Tight-Binding Parameterizations of Ti and Ba Oxides and Their Application for the Prediction of 2D Phases

Ahmad W. Huran and Miguel A. L. Marques

Herein, a set of Slater–Koster parameters for the O–Ti–Ba system to be used within the self-consistent-charge, density-functional tight-binding method is developed. This parameterization follows the recently suggested procedure by Huran et al. in 2018, and is based on the fitting to density-functional theory (DFT) results. This approach yields improved energies and forces compared with existing parameterizations, and is, therefore, useful for the applications in molecular dynamics or global structural prediction. The O–Ba subset of the parameters is then used to investigate the low-dimensional phase diagram of Ba–O using global structural prediction techniques. The resulting convex hull of stability is validated using DFT, and the most interesting phases are subsequently analyzed and characterized. Among the stable systems, superoxides, peroxides, BaO, and oxygen-deficient phases are found with different geometrical arrangements and electronic properties.

1. Introduction

One of the most successful theories of the last decades is undoubtedly density-functional theory\textsuperscript{[1]} (DFT). Mathematically, this can be seen as a reformulation of quantum mechanics that is based on the electronic density, instead of the more complicated many-body wavefunction. Within this theory, many of the complexities of many-body physics are contained in the so-called exchange–correlation functional, for which hundreds of approximations exist.\textsuperscript{[2]} The success of DFT stems from the unparalleled accuracy achieved by those functionals combined with rather modest computational requirements, allowing its use for the study and understanding of a myriad of physical and chemical systems.

Limitations still exist, however, on the applicability of DFT, both from a physical and a practical point of view. Physically, standard DFT fails to describe a series of physical systems (such as strongly correlated systems) and properties (like electronic bandgaps). From a practical point of view, DFT calculations are still impractical for very large systems, or for dynamical simulations that require a considerable amount of energy and force evaluations. To resolve this problem, one often resorts to more approximate schemes, such as semiempirical methods,\textsuperscript{[3–5]} or classical force fields.\textsuperscript{[6,7]} Of course, these approaches alleviate the computational effort at the cost of some accuracy, so a great care has to be taken in their construction and validation.

Here, we are concerned by one of such schemes, density-functional tight binding\textsuperscript{[8]} (DFTB). This method, along with its numerous extensions,\textsuperscript{[9–22]} mainly targets large molecular structures and extended systems with periodic boundary conditions involving up to tens of thousands of atoms in the unit cell,\textsuperscript{[23]} while maintaining a rather accurate quantum mechanical description of the electrons. It is, therefore, not surprising that it found a wide range of applications, from the modeling of chemical reactions\textsuperscript{[24–26]} to biomolecular science,\textsuperscript{[27–29]} solid-state physics,\textsuperscript{[30,31]} and material science.\textsuperscript{[32–34]}

The efficiency of DFTB ultimately comes from the use of a set of precomputed and tabulated numbers, the Slater–Koster parameters, which are prepared beforehand for each pair of chemical elements. They contain an electronic part that is required for formulating the quantum-mechanical problem, and a classical potential describing the repulsion between atomic cores and other terms of corrective nature. The construction of such parameter sets is highly nontrivial and often requires a large amount of human intervention. In the past years, a series of strategies were put forward\textsuperscript{[35–38]} with the purpose of reducing human intervention and to accelerate the training process. Recently, we proposed a methodology to train DFTB parameters that are transferable (i.e., that can be used for a variety of systems) and that yield accurate energies and forces.\textsuperscript{[39]} We then used it to generate Slater–Koster parameters for group IV elements.\textsuperscript{[39]}

In this article, we give a step forward and use our methodology to create Slater–Koster sets for the O–Ti–Ba system, i.e., for the elements O, Ti, and Ba, and for the binary systems O–Ti, O–Ba, and Ti–Ba. Several reasons motivated our choice of this system. First, it includes oxides, much more complicated systems than the group IV compounds studied by Huran et al.,\textsuperscript{[39]} and certainly more difficult to treat within DFTB. Second, it includes the BaTiO\textsubscript{3} compound, which is one of the most studied and interesting oxide perovskites. Finally, under some conditions, BaTiO\textsubscript{3} forms a remarkable 2D quasicrystal\textsuperscript{[30,41]} when deposited on a...
platinum surface. The creation of DFTB parameters for the O–Ti–Ba systems opens the way for the study of large, complex BaTiO$_3$ geometries, such as defects, surfaces, interfaces, quasi-crystals, and so on. It also allows us to perform long molecular dynamic (MD) simulations or global structural prediction runs of the ternary phase diagram, a task well beyond the reach of standard DFT approaches.

The remainder of this article is structured as follows. In Section 2, we give a brief account of DFTB. Section 3 describes the generation of the Slater–Koster sets, passing by the creation of training and testing sets, the optimization procedure, and the validation of the parameters. In Section 4, we use these parameters to unveil the binary phase diagram of 2D Ba$_x$O$_{1-x}$. This is performed by the use of global structural prediction methods, based on DFTB energies and forces, enabling a completely unbiased exploration of the phase diagram. We describe the structural prediction runs, the binary convex hull, and the geometric and electronic structure of the most interesting crystal structures found. Finally, we present our conclusions in Section 5.

