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Tight-binding modeling of titanium

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Tight-binding modeling of titanium

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Abstract

We develop a code to compute the electronic states and energies and total energy of titanium-only structures the tight-binding method. We adopt the parameterization of Ref. [1] for the Slater-Koster integrals and construct the tight-binding matrices. We obtain the **k**-dependent electron eigenenergies by solving the secular equation, thus we can construct the electronic bands. We evaluate the total energy as the sum of the occupied band energies. We repeat this process for different lattices and lattice spacings to establish the equilibrium structure for a titanium crystal. We determine the stablest structure to be the α hexagonal close-packed crystal with $\frac{c}{a} = 1.618$ and $a = 2.941$, not far from experiment. We utilize the same method to study titanium molecules and obtain non-physical results, proving that this parameterization retains a quite narrow range of applicability.

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1 Introduction

Titanium is the second transition metal in the periodic table. At room temperature and pressure it is a crystalline solid with a hexagonal close-packed structure. In this work, we study the electron motion within the adiabatic approximation, and we aim to compute the electronic bands of a titanium crystal through the tight-binding method. For this purpose we adopt the parameterization provided in Ref. [1] to evaluate the two-center Slater-Koster integrals [2].

We then construct and diagonalize the tight-binding matrix to obtain the single electron eigenenergies, which we use to calculate the total energy per atom. At this point, we study how the total energy changes as we alter the crystal lattice type and the cell volume. The equilibrium structure corresponds to the minimum of this total energy.

2 Electrons in crystals

In this section we revise the key aspects of the tight-binding model for the electronic bands of solids.

2.1 Crystal structures

Crystalline solids are characterized by discrete translational symmetry. This means that, assuming the crystal is large enough to be considered infinite, we can identify a translation lattice, called the Bravais lattice, such that, given a point $\mathbf{r}$ within the crystal, equal physical properties are observed at all points $\mathbf{r'} = \mathbf{r} + \mathbf{R}$, where $\mathbf{R}$ is a vector of the Bravais lattice. We can obtain all vectors of the Bravais lattice as combinations of three primitive vectors:

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3, \tag{1}$$

where n_1, n_2, n_3 are integers. We can then identify a primitive crystalline cell as the smallest volume that contains all translationally inequivalent points. There is an infinite number of primitive cells in a lattice; for example, we consider the parallelepiped generated by the primitive vectors. A primitive cell may contain one or more atoms depending on the crystal; if the cell contains more than one atom, we need to introduce a basis: a list of the coordinates and types of all atoms within the cell. To fully describe the structure of a crystal we need its Bravais lattice and its basis.

2.2 The reciprocal lattice

In order to study the motion of electrons in crystals, we introduce the reciprocal lattice. When we calculate the Fourier expansion of any periodically repeating crystal property, all components vanish except for those at $\mathbf{k}$ points whose $e^{i\mathbf{kr}}$ term has the same periodicity as the crystal. We will call these special $\mathbf{k}$ points $\mathbf{G}$. In order to maintain function periodicity, the $\mathbf{G}$ points must be such that $e^{i\mathbf{G}\cdot\mathbf{R}} = 1$, hence:

$$\mathbf{G} = l_1\mathbf{b}_1 + l_2\mathbf{b}_2 + l_3\mathbf{b}_3, \tag{2}$$

where l_1, l_2, l_3 are integers, and

$$\mathbf{b}_1 = \frac{2\pi}{V_c}\mathbf{a}_2 \times \mathbf{a}_3, \qquad \mathbf{b}_2 = \frac{2\pi}{V_c}\mathbf{a}_3 \times \mathbf{a}_1, \qquad \mathbf{b}_3 = \frac{2\pi}{V_c}\mathbf{a}_1 \times \mathbf{a}_2, \tag{3}$$

where $V_c = (\mathbf{a}_1 \times \mathbf{a}_2) \cdot \mathbf{a}_3$ is the volume of the primitive cell. We see that the $\mathbf{G}$ points form a Bravais lattice in the reciprocal space, and $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{b}_3$ are its primitive vectors.

2.3 Independent-electron methods and Bloch's theorem

We operate within the adiabatic approximation, where the atomic nuclei assume specific positions within the crystal and are considered still, so their kinetic energy can be neglected. Thus we can write the Schrödinger equation for electron motion:

$$H\Psi(\mathbf{w}) = [T_e + V_{ee} + V_{ne}]\Psi_e(\mathbf{w}) = \varepsilon_e\Psi_e(\mathbf{w}), \tag{4}$$

where T_e is the electronic kinetic energy, V_{ee} is the electron-electron Coulomb potential, V_{ne} is the nuclei-electron Coulomb potential, and $\mathbf{w}$ is a variable that contains the positions and spins of all electrons. This equation is generally too complicated to solve due to the large number of electrons in the crystal, however it can be approached through some approximate mean-field one-electron method, e.g. the Hartree-Fock method. With this method, rather than solving the N electron equation, we solve the equation for one electron within the potential generated by the nuclei and the $N-1$ remaining electrons. This way we construct an effective potential V_{eff}, which has the same symmetry as the nuclei-electron potential. The problem is rewritten as:

$$H_1\psi(\mathbf{w}_1) = [T_{e1} + V_{\text{eff}}]\psi(\mathbf{w}_1) = \varepsilon_{e1}\psi(\mathbf{w}_1). \tag{5}$$

The electronic wave function can be factorized into a spatial component and a spin component:

$$\psi(\mathbf{w}_1) = \phi(\mathbf{r}_1)\chi(\sigma_1). \tag{6}$$

We can assume that the spin wave function $\chi(\sigma_1)$ is trivial, and only provides a twofold degeneracy. We then focus on the spatial dependence of the single-electron wave function:: $\psi(\mathbf{w}) = \psi(\mathbf{r})$.

If we take the periodicity of the crystalline structure into account, the nuclear attraction V_{ne} is seen as a periodic function by each electron and, as a result, the effective potential is usually periodic with the same periodicity. Under such conditions, the electronic wave functions take the form expressed in *Bloch's theorem*:

$$\psi_j(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k},j}(\mathbf{r}). \tag{7}$$

Here the function $u_{\mathbf{k}}(\mathbf{r})$ has the same periodicity as the effective potential, $\mathbf{k}$ is an arbitrary wave vector, and j is the band index. This factorization means that the calculation of the periodic part of the electron eigenfunctions can be limited to a primitive cell of the crystal: a Bravais translation $\mathbf{R}$ would leave the wave function unchanged, apart from a constant phase term $e^{i\mathbf{k}\cdot\mathbf{R}}$. Another simplification comes from restricting the $\mathbf{k}$ points to a single primitive cell of the reciprocal lattice, such as the first Brillouin zone. If we consider a $\mathbf{k}$ point outside of the first Brillouin zone, we can always find a $\mathbf{G}$ vector of the reciprocal lattice such that $\mathbf{k'} = \mathbf{k}+\mathbf{G}$ is in the first Brillouin zone. Then we would have $\psi_j(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k},j}(\mathbf{r}) = e^{(i\mathbf{k'}-\mathbf{G})\cdot\mathbf{r}} u_{\mathbf{k},j}(\mathbf{r}) = e^{i\mathbf{k'}\cdot\mathbf{r}} e^{-i\mathbf{G}\cdot\mathbf{r}} u_{\mathbf{k},j}(\mathbf{r})$, and the function $u'_{\mathbf{k}',j}(\mathbf{r}) = e^{-i\mathbf{G}\cdot\mathbf{r}} u_{\mathbf{k},j}(\mathbf{r})$ is lattice periodic, therefore $e^{i\mathbf{k}'\cdot\mathbf{r}} u'_{\mathbf{k}',j}(\mathbf{r})$ is an equivalent Bloch function. We can now rewrite the stationary Schrödinger equation:

$$\left[-\frac{\hbar^2}{2m_e}\nabla^2 + V_{\text{eff}}(\mathbf{r})\right] e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k},j}(\mathbf{r}) = \varepsilon e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k},j}(\mathbf{r}). \tag{8}$$

