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A METHOD TO FORMULATE THE UNIT CELL FOR DENSITY FUNCTIONAL THEORY (DFT) CALCULATIONS OF THE ELECTRONIC BAND STRUCTURE OF HETEROSTRUCTURES OF TWO-DIMENSIONAL NANOSHEETS

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April 2015

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Munitions Engineering Technology Center

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14. ABSTRACT

A method for formulating the unit cell of arbitrarily stacked, two-dimensional (2D) transition metal dichalcogenides is presented. Geometrical considerations and genetic algorithms are used to minimize the number of "unit cells" utilized in the construction of a "supercell" which may accommodate the lattice constants of arbitrary 2D and other close-packed materials. Supercells for various combinations of layered 2D transition metal dichalcogenides are calculated and their electronic band structures are simulated using density functional theory. Results are compared with previously reported density functional theory simulations from the literature.

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Density functional theory; Molybdenum disulfide; Transition metal dichalcogenides; Unit cell; Electronic band structure; Periodic lattice structure; Genetic algorithm

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INTRODUCTION

Two-dimensional (2D) material heterostructures offer novel and compelling electronic and optical properties. Density functional theory (DFT) is often used to derive the electronic band structure of the 2D heterostructures from first principles as well as to validate experimental results. However, the implementation of DFT requires an in-depth understanding of the geometric properties of the system being analyzed. The creation of a unit cell that accurately describes the system remains one of the largest challenges for DFT calculations. As the unit cell size increases, computational requirements increase exponentially. However, too small of a unit cell may fail to represent short- to mid-range order in the lattice. Balancing these conflicting requirements of cost and accuracy is still one of the biggest barriers to implementing DFT calculations. An algorithm to automatically optimize the process would greatly streamline the method of creating a unit cell. While many methods have undoubtedly been created for matching lattice constants of dissimilar nanomaterials, very few are actually covered explicitly in literature. To rectify this, and to ensure other researchers will not have to resolve this problem, this report will review the underlying geometry of popular 2D materials, draw comparisons to other common unit cells, then offer a solution which facilitates the creation of an optimal unit cell for any heterogeneous structure consisting of multiple layers of 2D and close-packed materials.