2. DFTB

Starting from the exact Kohn–Sham total energy,\cite{42} an approximate energy functional can be constructed by expanding the charge density around some suitably chosen reference density $n_0(r)$ that approximate the correct density $n(r)$ up to a fluctuation $\delta n(r)$\cite{48}. Admitting an error that is second order in the charge fluctuation, one arrives at the Harris–Foulkes energy functional, which is the basis on which DFTB is built.\cite{43,44} The reference density is usually expressed as a superposition of atomic-like densities, and the resulting energy expression is composed of a band structure term and a pairwise repulsive potential that contains the double counting terms as well as the repulsion among atomic cores

$$E_{\text{DFTB}}[n_0] = \sum_i f_i (\langle \psi_i | \hat{H} | \psi_i \rangle + \sum_{lj} \delta \mu_{lj}^\text{rep}(R_{lj})) \tag{1}$$

where $\hat{H}[n_0]$ is the Kohn–Sham Hamiltonian built from a superposition of atomic-like reference densities, the index $i$ runs over Kohn–Sham orbitals $\psi_i$ with occupation numbers $f_i$, and $\delta \mu_{lj}^\text{rep}(R_{lj})$ is the repulsive potential between the atoms $I$ and $J$ at a distance $R_{lj}$ from each other. At this stage, two more approximations are required. The Kohn–Sham states are approximated within a minimal basis set consisting of localized atomic-centered basis functions (in some cases, polarization functions are also added). Moreover, a many-center expansion is conducted to express the Hamiltonian, with the subsequent neglect of all crystal-field- and three-center-like terms (this is the two-center approximation; for a theoretical justification, see ref. [45]).

With this in mind, minimizing the energy functional of Equation (1), with the orthonormality constraints, leads to the generalized eigenvalue problem

$$\sum_i (\mu_{\mu\nu} - \epsilon_i S_{\mu\nu}) \epsilon_{\nu i} = 0, \quad \forall \mu, i \tag{2}$$

where $\epsilon_{\nu i}$ are expansion coefficients of the Kohn–Sham states in the aforementioned basis set $\{\psi_i\}$, and for basis functions $\varphi_\alpha$ and $\varphi_\beta$ centered on atoms $\alpha$ and $\beta$, respectively, we have

$$S_{\alpha\beta} = \begin{cases} \langle \psi_\alpha | \psi_\beta \rangle, & \alpha \neq \beta \\ \delta_{\alpha\beta}, & \alpha = \beta \end{cases} \tag{3}$$

$$H_{\alpha\beta} = \begin{cases} \langle \varphi_\alpha | \hat{H} | \varphi_\beta \rangle, & \alpha \neq \beta \\ \epsilon_\alpha \delta_{\alpha\beta}, & \alpha = \beta \end{cases} \tag{4}$$

where $\epsilon_\alpha$ is the corresponding Kohn–Sham eigenvalue in the free, spin-averaged atom.

The approach described thus far utilizes a Hamiltonian with contributions coming solely from the pristine atomic-like charge densities. This can be problematic when significant charge migration occurs upon bonding, because the effective potential is then a very poor approximation to the correct Kohn–Sham potential. A popular solution to this problem, accounting for effects that are second order in the charge fluctuations, is the self-consistent-charge (SCC) DFTB.\cite{49} This approach treats charge fluctuation effects as a pairwise effective interaction between point-like charges estimated via Mulliken population analysis. The resulting total energy becomes

$$E_{\text{SCC}} = E_{\text{DFTB}} + \frac{1}{2} \sum_{ij} \gamma_{ij}(R_{ij}) \Delta q_i \Delta q_j \tag{5}$$

where $\Delta q_i$ is the partial charge on atom $I$ computed by the Mulliken method. The effective interaction $\gamma_{ij}(R_{ij})$ interpolates between the onsite exchange–correlation-dominated limit and the long-ranged Coulombic tail. It is given as a function of the Hubbard parameter of the free, spin-compensated atom. The Hubbard parameters are computed as the negative derivative of the highest occupied orbital eigenvalue with respect to the number of electrons.\cite{46} These parameters describe the exchange and correlation effects as well as the decay of the charge fluctuation in the monopole approximation (see Appendix in the study by Elstner et al.\cite{47}). Unfortunately, the resulting set of algebraic equations is no longer equivalent to a generalized eigenvalue problem, and iterative solution schemes are required.

Despite remarkable successes of the SCC-DFTB approach when applied to a wide variety of systems, it does not come without limitations. Recently, it was shown that the use of the monopole approximation coupled with Mulliken atomic charges results in very poor higher multipole models.\cite{48} It is suggested that the solution to such issues lies in going beyond the monopole approximation as in the SCC and dipole DFTB method,\cite{50} coupled with a different kind of charges such as the charge model 3.\cite{48} Another source of problems in the SCC-DFTB approach regards the truncation of the energy at the second order in the charge fluctuation. The approach known as DFTB3\cite{49} includes third-order terms in a fashion similar to the SCC-DFTB method. The resulting third-order corrections introduce an extra level of self-consistency via derivatives of the Hubbard parameters with respect to charges. The DFTB3 approach was found to be especially successful for the description of hydrogen bonding and proton affinities which are paramount to studying countless biochemical processes.\cite{50}

