Electronic band structure of platinum low–index surfaces: 
an ab initio vs. tight–binding study. II

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As a second part of a previous paper, here the calculated electronic band structure of ideal Pt(100) and Pt(110) surfaces, studied using density functional theory and the empirical tight–binding method, is presented. A detailed discussion of the surface– and resonance–states is given. It is shown that the calculated surface– and resonance–states of ideal Pt(100) surfaces agree very well with the available experimental data. For Pt(110), some of the surface– and resonance–states are characteristic of the low degree of symmetry of the surface and are identified as being independent of surface reconstruction effects. As in the previous paper, the density functional calculations were performed using the full potential linearized augmented plane wave method, and the empirical calculations were performed using the tight–binding method and Surface Green’s Function Matching Method.

PACS numbers: 73.20.At,71.15.Ap,71.15.Mb

I. INTRODUCTION

This work presents the continuation of our study of the Pt low–index surfaces. In a previous paper we have discussed our calculations on Pt(111) surface [1], and in this paper we will discuss our results on Pt(100) and Pt(110) surfaces.

The Pt(100) surface is usually studied in the (1 × 1) and (5 × 1) phases. The unreconstructed (1 × 1) phase is metastable, whereas the reconstructed (5 × 1) phase is obtained after the sample is annealed at 400 K [2–4]. The reported surface– and resonance–states of the metastable (1×1) phase were accurately reproduced in the present work. The experimental reports of controversial surface–states are clarified in this work. A surface–state that was recently reported by Subaran et al. [3], and was not observed in previous reports is properly identified in these calculations.

It is established that the Pt(110) surface exhibits the so–called (1 × 2) missing row reconstruction, whereas the (1 × 1) phase is metastable [4]. In this work, however, the calculation was performed on an ideal Pt(110) surface. Although we did not find experimental data related to this phase, for completeness, we will discuss our results and will qualitatively compare our results with previous experimental data on the (1 × 2) missing row phase [4]. These calculations reveal several surface– and resonance–states that are reported to be characteristic of a low degree of symmetry of the surface. These states are identified as being independent of surface reconstruction effects, and these facts support our approach to computations of the characteristics of this surface.

The rest of the paper is organized as follows: In Section II the essentials of the calculation methods are given. Sections III–IV contain the results and a discussion of the studied surfaces. A comparison of these results with ETB calculations is also presented in these sections. Section V summarizes our work.

II. COMPUTATIONAL STRATEGY

The DFT calculations were done using the full potential linearized augmented plane wave (LAPW) method [10], while the empirical tight–binding (ETB) calculations were done using the parametrization of Papaconstantopoulos [11] and the surface Green function matching (SGFM) method of García–Moliner and Velasco [12]. The details of the DFT and ETB methods used in our calculations can be seen in Reference [1]. Here we only comment the essentials of the DFT variational parameters used in our supercell calculations. The ETB parameters and model used in the empirical calculations are the same as those discussed in Ref. [1].

To minimize the total energy of the Pt(100) surface, a supercell with 15–atomic layers and 9–vacuum layers was used, whereas a supercell of 21–atomic layers and 13–vacuum layers was used for the Pt(110) surface.

In the calculations, the step analysis was carefully performed to ensure the convergence of the total energy in terms of the variational parameters. At the same time, an appropriate set of k points was used. The varia-
tional parameters used for the two studied surfaces were $R_{k\text{max}} = 9$ Ry and $G_{\text{max}} = 14$. The total energy of the Pt(100) surface was minimized using a set of 91 $k-$points in the irreducible portion of the BZ, equivalent to a $25 \times 25 \times 1$ Monkhorst–Pack grid in the unit cell. For the Pt(110) surface, the total energy was minimized using a set of 88 $k-$points in the irreducible portion of the BZ, equivalent to a $22 \times 16 \times 1$ Monkhorst–Pack grid. Finally, the total energy converged with a resolution better than 0.0001 Ry.

