{\sigma_{max}},$$  \hspace{1cm} (1)

where $\sigma$ is the solid angle and $\sigma_{max}$ defines the neighboring atom whose polyhedron site subtends the largest solid angle. Following the recent findings on benchmarking nearest neighbors algorithms by Pan et. al., we consider an atom a neighbor if the solid angle is larger than 50% of the maximum solid angle, i.e. $\sigma > 0.5 \times \sigma_{max}$. [25];

(4) Create faces enclosing the current position;

(5) Investigate each face found in step (4) and find the center ($E_a$). In order to account for possible unequal ionic radii on the edges of the face, we define the center as the Chebyshev center of the face, which is the largest inscribed circle within a polygon (see Figure 2 (a)). For creating the polygon for which the Chebyshev center is calculated,
all vertices of the face are considered. From each vertex, a line is drawn from the
center of the atom site with an angle $\theta/2$ that intersects with the circle representing
the atomic radius (orange crosses). $\theta$ is the angle spanned by the two edges intersecting
at the vertex. The tangent on the ion going through the orange crosses makes up the
dges of the inner polygon for which the Chebyshev center is calculated;

(6) Investigate each edge of the face at the center in between the two vertices again con-
sidering ionic radii. Find the CNN at this "bridge site" according to the definition in
step (3) (see also image on top in Figure 2 (b)). If the CNN is larger than the CNN
at the Chebyshev center, choose the bridge position;

(7) Consider all valid bridge and Chebyshev center and choose the position that minimizes
the distance to the final position;

(8) Consider the next position, being either an accessible unoccupied site $E_i$ or the final
position. If an unoccupied site is accessible, repeat steps (3) - (8) until final position
is reached.

The critical radius along the path is then defined as the minimum radius of a sphere
in all possible bridge and face positions along the path. Moreover, this position is then
denoted as possible transition state configuration. Considering the bridge site is motivated
through the example shown in Figure 2 (b). The atom sites are arranged in a rhombus.
The Voronoi tesselation identifies the Voronoi vertex as a possible transition state of the
face under investigation (grey shaded triangle). A secondary Voronoi tesselation around
this vertex results in three nearest neighbors. Applying the Voronoi tessellation around the
bridge site at the center of the rhombus (Figure 2 (b) case "(2) include bridge site") leads
to four nearest neighbors being identified. While this case only shows a simplified example
in 2D, the approach directly translates into three-dimensional spaces. For instance, we find
that the transition state configuration for the Chevrel phase can be best described through

8
3 Results and Discussion

The path finder tool is able to give a good estimate of the unrelaxed transition state geometry based on solely the relaxed supercell. This is important, since it allows to study features of the unrelaxed initial and transition state of the NEB path. For instance, for the case of the spinel structure, the path finder tool takes as an input the initial and final positions of the Magnesium ion residing in a tetrahedral coordination. As a results, it predicts the path to traverse through a triangular face, into an octahedral unoccupied site. From this intermediate state it subsequently traverses through a second triangular face to the final position of the NEB path. The critical radius is predicted to be found at the triangular faces in agreement with literature. [7, 8]

The considered activation barriers obtained from the CI-NEB calculations for the 40 paths range from 0.23 eV up to 1.42 eV. The lowest barrier is obtained for one of the symmetry inequivalent paths of the Chevrel phase, which is known to be a working cathode with reasonably fast magnesium-ion diffusion rates. [2] Interestingly, the path finder tool finds for the Chevrel phase, that the transition state is located at a bridge site (see Figure 2 (b)). While the face is three fold coordinated, investigating the bridge site leads to four nearest sulfur neighbors being accessible. The fourth nearest neighbor is in fact a coordinating atom of the final site. We note that while this is the only material in the dataset that exhibits this geometrical feature, it coincides with the smallest barrier observed. It is therefore a specific geometrical characteristic that can be exploited automatically through using the presented tool.

Using DFT-NEB calculations allows us to study electronic and ionic relaxation effects on the transition state, which have been found to impact the barrier. [21, 22] This information is not
accessible when using methods that assume the host structure to be immobile (i.e., Bond Valence Site Energy methods [9]). As a possible descriptor for studying these effects we use the root mean square deviation (RMSD) in between the first-shell nearest neighbor anionic positions (anion_{NN} according to equation 1) of the initial and relaxed supercell structure upon vacancy defect creation. The mobility of nearby anions is expected to directly influence their ability to stabilize the transition state. This feature still circumvents relaxing the full NEB-path.

In order to study the statistical relationship of the structural distortions of the coordinating anions on the barrier, Pearson correlation coefficients are calculated. Separating the spinel structure group (accounting for 24/40 data points) from the remaining five groups leads to a medium correlation with a Pearson coefficient of +0.37. Magnesium can attract anions more easily in the dilute vacancy case leading to a stronger distortion. At the same time, the decreased volume upon removing all remaining magnesium ions increases the kinetic barrier for spinel structures. Conversely, the Pearson correlation coefficient for the remaining five groups when plotted against the barrier is -0.24. This trend can be explained by taking for instance the garnet structures, for which the increased ion mobility at the charged states leads to a stabilization of the transition state and therefore lower barriers. In the case of the garnet structures in the charged state, the increased anion mobility can also be directly related to the weak stability, i.e., the convex hull energies are above 0.35 eV/atom. When choosing to correlate all barrier values obtained in this work, the Pearson coefficient suggests only a very weak correlation of -0.07 (see Table 1 - feature 7). In addition to the dataset being rather limited in terms of data points, this clearly indicates that it would be beneficial to group the symmetry inequivalent NEB paths in order to find relations to similar path geometries and structure groups.

