

**Tight-binding model for iron pnictides**M. J. Calderón,<sup>1,\*</sup> B. Valenzuela,<sup>1,2,†</sup> and E. Bascones<sup>1,‡</sup><sup>1</sup>*Instituto de Ciencia de Materiales de Madrid, ICMM-CSIC, Cantoblanco, E-28049 Madrid, Spain*<sup>2</sup>*Departamento de la Materia Condensada, Universidad Autónoma de Madrid, Cantoblanco, E-28049 Madrid, Spain*

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We propose a five-band tight-binding model for the Fe-As layers of iron pnictides with the hopping amplitudes calculated within the Slater-Koster framework. The band structure found in density-functional theory, including the orbital content of the bands, is well reproduced using only four fitting parameters to determine all the hopping amplitudes. The model allows to study the changes in the electronic structure caused by a modification of the angle  $\alpha$  formed by the Fe-As bonds and the Fe plane and recovers the phenomenology previously discussed in the literature. We also find that changes in  $\alpha$  modify the shape and orbital content of the Fermi-surface sheets.

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**I. INTRODUCTION**

Since the discovery of high-temperature superconductivity in iron pnictides<sup>1,2</sup> a lot of attention has been devoted to their understanding. Iron pnictides are layered materials with arsenic (or another pnictogen) atoms at the center of the Fe plaquettes, out of plane, and arranged upward and downward in a checkerboard form (see Fig. 1) in tetrahedral configuration. Fe-As bonds form an angle  $\alpha$  with the Fe plane, called in the following Fe-As or iron-pnictogen angle, which differs among compounds<sup>3,4</sup> and depends on doping<sup>3,5,6</sup> or applied pressure.<sup>7</sup> A possible connection between the value of  $\alpha$ , the critical temperature and electronic properties has been discussed by several authors.<sup>6,8,9</sup> Recently Kuroki *et al.*<sup>10</sup> have proposed that the pnictogen height above the Fe plane is the key factor that determines both  $T_c$  and the form of the superconducting gap.

From a density-functional theory (DFT) point of view iron superconductors have multiband character mostly due to Fe  $d$  orbitals.<sup>11–13</sup> In the iron (unfolded) Brillouin zone<sup>14</sup> the Fermi surface consists of electron pockets at the  $X$  and  $Y$  points, two hole pockets in  $\Gamma$  and a hole pocket at  $M$ , in reasonable agreement with de Haas van Alphen<sup>15</sup> experiments in the nonmagnetic state. Angle-resolved photoemission (ARPES) measurements give also evidence of Fermi pockets at these symmetry points.<sup>16–20</sup> Interband scattering between electron and hole pockets has been proposed as a mechanism for superconductivity.<sup>14,21</sup> In this context the importance of nesting for superconductivity and magnetism is discussed.<sup>22,23</sup> More recently, the relevance of the anisotropic orbital weight of each Fermi pocket in determining the symmetry of the superconducting order parameter has been emphasized.<sup>10,24,25</sup> Electron pockets at  $X$  and  $Y$  have, respectively,  $yz/xy$  and  $xz/xy$  origin while the hole pockets in  $\Gamma$  arise from  $zx$  and  $yz$  orbitals.<sup>26</sup> Due to closeness of two hole bands and different dependence of their energy on  $\alpha$  the orbital character of the pocket in  $M$  switches between  $xy$  or  $3z^2-r^2$  depending on the value of  $\alpha$ .<sup>27,28</sup> Experimentally, the orbital content can be studied by changing the polarization of the light used in ARPES.<sup>29–32</sup>

A good tight-binding model is the basic building block of any theoretical treatment in a lattice. Initial attempts tried to describe the iron pnictides using two-<sup>22,33,34</sup> or three-orbital<sup>35</sup> models. Several proposals based on the symmetry properties

of  $zx$  and  $yz$  (and  $xy$  as third orbital) were put forward to describe the bands close to the Fermi level. However crystal-field splittings among the Fe  $d$  orbitals are small compared with the bandwidth resulting in strong hybridization of all  $d$  orbitals. At present it is believed that inclusion of all five Fe  $d$  orbitals is necessary to obtain a good description of the properties of iron pnictides.<sup>36–38</sup> The placement of As at the center of the plaquettes suggests that hopping between Fe atoms to second-nearest neighbors cannot be disregarded.

In this paper we propose a five-orbital tight-binding model to describe the Fe-As layers with the hopping amplitudes calculated within the Slater-Koster framework.<sup>39</sup> Compared to DFT tight-binding fits, the procedure presented here greatly reduces the number of fitting parameters necessary to calculate the bands and allows to study changes in the iron-pnictogen angle  $\alpha$ . We show that the bands close to the Fermi level can be described giving all the hopping amplitudes in terms of just four parameters. The agreement between our results and DFT predictions extends to the orbital weight of each band. We also reproduce the switch in orbital character of the hole pocket in  $M$  when  $\alpha$  varies. Furthermore, we predict that changes in  $\alpha$  can induce modifications in the shape and orbital content of the Fermi pockets, including the disappearance of the hole pockets in  $\Gamma$  when the tetrahedron is elongated. Within the present theoretical understanding these results have strong implications in the superconducting and magnetic properties of these compounds.<sup>10,24,25</sup>

**II. TIGHT-BINDING MODEL**

We construct a tight-binding model to describe the band structure of the FeAs layers including the five Fe  $d$  orbitals. Arsenic atoms only enter in the model indirectly via the Fe-Fe hopping amplitudes. Indirect hopping via arsenic is treated to second order in perturbation theory. Direct hopping between Fe atoms is also included. Hopping is restricted to first and second-nearest Fe neighbors. Both the mathematical form of the Hamiltonian and the hopping amplitudes are computed within the Slater-Koster formalism.<sup>39</sup> We take  $X$  and  $Y$  directed along the Fe bonds (see Fig. 1). The same axis convention applies for the orbitals, i.e.,  $x^2-y^2$  orbital lobes are directed along the Fe-Fe bonds. Under these assumptions the Hamiltonian is given by