As in the case of Pt(111), and to check the accuracy of the electronic properties calculated from the supercell approach, the calculated bulk density of states (DOS) is compared with the DOS projected onto the central atomic layers of the different supercells. It should be noted that in this approach, the DOS projected onto the central atomic layer must be similar to the calculated bulk DOS. Figure 1 shows that this is the case. In the figure, the calculated bulk DOS is shown as a solid line, the calculated DOS projected onto the central atomic layer is presented as a dotted line, and the calculated DOS projected onto the outer atomic layer is presented as a broken line. In the upper panel, the partial bulk–DOS projected onto the outer atomic layer is presented as a dotted line, and the calculated DOS projected onto the central atomic layer is presented as a solid line, properly reproduces the main features of the bulk DOS. The comparison of the DOS calculated using the ETB method with the DOS projected onto the central atomic layers of the different supercells. It should be noted that in this approach, the DOS projected onto the central atomic layer must be similar to the calculated bulk DOS. Figure 1 shows that this is the case. In the figure, the calculated bulk DOS is shown as a solid line, the calculated DOS projected onto the central atomic layer is presented as a dotted line, and the calculated DOS projected onto the outer atomic layer is presented as a broken line. In the upper panel, the partial bulk–DOS projected onto the Pt–5$d$ orbitals is also shown. The figure shows that in the energy range from approximately –7.0 eV to 0.5 eV, the main contribution to the bulk DOS is obtained from the $d$ electrons. This symmetry composition should be reflected in the obtained surface electronic band structure. The upper panel shows the calculated DOS of Pt(100) and the lower panel shows the results for Pt(110). In the figures, the zero of the energy axis represents the Fermi level ($E_F$). The figure shows that below $E_F$, the DOS projected onto the central layer (broken line) properly reproduces the main features of the bulk DOS (solid line) for each studied surface. The bulk DOS exhibits four main peaks that are accurately reproduced by the DOS projected onto the central atomic layer. The same is true of the width and energy of the main peak. The small observed differences are related to the shape of the main peaks. Above $E_F$, Fig. shows that the DOS projected onto the central layer properly reproduces the bulk DOS up to 6.0 eV, at which point some differences between the two calculations were observed.

However, it is clear from Fig. that the calculated DOS projected onto the outer atomic layer is significantly different from the bulk DOS. There are important features obtained from the projected surface DOS: these features were obtained below and above $E_F$ but were not obtained for the bulk DOS. Information about the surface– and resonance–states will be found from these differences. Below $E_F$, resonance–states are expected to be obtained, primarily because these energies represent the continuum of the projected bulk bands, and few energy gaps exist at these energy values. The surface–states will be obtained above $E_F$ because energy gaps are more frequently observed at these energies.

The comparison of the DOS calculated using the ETB and the DFT methods is shown in the inset of each figure. As can be observed the calculated DOS using both methods are quite similar, mainly for energies below $E_F$. From these facts, it will be shown that the found surface electronic band structure is also quite similar in both calculations.

## III. RESULTS AND DISCUSSION

### A. Platinum(100)

Figure 2 shows the calculated DFT pbs as well as the SSs and RSs of Pt(100). Table I shows the wavefunction compositions of the different SSs and RSs.

For this surface, at the $\bar{X}$ point, an SS was found approximately 4.3 eV above $E_F$. An RS was also found at the $\bar{M}$ point at energies that range from 9.0 eV to 10.0 eV, as shown in Fig. 2. These states are supported by the calculated DOS projected onto the surface as noted in Fig. 1. According to the DFT calculations, the wavefunctions of these states have the symmetries of the $s$, $d_{x^2+y^2}$ and $d_{xy}$ orbitals, respectively.

However, as can be observed in Fig. 2 a number of SSs and RSs were obtained at energies below $E_F$.

According to the convention for a resonance state given above, an RS was obtained at lower energies, approximately 6.4 eV below $E_F$. The state seems to begin at the $\bar{M}$ point at energies that range from 9.0 eV to 10.0 eV, as shown in Fig. 2. These states are supported by the calculated DOS projected onto the surface as noted in Fig. 1. According to the DFT calculations, the wavefunctions of these states have the symmetries of the $s$, $d_{x^2+y^2}$ and $d_{xy}$ orbitals, respectively.