One approach to visualize possible clusters of similar NEB-paths can be obtained through a Principal Component Analysis (PCA). PCA is a technique to find a lower-dimensional
Table 1: Pearson Correlation coefficients for seven different features measuring the correlation with the kinetic barrier obtained through the NEB-calculations. The anion$_{NN}$ contain all first-shell anionic nearest neighbors obtained using equation 1. Features 1 - 6 are considered for the Principal Component Analysis.

<table>
<thead>
<tr>
<th>Feature</th>
<th>Pearson correlation coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Minimum ion-anion$_{NN}$ separation distance initial configuration</td>
</tr>
<tr>
<td>2</td>
<td>Maximum ion-anion$_{NN}$ separation distance initial configuration</td>
</tr>
<tr>
<td>3</td>
<td>Minimum ion-anion$_{NN}$ separation distance transition state</td>
</tr>
<tr>
<td>4</td>
<td>Maximum ion-anion$_{NN}$ separation distance transition state</td>
</tr>
<tr>
<td>5</td>
<td>Minimum ion-atom$_{host}$ separation distance transition state</td>
</tr>
<tr>
<td>6</td>
<td>Change of CNN between initial and transition state</td>
</tr>
<tr>
<td>7</td>
<td>Distortion of anion$_{NN}$ atoms upon vacancy creation</td>
</tr>
</tbody>
</table>

representation of a high-dimensional dataset while maximizing the variance captured by the different descriptors in the dataset. Here, we try to use a minimal set of descriptors given the limited amount of data points. Geometric descriptors have been found to be most relevant for finding fast lithium-ion conductors. [26] The barrier is calculated as the total energy difference between the initial and transition state configuration. If a path is symmetry inequivalent, at least one of these configurations is most likely structurally unique. Using the unrelaxed transition state configuration $E_a$ obtained from the path finder tool as well as the initial unrelaxed configuration $E_s$ we extract for both configurations a total of six geometrical descriptors given in Table 1 (features 1 - 6). While searching for nearest neighbors using a Voronoi tessellation finds all atoms in the first neighbor shell, it does not contain information on possible interactions with elements in the second nearest neighbor shell. Therefore, we also include the minimum ion-atom$_{host}$ separation distance where the atom$_{host}$ structure comprises all elements that are not an anion$_{NN}$ or the moving species. Finally, the change of coordination number in between the initial and transition configuration is included which has been found to be correlated to the barrier. [1] In general, we find a better correlation
between the barrier and the local geometry for the transition state (Features 4+5 < -0.3) than the initial state (Features 1+2) underlining the importance of describing the transition configuration when trying to estimate the associated kinetic barrier of the path. All six features are readily available and only require the relaxation of the supercell.

Figure 3: PCA analysis of the six descriptors based on the unrelaxed initial and transition state configuration. The grey square indicates the structure \(\delta-V_2O_5\), which has been discarded during the screening process before estimating kinetic barriers.

Figure 3 shows the PCA analysis using the six discussed descriptors for the symmetry inequivalent NEB paths. The two first components of the PCA carry \(\sim 94\%\) of the variance in the data meaning it is reasonable to visually inspect the data projected on only two dimensions. The different crystal groups spinel, chevrel, layered and garnet appear well separated. Additionally, the two symmetry inequivalent paths found in the Chevrel structure appear separated. Especially the smallest barrier found in the dataset for the path in the
dilute vacancy limit for the Chevrel structure can be distinguished from paths with larger barriers (blue point in group marked as "Chevrel" in Figure 3). The separation of data points for the Spinel group can be mainly attributed to the different anions O, S, Se and Te. All spinel compounds containing oxygen are lumped together on the left hand side due to the short bond length distances Mg-O. For spinel compounds, larger anions (S, Se and Te) lead to improved ion diffusivity due to an increased critical radius. [27] All barriers for the NEB paths in the Spinel group are found to be 0.8 eV at most, while all 24 paths only differ by 0.47 eV. Thus, adding additional data points from other Spinel compounds falling in the same area will only add minor information.

An example of how to use this approach to more efficiently find new structures that have not been explored is to look at areas, where data points are sparse or the barrier values vary in between data points close by. The latter indicates that the given descriptors do not capture all information necessary to determine the barrier which will be the topic of a subsequent study. For instance, NEB barriers of the five paths of the group of layered materials differ by 1.0 eV. Nevertheless, we find the material Mg₃Nb₃O₁₁ to have percolating paths with low barriers. In the dilute vacancy limit (discharged) the NEB barrier is 0.42 eV, while at the high vacancy limit (charged) it is 0.53 eV. To fully characterize this structure and its ionic conductivity, all non-reflective percolating paths need to be investigated which is beyond the scope of this study.