TWO-DIMENSIONAL MATERIAL GEOMETRY AND ANALOGS WITH CLOSE-PACKED SYSTEMS

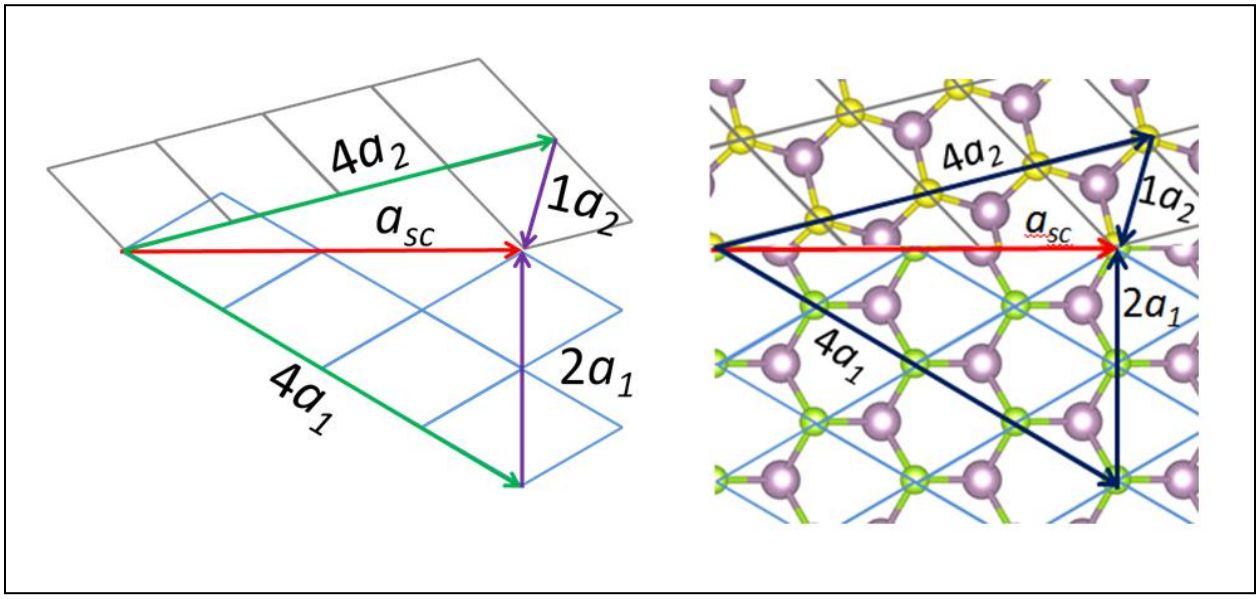
The vast majority of 2D materials currently under research focus, including graphene, graphane, silicine, germanane, and all transition metal dichalcogenides (TMDCs), form hexagonal planes (ref. 1). These structures are all easily expressed using 60 deg monoclinic Bravais lattices where the rhombic sides of the Bravais lattices fit together to form hexagonal monolayers. When metals are deposited as electrodes on top of these 2D layers, the face-centered cubic (fcc) or hexagonal close-packed (hcp) lattice structure of the metals can also be modeled as rhombic unit cells for consistency with the underlying stacked heterostructures. The hcp structures are described using the primitive hexagonal lattice, with $a = b \neq c$, $\alpha = \beta = 90°$, $\gamma = 60°$ and two atoms, at (0,0,0) and (⅓,⅔,½). We can also represent a fcc crystal using a rhombic unit cell by rotating the unit cell 45 deg and making the close-packed plane the base of the unit cell, with $a = b \neq c$, $\alpha = \beta = 90°$, $\gamma = 60°$ and four atoms, at (0,0,0), (½,½,0), (½,0, ½), and (0, ½,½). As the primary difference between hcp and fcc structures lies in differing stacking sequences (ABAB and ABCABC, respectively), it makes sense that a fcc cell taken using the close-packed plane as the base is similar to the hcp unit cell but with one more layer added.

MATCHING SYSTEM LATTICE VECTORS: AN OPTIMIZATION PROBLEM

Now that we are able to express various crystal structures as hexagonal lattices with a rhombus base, we can address the core issue of matching differing lattices into a larger primitive cell. In order for each of the materials in the system to repeat correctly, the overall system cell must be represented as a linear combination of each individual material's unit cell (fig. 1). We define a supercell for each material with lattice constant

$$|a_{sc}|_i = \sqrt{a_i^2 * (m_i^2 + n_i^2 - m_i * n_i)} \tag{1}$$

where a_i is the lattice parameter for a given material, and m_i and n_i are integers representing the number of unit cells in each direction. We then seek the minimum value $|a_{sc}|_i$ such that it is equal for each material. By generating a value for $|a_{sc}|_i$ for each material in the system then minimizing the variance and magnitude, an amorphous geometric problem turns into a fairly simple optimization problem.



Note: In this example, $m_1 = m_2 = 4$, $n_1 = 2, n_2 = 1$. $a_1/a_2 \approx 1.04$, $a_{sc}/a_2 \approx 3.6$. Purple spheres denote Mo, Green Se, and Yellow S.

Figure 1
Matching the system lattice vector for two different transition metal dichalcogenides (TMDs), $MoSe_2$ and MoS_2

In order to solve the optimization problem, constraints are necessary. m_i and n_i must be integers, and the unit cell lattice parameters of each material were allowed to vary by up to 1%, which significantly decreased the cell size while imposing minimal total strain in the structure. A maximum value of 6 was set for m_i and n_i, as a larger system would prove extremely computationally expensive. A minimum of 1 for m_i and 0 for n_i forces the system lattice parameter to have a non-zero value but allows for the smallest possible system. For this work, a genetic algorithm was used to solve the optimization problem. Genetic algorithms begin with a large population of potential solutions and then undergo an iterative process mimicking evolution. Each solution is evaluated compared to a 'fitness function' that defines the end goal of the optimization problem. For this problem, the fitness function minimized the variance in the vector of each individual material a_{sc}. Genetic algorithms converge quickly and, depending on the initial population, effectively find global minima. Reference 2 provides an excellent primer on genetic algorithms.