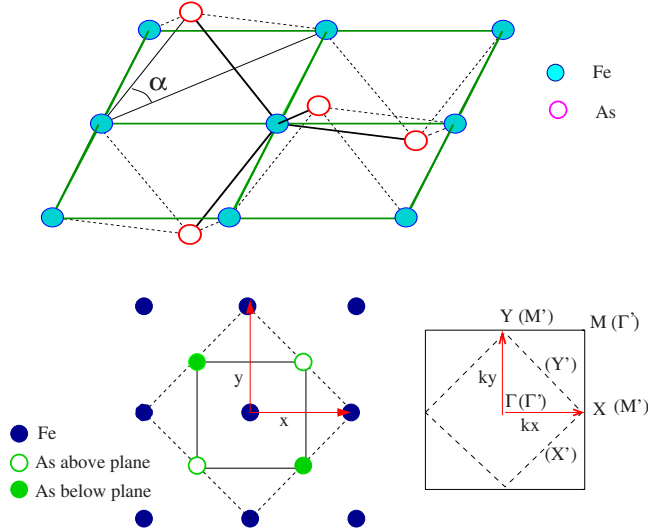


FIG. 1. (Color online) Top figure: sketch of the lattice structure. Fe-As bonds form an angle  $\alpha$  with the Fe plane which changes among compounds, with doping and with pressure. Bottom figure: on the left, in a top view of the Fe-As layer, the real (extended) and the Fe unit cells are shown in dashed and solid lines, respectively. The  $X$  and  $Y$  axes of the Fe unit cell, used in the paper, and shown with arrows, are directed along the Fe bonds. On the right the experimental (folded) Brillouin zone is shown with dashed lines. Its symmetry points are denoted with primed letters. The extended Brillouin zone, used in the paper, is delimited by solid lines. It is double sized and rotated  $45^\circ$  with respect to the experimental Brillouin zone. Bands and Fermi pockets at  $\Gamma$  and  $M$  in the extended Brillouin zone and discussed through the text will appear experimentally at  $\Gamma'$ .

$$\begin{aligned}
 H = & \sum_{m,n,\sigma} \left( \sum_{\gamma} \left( \epsilon_{\gamma} d_{m,n;\gamma,\sigma}^{\dagger} d_{m,n;\gamma,\sigma} + \sum_{s_x=\pm 1} t_{\gamma,\gamma}^x d_{m+s_x,n;\gamma,\sigma}^{\dagger} d_{m,n;\gamma,\sigma} \right. \right. \\
 & + \sum_{s_y=\pm 1} t_{\gamma,\gamma}^y d_{m,n+s_y;\gamma,\sigma}^{\dagger} d_{m,n;\gamma,\sigma} \\
 & + \left. \sum_{s_x,s_y=\pm 1} \tilde{t}_{\gamma,\gamma} d_{m+s_x,n+s_y;\gamma,\sigma}^{\dagger} d_{m,n;\gamma,\sigma} \right) \\
 & + \sum_{[\gamma \neq \beta]} t_{\gamma,\beta} \left( \sum_{s_x=\pm 1} d_{m+s_x,n;\beta,\sigma}^{\dagger} d_{m,n;\gamma,\sigma} \right. \\
 & - \left. \sum_{s_y=\pm 1} d_{m,n+s_y;\beta,\sigma}^{\dagger} d_{m,n;\gamma,\sigma} \right) \\
 & + \sum_{\langle \gamma \neq \beta \rangle} \sum_{s_x,s_y=\pm 1} s_x s_y \tilde{t}_{\gamma,\beta} d_{m+s_x,n+s_y;\beta,\sigma}^{\dagger} d_{m,n;\gamma,\sigma} \\
 & + (-1)^{m+n} \left\{ \sum_{(\gamma \neq \beta)} \sum_{s_x=\pm 1} s_x t_{\gamma,\beta}^x d_{m+s_x,n;\beta,\sigma}^{\dagger} d_{m,n;\gamma,\sigma} \right. \\
 & + \sum_{[\gamma \neq \beta]} \sum_{s_y=\pm 1} s_y t_{\gamma,\beta}^y d_{m,n+s_y;\beta,\sigma}^{\dagger} d_{m,n;\gamma,\sigma} \\
 & + \sum_{(\gamma \neq \beta)} \sum_{s_x,s_y=\pm 1} s_x \tilde{t}_{\gamma,\beta} d_{m+s_x,n+s_y;\beta,\sigma}^{\dagger} d_{m,n;\gamma,\sigma} \\
 & \left. + \sum_{[\gamma \neq \beta]} \sum_{s_x,s_y=\pm 1} s_y \tilde{t}_{\gamma,\beta} d_{m+n+s_y;\beta,\sigma}^{\dagger} d_{m,n;\gamma,\sigma} \right\} - \mu. \quad (1)
 \end{aligned}$$

Here  $m, n$  refer to lattice sites,  $\gamma, \beta$  are the orbital indices,  $\sigma$  the spin, and  $\mu$  the chemical potential. Only the first sum runs through all the orbitals. Brackets and parentheses restrict the orbitals to which the other sums apply. In particular,  $\langle \gamma \neq \beta \rangle$  is restricted to the pairs  $\{\gamma, \beta\} = \{yz, zx\}$ ,  $\{xy, 3z^2 - r^2\}$ ,  $[ \gamma \neq \beta ]$  to the pair  $\{\gamma, \beta\} = \{3z^2 - r^2, x^2 - y^2\}$ ,  $(\gamma \neq \beta)$  to the pairs  $\{\gamma, \beta\} = \{yz, 3z^2 - r^2\}$ ,  $\{yz, x^2 - y^2\}$ ,  $\{zx, xy\}$ , and  $[ (\gamma \neq \beta) ]$  to the pairs  $\{\gamma, \beta\} = \{yz, xy\}$ ,  $\{zx, 3z^2 - r^2\}$ ,  $\{zx, x^2 - y^2\}$ .  $\epsilon_{\gamma}$  are the on-site energies of the  $d$  orbitals. Due to the degeneracy of  $yz$  and  $zx$ ,  $\epsilon_{yz} = \epsilon_{zx}$ . From the orbital symmetry it follows  $t_{\gamma,\gamma}^x = t_{\gamma,\gamma}^y$  for  $\gamma = xy, 3z^2 - r^2, x^2 - y^2$ . Second-nearest-neighbor hopping parameters  $\tilde{t}_{\gamma,\beta}$  where  $\gamma = xz, yz$  and  $\beta = xy, 3z^2 - r^2, x^2 - y^2$  change sign when  $\gamma$  and  $\beta$  orbitals are exchanged. In any other case  $\tilde{t}_{\gamma,\beta} = \tilde{t}_{\beta,\gamma}$  and  $t_{\gamma,\beta}^a = t_{\beta,\gamma}^a$  with  $a = x, y$ . Other equalities brought by the symmetry are