The equation can be transformed into an equation for the periodic function $u_{\mathbf{k},j}(\mathbf{r})$ as follows:

$$\begin{aligned}\nabla^2 e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k},j}(\mathbf{r}) &= \nabla\cdot\left[e^{i\mathbf{k}\cdot\mathbf{r}}\nabla u_{\mathbf{k},j}(\mathbf{r}) + i\mathbf{k}e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k},j}(\mathbf{r})\right] \\ &= e^{i\mathbf{k}\cdot\mathbf{r}}(\nabla + i\mathbf{k})^2 u_{\mathbf{k},j}(\mathbf{r})\end{aligned}$$

by substituting and simplifying the common factor $e^{i\mathbf{k}\cdot\mathbf{r}}$, we obtain:

$$\left[-\frac{\hbar^2}{2m_e}(\nabla + i\mathbf{k})^2 + V_{\text{eff}}(\mathbf{r})\right] u_{\mathbf{k},j}(\mathbf{r}) = \varepsilon_{\mathbf{k},j} u_{\mathbf{k},j}(\mathbf{r}). \tag{9}$$

In conclusion, we have factorized the electron eigenfunctions in such a way that reduces the problem to a single primitive cell in the real lattice. The problem must be solved for each fixed $\mathbf{k}$ point in a given cell of the reciprocal lattice. The electron eigenvalues $\varepsilon \equiv \varepsilon_{k,j}$ are $\mathbf{k}$-dependent and form continuous bands as $\mathbf{k}$ varies within a reciprocal-lattice cell, e.g. the first Brillouin zone.

2.4 The tight-binding model

In the tight-binding method, we calculate the electronic band structure by constructing the Bloch functions through linear combinations of atomic orbitals. The first assumption we make is that in the proximity of an atom within the crystal, the electron wave functions nearly coincide with the atomic orbitals. In practice, this means that in our calculations we only consider the electrons in the outer valence orbitals, while the core shells are nearly unaffected by the presence of other atoms. We follow the procedure shown in Ref. [3] and decompose the single-electron Hamiltonian as

$$H_1 = H_{\text{at}} + \Delta V(\mathbf{r}) \tag{10}$$

where H_{at} is the one atom Hamiltonian, and $\Delta V(\mathbf{r})$ is the potential generated by all remaining ions, which produces the effective potential when added to the potential of the atom. We can then form Bloch states through the following linear combination:

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \phi(\mathbf{r} - \mathbf{R}), \tag{11}$$

where ϕ is a linear combination of atomic wave functions:

$$\phi(\mathbf{r}) = \sum_{n} b_n \varphi_n(\mathbf{r}). \tag{12}$$

It is easy to prove that $\psi_{\mathbf{k}}$ satisfies Bloch's theorem (7):

$$
\begin{aligned}
\psi_{\mathbf{k}}(\mathbf{r}+\mathbf{R}) &= \sum_{\mathbf{R}'} e^{i\mathbf{k}\cdot\mathbf{R}'}\phi(\mathbf{r}+\mathbf{R}-\mathbf{R}') \\
&= e^{i\mathbf{k}\cdot\mathbf{R}}\left[\sum_{\mathbf{R}'} e^{i\mathbf{k}\cdot(\mathbf{R}'-\mathbf{R})}\phi(\mathbf{r}-(\mathbf{R}'-\mathbf{R}))\right] \\
&= e^{i\mathbf{k}\cdot\mathbf{R}}\left[\sum_{\mathbf{R}'} e^{i\mathbf{k}\cdot(\mathbf{R}'-\mathbf{R})}\phi(\mathbf{r}-\overline{R})\right] \\
&= e^{i\mathbf{k}\cdot\mathbf{R}}\psi_{\mathbf{k}}(\mathbf{r}).
\end{aligned}
$$

If we multiply the crystal Schrödinger equation

$$
[H_{\mathrm{at}} + \Delta V(\mathbf{r})]\psi_{\mathbf{k}} = \varepsilon_{\mathbf{k}}\psi_{\mathbf{k}}(\mathbf{r}) \tag{13}
$$

by the atomic wave function $\varphi_m^*(\mathbf{r})$ and integrate over $\mathbf{r}$, we obtain

$$
\int \varphi_m^*(\mathbf{r})[H_{\mathrm{at}} + \Delta V(\mathbf{r})]\psi_{\mathbf{k}}(\mathbf{r})d\mathbf{r} = \varepsilon_{\mathbf{k}}\int \varphi_m^*(\mathbf{r})\psi_{\mathbf{k}}(\mathbf{r})d\mathbf{r}. \tag{14}
$$

Through equations (11) and (12), we reach the secular equation:

$$
\sum_n H_{\mathbf{k},mn}b_n = \varepsilon_{\mathbf{k}}\sum_n S_{\mathbf{k},mn}b_{\mathbf{k},n} \tag{15}
$$

where:

$$
H_{\mathbf{k},mn} = \sum_{\mathbf{T}_i} e^{i\mathbf{k}\cdot(\mathbf{T}_i-\mathbf{T}_j)}\int \varphi_m^*(\mathbf{r}-\mathbf{T}_j)[H_{\mathrm{at}} + \Delta V(\mathbf{r})]\varphi_n(\mathbf{r}-\mathbf{T}_i)d\mathbf{r} \tag{16}
$$

$$
S_{\mathbf{k},mn} = \sum_{\mathbf{T}_i} e^{i\mathbf{k}\cdot(\mathbf{T}_i-\mathbf{T}_j)}\int \varphi_m^*(\mathbf{r}-\mathbf{T}_j)\varphi_n(\mathbf{r}-\mathbf{T}_i)d\mathbf{r} \tag{17}
$$

where $\mathbf{T}_i$ and $\mathbf{T}_j$ are the positions of the i-th and j-th atoms within the crystal, which can be expressed as the sum of a Bravais translation $\mathbf{R}_{i/j}$ and the position of the atom within the cell $\mathbf{d}_{i/j}$: $\mathbf{T}_{i/j} = \mathbf{R}_{i/j} + \mathbf{d}_{i/j}$. We will refer to $H_{\mathbf{k},mn}$ and $S_{\mathbf{k},mn}$, respectively, as the Hamiltonian matrix and the overlap matrix. Both matrices, and the resulting generalized secular problem (15), are parametrically dependent on the wave vector $\mathbf{k}$. The solution of the secular equation (15) provides the band structure of the crystal.