Komsa and Krasheninnikov (ref. 3) took a similar approach for optimizing the unit cell for a heterostructure of two-dimensional metal chalcogenides (TDMCs). However, the method used in this report differs from theirs in a few key respects. For example, in considering the bilayer heterostructure of TDMCs with one member of the bilayer being always MoS_2 and the other varied between WS_2, $MoSe_2$, $MoTe_2$, BN, or graphene, Komsa and Krasheninnikov fixed the lattice parameter of MoS_2 and only allowed the second layer to strain. We let both of the bilayers undergo a strain up to 1%, allowing us to more effectively find a minimum and to distribute the strain from the lattice mismatch among both layers of the heterostructure. Additionally, while Komsa and Krasheninnikov chose the smallest unit cell with <1% strain, we used a weighting algorithm to choose a unit cell with near-optimal size and minimal strain.

GENERATING THE SYSTEM UNIT CELL

The found values for a_{sc}, a_i, m_i, and n_i allow us to generate the crystal lattice for each material. The angle α between the system unit cell lattice vector and the material lattice vector is given by

$$\alpha_i = \cos^{-1}\left(a_{sc}^2 + a_i^2 \frac{m_i^2 - n_i^2}{2\, a_{sc} m_i a_i}\right). \quad (2)$$

The periodicity of the material lattices makes generating the structure unit cell fairly straightforward. From the top left corner of the system unit cell, every atom in a given material repeats at every linear combination of moving a_i in the α direction and moving a_i in the α + 60° direction (fig. 2).