The orbital basis set and the atomic-like charge densities ($\varphi_\alpha$ and $n_\alpha^0$ in Equation (4)) are yet to be determined. We obtain
these quantities from solving the radial Kohn–Sham problem for the free spin-averaged atom within a confinement potential (pseudoatom) as is usually done. For the confinement potential, we use the Woods–Saxon potential, given by

\[ V_{WS}(r) = \frac{\hbar^2}{1 + e^{r/r_0}} \]

where \( h \) is the saturation limit of the potential at large distances, \( r_0 \) gives the inflection point, and \( \Delta \) determines the slope at \( r_0 \). What is left to be determined is the pairwise repulsive potential, which is expanded in a cutoff-polynomial basis:\[37\]

\[ V_{rep}(\phi_{rep}, R) = \sum_{j=3}^{\infty} \phi_{rep} \left( R_{cut} - R \right)^j \]

where \( R_{cut} \) is the cutoff of the repulsive potential, and \( \phi_{rep} \) are the expansion coefficients to be determined via a linear least-squares fit.

3. Parameters

3.1. Data

Following the procedure developed in our previous work,\[39\] we start by generating the data required for fitting the ingredients of the DFTB model and for testing the quality of the parameter sets. We target a parameter set that is suitable for MD simulations and global structural prediction. In this context, the models need to handle a wide variety of atomic arrangements on equal footing, which necessitates an unbiased, ample representation of crystal structures in the training data. Our data pool was generated with Kohn–Sham DFT, within the projector augmented wave (PAW) method,\[34,35\] as implemented in the Vienna ab initio simulation package (VASP, version 5.4.4), and with the Perdew–Burke–Ernzerhof (PBE)\[36\] approximation to the exchange–correlation functional. Dense k-point meshes were used throughout (the chosen value is shown in Table 1). Confinement potentials for the input density and the different angular momentum channels were allowed to be different, yielding four potentials in the case of an spd valence. The value of 1 a.u. was used as an initial guess for all the parameters in the confinement potentials, except for orbitals that were unbound in the free atom. For this case, the initial guess for the height of the potential was increased until all the involved overlap matrices were positive-definite.

3.2. Optimization

The optimization of the parameters proceeds as in the study by Huran et al.,\[39\] as well. The objective for the optimization is an equally weighted scalarization of two error estimates related to formation energies and forces.

\[ \mu_{\Delta E} = \sum_i w_i \left( \Delta E_i^{\text{DFT}} - \Delta E_i^{\text{DFTB}} \right)^2 \]

\[ \mu_F = \sum_i \sum_j \sum_k \frac{\sum_q \left( F_i^{\text{DFT}} - F_i^{\text{DFTB}} \right)_{qj}}{w_i} \]

where \( \Delta \) is the saturation limit of the potential at large distances, \( r_0 \) gives the inflection point, and \( \Delta \) determines the slope at \( r_0 \). What is left to be determined is the pairwise repulsive potential, which is expanded in a cutoff-polynomial basis:\[37\]

\[ V_{rep}(\phi_{rep}, R) = \sum_{j=3}^{\infty} \phi_{rep} \left( R_{cut} - R \right)^j \]

where \( R_{cut} \) is the cutoff of the repulsive potential, and \( \phi_{rep} \) are the expansion coefficients to be determined via a linear least-squares fit.

3.3. Results

Although the SCC-DFTB is the standard in the community, it is of interest to test non-SCC parameterizations as they offer significant savings in computation costs. Especially for the study...
of elementary substances, the non-SCC approach can be a viable option because charge fluctuations are usually of small magnitude (if not entirely absent due to symmetry). Nonetheless, we found the non-SCC description of elementary oxygen phases to be unsatisfactory as it results in a severe underestimation (≈50%) of bond lengths. This can be explained by the relative importance of the second-order corrections for different elements originating in the different values of their Hubbard parameters. Figure 1 shows a comparison of the effective interaction between charge fluctuations for O, Ba, Ti, and Si as a function of internuclear distance. Silicon is a typical example for which the non-SCC DFTB can yield a good treatment (for a recent application, see ref. [64]). Both Ti and Ba exhibit an effective interaction weaker than Si. In contrast, oxygen shows an effective interaction almost twice that of silicon both for the on-site case and near the respective nearest-neighbor distances. This problem can be aggravated by the fact that the optimization procedure is purely numerical and lacks any physically motivated components. Therefore, in what follows, we present only SCC compatible parameter sets.

The parameters defining the confinement potentials resulting from the pattern-search runs are given in the Supporting Information. It is worth noting that the details of the confinement potentials are usually associated with physical features of the relevant species, such as the covalent radius and the spatial extent of the corresponding orbitals. We emphasise that this is not the case here, as these potentials are solely determined by the optimization procedure. Having obtained the electronic parameters and the homonuclear repulsive potentials, we proceed to construct the repulsive potentials for the heteronuclear cases. Expansion coefficients for the final repulsive potentials are shown in the Supporting Information.

Once the parameters are constructed, they are validated using structures that were not including in the fitting set. This step is very important because obtaining reasonable error estimates in the fitting process is not enough to judge the quality of the resulting parameters set. The quality of the fitting process is assessed by comparing the errors in the fitting set against the test set, and discrepancies of large magnitudes indicate problems related to over-fitting.