An RS was obtained at energies of approximately 3.6 eV in the $\bar{G}$–$\bar{X}$ interval and seems to have an oscillatory shape. That is, the state seems to extend throughout the SBZ, crossing the $\bar{X}$–point at 3.5 eV, then crossing the $\bar{M}$–$\bar{F}$ point at 0.2 eV, and finally ending at 3.6 eV in the middle of the $\bar{M}$–$\bar{G}$ interval. Although the state seems to be discontinuous in its trajectory, this could be a consequence of the numerical accuracy; the state should be a single band crossing the entire SBZ. A similar pattern was observed for the Pt(111) surface. The wavefunction composition of this RS has the $s$, $d_{x^2+y^2}$ symmetry.

Similar comments are appropriate for the RS that begins at 2.1 eV in the $\bar{G}$–$\bar{X}$ interval and seems to continue through the $\bar{X}$–point before going through the $\bar{M}$–point and mixing with the previously discussed RS. This state finally ends at the $\bar{X}$–point once again. Although it is difficult to establish a unique pattern for these RSs, it could be possible that they represent one band that crosses the entire SBZ. A similar pattern was observed for the Pt(111) surface. The wavefunction composition of this RS has the $d_{x^2+y^2}$ and $d_{xy}$ symmetry.

At $\bar{M}$, a lower RS with a parabolic shape as a function of $k_{||}$ was found. This state begins near the local gap located between 4.0 – 5.0 eV and ends in the middle of the $\bar{M}$–$\bar{G}$ interval. The wavefunction composition of this RS is $s$, $d_{x^2+y^2}$.
Near $E_F$ at the $\tilde{M}$ point, a surface state with a negative curvature is observed. The state goes into the local gap above $E_F$ with a bandwidth of approximately 1.1 eV. The calculated wavefunction composition of this SS is $d_{x^2+y^2}$.

B. Comparison with experiment

It is well known that Pt(100) exhibits both the unreconstructed (1 x 1) surface and the reconstructed (5 x 1) surface [2,4]. However, the ideal surface was studied in this work, and the results will be compared with experimental data found for the (1 x 1) phase.

Using angle–resolved photoemission spectroscopy, Stampfl et al. [2] reported the SSs of Pt(100)(1 x 1) at energies below $E_F$. These authors present a rich number of SSs along the $\tilde{M} - \tilde{\Gamma} - \tilde{X}$ interval for the (1 x 1) phase (see Fig. 2 in Ref. [2]). Although these states are not discussed in detail in Ref. [2], it will be shown that the general shape of the reported states is reproduced accurately in the present work.

As was reported by Stampfl et al. [2], there is an RS near $E_F$ for the $\tilde{M} - \tilde{\Gamma}$ interval that follows the border of the $E_F$. The state shows almost zero dispersion as a function of $k_{||}$ (see Fig. 2 in Ref. [2]). The DFT calculations found a state around the $\tilde{M}$ point located mainly in the local gap just above $E_F$, and this state could be identified with the experimental one.

There are two RSs reported at 0.6 and 0.9 eV at the $\tilde{M}$ point. These states are dispersed throughout nearly the entire $\tilde{M} - \tilde{\Gamma} - \tilde{X}$ interval (see Fig. 2 in Ref. [2]). The energy dispersion of these states is worth noting and is reproduced properly in the DFT calculations (see Fig. 2). As mentioned above, these states show quasi–oscillatory behavior in this portion of the SBZ. A similar pattern can also be observed from the calculated bands shown in Fig. 2(b) in Ref. [2].

Stampfl et al. [2] reported another RS at low energies around 5.5 eV at the $\tilde{M}$ point. This state is reproduced accurately in the DFT calculation as discussed above (see Fig. 2 and Table I).

Near the $\tilde{X}$ point, an RS that reaches the $\tilde{X}$ point was found around 2.3 eV. This state seems to be related to the state around 2.5 eV reported by Stampfl et al. [2].