We follow Ref. [2] to calculate the integrals in equations 16 and 17. The basic geometric element is the vector $\mathbf{T}_i - \mathbf{T}_j$ joining the two interacting atoms. By writing the atomic basis φ functions as linear combinations of functions quantized

with respect to the joining vector, we obtain the appropriate overlap matrix elementsi. For example a p orbital can be expressed as a linear combination of a $p\sigma$ and a $p\pi_{\pm}$ function. Assume that φ_m is a p_x function and φ_n is a d_{xy} function: we can symbolize the integral as $E_{x,xy}$. This function can be written in terms of two distance-dependent integrals: one between a $p\sigma$ orbital on the first atom and a $d\sigma$ orbital on the second, which we name $(pd\sigma)$; and one between a $p\pi$ orbital on the first and a $d\pi$ on the second, which we name $(pd\pi)$. All other components vanish due to the orthogonality of the atomic orbitals. By carrying out the calculations we obtain $E_{x,xy} = \sqrt{3}l^2m(pd\sigma) + m(1-2l^2)(pd\pi)$ where l, m, n are the direction cosines of the $\mathbf{R}_i - \mathbf{R}_j$ vector. Similar results can be obtained for other integrals, as reported in table 1 of Ref. [2]. The same procedure applies to both the energy and overlap integrals, although the distance-dependent integrals obviously have different values. The calculation of the distance-dependent integrals is detailed in the next chapter.

3 Implementation

The calculation of the electronic bands and total energy involves 5 steps, which are carried out through a C++ code:

1. the construction of the crystal through the input of a primitive cell and basis vectors;

2. the evaluation of the distances involved in the specific lattice structure considered, and correspondingly of the resulting two-center Slater-Koster energy integrals to construct the tight-binding matrices: for this step we make use of the parameterization provided by Ref. [1], which will be further explained in the next section;

3. the construction of a uniform grid of $\mathbf{k}$ points in a primitive cell of the reciprocal lattice;

4. the resolution of the secular equation (15), at each point of the $\mathbf{k}$-space grid: this diagonalization is carried out through the Eigen library [4];

5. the calculation of the chemical potential to determine which band states are full and which are empty, which then allows us to determine the total energy of the crystal.

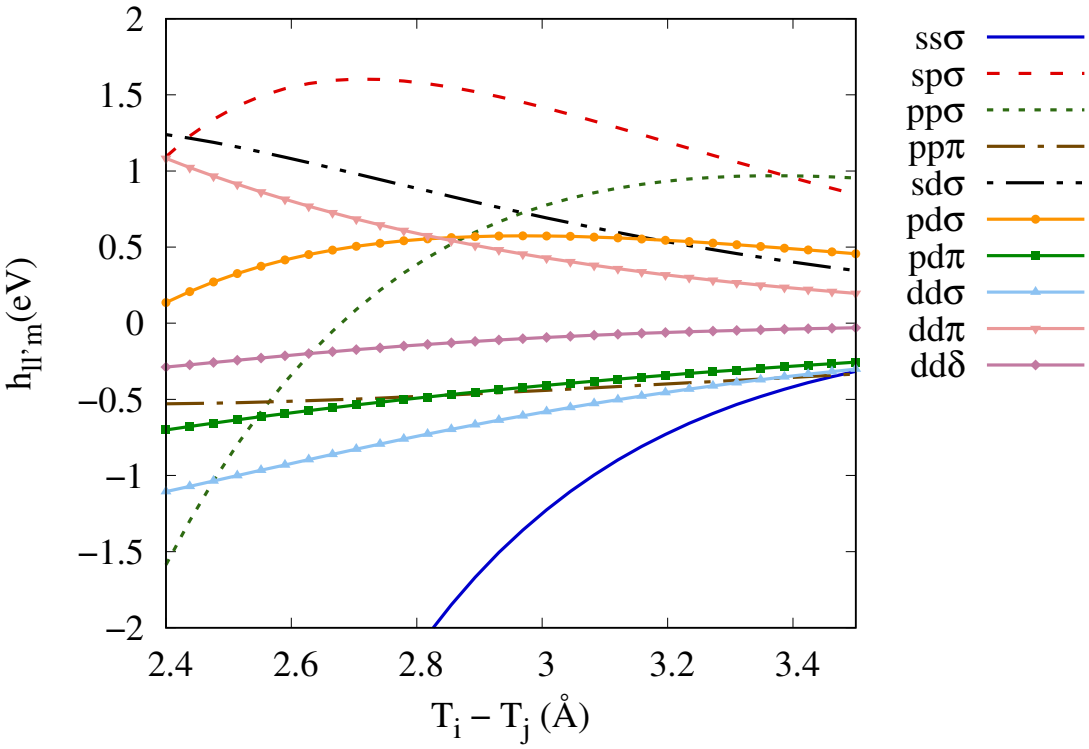

Figure 1: Tight-binding Hamiltonian Slater-Koster amplitudes as a function of the Ti-Ti distance $\mathbf{T}_i - \mathbf{T}_j$.

3.1 The parameterization

Following Ref. [2] we can simplify the energy and overlap matrix elements from equations (16), (17). Thus the matrix elements take the following form:

$$H_{\mathbf{k},mn} = \sum_{\mathbf{T}_i} e^{i\mathbf{k}\cdot(\mathbf{T}_i-\mathbf{T}_j)} E_{mn}(\mathbf{T}_i - \mathbf{T}_j) \tag{18}$$

$$S_{\mathbf{k},mn} = \sum_{\mathbf{T}_i} e^{i\mathbf{k}\cdot(\mathbf{T}_i-\mathbf{T}_j)} S_{mn}(\mathbf{T}_i - \mathbf{T}_j) \tag{19}$$

where E_{mn} and S_{mn} are respectively the energy and overlap Slater-Koster integrals reported in table 1 of Ref. [2]. We can also note that for $\mathbf{T}_i - \mathbf{T}_j = 0$ the non-diagonal terms vanish, therefore:

$$H_{\mathbf{k},mn} = \delta_{mn}\varepsilon_m + \sum_{\mathbf{T}_i \neq \mathbf{T}_j} e^{i\mathbf{k}\cdot(\mathbf{T}_i-\mathbf{T}_j)} E_{mn}(\mathbf{T}_i - \mathbf{T}_j) \tag{20}$$

$$S_{\mathbf{k},mn} = \delta_{mn} + \sum_{\mathbf{T}_i \neq \mathbf{T}_j} e^{i\mathbf{k}\cdot(\mathbf{T}_i-\mathbf{T}_j)} S_{mn}(\mathbf{T}_i - \mathbf{T}_j). \tag{21}$$

In Ref. [1] the Slater-Koster integrals are parameterized through three functions: hopping and overlap functions and onsite energies. A key observation is