Validation results for our parameters (and for the pbc-0-3,[65,66] matsci-0-3 parameter sets when applicable) are shown in Table 2. The largest difference between the fitting and testing sets for the error in formation energy was for O–Ti (13.6 meV atom$^{-1}$), whereas for the error in the forces was for Ti (18.9 meV Å$^{-1}$), indicating the absence of overfitting. The elemental substances show very different behavior when evaluated with our parameters set. Barium exhibits the lowest error estimates for both the formation energy and forces. The errors are almost double while considering Ti, with a significant increment as we go to O. This can be explained in light of the valence configuration (assuming everything else being equal): for Ba, we have two electrons in nine orbitals, Ti has four electrons in nine orbitals, whereas for O it is six electrons in four orbitals. On average, the error estimate for the binary systems is larger than the errors averaged over the elemental systems. This discrepancy amounts to ≈50 meV atom$^{-1}$ in formation energies and ≈90 meV Å$^{-1}$ in the forces. This is in fact an acceptable result given that the only freedom in the models for the binary systems are the heteronuclear repulsive potentials. For the O–O system, both pbc-0-3 and matsci-0-3 yield similar errors in formation energy compared with the present work. However, errors in the forces are more than three times larger. For Ti–Ti and O–Ti systems, the matsci-0-3 parameter set was found to yield very large errors in both formation energies and forces. More results using the mio-1-1 [9] tiorg-0-1 [68] and trans3d-0-1 [69] parameter sets are given in the Supporting Information. Note that, for the Ti–O systems, both the tiorg-0-1 and trans3d-0-1 sets use the O–O parameters from the mio-1-1 set.

The improvements offered by our parameter sets can be attributed to two reasons, namely the diversity of the fitting and testing data sets, and the fact that the electronic and repulsive parts are fitted together, leading to considerable cancellation of errors. We emphasize that we try to reproduce solely energies and forces; therefore, we can not expect an accurate description of band structures. This is indeed the case as we can see in the Supporting Information where we compare the band structure computed by the parameters of this work to DFT for rutile TiO$_2$ and bulk BaO.

![Figure 1](image_url)

**Figure 1.** The effective interaction $\gamma(R_{ij})$ for O, Ba, Ti, and Si. Markers denote a typical bond length of the respective species on the corresponding curve.

| Type   | $\sqrt{\mu_{\text{fit}}}$ | $\sqrt{\mu_{\text{fit}}}$ |
|--------|--------------------------|--------------------------|
| O      | Present                  | 131.3                    | 195.2                    |
| pbc-0-3| Present                  | 141.5                    | 713.6                    |
| matsci-0-3 | Present               | 132.2                    | 613.8                    |
| Ti     | Present                  | 81.5                     | 113.0                    |
| matsci-0-3 | Present               | 573.9                    | 903.1                    |
| Ba     | Present                  | 35.7                     | 40.6                     |
| O–Ti   | Present                  | 125.1                    | 241.9                    |
| matsci-0-3 | Present               | 718.7                    | 825.7                    |
| Ti–Ba  | Present                  | 145.7                    | 205.0                    |
| O–Ba   | Present                  | 125.3                    | 176.7                    |

Table 2. Error in the formation energies (meV atom$^{-1}$) and forces (meV Å$^{-1}$) at the SCC DFTB level (see Equation (8) and (9)).
4. 2D Ba–O Phase Diagram

4.1. Structural Prediction

As a first application of the parameterizations developed here, and to showcase the power and numerical efficiency of this approach, we decided to investigate the phase diagram of 2D Ba–O. The main motivation for this study was the remarkable discovery of 2D quasicrystals on the BaTiO$_3$ system on top of a platinum substrate.\cite{40,41} Of course, before embarking on the study of such complicated quaternary system, it is important to understand how the elementary and binary substances behave in confined geometries. The study of this 2D diagram is also a very stringent test on the quality of our tight-binding parameters. In fact, the training sets used in the training of the parameters included exclusively 3D bulk systems. By testing 2D systems, we are in fact verifying the transferability of our approach to completely different chemical environments.

Very little is known on the chemistry and the behavior of free-standing atomically thin oxides. As such, we do not have any information about the preferred crystal structures of 2D BaO, nor even which stoichiometries are stable in these highly constrained geometries. We decided, therefore, to use a fully unbiased approach based on global structural prediction methods.\cite{70} These techniques allow us to obtain the ground-state crystal structure (and some low-lying metastable phases) of a given stoichiometry without any a priori knowledge. The input for these methods are forces and energies that we calculate using DFTB$_4$.\cite{79} with our parameterizations for the Ba–O system.

Here, we use the constrained minima-hopping algorithm\cite{57,58} that uses a confining potential along the nonperiodic direction to ensure a 2D geometry. Furthermore, by varying the width of this confining potential, we can access flat monolayers (with width approaching zero), buckled monolayers, bilayers, and so on. This approach has proved its efficiency in the discovery of new 2D polymorphs\cite{33,64,71} of C, Si, and TiO$_2$. Of course, here we are interested in investigating the complete phase diagram, so we need to perform simulations by varying the stoichiometry from pure barium to pure oxygen. We emphasize that due to the large number of stoichiometries, the large number of atoms in the unit cell, and the large supercells required for our calculations (that include a vacuum buffer in the nonperiodic dimension), these calculations are only possible due to the numerical efficiency offered by tight-binding methods.