$$t_{zx,zx}^x = t_{yz,yz}^y,$$

$$t_{zx,zx}^y = t_{yz,yz}^x,$$

$$t_{zx,xy}^x = t_{yz,xy}^y,$$

$$t_{zx,3z^2-r^2}^y = t_{yz,3z^2-r^2}^x,$$

$$t_{zx,x^2-y^2}^y = -t_{yz,x^2-y^2}^x,$$

$$\tilde{t}_{yz,xy} = \tilde{t}_{zx,xy},$$

$$\tilde{t}_{yz,3z^2-r^2} = \tilde{t}_{zx,3z^2-r^2},$$

$$\tilde{t}_{yz,x^2-y^2} = -\tilde{t}_{zx,x^2-y^2}. \quad (2)$$

The complex sign structure of the hopping terms included in the  $s_x$  and  $s_y$  factors arises from changes in sign in the orbital wave functions. The factor  $(-1)^{m+n}$  in the terms which mix  $yz, zx$  with  $xy, 3z^2 - r^2, x^2 - y^2$  reflect the doubling of the unit cell due to the checkerboard alternance of the arsenic atoms displaced up and down from the center of the Fe-square plaquettes. These terms vanish when the arsenic atoms are in the Fe planes (see Fig. 2 and Appendix A). Due to the enlargement of the unit cell, in the reduced Brillouin zone  $-\frac{\pi}{2} < k'_x, k'_y < \frac{\pi}{2}$ , the Hamiltonian is a  $10 \times 10$  matrix. As discussed in the context of three and four band models<sup>35,40</sup> and in Appendix B, it is possible to work in an unfolded Brillouin zone  $-\pi < k_x, k_y < \pi$  where  $\mathbf{k} = \mathbf{k}'$  for orbitals  $yz$  and  $zx$  and  $\mathbf{k} = \mathbf{k}' + \mathbf{Q}$  in the case of  $xy, 3z^2 - r^2$  and  $x^2 - y^2$ . In this unfolded Brillouin zone, the system is described by a five-band Hamiltonian  $H_{5 \times 5}(\mathbf{k})$ . The relation between the unfolded and the reduced Brillouin zones is displayed in Fig. 1.

In previous five-band Hamiltonians,<sup>36,41</sup> the hopping amplitudes  $t_{\gamma,\beta}^x$ ,  $t_{\gamma,\beta}^y$ , and  $\tilde{t}_{\gamma,\beta}$  were determined from a fitting to DFT bands. In contrast, here they are calculated within the Slater-Koster framework.<sup>39</sup> This method had been used before in two- and three-band models for iron pnictides.<sup>33,42,43</sup> It involves a small number of fitting parameters as all the hopping terms depend on a few disposable constants, the Fe-As and Fe-Fe orbitals overlap integrals. The final expres-

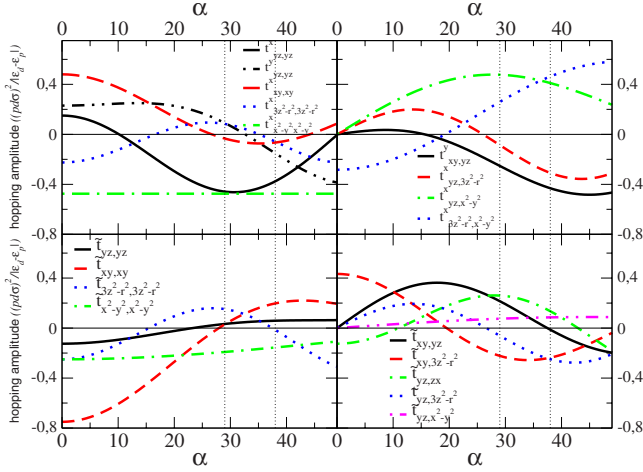


FIG. 2. (Color online) Dependence of the hopping amplitudes on  $\alpha$ . Experimental values of  $\alpha$  are between  $29^\circ$  and  $38^\circ$ . Top (bottom) graphs: first- (second-) nearest-neighbor hopping amplitudes corresponding to  $pd\pi = -0.5$ ,  $(dd\sigma)_1 = -0.6$ ,  $(dd\pi)_1 = 0.48$ , and  $(dd\delta)_1 = -0.1$ . Direct Fe hopping between second-nearest neighbors via  $(dd\sigma)_2$ ,  $(dd\pi)_2$ , and  $(dd\delta)_2$  is neglected. All the energies are in units of  $(pd\sigma)^2/|\epsilon_d - \epsilon_p|$  except  $pd\sigma$  and  $pd\pi$  which are in units of  $pd\sigma$ . Here  $\epsilon_p$  and  $\epsilon_d$  are the on-site energies of the pnictogen- $p$  and the Fe  $d$  orbital (see Appendix A). The same fitting parameters and energy units are used through all the text.

sions for the hopping amplitudes are given in Appendix A. Indirect hopping via As induces a dependence of the hopping amplitudes on the angle  $\alpha$  formed by Fe-As bonds and the Fe plane. This dependence is shown in Fig. 2. In the range of experimental interest of  $\alpha$  ( $29^\circ - 38^\circ$ ) a strong variation in the hoppings is seen indicating important implications for any proposed model either in the weak<sup>14,22,23,44</sup> or strong-coupling limit<sup>33,45-47</sup> to describe these compounds.

In Fig. 2 and in the rest of the paper the values of the overlap integrals and crystal-field parameters have been chosen to reproduce the main features of the band structure of LaFeAsO when  $\alpha$  equals the angle measured experimentally<sup>48</sup> in this compound  $\alpha^{\text{LaFeAsO}} = 33.2^\circ$ . While the expressions for the hopping amplitudes given in Appendix A include both Fe-Fe overlap integrals up to second-nearest neighbors, we have found that the band structure is well described including only Fe-As and Fe-Fe overlap to nearest neighbors and neglecting Fe-Fe direct overlap to second-nearest neighbors. With such a choice, hopping between Fe atoms to next-nearest neighbors is completely mediated by As while hopping to first-nearest neighbors has contributions from both direct hopping between Fe atoms and indirect hopping via As.

The same values for the overlap integrals and crystal-field splittings are used in all the figures throughout the paper. In Sec. IV we analyze the effect of changing  $\alpha$  on the band structure, using in the analysis values of  $\alpha$  which have been found experimentally in several pnictides. However, we caution on the application of the results obtained here on the angle dependence to compare different compounds. Substitution of arsenic atoms by P or a change in the lattice constant could modify to some extent the values of the integral overlaps.

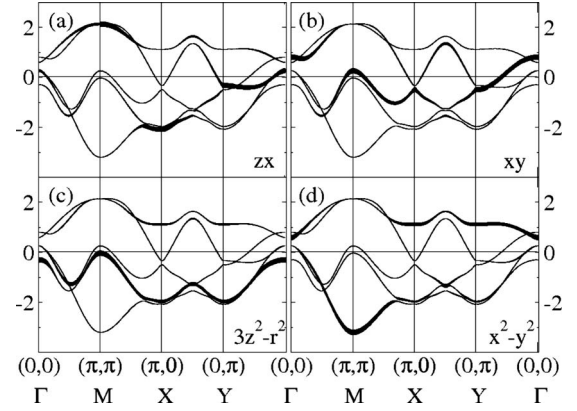


FIG. 3. Band structure in the unfolded Brillouin zone obtained from the tight-binding Hamiltonian (1) with the hopping amplitudes computed within the Slater-Koster framework as described in Appendix A. Values used for the overlap integrals are given in Fig. 2,  $\alpha^{\text{LaFeAsO}} = 33.2^\circ$ , as found experimentally in LaFeAsO. For on-site energy values see text. From (a) to (d) the width of each bandline is proportional to its  $zx$ ,  $xy$ ,  $3z^2 - r^2$ , and  $x^2 - y^2$  weight.