However, Subaran et al. [3] used angle–resolved photoemission spectroscopy and reported a flat band around 4.0 eV at the $\tilde{X}$ point, which differs from the experimental data reported in Ref. [2]. It was speculated that this band represents emission from the surface layer or that it arises from adsorbate atoms [3].

As was shown above, our calculations found an RS around 3.6 eV that very accurately reproduces the dispersion and shape of the state reported by Subaran et al. [3]. As was mentioned there, this state seems to be part of a continuous band that crosses the entire SBZ (see Fig. 2 and Table I).

Stampfl et al. [2] reported another RS at energies around 6.5 eV at the $\tilde{\Gamma}$ point. This state exhibits parabolic dispersion as a function of $k_{||}$, and as mentioned above, our DFT calculations properly reproduce this state.

Stampfl et al. [2] reported an RS around –0.3 eV at the $\tilde{\Gamma}$ point, and this state is also reproduced in the DFT calculations.

It is well known that it is difficult to reproduce experimental measurements individually. However, the accuracy of our calculated SSs and RSs in comparison with those reported by Stampfl et al. [2] for the Pt(100) surface is worth noting.

In an early experimental work Drube et al. [4] used angle–dependent inverse photoemission. To measure the SSs of Pt(100)(1 x 1) at energies above $E_F$. Energy band dispersion was found in the $\tilde{\Gamma} - \tilde{X}$ interval.

These authors found an SS in the local gap above $E_F$, which is labeled $S_1$ in Fig. 3 of Ref. [4].

The authors also report a state at 0.6 eV above $E_F$ that seems to be an RS: the state labeled $B_1$ in Fig. 3 of Ref. [4].

They also report a state labeled $D$. The authors mention that they did not find an explanation for this state.

A state labeled $B_2$, which exhibited significant dispersion, was also reported. Although this state is found nearly inside the bulk bands, there is a portion of the state that penetrates into the local gap near the $\tilde{X}$ point.

Discussion of these states and comparison with our DFT calculations is left for the next section, where the ETB results for the Pt(100) surface will be presented.

C. Tight–Binding Calculations

Figure 2 shows the calculated pbbs, SSs, and RSs for Pt(100) using the FLAPW method and compares them with those obtained using the ETB method. Table I shows the wavefunction compositions of the different SSs and RSs. As in the Pt(111) case, the ETB calculation properly reproduces the pbbs, SSs, and RSs that were found in the DFT calculations. A few discrepancies are observed and will be discussed below. The observed differences include the fact that the ETB calculations do not find the same number of states as the DFT calculations.

Figure 2 shows that the local energy gaps found in the ETB calculations are identical to those calculated using DFT. More importantly, the dispersion of the SSs in the local gaps found by the ETB calculations is almost the same as those found by the DFT calculations.

However, the ETB calculations predict an SS located in the local gap above $E_F$ at the $\tilde{\Gamma}$ point that seems to be related to the state that was reported by Drube et al. [4]. This state was not found in the DFT calculations. This SS was reported at approximately 5.5 eV, and the state was found at 4.3 eV in the ETB calculation. The state increases in energy to approximately 6.0 eV and seems to mix with the bulk bands. The calculated ETB wavefunction composition of this state exhibits $s, p_z$ symmetry (see Table I).
Another SS was found in the ETB calculations but not in the DFT calculation. The state exhibits significant dispersion as a function of \( k_{||} \), is located at approximately 2.1 eV in the local gap around the \( \bar{X} \) point, and disperses following the lower edge of the local gap. The calculated ETB wavefunction composition of this state has the \( p_x, p_y \) symmetry (see Table I).

An SS following the upper edge of the local gap at \( \bar{X} \) was found at approximately 4.3 eV. It was found that both calculations predict this state, but no experimental evidence for this state was found.

At energies below \( E_F \), the ETB calculation properly reproduces most of the SSs and RSs found in the DFT calculations, as shown in Fig. 2. In some cases, there are some small numerical differences in the calculated energy values of these states, but in general, most of the features found in the DFT calculation were also found in the ETB calculation.

The ETB calculations also reproduce most of the experimental data reported by Stampfl et al. [2]. These facts demonstrate the predictive power of the ETB method.