The structure prediction runs were performed for all possible unit cells containing a maximum of 16 atoms. This resulted in 81 different stoichiometries, and a total of 431 possible unit-cell sizes. For each of these cases, we performed four independent minima-hopping runs always starting from a random configuration of the atoms and the cell parameters. As a constraining potential, we used a parabolic confinement that was activated for widths larger than 3 Å. We chose this value to allow for the appearance of buckled atomic layers or even bilayers. We note that, however, this setup does not forbid thicker slabs, and these were indeed found in some of the simulations. Each individual run arrived at 80–400 minima, yielding a total of 113 783 crystal structures. These were then filtered to remove duplicated structures to arrive at 29 252 different Ba–O phases.

![Figure 2. Phase diagram of 2D Ba–O, calculated with tight binding with the parameterizations presented here (and including the constraining potential). Each point corresponds to a different crystal structure, and the color gradient indicates the composition. The two lines depict the convex hull of stability considering only structures with less than 1.75 Å of thickness (blue line) and 3.75 Å of thickness (black line). The circles on the convex hull denote thermodynamically stable phases.](image-url)

In Figure 2, we plot the formation energy of this final set of structures. Formation energies were calculated with respect to the ground states configurations of low-dimensional elemental substances and not with respect to the usual bulk chemical potential. Each point corresponds to one of the 29 252 different phases, and the color gradient indicates the chemical composition. To help in the interpretation of the data, we depict two different convex hulls of thermodynamic stability. The first (in light blue) is constructed by restricting the thickness of the layers to be smaller than 1.75 Å, whereas the second (in dark blue) includes structures with thickness up to 3.75 Å. Clearly, by allowing for thicker layers, the systems have more degrees of freedom to decrease their energy, so the latter curve has by construction to lie beneath the former.

As expected from the conventional oxidation states of Ba and O, the most stable composition is BaO, with a formation energy of $-2.64$ eV (calculated with tight binding). On the oxygen-rich side of the phase diagram, we find a series of structures that lie on the convex hull. Furthermore, the two convex hulls lie in close vicinity, which tells us that atomically thin oxygen-rich phases are energetically competitive. On the barium-rich side, we do not find any phase exactly on the convex hull, but many different points are rather close to it. In this region, we also see a large difference between the two hulls, indicating that geometries are significantly stabilized by assuming the form of thick slabs.

4.2. Validation and Analysis

To validate the phase diagram obtained with DFTB, and to analyze our results in detail, the selected structures were reoptimized using VASP. All structures within 100 meV atom$^{-1}$ of the convex hull were reoptimized, resulting in 876 crystal structures of 74 different stoichiometries. In principle, this energy threshold should be as large as possible, to include all structures
that were misidentified by tight binding. However, the large size of the unit cells severely limits the amount of structures that can be reoptimized. Our choice of 100 meV atom$^{-1}$ is, therefore, a compromise between the typical error of our tight-binding parameterizations (Table 2) and available computational resources.

We performed collinear spin-polarized calculations (starting from the ferromagnetic configuration). The PBE$^{[56]}$ approximation to the exchange–correlation functional was used along with a plane-wave cutoff energy of 520 eV. Geometry optimizations were performed so that forces were converged to 5 meV Å$^{-1}$, together with Γ-centred k-point grids, determined such that total energies were converged to better than 2 meV atom$^{-1}$. A vacuum region of 15 Å was used to separate periodic copies in the direction perpendicular to the layers. Note that the geometry optimizations were performed without the confining potential. The removal of this constraint sometimes led to large reconstructions of the geometry into considerably thicker structures. In most other cases, however, the tight-binding geometry was already rather close to the DFT minimum; therefore, the geometry optimization required few iterations to converge.

Figure 3 shows the convex hull of stability calculated within DFT with the PBE approximation. As previously mentioned, formation energies were calculated with respect to the ground-state configurations of low-dimensional elemental substances. At first sight, the overall shape of the phase diagram is similar to the one obtained with tight binding and shown in Figure 2. The most stable composition is BaO, with a formation energy of $-2.52$ eV, a difference of 0.12 eV with respect to the tight-binding result. As shown in Table 2, this is perfectly within the typical errors for our tight-binding parameterizations. Moreover, a large majority of the structures remain within a $\approx 100$ meV stripe above the convex hull, which in our opinion fully validates our approach.

The tight-binding and the DFT convex hulls for a thickness of 3.75 Å are rather similar. We find some differences in some of the stoichiometries that are on the hull, that arise from DFT slightly stabilizing or destabilizing phases that were already very close to the tight-binding hull. A larger difference can be seen in the convex hull for a thickness of 1.75 Å. The reason for this is a thin BaO structure that is destabilized by DFT, allowing for other compositions to appear on the hull.

### 4.3. Selected Structures

In the following, we discuss in more detail a few selected systems that we chose from the DFT phase diagram. Although our systems are 2D, for convenience we label the structures using the 3D space groups.