### III. BAND STRUCTURE FOR $\alpha^{\text{LaFeAsO}}$

Figure 3 shows the band structure obtained from Eq. (1) for  $\alpha = 33.2^\circ$ , the experimental Fe-As angle in LaFeAsO and the overlap integrals given in Fig. 2. For the crystal-field splitting we take  $\epsilon_{xy} = 0.02$  and  $\epsilon_{zx,yz} = 0$ , which defines the zero of energy,  $\epsilon_{3z^2-r^2} = -0.55$  and  $\epsilon_{x^2-y^2} = -0.6$ , in units of  $(pd\sigma)^2/|\epsilon_d - \epsilon_p|$ . The order of the on-site energies taken here has been discussed extensively in the literature and the values chosen are similar to those used previously by other authors.<sup>24,36,38,40,49</sup> The Fermi level corresponds to filling the bands with six electrons (including spins), as found in undoped pnictides or compensated FeAs layers. All the figures are shown in the Fe or unfolded Brillouin zone. Bands in Fig. 3 have a strong resemblance with those obtained from local-density approximation (LDA) calculations, once they are represented in the unfolded Brillouin zone. Pockets at the Fermi level include: two hole pockets at  $\Gamma = (0,0)$ , a hole pocket in  $M = (\pm\pi, \pm\pi)$ , and electron pockets in  $X = (\pm\pi, 0)$  and  $Y = (0, \pm\pi)$ . The resulting Fermi surface is plotted in Fig. 5. The two hole pockets in  $\Gamma$  originate in two hole bands degenerate at the top due to the degeneracy of  $zx$  and  $yz$  orbitals. The so-called Dirac point<sup>10,25</sup> which results from the crossing of  $zx$  and  $xy$  derived bands is located close to the Fermi level in the vicinity of  $(0, \pi)$ . From the expression of the Hamiltonian in Appendix B, it can be seen that these two orbitals do not mix in the  $(0,0) - (\pi,0)$  direction.

The agreement between our results and LDA calculations also extends to their orbital character. From top to bottom in Fig. 3 we show the energy bands weighted by their  $zx$ ,  $xy$ ,  $3z^2 - r^2$ , and  $x^2 - y^2$  orbitals content, which can be compared with the results by Boeri *et al.*<sup>26</sup> The  $yz$  weight is equivalent to the  $zx$  weight if  $X$  and  $Y$  axes are interchanged. The two hole bands in  $\Gamma$  which cross the Fermi level have mostly  $zx$  and  $yz$  characters while some  $x^2 - y^2$  weight can also be appreciated. The electron pockets at  $(\pm\pi, 0)/(0, \pm\pi)$  arise from  $yz/zx$  and  $xy$  orbitals.  $3z^2 - r^2$  contributes mostly to bands below the Fermi level. The orbital content of the Fermi pockets is better seen in Fig. 6.

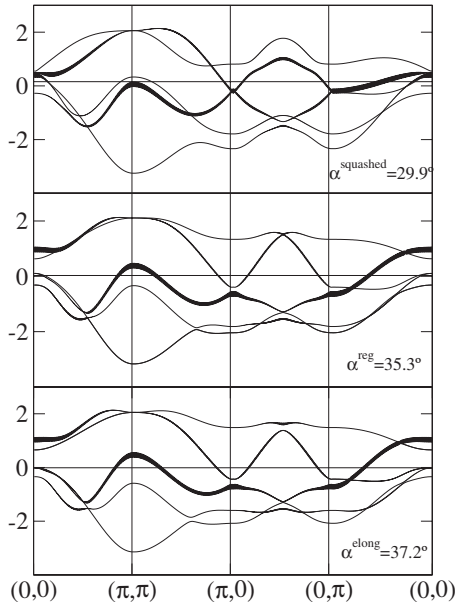


FIG. 4. From top to bottom, energy bands corresponding to  $\alpha^{\text{squashed}}=29.9^\circ$  (as found in LaFePO),  $\alpha^{\text{reg}}=35.3^\circ$  (regular tetrahedron), and  $\alpha^{\text{elong}}=37.2^\circ$  (elongated tetrahedron). The width of the curves is proportional to their  $xy$  weight.

Around  $(\pm\pi, \pm\pi)$  a  $3z^2-r^2$  hole band nearly touches the Fermi level, without crossing it. This band is close to another  $xy$  hole band which produces the pockets at  $(\pm\pi, \pm\pi)$ . All these features are also present in the LDA bands. The pocket at  $(\pi, \pi)$  has been a matter of discussion in the literature. Initially,<sup>12</sup> it was proposed that there was a small three-dimensional pocket with  $3z^2-r^2$  character which in the reduced Brillouin zone appeared at  $\Gamma'$ . This conclusion was reached using the relaxed lattice structure and not the experimental one. It was later shown that using the experimental lattice parameters, in particular, the experimental Fe-As angle, the position of the top of the  $xy$  and  $3z^2-r^2$  hole bands at  $\Gamma'$  in the reduced Brillouin-zone switch and the Fermi

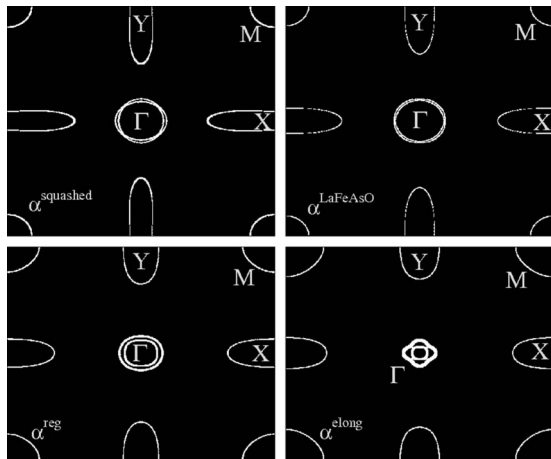


FIG. 5. Fermi surface corresponding to  $\alpha^{\text{squashed}}=29.9^\circ$  (as found in LaFePO),  $\alpha^{\text{LaFeAsO}}=33.2^\circ$  (as found in LaFeAsO),  $\alpha^{\text{reg}}=35.3^\circ$  (regular tetrahedron), and  $\alpha^{\text{elong}}=37.2^\circ$  (elongated tetrahedron) with the same fitting parameters as in Fig. 3.

pocket has  $xy$  character.<sup>27</sup> This apparent disagreement between the results obtained with the relaxed and the experimental lattices originates in a strong dependence of the band structure on the Fe-As angle.<sup>13,26-28</sup> We show in Sec. IV that the tight binding proposed here reproduces this angle dependence of the band energies for the pocket which appears at  $(\pi, \pi)$ .