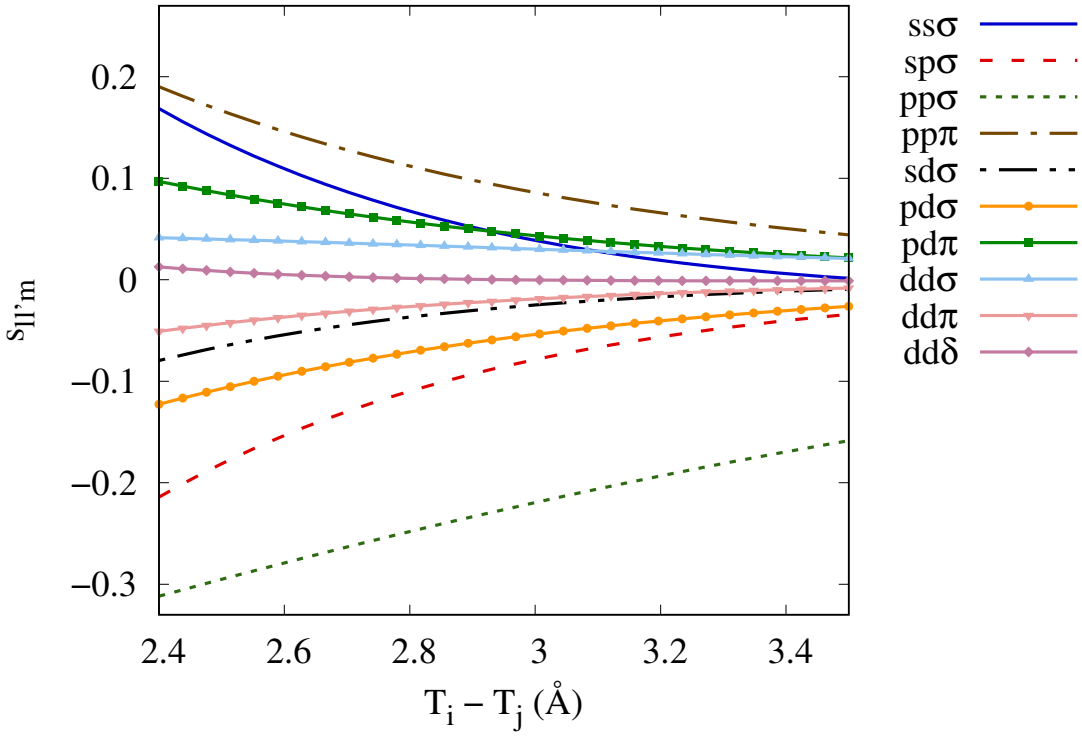

Figure 2: Tight-binding overlaps as a function of the Ti-Ti distance $\mathbf{T}_i - \mathbf{T}_j$.

that this model involves no explicit classic pair potential in the total energy, but it incorporates the effective potential into the 1-electron Hamiltonian through density-dependent onsite energies:

$$\varepsilon_{l,i} = a_l + b_l \rho_i^{2/3} + c_l \rho_i^{4/3} + d_l \rho_i^2, \tag{22}$$

where

$$\rho_i = \sum_{j \neq i} \exp(-\lambda^2 r_{ij}) f_c(r_{ij}) \tag{23}$$

is the local atomic density, i and j are atomic indices, l is the angular quantum number of the orbital, and $f_c(r)$ is a smooth cut-off function

$$f_c(r) = \left[1 + \exp\left(\frac{r - R_0}{l_0}\right)\right]^{-1}. \tag{24}$$

The intersite and overlap functions are as follows:

$$P_{ll'm}(r) = (e_{ll'm} + f_{ll'm} r) \exp(-g_{ll'm}^2 r) f_c(r). \tag{25}$$

The cut-off function $f_c(r)$ is the same for every parameter.

Crystal structures	Primitive vectors	Basis
sc	$\mathbf{a}_1 = a(1,0,0)$ $\mathbf{a}_2 = a(0,1,0)$ $\mathbf{a}_3 = a(0,0,1)$	$\mathbf{d}_1 = (0,0,0)$
bcc	$\mathbf{a}_1 = \frac{a}{2}(1,1,-1)$ $\mathbf{a}_2 = \frac{a}{2}(1,-1,1)$ $\mathbf{a}_3 = \frac{a}{2}(-1,1,1)$	$\mathbf{d}_1 = (0,0,0)$
fcc	$\mathbf{a}_1 = \frac{a}{2}(1,1,0)$ $\mathbf{a}_2 = \frac{a}{2}(1,0,1)$ $\mathbf{a}_3 = \frac{a}{2}(0,1,1)$	$\mathbf{d}_1 = (0,0,0)$
α-hcp	$\mathbf{a}_1 = a(1,0,0)$ $\mathbf{a}_2 = a(\frac{1}{2}, \frac{\sqrt{3}}{2}, 0)$ $\mathbf{a}_3 = c(0,0,1)$	$\mathbf{d}_1 = (0,0,0)$ $\mathbf{d}_2 = (\frac{1}{2}a, \frac{\sqrt{3}}{6}a, \frac{c}{2})$

Table 1: Primitive vectors and basis for different crystal structures.

The adopted parameterization includes the 4s, 4p and 3d orbitals of titanium. As a result it requires 3 onsite energy functions, labeled by the angular quantum number l; 10 hopping functions and 10 overlap functions, labeled by the kind of interaction: $ss\sigma$, $sp\sigma$, $pp\sigma$, $pp\pi$, $sd\sigma$, $pd\sigma$, $pd\pi$, $dd\sigma$, $dd\pi$, $dd\delta$. Overall this model relies on 60 parameters for the hopping and overlap functions, plus 15 parameters for the onsite energies. Figures 1 and 2 show the hopping and overlap functions as a function of the interatomic distance.

3.2 Bulk calculations

The adopted tight-binding model focuses on titanium crystals within the bulk approximation, i.e. ideal infinite crystalline structures. For this reason we write a C++ code that takes as input the basis and primitive vectors for selected periodic structures and the lattice spacing a, then it constructs the crystal by calculating the positions of all atoms within a pre-defined cut-off distance of the central cell. Following Ref. [1], we set the cut-off at 8 Å. The code then proceeds to calculate the onsite energies.

We use a regularly spaced $\mathbf{k}$ point mesh within the reciprocal primitive cell, as explained in Ref. [5]:

$$\mathbf{k} = \frac{n_1}{N}\mathbf{b}_1 + \frac{n_2}{N}\mathbf{b}_2 + \frac{n_3}{N}\mathbf{b}_3, \tag{26}$$

where n_1, n_2, n_3 are integers, $0 \leq n_1, n_2, n_3 < N$. We adopt $N = 15$that we verified leads to a sufficiently fine mesh to produce well-converged results. For each $\mathbf{k}$ point, the code cycles through all the atoms within the cutoff distance and calculates the intersite and overlap functions and constructs the matrices through equations (20) and (21). Next, using the `GeneralizedSelfAdjointEigenSolver` method provided by the Eigen library [4], it solves the generalized secular equation (15) and determines the energy levels of that $\mathbf{k}$ point. At the end of the $\mathbf{k}$ loop, the code sorts all energy levels (all bands at all $\mathbf{k}$ points) in ascending order: this is useful for the evaluation of the chemical potential.

Based on the obtained band energies, the code proceeds to evaluate the total energy. For this purpose, the code must first evaluate the number of electrons in the portion of the crystal we are considering: $N_{\text{el}} = N^3 \times N_{basis} \times 4$, where N_{basis} is the number of atoms in the primitive cell, and 4 is the number of electrons per titanium atom in the 4s, 4p and 3d orbitals included in this model: 2 3d electrons, and 2 4s electrons. To calculate the total energy of the crystal we fill the lowest $\frac{N_{\text{el}}}{2}$ energy levels with 2 electrons each. The total energy is obtained by adding up all sorted band energies of the filled states:

$$E_{tot} = 2 \sum_{\alpha \leq N_{\text{el}}/2} \varepsilon_\alpha. \tag{27}$$

We calculate the chemical potential as the average of the energies of the *Highest Occupied Molecular Orbital* (HOMO), i.e. level number $\frac{N_{\text{el}}}{2}$ in the sorted list, and the *Lowest Unoccupied Molecular Orbital* (LUMO), i.e. the successive level number $\frac{N_{\text{el}}}{2} + 1$ in the sorted list:

$$\mu = \frac{\varepsilon_{\text{LUMO}} + \varepsilon_{\text{HOMO}}}{2}. \tag{28}$$

The entire calculation is then repeated after varying the lattice spacing (and, proportionally, the basis vectors too): this allows us to calculate the total energy as a function of the volume of the cell, and therefore to determine the stablest structure of titanium. All calculations are done at the temperature $T = 0$ K.