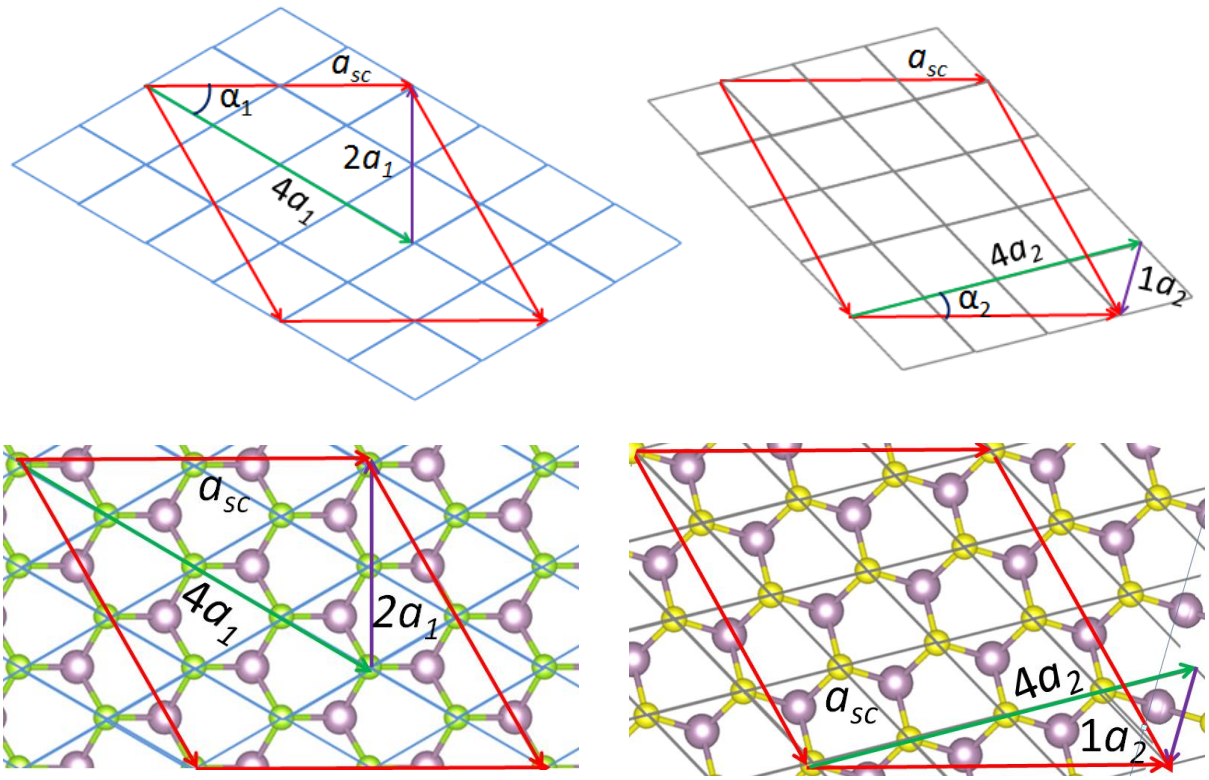


Figure 2
Matching the system lattice vector to our two respective crystal lattices

TRANSITION METAL DICHALCOGENIDES (TMDCS) WITH MISMATCHED LATTICE PARAMETERS

A bilayer of MoS_2 and $MoSe_2$ was chosen as the first system to evaluate. In the calculations, a relaxed $MoSe_2$ layer has a lattice parameter of 3.28 Å and a relaxed MoS_2 layer has a lattice parameter of 3.16 Å. This genetic algorithm successfully matched the two layers, as shown in figure 3. We also used it to match a series of different TMDCs. The results are summarized in table 1. The strain (ε) in the individual layers as shown in table 1 is less than 1% for all the cases considered.