The good agreement (shown in Fig. 3) is not restricted to the energies closest to the Fermi level but it is quite generic to all the bands. The correspondence is more impressive having in mind that all the hopping amplitudes are given in terms of just four free parameters. We emphasize that the orbital overlaps and crystal-field values have not been optimized to fit the LDA bands of LaFeAsO but just correspond to the minimum set of parameters that reproduce the qualitative features of the band structure using the expected orbital energy splitting.

As discussed above the value of the overlap integrals is expected to depend to some extent on the lattice parameters and atomic radii. We have found that the band structure is sensitive against small changes in the fitting parameters. Close to the Fermi level the largest variations appear in the relative position of the top of the  $xy$  and  $3z^2-r^2$  hole bands in  $M$  between them and with respect to those in  $\Gamma$ , and the energies of  $xy$  and  $zx$  bands in  $Y$ . This behavior might be an indication of the experimentally found strong sensitivity of these compounds to modifications in structural parameters.

#### IV. Fe-As ANGLE DEPENDENCE

We now focus on the changes in the band structure produced by a modification of the angle  $\alpha$ . We assume that all dependence enters via the hopping amplitudes. The crystal-field splitting of the Fe  $d$  orbitals results from both the As and Fe environment of each Fe atom. Modifications in  $\alpha$  change the electrostatic environment produced by arsenic atoms but not the one due to Fe atoms. We assume that in the range of  $\alpha$  values of interest the change in the crystal-field parameters is small and we neglect the dependence of the on-site energies on  $\alpha$ . As discussed in Appendix B to analyze the effect of a possible change in crystal field with  $\alpha$  is straightforward. In Fig. 4 we plot the energy bands corresponding to  $\alpha^{\text{squashed}}=29.9^\circ$  (squashed tetrahedron),  $\alpha^{\text{reg}}=35.3^\circ$  (regular tetrahedron), and  $\alpha^{\text{elong}}=37.2^\circ$  (elongated tetrahedron) and the fitting parameters used in Fig. 3. The bandline width is proportional to the weight of the  $xy$  orbital. The first two values of  $\alpha$  used have been found in LaFePO and in BaFe<sub>2</sub>As<sub>2</sub> at optimal doping, respectively. The FeAs<sub>4</sub> tetrahedron is slightly elongated in CaFeAsF.

As evident in Fig. 4, even small modifications of the Fe-As angle have an impact on the band structure. Around the Fermi level  $E_F$ , the most clear change appears close to  $(\pi, \pi)$ . There are two hole bands with maximum close to  $E_F$ , with mostly  $xy$  or  $3z^2-r^2$  character. For  $\alpha^{\text{squashed}}$  the  $3z^2-r^2$  is higher in energy and crosses the Fermi level. However the relative position of the two bands changes as  $\alpha$  increases and the hole pocket around  $(\pi, \pi)$  has  $xy$  character in the other two cases considered here. The energy difference between both bands increases as the tetrahedron is elongated.