We repeat this procedure for the following crystalline structures: simple cubic (sc), body-centered cubic (bcc), face-centered cubic (fcc), α hexagonal close-packed (α-hcp). Table 1 reports their basis and primitive vectors. Since in the hcp structure the entire calculation depends on 2 parameters, namely c and a, or equivalently on a and the $\frac{c}{a}$ ratio, the determination of the most stable structure cannot rely on a simple 1-parameter optimization as for the cubic structures. Therefore, we implement a simplex minimization method [6] to determine which values of a and c return the minimum energy. We then calculate the band struc-

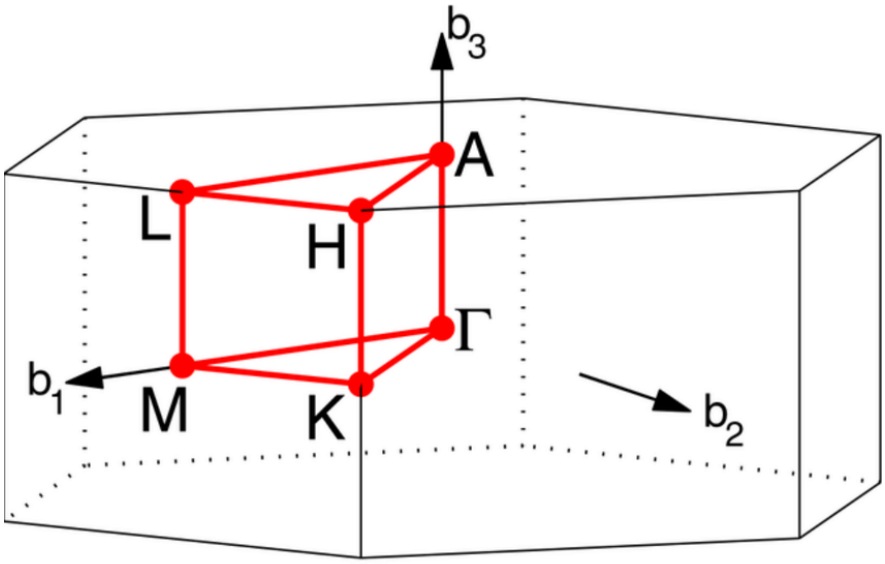

Figure 3: First Brillouin zone of the α-hcp structure with high symmetry points highlighted. In our computation of the electronic bands, we follow the path $\Gamma-M-K-\Gamma-A-L-H-A$.

ture for the equilibrium structure obtained in this way along a path in the first Brillouin zone, illustrated for the α-hcp example in Figure 3.

We also evaluate the bulk modulus for the equilibrium structure. The bulk modulus is defined as:

$$B = -V\frac{\partial P}{\partial V} = V\frac{\partial^2 F}{\partial V^2}, \tag{29}$$

where V is the volume per atom, P is the pressure, and F is the Helmholtz free energy per atom, which, at $T = 0$ K is equal to the total energy per atom E_{at}, therefore:

$$B = V\frac{\partial^2 E_{\mathrm{at}}}{\partial V^2}. \tag{30}$$

To evaluate the bulk modulus we fit our data near the equilibrium point to a second-degree polynomial $\alpha(x-\beta)^2+\gamma$, the bulk modulus is obtained as $B = 2\alpha\beta$.

3.3 Molecules and clusters

We can also run tight-binding calculations for molecules and finite clusters of titanium, with a few minor changes to the procedure. For isolated molecules, there is no need of a Bravais lattice. The code takes as input the positions of the

Atomic shell	Energy (eV)
4s	−3.272
3d	0.3632
4p	4.974

Table 2: Energy levels for the single titanium atom. The resulting total energy is $E_{\text{atom}} = -5.8176$ eV.

atoms, while the dimensions of the cell are set to be much greater than the cut-off distance, thus limiting the computation to just one cell. The lack of periodic boundary conditions also reduces the $\mathbf{k}$ point mesh to a single point ($N = 1$), making the computation of the energy levels generally faster. We attempted these calculations for the titanium dimer and for an icosahedral cluster consisting of 13 atoms (12 at the vertices plus 1 at the center). In order to determine the equilibrium positions of the atoms, we adopt a simplex minimization.

4 Results

In this section we report the results of our tight-binding simulations.

4.1 The titanium atom

We need a single titanium atom to provide the reference energy of the unbound atomized state. As previously mentioned, the model considers the 4s, 3d and 4p shells: as expected, we find three distinct energy levels, listed in table 2. In its ground state, the titanium atom has two electrons in the 4s shell plus 2 electrons in the 3d shell, resulting in a total energy $E_{\text{atom}} = -5.8176$ eV.

4.2 The Ti_2 dimer

Figure 4 reports the computed total energy per atom for the titanium dimer. The results appear of little physical significance for at least two reasons: (i) at distance $r > 2.9$ Å this adiabatic energy is a decreasing function of distance, indicating an unphysical repulsive character; (ii) attraction develops at smaller distance, but at distances smaller than 2 Å jump discontinuities appear, indicating serious problems with the model. At small distance, the dimer energy keeps decreasing, instead of becoming positive, indicating that the interaction is attractive, rather than repulsive as expected due to the overlap of the core shells. At large distances

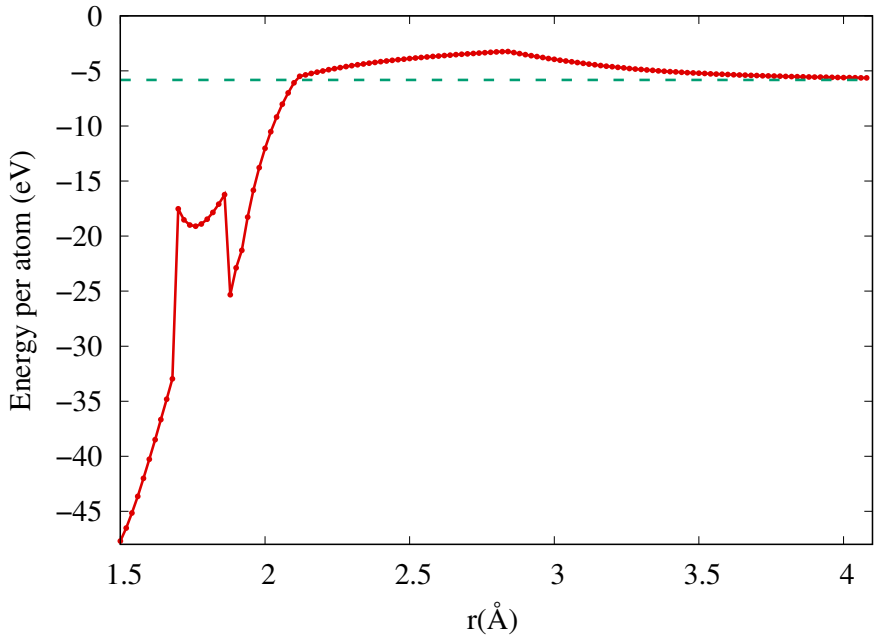

Figure 4: Energy per atom of the titanium dimer as a function of the interatomic distance. The dashed line represents the reference energy of an isolated atom. The jump discontinuities at small distance and the repulsive regime at large distance are both unphysical.

the total energy is greater than the energy of an isolated atom, indicated by the dashed line in 4, suggesting that if titanium was to follow this model, the Ti_2 dimer would decompose spontaneously into single atoms. The energy levels, reported in Figure 5 display the same discontinuities at short distances, although at long distances they behave as expected, converging into the 4s, 3d and 4p levels. The simplex method yielded no meaningful results, as the total energy has no minimum.