### IV. PLATINUM(110)

Figure 3 shows the calculated pbbs, SSs, and RSs for Pt(110). Table II shows the calculated wavefunction compositions of the different SSs and RSs of this surface.

As in previous cases, the figure shows the pbbs as small black dots, and the SSs and RSs are shown as red dots.

The figure shows four local gap above \( E_F \), and three local gaps are found at energies below \( E_F \).

Three SSs above \( E_F \) were found from the calculations. An SS is found in the local gap at the \( \bar{X} \) point around 5.3 eV. This state exhibits nearly parabolic behavior as a function of \( k_{||} \), and its energy bandwidth is approximately 1.0 eV. The state mixes with a calculated RS obtained at the \( \bar{S} \)–point at approximately 6.2 eV. The wavefunction of this SS has \( s, p_z \) symmetry.

Another SS was located near the bottom of this local gap. This state is located at 2.4 eV and extends a few \( k \)-values from the \( \bar{X} \) point. The computed wavefunction composition of this state is \( s, d_{x^2+y^2}, d_{xz} \).

Near the \( \bar{X} \) point, there is an RS that should be noted. This state shows peculiar behavior as a function of \( k_{||} \). The state seems to originate in the group of RSs located in the energy range from 0 to 1.0 eV below \( E_F \) and exhibits significant energy dispersion following the edge of the local gap.

An SS was obtained in the local gap at the \( \bar{Y} \) point. This state exhibits little dispersion as a function of \( k_{||} \). The state is located at approximately 2.1 eV, and the calculated wavefunction composition of this state is \( s, d_{x^2+y^2}, d_{xz} \).

As for the previous surfaces, a number of RSs were found at energies below \( E_F \) and are shown in Fig. 3. The main characteristics of these states are as follows:

A noticeable SS was found at low energies, approximately 5.9 eV in the \( \bar{Y} \)–\( \bar{\Gamma} \) interval. The state begins in the lower local gap at \( \bar{Y} \) and then continues into the continuum of the pbbs in the \( \bar{Y} \)–\( \bar{\Gamma} \) interval. The wavefunction composition of this state is \( s, d_{x^2+y^2} \).

Similarly, a series of RSs were found near \( E_F \) in the \( \bar{Y} \)–\( \bar{\Gamma} \) interval located at energies that range from 0.0 to 3.0 eV. The states then go through the \( \bar{\Gamma} \)–\( \bar{X} \) interval.

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**Table I: Calculated energy values and wave function compositions of the different surface states found for Pt(001).**

| Point | State | Energy value (eV) | Wave function |
|-------|-------|------------------|--------------|
| \( \bar{\Gamma} \) | SS | 4.3 | \( d_{xz}, d_{z^2} \) | \( s, p_x \) |
| | RS | 0.0 | \( d_{xy} \) | \( s, d_{xy} \) |
| | RS | -6.4 | \( d_{xy}, d_{z^2} \) | \( s, d_{xy}, d_{z^2} \) |
| \( \bar{X} \) | SS | 4.3 | \( s, d_{x^2+y^2} \) | \( s, d_{xy} \) |
| | RS | 2.1 | \( d_{xz} \) | \( p_x, p_y \) |
| | RS | -2.3 | \( d_{xy}, d_{xz} \) | \( d_{xy} \) |
| | RS | -4.0 | \( d_{x^2+y^2}, d_{xz} \) | \( d \) |
| | SS | -5.0 | \( d_{x^2+y^2} \) | \( s, d_{xy} \) |
| \( \bar{M} \) | RS | 9.0–10.0 | \( d_{xy} \) | \( s, d_{xy} \) |
| | SS | ~0.0 | \( d_{x^2+y^2} \) | \( s, d_{xy} \) |
| | RS | -0.6 | \( d_{xy} \) | \( d_{xy} \) |
| | RS | -0.9 | \( d_{xy} \) | \( d_{xy} \) |
| | RS | -1.7 | \( d_{x^2+y^2}, d_{xz} \) | \( d_{x^2+y^2} \) |

*Value calculated by Benesh et al. [5]*
At energies near $E_F$, around 0.1 eV at the $\bar{S}$ point, an RS was found that follows the dispersion of the upper pbbs. This state extends from the middle of the $\bar{X} - \bar{S}$ through the $\bar{S} - \bar{Y}$ intervals. This state is a hybridization of the $s, d_{xz}$, $d_{yz}$ orbitals.