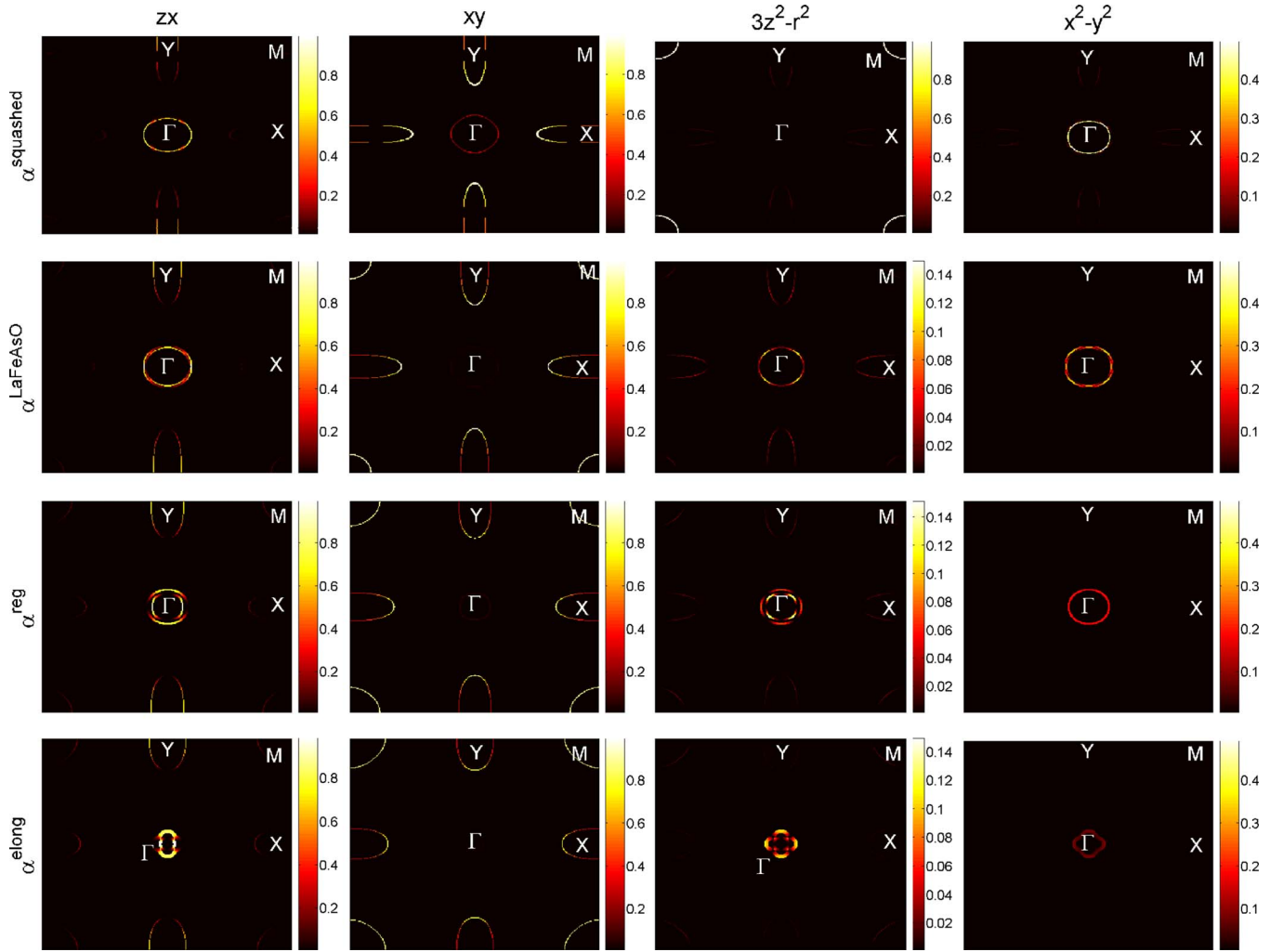


FIG. 6. (Color online) From left to right: orbital content of the Fermi surface corresponding to orbitals  $zx$ ,  $xy$ ,  $3z^2-r^2$ , and  $x^2-y^2$ . From top to bottom, each of the figures is plotted for  $\alpha^{\text{squashed}}=29.9^\circ$  (as found in LaFePO),  $\alpha^{\text{LaFeAsO}}=33.2^\circ$  (as found in LaFeAsO),  $\alpha^{\text{reg}}=35.3^\circ$  (regular tetrahedron), and  $\alpha^{\text{elong}}=37.2^\circ$  (elongated tetrahedron) and the same fitting parameters used in Fig. 3.

This behavior was first obtained from LDA calculations. In our tight-binding model it is easy to understand the origin of this shift. At  $(\pi, \pi)$  the energy of  $xy$  and  $3z^2-r^2$  orbitals is  $E_\beta(\pi, \pi) = 4t_\beta^x + \tilde{t}_\beta$  for  $\beta = xy, 3z^2-r^2$ . The upward shift in  $E_{xy}(\pi, \pi)$  with increasing  $\alpha$  is due to the increase in  $xy$  second-nearest neighbors  $\tilde{t}_{xy}$  while the first-nearest neighbors  $t_{xy}^x$  remains almost constant (see Fig. 2). On the other hand both  $t_{3z^2-r^2}^x$  and  $\tilde{t}_{3z^2-r^2}$  decrease when  $\alpha$  increases.

The dependence of the band structure on the Fe-As angle is also seen at  $\Gamma$ . The gap between the top of the hole bands which cross  $E_F$  and the  $xy$  band at higher energies is strongly reduced with decreasing  $\alpha$ , in part due to a change in  $\tilde{t}_{xy,xy}$  (see Appendix B). This gap reduction is, however, not only due to a decrease in energy of the  $xy$  band. The top of the  $yz, zx$  hole bands shifts upward as  $\alpha$  is reduced. On the other hand, elongation of the tetrahedron can lead to the disappearance of the hole pockets at  $\Gamma$ .

As  $\alpha$  decreases, a transfer of  $xy$  orbital weight from the third to the second band can be appreciated in the  $(\pi, 0) \rightarrow (0, \pi)$  direction. This is accompanied by a shift of the

Dirac point toward  $(0, \pi)$ . Other changes in the band structure with  $\alpha$  are discussed in Appendix B.

Somehow weaker but still observable is the change in shape of the electron and hole pockets at  $\Gamma$  and  $X$  ( $Y$ ). This feature is better observed in Fig. 5. The electron pockets at  $X$  and  $Y$  are more elongated toward  $\Gamma$  as  $\alpha$  is reduced. The shape of hole pockets is qualitatively modified as  $\alpha$  increases. For the smallest angle,  $\alpha^{\text{squashed}}=29.9^\circ$ , the hole Fermi pockets at  $\Gamma$  resemble two ellipses centered at  $\Gamma$  with axis directed along  $X$  and  $Y$  directions. For both  $\alpha^{\text{squashed}}=29.9^\circ$  and  $\alpha^{\text{LaFeAsO}}=33.2^\circ$  the two Fermi sheets are very close to each other and would be hardly distinguishable in ARPES or quantum oscillation experiments. With increasing  $\alpha$ , for a value corresponding to a regular tetrahedron we find two concentric pockets. Finally, when the tetrahedron is elongated the inner hole has a squarelike shape while the outer one has a flowerlike shape. Similar Fermi surfaces have been found in an *ab initio* study of the effect of pressure in the 122 family.<sup>50</sup> Both circularlike and squarelike hole pockets at  $\Gamma$  have been reported from ARPES measurements.<sup>16–20,29–32</sup> We emphasize that we are working

in the unfolded Brillouin zone. ARPES experiments sample the folded Brillouin zone where the pocket that we found at  $M$  would be also expected at  $\Gamma$ . Its relative size, compared to the other two hole pockets in  $\Gamma$ , will depend on the Fe-As angle.

In our model, the exact shape of the hole Fermi pockets found for a given angle can depend on the exact fitting parameters used. However, the change in the Fermi pockets shape with  $\alpha$  is a robust feature.

Recently it has been proposed that the anisotropic orbital makeup of the states on the Fermi surface is crucial to determine the superconducting and magnetic properties since it controls the anisotropy of the interband pair scattering. Figure 6 shows that this orbital makeup is also sensitive to changes in  $\alpha$ . Such orbital dependence on  $\alpha$  will influence the value and anisotropy of the pair scattering potential. The most dramatic example of such sensitivity is the change in the hole pocket at  $M$  from  $3z^2-r^2$  for  $\alpha=29.9^\circ$  to  $xy$  character for larger  $\alpha$  discussed above. The  $zx$  and  $yz$  weights in the hole pockets in  $\Gamma$  also reverses. For  $\alpha^{squashed}$ , the  $zx$  weight is larger around  $(k_F, 0)$  in the inner pocket and  $(0, k_F)$  in the outer pocket. On the contrary, for the regular tetrahedron  $\alpha^{reg}$  the situation is the opposite: the  $zx$  weight is larger around  $(0, k_F)$  in the inner pocket and  $(k_F, 0)$  in the outer pocket. Note that, in the reference frame that we use,  $zx$  and  $yz$  orbitals lie in the plane of the Fe-Fe bonds and are not directed toward the diagonals. Other  $\alpha$ -dependent effects seen in Fig. 6 include smaller  $x^2-y^2$  weight in the hole pockets in  $\Gamma$  for larger  $\alpha$  and changes in the  $3z^2-r^2$  content of the hole pockets.