#### 4.3.1. BaO$_4$

On the oxygen-rich side of the convex hull, we first encounter the superoxide composition BaO$_4$. The lowest energy structure of this composition (BaO$_4$-I) is an orthorombic system belonging to the Cmmm space group. Figure 4 shows the crystal structure that consists of a planar Ba subsystem with the barium atoms forming a centered rectangular lattice. Parallel O$_2$ units are situated above and below the Ba plane along the long diagonal of the rhombi formed by the barium atoms. Each barium atom is surrounded by 12 equivalent oxygen atoms to form a network of face-sharing cuboctahedra. Bader charge analysis$^{[72,73]}$ indicates a loss of 1.6 electrons per barium atom and a 0.8 electron excess per O$_2$, as expected for a superoxide species. Nevertheless, the...
absence of magnetization suggests the lack of superoxide \( \text{O}_2^- \) anions in the structure. A possible consideration is that oxygen exists in this structure in the form of \( \text{O}_2^2^- \). The PBE electronic band structure (Figure 4) shows a direct gap of 0.31 eV. Above the Fermi level, there is a low lying, flat band with main contributions from oxygen p orbitals. Beyond that, we find a range of forbidden energies 3.13 eV wide. This is an interesting feature making BaO4-I a four-band system with, effectively, a single conduction band.

Around 3 meV atom\(^{-1}\) above BaO4-I, we have BaO4-II. The structure at hand is a hexagonal system crystallizing in the P6/mmm space group. Similar to BaO4-I, we have a planar Ba subsystem but the atoms now lay on the lattice points of hexagonal lattice (Figure 5). O2 units are perpendicular to the Ba subsystem and situated at the centers of all equilateral triangles formed by the Ba–Ba first neighbors. Bader charge analysis is also in agreement with a superoxide structure. Unlike BaO4-I, we find 0.5 a.u. of local magnetization per O2 unit with a ferromagnetic ordering. The electronic band structure at the PBE level (Figure 5) shows a half-metallic behavior with the majority channel being an insulator with a 3.47 eV gap, and the minority channel having a finite density of states (DOS) at the Fermi level.

### 4.3.2 BaO2

Increasing the Ba fraction in the composition we reach the next point on the convex hull, namely the BaO2 stoichiometry. The ground-state configuration for this composition (BaO2-I) crystallizes in the hexagonal P6m2 space group. The crystal structure shown in Figure 6 shows the same Ba subsystem encountered in BaO4-II, however with 8.6% shorter Ba–Ba distances due to the absence of the O2 units from the centers of the Ba–O2 hexagons found in BaO4-II. PBE electronic band structure analysis (Supporting Information) shows an indirect bandgap of 2.89 eV. Partial charges on the atoms indicate that the O2 units are present in the form of peroxide anions \( \text{O}_2^2^- \).

### 4.3.3 BaO

Further reduction of the oxygen content takes us to the most stable composition on the convex hull, that is BaO. The lowest energy structure (BaO-I) is a trigonal crystal pertaining to the P\( \overline{3}\)m1 space group. The structure (Figure 7) is a strongly bound bilayer. In each layer, the barium and oxygen atoms alternate the occupation of the vertices of hexagons. These hexagons are not completely planar as the plane of the oxygen atoms lies slightly below the plane of barium atoms in the top layer, whereas the converse is true for the other layer. The layers are stacked such that the oxygen atoms in the top layer are vertically aligned with the barium atoms from the bottom layer.

As expected from the stoichiometry, Bader charge analysis shows the transfer of 1.5 electrons from barium to oxygen. The electronic band structure at the PBE level (Supporting Information) presents an indirect gap of 1.50 eV. The monolayer analogue of this system was found to be a planar structure lying around 262 meV atom\(^{-1}\) above the bilayer. We note that BaO-I is
a mere 117 meV atom\(^{-1}\) above the lowest-energy BaO 3D crystalline phase. This energy difference is more than five times smaller than the corresponding difference in the case of silicene.\[^{[64]}\]

These values hint at the possibility of the synthesis of this material on appropriate substrates.

### 4.3.4. Ba\(_4\)O\(_3\)

Arriving at the barium-rich side of the convex hull, we encounter the Ba\(_2\)O\(_3\) composition. The ground-state geometry for this composition (Ba\(_2\)O\(_3\)-I) crystallizes in the monoclinic P2\(_1/m\) space group, and has the structure of BaO-I with an ordered array of O vacancies in each one of the layers. The removal of oxygen atoms from BaO-I to form Ba\(_4\)O\(_3\)-I comes with an energetic cost of 4.7 eV per Ba\(_2\)O\(_3\) unit formula. The oxygen-deficient structure (Figure 8) exhibits three inequivalent barium site and two inequivalent oxygen sites. The barium atoms that are vertically aligned with the oxygen vacancies are all equivalent (Ba-I). The second type of barium sites (Ba-II) alternates with the first type Ba atoms along a straight line.

One of the two inequivalent oxygen sites is occupied by those atoms that alternate with the vacancy site in a collinear fashion throughout the structure. The electronic band structure (Supporting Information) shows a narrow bandgap with a width of 0.16 eV. Bands below the topmost valence ones present large contributions from Ba d states in contrast to the structures we have discussed thus far. Partial charges on the barium sites are +0.9, +1.1, and +1.3 for Ba-III, Ba-II, and Ba-I, respectively, whereas all the oxygen sites have a charge of −1.4. We finally remark that the electron localization function (ELF) shows strongly localized electrons in the empty space created by the vacancies (Figure 8).