A series of RSs were found at the $\bar{X}$ point. There is one RS around 0.7 eV that seems to be part of the states coming from the $\bar{X} - \bar{S}$ interval and going to the $\bar{S}$ point. The wavefunction composition of this state is $s, d_{yz}, d_{z^2}$. Another RS is located around 2.1 eV. An RS located at approximately 4.2 eV was also found. The wavefunction compositions of these states primarily have the symmetries of the $d_{zz}$ and $s, d_{xy}$ orbitals, respectively.

A local gap at 0.5 eV is observed at the $\bar{S}$ point, and an SS is located there. The wavefunction composition of this state is primarily $d_{yz}$. The already mentioned SS at 1.4 eV was also found at this point and shows the wavefunction composition is $d_{zz}, d_{z^2}$. Another RS with a parabolic shape is located around 2.2 eV and has the wavefunction composition $d_{yz^2}$. An RS around 4.0 eV was also found. The wavefunction composition of this state has the $d_{xy}$ symmetry. The final RS is located in the $\bar{X} - \bar{S}$ interval around 4.5 eV. The wavefunction of this state has $s, d_{xy}$ symmetry.

A. Comparison with experiment

For energies above $E_F$, experimental reports of the electronic band structure of this surface can be found \cite{6, 7} report an SS at approximately 5.1 eV, labeled $S_0^+$ in Fig. 3 of Ref. \cite{6}. However, the DFT calculations do not reproduce this state.

Just above $E_F$ in the rest of the SBZ, Memmel et al. \cite{6} report several states mixed with the pbbs. The flat state at $E_F$ in the $\bar{X} - \bar{Y}$ interval, which should represent an RS, should be noted.

There is also a state labeled $C$ that shows a negative slope centered at $\bar{\Gamma}$, around 3.0 eV.

Finally, there is a series of states around 1.0 eV at $\bar{\Gamma}$, shown in Fig. 3 of Ref. \cite{6}, as well as a state labeled $IS$ around 5.0 eV at $\bar{\Gamma}$.

The DFT calculations do not reproduce these states in detail. However, a series of states was found near $E_F$ that show little dispersion as functions of $k_{\parallel}$ and covered the $S\bar{Y}$ interval (see also the above discussion related to Fig. \cite{6}).

As discussed above, a number of SSs and RSs were found at energies below $E_F$. However, because we did not find enough experimental data in this energy region, we only comment on our results for the RS near $E_F$ at the $\bar{S}$ point, and further commentaries on the rest of the states will be omitted.

The RS at 0.0 eV around the $\bar{S}$ point was previously discussed by Menzel et al. \cite{8}. These authors mentioned that this state is observed in clean Pt(110) surfaces as well as in the Br/Pt(110)–c(2 $\times$ 2) system. In a related work, Minca et al. \cite{8} also discuss an RS at the $\bar{X}$ point. The authors mention that this state appears because the bulk energy bands present a flat band along the $W\bar{L}\bar{W}$ line just below $E_F$. This band creates a van Hove singularity at $E_F$. The bulk band, when projected onto the $\bar{S}$ point of the (110) SBZ, is the origin of the observed resonance state. The results obtained for the ideal Pt(110) surface show that the RS at the $\bar{S}$ point is a characteristic of this surface and is independent of the reconstruction.

Similar observations were noted for the one-dimensional SS at the $\bar{X}$ point above $E_F$, as described by Memmel et al. \cite{6}.