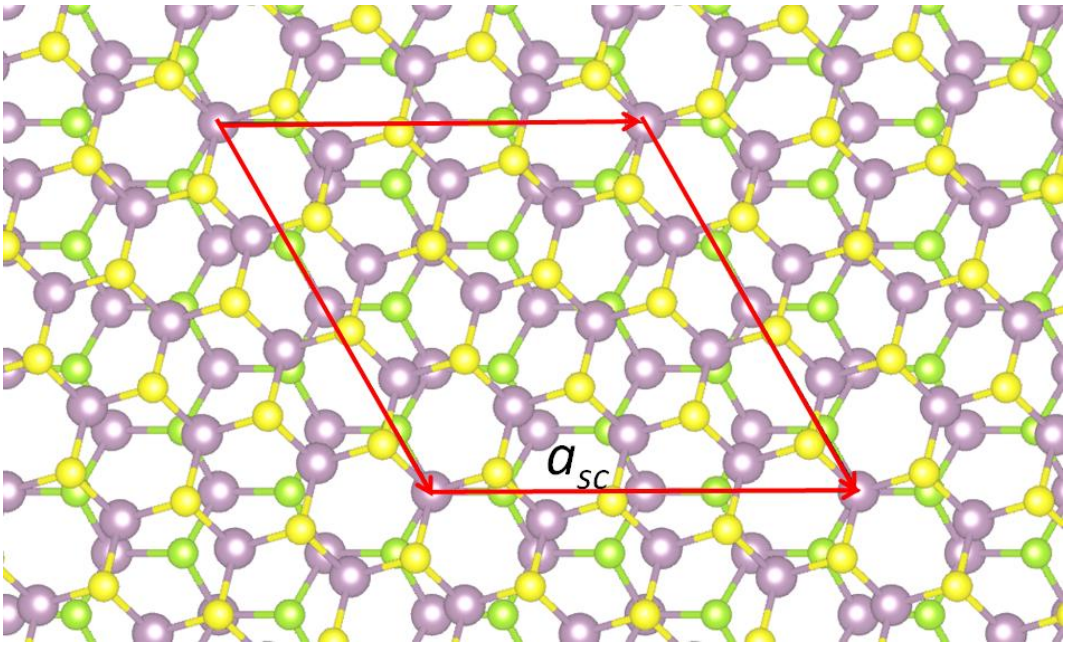


Figure 3
The generated unit cell of a $MoS_2/MoSe_2$ heterostructure bilayer

Table 1
Multiple matched monolayers

	m_1	n_1	m_2	n_2	Strained a_1[Å]	(Un)Strained a_2[Å]	α [°]	a_{sc} [Å]	ε_1	ε_2
$MoS_2/MoSe_2$	4	1	4	2	3.16	(3.28) 3.29	16.1	11.4	0.00%	0.30%
$MoS_2/MoTe_2$	3	3	3	1	3.14	(3.55) 3.56	40.9	9.42	0.63%	0.28%
MoS_2/WS_2	1	0	1	0	3.18	(3.21) 3.18	0	3.18	0.63%	0.93%
MoS_2/WSe_2	4	1	4	2	3.18	(3.33) 3.31	16.1	11.48	0.63%	0.60%
$MoSe_2/MoTe_2$	5	3	4	4	3.28	(3.55) 3.57	23.4	11.46	0.00%	0.56%
$MoSe_2/WS_2$	4	2	3	4	3.31	(3.21) 3.18	13.9	11.46	0.90%	0.93%
$MoSe_2/WSe_2$	1	0	1	0	3.31	(3.33) 3.31	0	3.3	0.90%	0.60%

With the optimized unit cell in place, DFT calculations to calculate the band structure and projected density of states for the material can begin. This simulation was run in SIESTA using the Perdew-Burke-Ernzerhof (PBE) functional for the exchange correlation contributions. All ions were relaxed to less than 0.01 eV/Å. The initial interlayer spacing was set to 12.5 Å, and then the structure was relaxed until reaching an energy minimum at a spacing of 6.4 Å. An 8x8x1 Monkhorst-Pack k-point mesh. The basis set was double zeta polarized, and a mesh cutoff of 300 Rydberg was implemented.

DENSITY FUNCTIONAL THEORY RESULTS

As figure 4 shows, the direct bandgap at the K point was calculated to be 1.49 eV. Previous DFT calculations (refs. 3 and 4) reported a value of ~1.25 eV for the direct bandgap at the K point for the heterostructure. The difference may be attributed to the fact that we have let both layers of the heterostructure to strain while Komsa and Krasheninnikov (ref. 3) allowed only one layer to stretch or compress. Interestingly, the direct bandgap of 1.49 eV in our studies is comparable to that of the individual layers (ref. 4). Consistent with the previous DFT calculations, it can be observed in figure 4 that the valance band maximum occurs at the Γ point of the Brillouin zone thereby rendering the minimum energy gap to be indirect. The observed value of 1.15 eV for the indirect gap is comparable to that reported by Komsa and Krasheninnikov (ref. 3).