The non-physical behavior of the model at short distances is easily understood by examining the overlap matrix. For the secular equation (15) to be solvable, the overlap matrix $S_{\mathbf{k}}$ must be positive definite, otherwise the diagonalization fails. Figure 6 reports the eigenvalues of the overlap matrix S for the dimer: the lowest eigenvalue becomes negative at interatomic distances lower than approximately 2Å. As a result, the S matrix stops being definite positive, and thus all generalized diagonalizations of the TB equation (15) become meaningless under 2Å.

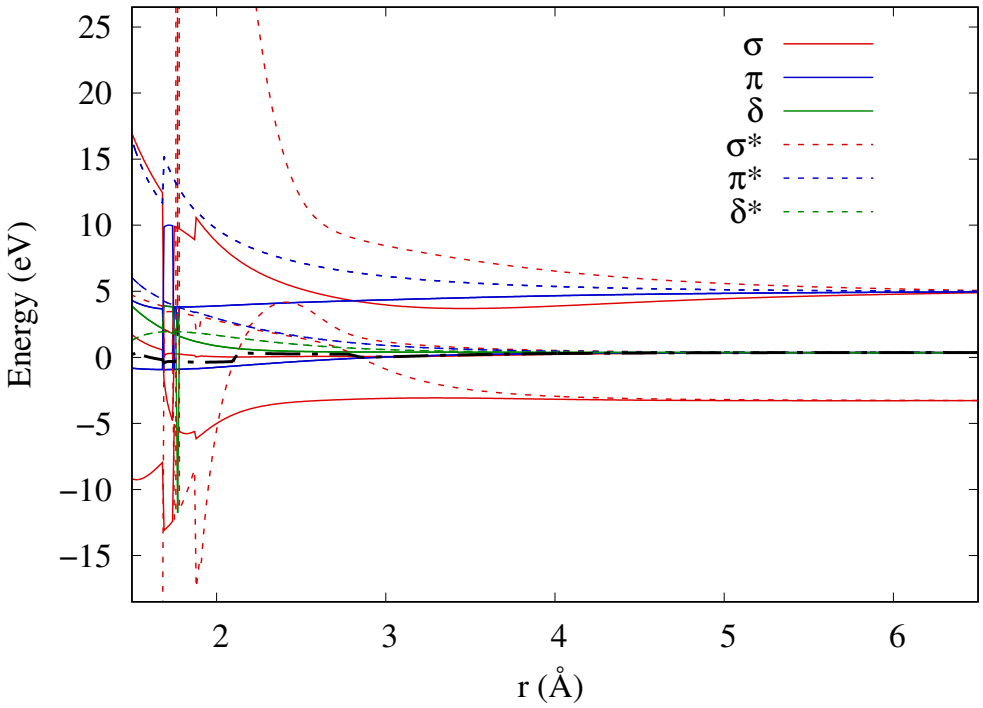

Figure 5: Molecular energy levels of the titanium dimer as a function of the interatomic distance. At short distances they show the same discontinuous behavior as the total energy, while at large distances they converge into the 4s, 3d and 4p atomic energies. The dashed black line represents the chemical potential.

4.3 Bulk structures

We must first check the convergence of the total energy as a function of the **k** point mesh used. Figure 7 shows that, for a **k** point mesh consisting of at least $15 \times 15 \times 15$ points, the discrepancy between the total energy and the value obtained with the finest mesh we could consider within reasonable execution times is smaller than 1 meV. Total-energy minimization for the α-hcp structure is carried out by means of the simplex method. The equilibrium structure is found for $\frac{c}{a} = 1.618$ and $a = 2.941$. Figure 8 reports the energy-volume curves for the α-hcp structure for different values of $\frac{c}{a}$. The results sketched in Figure 9 show that the α-hcp structure is the stablest one for a titanium crystal. The results we obtained are slightly different from those of Ref. [1]. This is likely due to a difference in the **k** point mesh: we cannot be sure because in Ref. [1] no clear indication is provided of what **k**-point mesh is adopted. Regardless of these details, the best structure shows a cohesive energy of just 0.3324 eV per atom, a

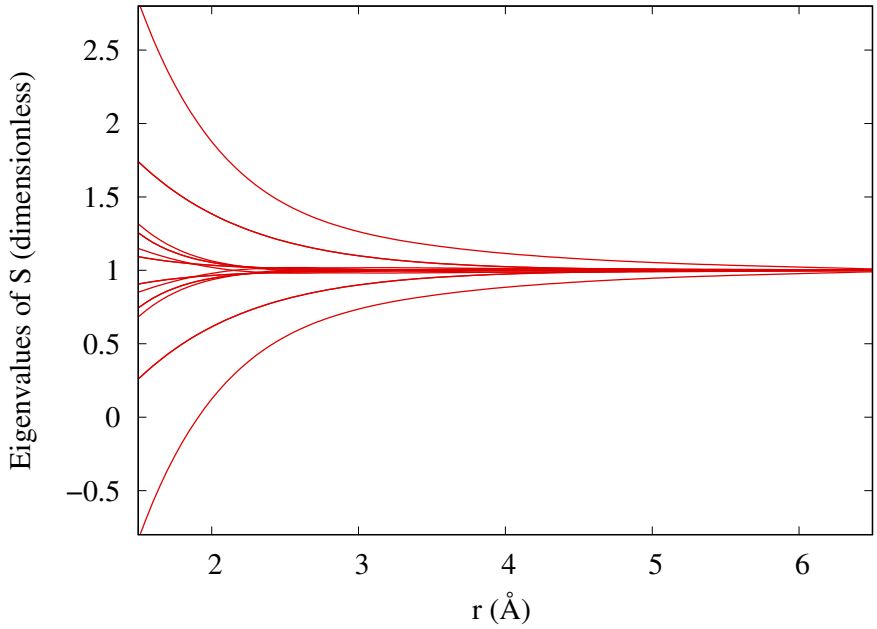

Figure 6: The eigenvalues of the overlap matrix S for the titanium dimer as a function of the interatomic distance. Around 2Å the lowest eigenvalue becomes negative, thus the matrix is no longer positive definite and the secular equation (15) cannot be solved.

stark variance from the accepted experimental value of 4.85 eV per atom (taken from Ref. [7]). The value obtained for the lattice constant a at the equilibrium structure is in good agreement with the experimental value of $a = 2.95$, while the value of $\frac{c}{a}$ is somewhat larger than the experimental value of $\frac{c}{a} = 1.59$. The value we obtained for the bulk modulus is $B = 115.8$ GPa, not far from the experimental value of 110 GPa (Ref. [8]).

Figure 10 shows the computed electronic bands of the titanium α-hcp crystal in its equilibrium geometry. As we can observe, the chemical potential crosses multiple bands: this is expected as titanium is a conductor. For comparison, in Fig. 11 we report the electronic bands computed with the FLAPW method in Ref. [9]. As we can observe, the graphs are qualitatively similar, except for the $M - K$ segment, where the bands exhibit different behaviors.