The importance of nesting between electron and hole pockets has been emphasized in weak-coupling models<sup>14,22,23,36,44</sup> which place interband scattering at the origin of the magnetic and superconducting properties of iron pnictides. Due to the change in shape of electron and hole bands with  $\alpha$  the amount of nesting will be sensitive to changes in the Fe-As angle. According to Fig. 5, for the fitting parameters used, the best nesting conditions are found between the inner hole pocket in  $\Gamma$  and the electron pockets in  $X$  and  $Y$  for the regular tetrahedron case. More recently, it has been argued that the scattering strength is not simply a consequence of nesting but it reflects the orbital weight structure factors. The effective pairing strength is larger between fermions which belong to the same orbital. In Fig. 6 it can be appreciated that this nesting is intraorbital, between segments of the inner hole pocket and those of the electron pocket around  $Y$  with  $d_{zx}$  character (and around  $X$  with  $d_{yz}$  character, not shown). Interestingly, the same result was obtained in *ab initio* studies of the evolution of the Fermi surface of  $\text{BaFe}_2\text{As}_2$  under pressure.<sup>50</sup>

## V. CONCLUSIONS

In conclusion, we have developed a five-orbital tight-binding model to describe FeAs layers in iron pnictides with hopping amplitudes calculated within the Slater-Koster framework. This method to determine the hopping amplitudes allows to analyze the dependence of the band structure on the Fe-As angle  $\alpha$ . A good description of the bands, in-

cluding its orbital content, can be obtained using only four fitting constants to parametrize all the hopping amplitudes which compare well with LDA bands.

The flexibility to study changes in the lattice and the small number of fitting parameters make this model a good starting point to which interactions can be added in order to study the magnetic and superconducting properties. We have shown that changes in iron-pnictogen angle  $\alpha$  induce changes in the shape of the Fermi surface and in its orbital makeup. In particular, in agreement with LDA calculations the hole pocket in  $(\pi, \pi)$  ( $\Gamma'$  in the reduced Brillouin zone) has  $3z^2-r^2$  character for  $\alpha^{squashed}$  and  $xy$  character for  $\alpha^{\text{LaFeAsO}}$ . In our tight-binding model these changes can be understood in terms of the evolution of the hopping parameters with  $\alpha$ . This sensitivity extends to the nesting properties of the Fermi surface. In a weak-coupling scenario changes in the shape, nesting and orbital content of the Fermi surface with  $\alpha$  could be at the origin of the different superconducting order parameters, critical temperature, and magnetic properties found in different iron pnictides. Within the strong coupling<sup>33,45-47</sup> point of view the superexchange interactions will also be affected by changes in  $\alpha$  via the hopping amplitudes.

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## APPENDIX A: HOPPING AMPLITUDES IN SLATER-KOSTER FRAMEWORK

In this appendix we give the expressions for the hopping amplitudes calculated within the Slater-Koster formalism.<sup>39</sup> Both Fe-Fe direct hopping as well as hopping via As are included in the expressions below. Fe-Fe direct hopping is described via first  $(dd\sigma)_1$ ,  $(dd\pi)_1$ , and  $(dd\delta)_1$  and second  $(dd\sigma)_2$ ,  $(dd\pi)_2$ , and  $(dd\delta)_2$  nearest neighbors overlap integrals between  $d$  orbitals. Fe-As hopping amplitudes are restricted to first-nearest neighbors and involve orbital overlap integral  $pd\sigma$  and  $pd\pi$  between As  $p$  and Fe  $d$  orbitals, which mediate both first- and second-nearest-neighbors hopping between Fe atoms. To compute hopping via arsenic atoms to second order in perturbation theory, we neglect the difference among the on-site energies of the  $d$  orbitals and that among the on-site energies of the  $p$  orbitals and take them equal to  $\epsilon_d$  and  $\epsilon_p$ , respectively. It is only in the expression for the indirect hopping amplitudes that the difference between the on-site energies of the  $d$  Fe orbitals has been neglected. The values  $\epsilon_\alpha$  are explicitly included and taken into account in the tight-binding expression (1). The resulting finite hopping amplitudes are between first-nearest neighbors

$$t_{xy,xy}^{x,y} = \frac{1}{|\epsilon_p - \epsilon_d|} \left( -\frac{3}{2}pd\sigma^2 - 2pd\pi^2 + 2\sqrt{3}pd\sigma p d\pi \right) \cos^4 \alpha \sin^2 \alpha + (dd\pi)_1, \quad (\text{A1})$$

$$t_{yz,yz}^x = \frac{1}{|\epsilon_p - \epsilon_d|} \left[ \left( \frac{3}{4} pd\sigma^2 \sin^2 \alpha + \sqrt{3} pd\sigma pd\pi \cos^2 \alpha \right) \sin^2(2\alpha) + pd\pi^2 (\cos^2 \alpha + 2 \sin^2 \alpha [1 - \cos^2 \alpha (3 + \cos(2\alpha))]) \right] + (dd\delta)_1, \quad (\text{A2})$$

$$t_{yz,yz}^y = \frac{1}{|\epsilon_p - \epsilon_d|} \left[ \left( -\frac{3}{4} pd\sigma^2 + \sqrt{3} pd\sigma pd\pi \right) \sin^2(2\alpha) \sin^2 \alpha - pd\pi^2 (1 - 3 \sin^2 \alpha + \sin^2(2\alpha) \sin^2 \alpha) \right] + (dd\pi)_1, \quad (\text{A3})$$

$$t_{3z^2-r^2,3z^2-r^2}^{x,y} = \frac{1}{|\epsilon_p - \epsilon_d|} \left[ pd\sigma^2 \sin^2 \alpha \left( \frac{1}{2} \cos^4 \alpha - \frac{1}{2} \sin^2(2\alpha) + 2 \sin^4 \alpha \right) + \frac{3}{2} pd\pi^2 \cos^2 \alpha \sin^2(2\alpha) + \sqrt{3} pd\sigma pd\pi \sin^2(2\alpha) \left( -\frac{1}{2} \cos^2 \alpha + \sin^2 \alpha \right) \right] + \frac{1}{4} (dd\sigma)_1 + \frac{3}{4} (dd\delta)_1, \quad (\text{A4})$$

$$t_{x^2-y^2,x^2-y^2}^{x,y} = \frac{3}{4} (dd\sigma)_1 + \frac{1}{4} (dd\delta)_1, \quad (\text{A5})$$

$$t_{xy,yz}^y = \frac{1}{|\epsilon_p - \epsilon_d|} \left[ -\frac{3}{8\sqrt{2}} pd\sigma^2 \sin^2(2\alpha) + \frac{\sqrt{2}}{2} pd\pi^2 \times \left( 1 - \frac{1}{2} \sin^2(2\alpha) \right) + \frac{\sqrt{6}}{4} pd\sigma pd\pi \sin^2(2\alpha) \right] \sin(2\alpha), \quad (\text{A6})$$