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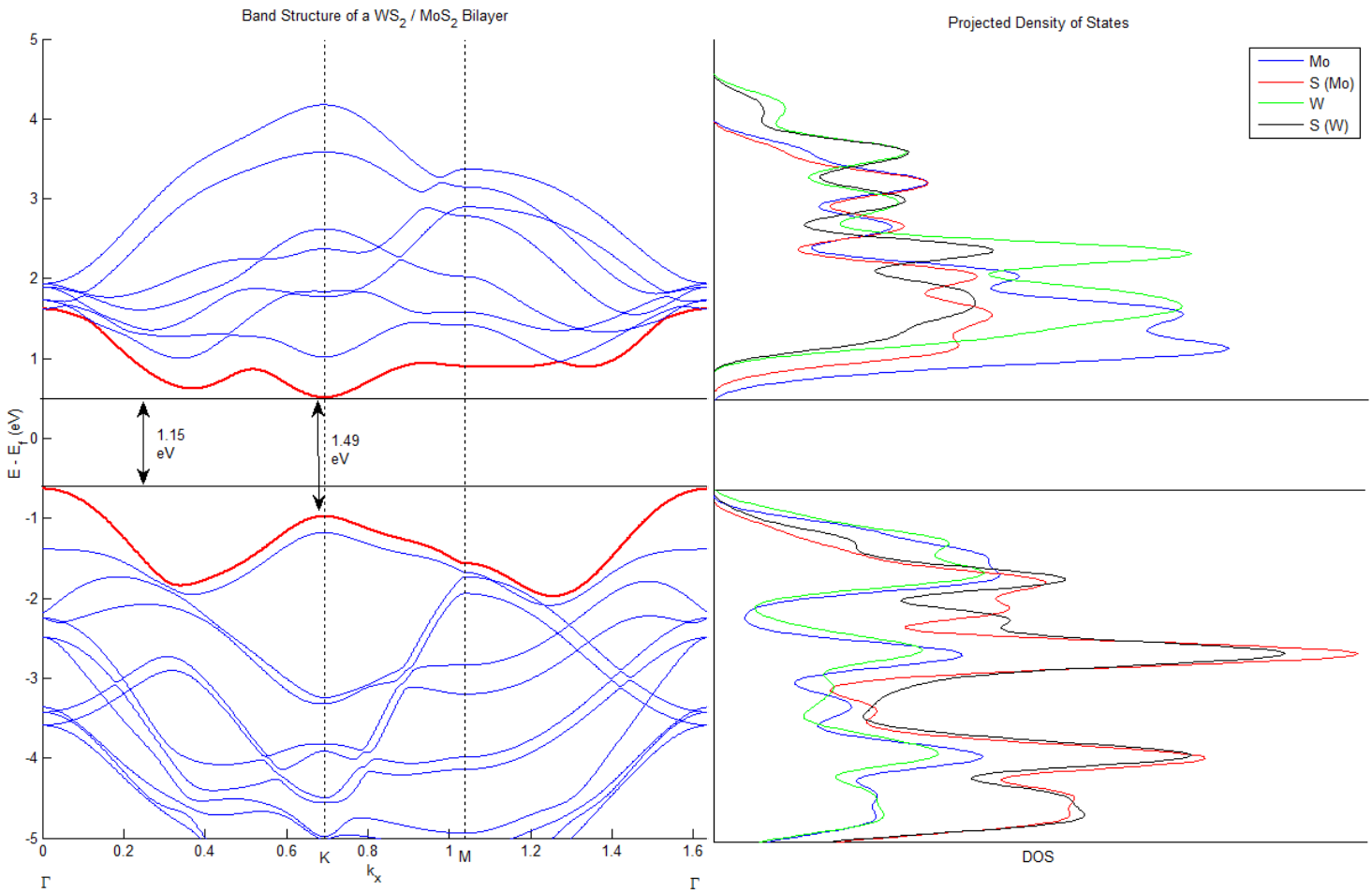

Figure 4
DFT calculation results of a WS_2 and MoS_2 heterostructure

Figure 4 also shows the projected density of states for the stacked heterostructure. The projected density of states shows that for MoS_2 / WS_2 most of the contribution to the conduction band comes from the molybdenum atoms. While the valence band contribution comes slightly more from the tungsten atoms than the molybdenum, the difference in contributions in the projected density of states is too small to make a meaningful conclusion about the exact nature of the valence band. However, the result suggests the interesting consequence of a type II band alignment of the heterostructure with the valence band maximum and conduction band minimum occurring in WS_2

and MoS_2 layers, respectively. Thus, in an excitonic optical transition, the electron-hole pair will be spatially separated. This will lead to interesting optical behavior of the heterostructure.

CONCLUSIONS

We have developed a genetic algorithm that allows us to rapidly optimize the unit cells for the calculation of the electronic band structures of heterostructures of two-dimensional (2D) nanomaterials. We applied the method to calculate the band structure of 2D MoS_2/WS_2 heterostructure, and our results are in good agreement with that of the earlier work of Komsa and Krasheninnikov. The flexibility of our method renders it applicable to any multilayer heterostructure where the individual layers can be expressed using rhombic unit cells. There are plans to use this technique to simulate combinations of different transition metal dichalcogenides (TMDCs) so as to better understand how stacking changes the electronic and optical properties. Further, this method will be used to model the electron transport in a heterostructure that uses other 2D materials as metal electrodes.

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