### 4.3.5. Ba\(_2\)O

Our last point on the convex hull is the severely oxygen-deficient Ba\(_2\)O. The lowest energy configuration (Ba\(_2\)O-I) crystallizes in the monoclinic P2\(_1/m\) space group as well. The structure is achieved by removing all oxygen atoms of the first type in Ba\(_4\)O\(_3\)-I (Figure 9) resulting in a ribbon-like structure with equivalent oxygen sites. Barium atoms occupy two inequivalent sites: Ba-I features atoms coordinated with a single oxygen atom, while Ba-II has the atoms coordinated with three oxygen atoms. The nature of the electronic structure is drastically changed in comparison to Ba\(_4\)O\(_3\)-I as the system is metallic (Supporting Information). Similar to Ba\(_4\)O\(_3\)-I, Ba\(_2\)O-I also presents regions with localized electrons, however, to a lesser extent (Figure 9), with the localized electrons stationed in the interribbon space.

### 5. Conclusions

We constructed a set of DFTB parameters for the O–Ti–Ba system. A pattern search algorithm was used for optimizing the electronic parameters, whereas the repulsive potentials were built on the fly during the optimization via least-square fits. A key feature of our approach is the use of large, unbiased, nonoverlapping data sets in the fitting process and the subsequent testing. These data sets were constructed from structural prediction runs ensuring that they cover an ample range of the possible structural arrangements. Evaluating the quality of the produced parameter sets showed very good performance especially in the case of elemental Ba. The error estimates for the testing set were \(\approx 36–146\) meV atom\(^{-1}\) and \(\approx 41–242\) meV Å\(^{-1}\) in the formation energies and forces, respectively. Our parameters set were found to bring significant improvements over parameter sets found in the literature.

These parameters were then used to investigate the low-dimensional phase diagram of Ba–O via extensive structural prediction runs using the MM. To validate these results, a set of 876 energetically relevant structures (within 100 meV atom\(^{-1}\) from the hull) were chosen and reoptimized using DFT. In the majority of cases, the DFTB geometry was found to be a very good approximation to the DFT one, which once again indicates the good quality of the parameterizations.

Low-energy structures of the stable compositions on the DFT convex hull were inspected and analyzed. The analyzed systems ranged from superoxides to conventional oxides and oxygen-deficient oxides. The superoxide composition BaO\(_4\) was found to feature a nonmagnetic system that suggests the lack of any superoxide anions (O\(_2^-\)). The selected peroxide and oxide systems were found to be nonmagnetic, wide-gaped systems similar to their bulk analogues. Two oxides with oxygen vacancies were analyzed, and one was found to have a narrow gap while the other was found to be metallic. Both systems with vacancies presented localized electrons in the space caused by the vacancies.

---

**Figure 8.** Structural model of Ba\(_2\)O-I and ELF isosurface at an isovalue of 0.65. Different shades of red and green indicate the different layers of oxygen and barium, respectively.

**Figure 9.** Structural model of Ba\(_2\)O-I and ELF isosurface at an isovalue of 0.65. Different shades of red and green indicate the different layers of oxygen and barium, respectively.
The quality of our parameter sets, together with the numerical efficiency of the DFTB method, allows for the accurate study of systems that could only be handled with classical force fields up to now. This includes not only complex or disordered crystal phases but also low-dimensional systems such as 2D layers, surfaces, or grain boundaries. Of course, the downside is that a complete set of Slater–Koster parameters is required for every pair of chemical elements present in the system. However, our training approach is systematic, and can be easily extended to other chemical elements. We believe, therefore, that in the near future we can generate DFTB parameterizations for a substantial amount of chemical elements, opening up the possibility of investigating systems across large regions of the periodic table.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements
The authors acknowledge support from the German Research Foundation within the Collaborative Research Centre 762 (project A11).

Conflict of Interest
The authors declare no conflict of interest.

Keywords
barium, density-functional tight binding, minima hopping, Slater–Koster, titanium, 2D oxides

Received: October 1, 2019
Revised: December 9, 2019
Published online: December 27, 2019