4.4 The icosahedral cluster

Our calculations for the icosahedral cluster, summarized in Figure 12, exhibit issues similar as those of the diatomic molecule: the total energy is discontinuous at short distances; the cluster is unstable, as it has higher energy than 13 isolated

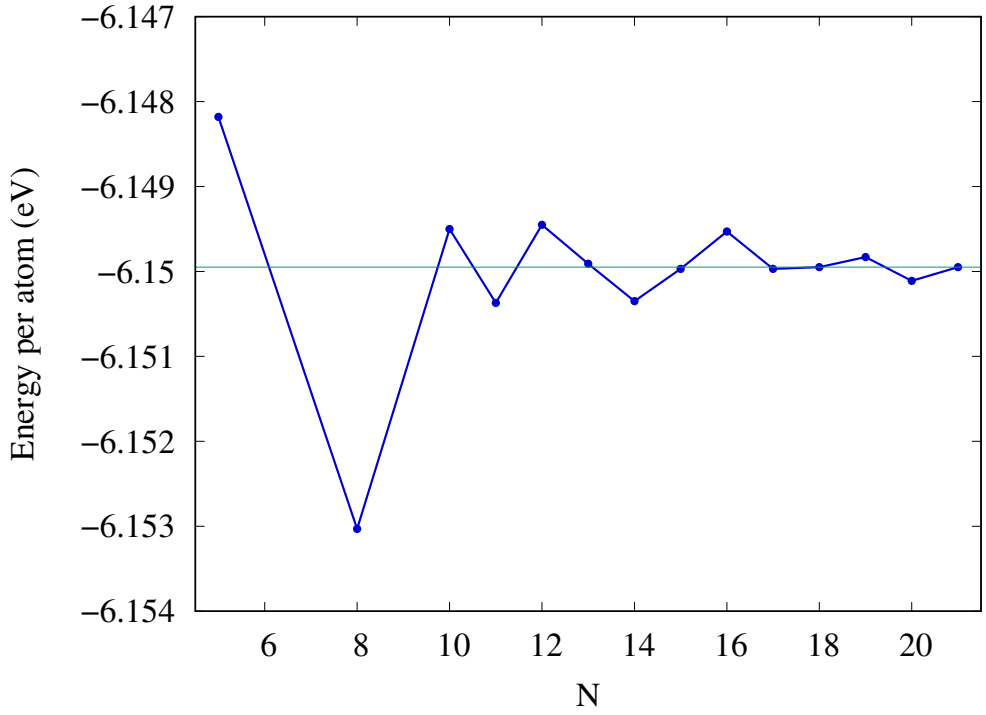

Figure 7: Total energy per atom of a titanium α-hcp crystal as a function of the number of $\mathbf{k}$ points used in the TB calculation. The total energy is computed at the equilibrium structure $a = 2.941$ and $\frac{c}{a} = 1.618$. The horizontal line represents the total energy obtained for the largest mesh computed ($N = 21$).

atoms, and the interaction is repulsive at large distances.

5 Discussion and conclusions

In summary, we implemented a code that calculates the total energy and band structure for arbitrary titanium crystals and molecules within a published tight-binding scheme [1]. We verified the results reported in Ref. [1] and obtained compatible results for the equilibrium structures. The most stable structure of this tight-binding model is the α-hcp crystal with $\frac{c}{a} = 1.618$ and $a = 2.941$, not far off the experimental structure. For the equilibrium structure we also report the energy bands, of course indicating metallic properties. Moreover, the crystal cohesive energy is dramatically smaller than expected based on experiment.

We applied the same method to calculate the bonding energy of titanium molecules and obtained more unphysical results. All these discussed problems

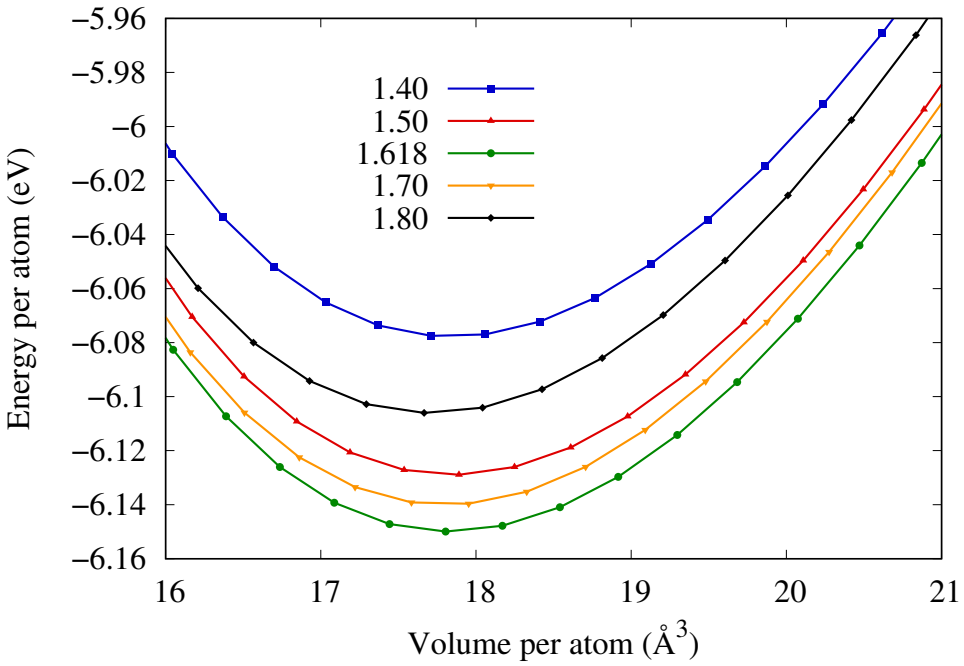

Figure 8: Total energy for the α-hcp structure calculated for a few values of $\frac{c}{a}$. The minimum energy, determined through the simplex method, is obtained for $\frac{c}{a} = 1.618$.

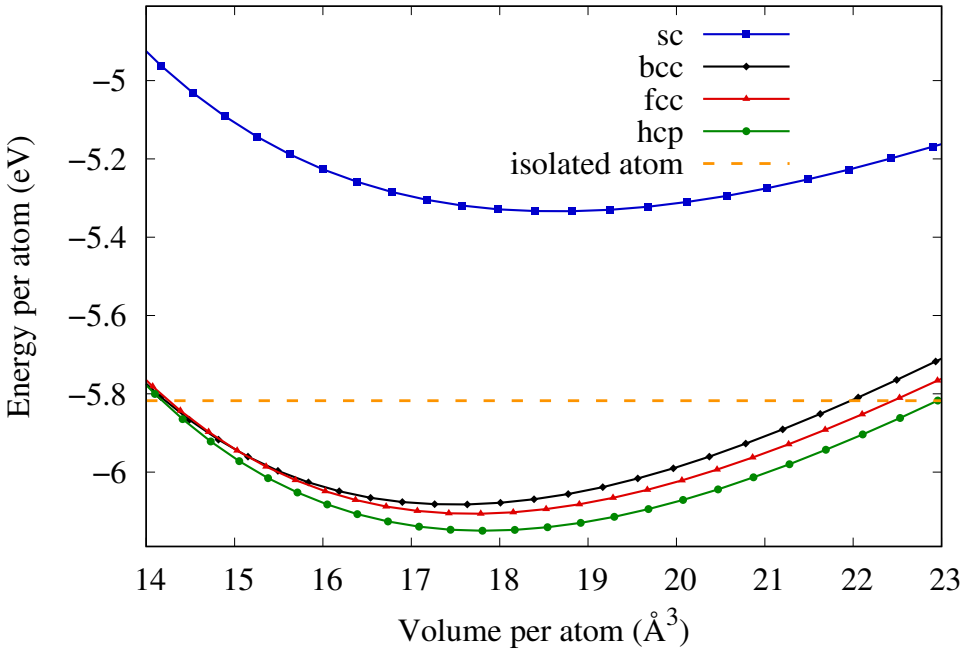

Figure 9: Total energy per atom of the crystal as a function of the volume per atom. The hcp curve is the same as if Figure 8, namely with $\frac{c}{a} = 1.618$.