B. Tight–Binding Calculation

Figure 4 shows the pbbs, SSs, and RSs of the Pt(110) ideal surface found using the ETB method. In the figure, the blue (black) dots represent the pbbs calculated using the ETB (FLAPW) method, while the green (red)
TABLE II: Calculated energy values and wave function compositions of the different surface states of Pt(110). For comparison, the calculated ETB wave functions are also given. For details, see the discussion in the text.

| Point | State | Energy value (eV) | Wave function |
|-------|-------|------------------|---------------|
|       |       | Experiment       | Calculated    | FLAPW         | ETB            |
| \(\bar{\Gamma}\) | SS    | 6.9              | \(\text{---}\) | \(s, p_x, p_y\) |
|       | RS    | 0 \(\rightarrow\) \(-1.2\) | \(d_{yz}, d_{x^2 - y^2}\) | \(\text{---}\) |
|       | RS    | \(-1.7\)         | \(\text{---}\) | \(d_{yz}, d_{x^2 - y^2}\) |
| \(\bar{X}\)   | SS    | 6.2              | \(\text{---}\) | \(s, p_x\) |
| \(\bar{X}\)   | RS    | 5.3              | \(s, p_x\) |
| \(\bar{X}\)   | SS    | 6.0 \([6]\)     | \(\text{---}\) | \(p_x\) |
| \(\bar{X}\)   | SS    | 3.6              | \(\text{---}\) | \(p_x\) |
| \(\bar{X}\)   | RS    | 2.4              | \(s, p_x\) |
| \(\bar{X}\)   | RS    | \(-0.7\)         | \(s, d_{xy} d_{x^2 - y^2}\) |
| \(\bar{X}\)   | RS    | \(-2.1\)         | \(d_{x^2}\) |
| \(\bar{X}\)   | RS    | \(-4.2\)         | \(s, d_{xy}\) |
| \(\bar{X}\)   | RS    | \(-5.7\)         | \(\text{---}\) | \(p_x, d_{xy}, d_{yz}\) |
| \(\bar{S}\)   | RS    | ~0.0 \([8]\)    | \(4.5\)       | \(\text{---}\) | \(d\) |
| \(\bar{S}\)   | RS    | \(0.1\)          | \(s, d_{x^2 + y^2}, d_{xy}\) | \(\text{---}\) |
| \(\bar{S}\)   | RS    | \(-1.4\)         | \(d_{xz}, d_{x^2}\) |
| \(\bar{S}\)   | RS    | \(-2.2\)         | \(d_{x^2 + y^2}\) |
| \(\bar{S}\)   | RS    | \(-4.0\)         | \(d_{xy}\) |
| \(\bar{S}\)   | RS    | \(-4.5\)         | \(s, d_{xy}\) |
| \(\bar{S}\)   | RS    | \(-5.2\)         | \(\text{---}\) | \(d_{x^2}\) |
| \(\bar{Y}\)   | SS    | 5.1 \([6]\)     | \(3.6\)       | \(s, p_x\) |
| \(\bar{Y}\)   | SS    | 1.3 \([6]\)     | \(2.1\)       | \(s, d_{x^2 + y^2}, d_{x^2}\) | \(p_y, d_{yz}\) |
| \(\bar{Y}\)   | RS    | \(-3.9\)         | \(\text{---}\) | \(d_{yz}, d_{x^2 + y^2}\) |
| \(\bar{Y}\)   | RS    | \(-5.9\)         | \(s, d_{x^2 + y^2}\) | \(s, p_x, d_{x^2 + y^2}, d_{x^2 - y^2}\) |

dots represent the SSs and RSs calculated using the ETB (FLAPW) method. For details, see the figure caption.

Although there are small differences at the edges of the calculated local gaps above \(E_F\), in general, the calculated pbbs at energies below \(E_F\) are similar in both methods.

At energies above \(E_F\), a series of SSs were found, and will be commented on in detail in the following paragraphs.

As mentioned above, an SS around 5.3 eV was found at the \(\bar{X}\) point in the DFT calculation. In the ETB calculation, however, an SS with a quasi–linear shape as a function of \(k_{||}\) was found at approximately 6.2 eV. Although this SS has different energies in the two calculations, the wavefunction symmetries bound by the two methods are the same (see Table II). The state also shows the trend reported by Memmel et al. \([6]\). The ETB calculation predicts a second SS around 3.6 eV at the \(\bar{X}\) point near the lower edge of the local gap. This state differs in its energy, although not in its shape, from the state found at 2.4 eV in the DFT calculation.