[1] E. Gross, R. Dreizler, Density Functional Theory: An Approach to the Quantum Many-Body Problem, Springer, Berlin 1990.
[2] S. Lehtola, C. Steigemann, M. J. Oliveira, M. A. Marques, SoftwareX2018, 7, 1.
[3] M. J. Dewar, E. G. Zoebisch, E. F. Healy, J. J. Stewart, J. Am. Chem. Soc. 1985, 107, 3902.
[4] J. J. Stewart, J. Mol. Model. 2007, 13, 1173.
[5] J. J. Stewart, J. Mol. Model. 2013, 19, 1.
[6] B. R. Brooks, R. E. Brucoleri, B. D. Olafson, D. J. States, S. A. Swaminathan, M. Karplus, J. Comput. Chem. 1983, 4, 187.
[7] D. A. Case, I. I. I. T. E. Cheatham, T. Darden, H. Gohlke, R. Luo, K. M. Merz Jr, A. Onufriev, C. Simmerling, B. Wang, R. J. Woods, J. Comput. Chem. 2005, 26, 1668.
[8] W. M. C. Foulkes, R. Haydock, Phys. Rev. B 1989, 39, 12520.
[9] M. Elstner, D. Porezag, G. Jungnickel, J. Eilsner, M. Haugk, T. Frauenheim, S. Suhai, G. Seifert, Phys. Rev. B 1998, 58, 7260.
[10] C. Köhler, G. Seifert, T. Frauenheim, Chem. Phys. 2007, 309, 23.
[11] C. Köhler, T. Frauenheim, B. Hourahine, G. Seifert, M. Sternberg, J. Phys. Chem. A 2007, 111, 5622.
[12] Q. Cui, M. Elstner, E. Kaxiras, T. Frauenheim, M. Karplus, J. Phys. Chem. B 2001, 105, 569.
[13] W. G. Han, M. Elstner, K. J. Jalkanen, T. Frauenheim, S. Suhai, Int. J. Quantum Chem. 2000, 78, 459.
[14] M. Elstner, P. Hobza, T. Frauenheim, S. Suhai, E. Kaxiras, J. Chem. Phys. 2001, 114, 5149.
[15] B. Hourahine, S. Sanna, B. Aradi, C. Köhler, T. Niehaus, T. Frauenheim, J. Phys. Chem. A 2007, 111, 5671.
[16] Y. Yang, H. Yu, D. York, Q. Cui, M. Elstner, J. Phys. Chem. A 2007, 111, 10861.
[17] T. A. Niehaus, S. Suhai, F. Della Sala, P. Lugli, M. Elstner, G. Seifert, T. Frauenheim, Phys. Rev. B 2001, 63, 085108.
[18] F. Trani, G. Scalmani, G. Zheng, I. Carneimeo, M. J. Frisch, V. Barone, J. Chem. Theory Comput. 2011, 7, 3304.
[19] H. Nishizawa, Y. Nishihara, M. Kobayashi, S. Irle, H. Nakai, J. Comput. Chem. 2016, 37, 1983.
[20] Y. Wu, A. Ille, S. Crampin, Comput. Mater. Sci. 2017, 134, 206.
[21] V. Lutsker, B. Aradi, T. A. Niehaus, J. Chem. Phys. 2015, 143, 184107.
[22] J. J. Kranz, M. Elstner, B. Aradi, T. Frauenheim, V. Lutsker, A. D. Garcia, T. A. Niehaus, J. Chem. Theory Comput. 2017, 13, 1737.
[23] A. W. Sakti, Y. Nishihara, H. Nakai, J. Phys. Chem. B 2017, 121, 1362.
[24] A. W. Sakti, Y. Nishihara, H. Sato, H. Nakai, Bull. Chem. Soc. Jpn. 2017, 90, 1230.
[25] A. Marutaghan, Y. Seekaew, C. Wongchoosuk, Nanoscale Res. Lett. 2017, 12, 90.
[26] J. Li, M. E. Foster, K. Sohlborg, Mol. Simul. 2017, 43, 428.
[27] M. Gaus, Q. Cui, M. Elstner, Wiley Interdiscip. Rev. Comput. Mol. Sci. 2014, 4, 49.
[28] H. Jin, P. Goyal, A. K. Das, M. Gaus, M. Meuwly, Q. Cui, J. Phys. Chem. B 2015, 120, 1894.
[29] X. Lu, V. Ovchinnikov, D. Demanap, D. Roston, Q. Cui, Biochemistry 2017, 56, 1482.
[30] S. Markov, B. Aradi, C. Y. Yam, H. Xie, T. Frauenheim, G. Chen, IEEE Trans. Electron Dev. 2015, 62, 696.
[31] J. Kullgren, M. J. Wolf, K. Hermansson, C. Köhler, B. Aradi, T. Frauenheim, P. Broqvist, J. Phys. Chem. C 2017, 121, 4593.
[32] Y. Ohta, Y. Okamoto, S. Irle, K. Morokuma, ACS Nano 2008, 2, 1437.
[33] P. Borlido, C. Steigemann, N. N. Lathiotakis, M. A. L. Marques, S. Botti, 2D Mater. 2017, 4, 045009.
[34] V. Sorkin, Y. Zhang, Nanotechnology 2016, 27, 395701.
[35] J. M. Knaup, B. Hourahine, T. Frauenheim, J. Phys. Chem. A 2007, 111, 5637.
[36] M. Gaus, C. P. Chou, H. Witek, M. Elstner, J. Phys. Chem. A 2009, 113, 11866.
[37] Z. Bodrog, B. Aradi, T. Frauenheim, J. Chem. Theory Comput. 2011, 7, 2654.
[38] M. P. Lourenço, M. C. da Silva, A. F. Oliveira, M. C. Quintão, H. A. Duarte, Theor. Chem. Acc. 2016, 135, 250.
[39] A. W. Huran, C. Steigemann, T. Frauenheim, B. Aradi, M. A. Marques, J. Chem. Theory Comput. 2018, 14, 2947.
[40] S. Förster, K. Meinel, R. Hammer, M. Trautmann, W. Widdra, Nature 2013, 502, 215.
[41] S. Förster, M. Trautmann, S. Roy, W. Adeagbo, E. Zollner, R. Hammer, F. Schumann, K. Meinel, S. Nayak, K. Mohsni, W. Hertger, H. L. Meyerheim, W. Widdra, Phys. Rev. Lett. 2016, 117, 095501.
[42] W. Kohn, L. J. Sham, Phys. Rev. 1965, 140, A1133.
[43] D. Porezag, T. Frauenheim, T. Köhler, G. Seifert, R. Kaschner, Phys. Rev. B 1995, 51, 12947.
[44] G. Seifert, D. Porezag, T. Frauenheim, Int. J. Quantum Chem. 1996, 58, 185.
[45] G. Seifert, J. Phys. Chem. A 2007, 111, 5609.
[46] Z. Bodrog, Ph.D. Thesis, Staats-und Universitätsbibliothek Bremen, 2012.