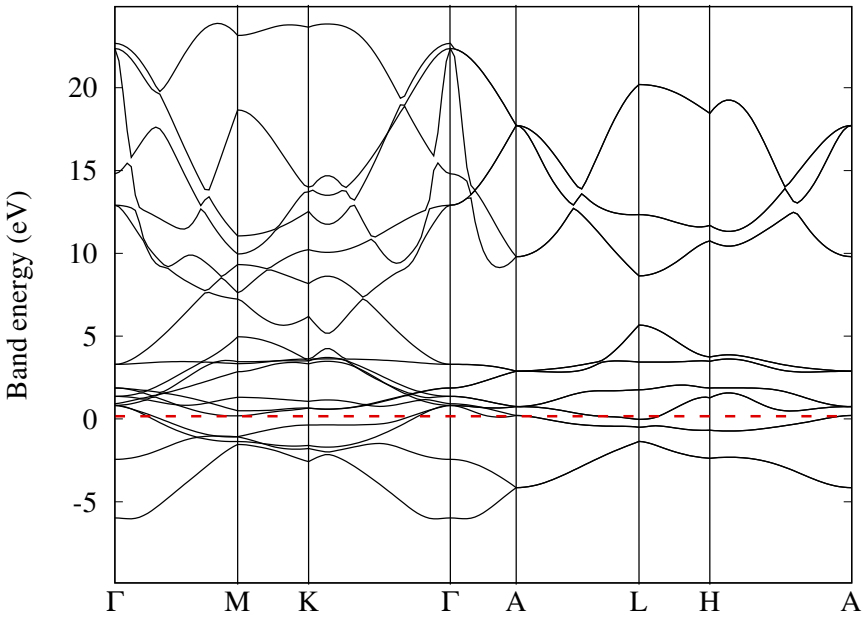

Figure 10: Titanium band structure for the α-hcp structure with $\frac{c}{a}$ = 1.618 and a=2.941. The calculation was made along the path shown in Figure 3. We evaluated the chemical potential at T = 0 K to be μ = 0.170 eV, represented by the red dashed line.

are to be attributed to the parameterization adopted. The most likely rationale is that this parameterization is based on a fitting database that only contains calculations with crystalline structures involving Ti-Ti distances greater than 2.350Å. As a results it is no surprise that this model fails for molecules, especially at small distances. In practice, the TB model of Ref. [1] proves to be a radically non-transferable model.

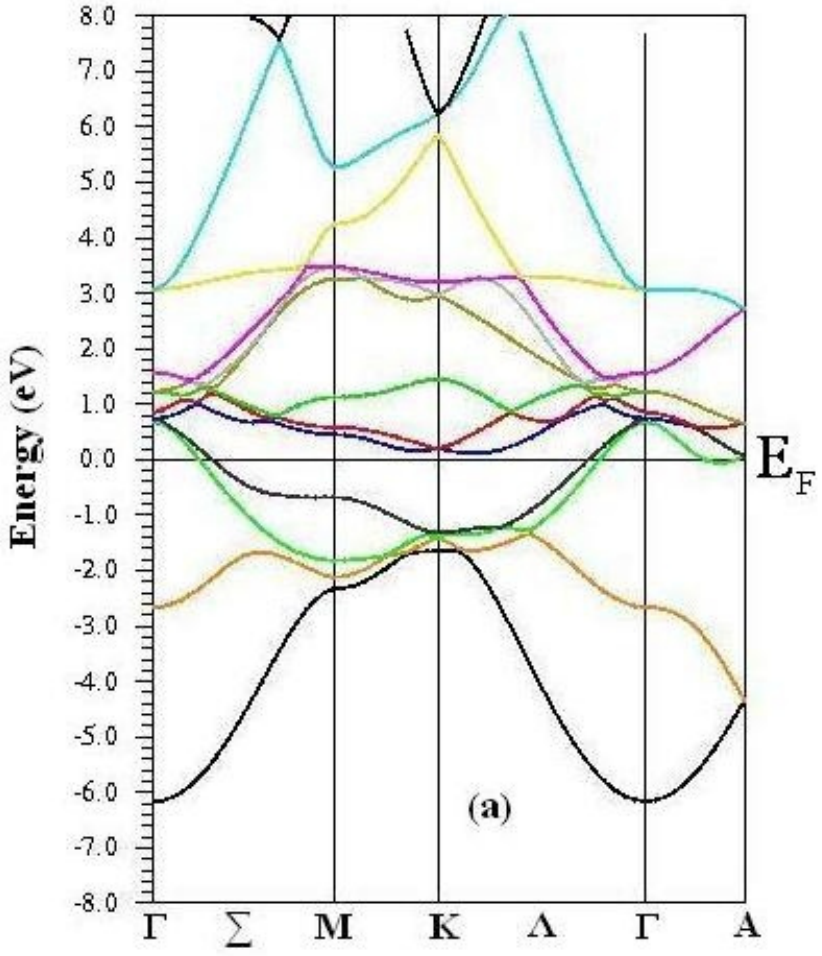

Figure 11: Titanium band structure computed through the FLAPW method for the α-hcp structure at $\frac{c}{a}$ = 1.584 and a = 2.957. This graph was taken from Ref. [9].

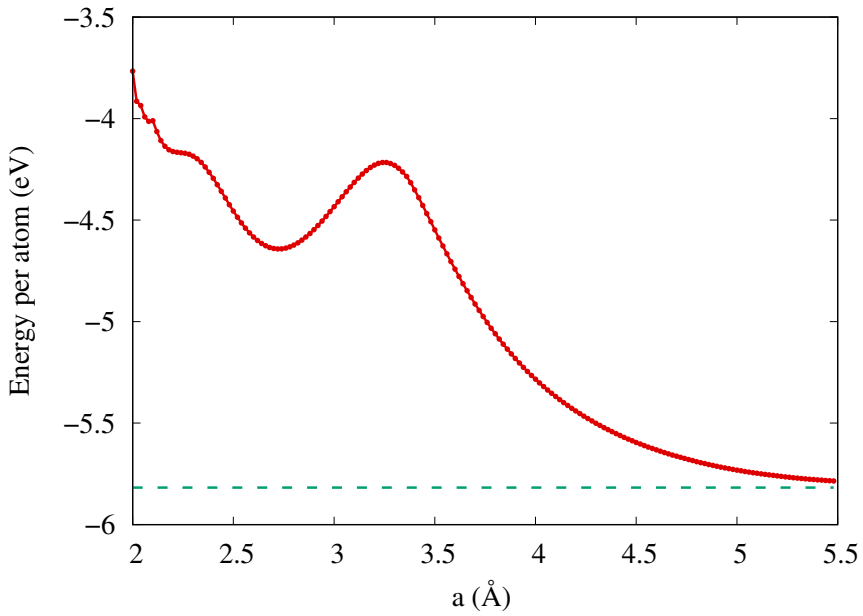

Figure 12: Total energy per atom of a titanium icosahedral cluster (13 atoms: 1 in the middle and 12 at the vertices of the regular icosahedron) as a function of the distance from the vertices to the center.

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