The ETB calculation predicts an RS at approximately 4.5 eV near the \(\bar{S}\) point. The wavefunction composition of this state has the full \(d\) symmetry.

The ETB calculation shows that an RS was found in the upper energies around the local gap at the \(\bar{S}\) point, around 9.5 eV. However, no experimental evidence for this state was found. The same is true of the SS calculated using the FLAPW method, which was located in the upper local gap near the \(\bar{S}\) point at approximately 9.0 eV.

Two SSs were found in the local gap around the \(\bar{Y}\) point. The lower state follows the dispersion found in the DFT calculation, and the state extends over the entire local gap. The ETB calculation predicts an upper SS around 3.6 eV that was not found in the DFT calculation. This state could be related to the state reported by Memmel et al. \([6]\) at these energies. To support this speculation, however, it is necessary to assume that this SS is independent of the missing row reconstruction.

At energies below \(E_F\), the calculated SSs in the main local gaps were accurately reproduced in both calculations. For example, the ETB calculation found an SS around 0.5 eV in the local gap at the \(\bar{S}\) point with negligible dispersion, in agreement with the state calculated using the FLAPW method.

In the lower local gap at \(\bar{Y}\), the SS found around 6.2 eV in the ETB calculation exhibits nearly the same dispersion as the state found using the FLAPW method.

On the other hand, Fig. 3 shows that a number of RSs were obtained from the ETB calculations. However, most of these RSs do not match any states calculated using the FLAPW method.
In this case, the two calculations provide us with different series of RSs, contrary to what was obtained for the Pt(100) surface (see Fig.2).

A possible explanation of these results could be the need to include reconstruction effects in the calculations. When compared with the experimental data, the ETB calculation properly predicts the SSs found in the local gaps, although some differences in the energies were observed because the calculations in this work were for an ideal surface. Nevertheless, these findings demonstrate the predictive power of the ETB calculations compared with the more computationally demanding methods. In this sense, the two methods complement each other.

V. CONCLUSIONS

We have calculated the electronic band structure of platinum low–index surfaces. In our calculations, we used both DFT and empirical methods. From our calculations, we report the pbbs, SSs, and RSs for ideal Pt(111), Pt(100), and Pt(110) surfaces. Comparisons with experimental data show that our calculations properly predict the SSs and RSs for Pt(111) and Pt(100) surfaces. Because the Pt(110) surface exhibits the so-called (2 × 1) missing row reconstruction that was not included in our calculations, our results compare poorly with the SSs reported for this surface. However, when the reported SSs are independent of the reconstruction, we found that our calculations properly reproduce the experimental states. The results of our calculations for ideal surfaces demonstrate the predictive power of the empirical method.

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FIG. 1: (Color online) Calculated DOS of the different Pt–surfaces studied in this work. The bulk DOS is presented as a black line, the DOS projected onto the central atomic layer is presented as a red line, and the DOS projected on the surface atomic layer is presented as a blue line. For comparison, the partial Pt–5d contribution to the DOS is also presented as a green line (upper panel). The inset in each panel shows the comparison of the bulk DOS calculated using the FLAPW (black line) method and the bulk projected DOS calculated using the SGFM–ETB (red line) method.
FIG. 2: (Color online) Projected bulk bands of Pt(100). Black dots represent the DFT calculated pbbs. Red dots represent the SSs or the RSs if the states are located in a local energy gap or in the continuum bulk bands, respectively. The blue dots represent the pbbs calculated by the ETB method, and the SSs and RSs are represented by green dots.
FIG. 3: (Color online) Projected bulk bands of Pt(110). The black dots represent the DFT calculated pbbs. Red dots represent SSs or RSs if the states are located in a local energy gap or in the continuum bulk bands, respectively. The blue dots represent the pbbs calculated using the ETB method, and the SSs and RSs are represented by green dots.