In order to test that the approach also works beyond the structures in the dataset, we include the δ-phase of the known cathode material V₂O₅ [28, 29] in the PCA analysis. Initially, this structure was removed during the screening process, since upon linear initialization of the path the moving ion is closer than 1 Å to an anion along the path. The path finder tool finds the transition state configuration at the three-coordinated oxygen face in accordance with literature. [8] Additionally, it finds the intermediate "square pyramid" site as an accessible unoccupied site. Replacing the linear initialization guess with the found intermediate states from the path finder tool can be seen as a viable approach to also find initial curved
path guesses for the NEB calculations. The added data point of the $\delta$-V$_2$O$_5$ structure in the PCA analysis (grey square in Figure 3) is in close vicinity to Mg(SbO)$_2$ ($P4_2/mbc$ - 0.81 eV barrier in the discharged state) and MgSb$_2$Cl$_2$O$_3$ ($Pnma$ - 0.88 eV barrier in the discharged state) that both have 1D-like diffusion channels, although $\delta$-V$_2$O$_5$ is a pseudolayered material. Published literature on the NEB-barrier for similar DFT input parameters (PBE instead of the chosen PBESol functional here) suggests the barrier at the discharged state to be at around $\sim$ 0.8 eV, which is in good agreement with the points close by. This underlines the importance of being able to group NEB-paths based on unrelaxed structures as it allows to focus on identifying new diffusion topologies (data points in close vicinity to others) or mechanisms enabling fast diffusion in similar topologies (e.g. lowered barrier for the garnet structure in the charged state enabled through high anion mobility).

4 Conclusion

We have conducted a screening study of the kinetic properties of magnesium diffusion in bulk cathode materials using the NEB method. 16 different materials were calculated resulting in a dataset containing 40 symmetry inequivalent diffusion paths. The anionic framework of the materials consisted of either O, S, Se, Te or Cl. In order to extract relevant descriptors for the NEB barrier, we introduce a path finder tool that takes as an input only the position of the initial and the final site of the moving ion. The tool is able to estimate a transition state configuration solely based on the relaxed supercell which gives a significant speed-up compared to calculating the relaxed transition state in screening studies. Investigating the relation of the distortion of the anionic framework upon vacancy defect creation to the barrier, reveals the importance of being able to distinguish NEB-paths into sub-groups. While the strong distortion of the anionic framework lowers the NEB barrier for garnet structures, it is non-beneficial to the diffusivity in the case of the spinel structures.

Extracting six geometrical descriptors from the initial and transition state configuration a
PCA analysis was carried out. We find that PCA can help to find sub-groups with similar diffusion topologies. In detail, we find that such an approach can support a more efficient screening study through: (1) Identifying points in the reduced-dimensionality space that are in no close vicinity to any other points, indicating a possible new diffusion topology in the dataset; (2) Finding points that are in close vicinity but show significant differences in the observed barriers pointing towards peculiarities in the ion migration. For instance, we find the latter case for the garnet structures. This study paves the way for more efficient screening studies when searching for fast ionic cathode conductors through employing simple but informative descriptors that can lead to a speed-up on the order of three-magnitudes compared to running the full calculations.

5 Computational Details

Density Functional Theory calculations were performed within the Perdew-Burke-Ernzerhof revised for solids (PBEsol) functional [30, 31] using the Vienna Ab-initio Simulation Package (VASP). [32, 33, 34] The energy cut-off for the plane wave basis set chosen is 520 eV. To sample the Brillouin zone, we ensure a k-pointdensity $> 4.7 / \text{Å}^{-1}$ and the forces on each atom are converged under 0.03 eV/Å. In order to reduce the Coulombic self-interaction error we employ a Hubbard $U$-correction [35] on the $d$-orbitals of the transition metal in structures containing oxygen (values taken from the materialsproject [23]): $U_{V} = 3.25$ eV, $U_{Co} = 3.32$ eV, $U_{Cr} = 3.7$ eV, $U_{Mn} = 3.9$ eV, $U_{Mo} = 4.38$ eV, $U_{Fe} = 5.3$ eV, $U_{Ni} = 6.2$ eV.

For estimating the phase stability of the structures, we construct the convex hull from all known stable structures as found in the materialsproject database and calculate the convex hull energy of the phase of interest. [23] The gas phase reference energy of oxygen at 0K is related to the energy difference between gas phase water and hydrogen molecules including the zero point energy corrections as suggested by Rossmeisl et al. [36].

All NEB-simulations have been carried out using the Atomic Simulation Environment. [37]
The forces acting on the images along the path are converged to less than 0.05 eV/Å. As discussed by Liu et al. [7], we do not apply a Hubbard correction for the NEB-calculations since the transition state is a less localized state than the initial and final states of the path. Defect-defect interactions are accounted for through assuring a minimum distance of 8 Å in between repeating supercells.

References


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\sqrt{17} + \Omega \int \delta e^{i\pi} = -1

\{2.7182818284\} \approx \lambda

\chi^2 \gg \Sigma!