$$t_{yz,3z^2-r^2}^x = \frac{1}{|\epsilon_p - \epsilon_d|} \left[ \frac{\sqrt{3}}{4\sqrt{2}} pd\sigma^2 \sin^2 \alpha (1 - 3 \cos(2\alpha)) + pd\pi^2 \sqrt{\frac{3}{2}} \left( -\frac{1}{4} + \cos(2\alpha) + \frac{1}{4} \cos(4\alpha) \right) + pd\sigma pd\pi \cos^2(\alpha) \left( \sqrt{2} - \frac{3}{\sqrt{2}} \cos(2\alpha) \right) \right] \sin(2\alpha), \quad (\text{A7})$$

$$t_{yz,x^2-y^2}^x = \frac{1}{|\epsilon_p - \epsilon_d|} \left[ -\frac{\sqrt{2}}{2} pd\pi^2 (1 - 2 \cos^2 \alpha) - \frac{\sqrt{6}}{2} pd\sigma pd\pi \cos^2 \alpha \right] \sin(2\alpha), \quad (\text{A8})$$

$$t_{3z^2-r^2,x^2-y^2}^x = \frac{1}{|\epsilon_p - \epsilon_d|} \left[ \frac{\sqrt{3}}{2} pd\pi^2 \sin^2(2\alpha) + pd\sigma pd\pi \cos^2 \alpha \times \alpha (1 - 3 \sin^2 \alpha) \right] - \frac{\sqrt{3}}{4} (dd\sigma)_1 + \frac{\sqrt{3}}{4} (dd\delta)_1 \quad (\text{A9})$$

and between second-nearest neighbors

$$\tilde{t}_{xy,xy} = \frac{1}{|\epsilon_p - \epsilon_d|} \left[ -\frac{3}{4} pd\sigma^2 \cos^2 \alpha \cos(2\alpha) + pd\pi^2 \cos(2\alpha) \sin^2 \alpha - \frac{\sqrt{3}}{2} pd\sigma pd\pi \sin^2(2\alpha) \right] \cos^2 \alpha + \frac{3}{4} (dd\sigma)_2 + \frac{1}{4} (dd\delta)_2, \quad (\text{A10})$$

$$\tilde{t}_{yz,yz} = \frac{1}{|\epsilon_p - \epsilon_d|} \left[ \left( \frac{3}{8} pd\sigma^2 - \frac{\sqrt{3}}{2} pd\sigma pd\pi \right) \cos(2\alpha) \sin^2(2\alpha) + \frac{1}{4} pd\pi^2 \left( 1 - \frac{5}{2} \cos(2\alpha) - \frac{1}{2} \cos(6\alpha) \right) \right] + \frac{1}{2} (dd\pi)_2 + \frac{1}{2} (dd\delta)_2, \quad (\text{A11})$$

$$\tilde{t}_{3z^2-r^2,3z^2-r^2} = \frac{1}{|\epsilon_p - \epsilon_d|} \left[ pd\sigma^2 \left( -\frac{1}{4} \cos^6 \alpha + \frac{5}{4} \cos^4 \alpha \sin^2 \alpha - 2 \cos^2 \alpha \sin^4 \alpha + \sin^6 \alpha \right) + \frac{3}{4} pd\pi^2 \cos(2\alpha) \sin^2(2\alpha) + \frac{\sqrt{3}}{2} pd\sigma pd\pi \sin^2(2\alpha) (3 \sin^2 \alpha - 1) \right] + \frac{1}{4} (dd\sigma)_2 + \frac{3}{4} (dd\delta)_2, \quad (\text{A12})$$

$$\tilde{t}_{x^2-y^2,x^2-y^2} = -\frac{1}{|\epsilon_p - \epsilon_d|} pd\pi^2 \cos^2 \alpha + (dd\pi)_2, \quad (\text{A13})$$

$$\begin{aligned} \tilde{t}_{xy,yz} = & \frac{1}{|\epsilon_p - \epsilon_d|} \frac{1}{4\sqrt{2}} [3pd\sigma^2 \cos^2 \alpha \cos(2\alpha) + pd\pi^2 \\ & \times (1 + \cos(4\alpha)) - \sqrt{3}pd\sigma pd\pi(\cos(2\alpha) \\ & + \cos(4\alpha))] \sin(2\alpha), \end{aligned} \quad (\text{A14})$$

$$\begin{aligned} \tilde{t}_{xy,3z^2-r^2} = & \frac{1}{|\epsilon_p - \epsilon_d|} \left[ \frac{\sqrt{3}}{8} pd\sigma^2 \cos^2 \alpha \left( \frac{3}{2} - \cos(2\alpha) \right. \right. \\ & \left. \left. + \frac{3}{2} \cos(4\alpha) \right) - \frac{\sqrt{3}}{4} pd\pi^2 \cos(2\alpha) \sin^2(2\alpha) \right. \\ & \left. + \frac{1}{4} pd\sigma pd\pi (1 + 3 \cos(2\alpha)) \sin^2(2\alpha) \right] \\ & - \frac{\sqrt{3}}{4} (dd\sigma)_2 + \frac{\sqrt{3}}{4} (dd\delta)_2, \end{aligned} \quad (\text{A15})$$

$$\begin{aligned} \tilde{t}_{yz,zx} = & \frac{1}{|\epsilon_p - \epsilon_d|} \left[ \frac{3}{8} pd\sigma^2 \cos(2\alpha) \sin^2(2\alpha) \right. \\ & \left. - \frac{1}{4} pd\pi^2 \left( 1 + \frac{1}{2} \cos(2\alpha) + \frac{1}{2} \cos(6\alpha) \right) \right. \\ & \left. - \frac{\sqrt{3}}{2} pd\sigma pd\pi \cos(2\alpha) \sin^2(2\alpha) \right] + \frac{1}{2} (dd\pi)_2 \\ & - \frac{1}{2} (dd\delta)_2, \end{aligned} \quad (\text{A16})$$

$$\begin{aligned} \tilde{t}_{yz,3z^2-r^2} = & \frac{1}{|\epsilon_p - \epsilon_d|} \left[ \frac{\sqrt{3}}{16} pd\sigma^2 (3 - 2 \cos(2\alpha) + 3 \cos(4\alpha)) \right. \\ & \left. + \frac{\sqrt{3}}{2} pd\pi^2 \cos^2(2\alpha) + \frac{1}{4} pd\sigma pd\pi (\cos(2\alpha) \right. \\ & \left. - 3 \cos(4\alpha)) \right] \frac{\sin(2\alpha)}{\sqrt{2}}, \end{aligned} \quad (\text{A17})$$

$$\tilde{t}_{yz,x^2-y^2} = \frac{1}{|\epsilon_p - \epsilon_d|} pd\pi^2 \frac{\sin(2\alpha)}{2\sqrt{2}}. \quad (\text{A18})$$

Any other hopping amplitude not listed here is zero or is related by symmetry to these ones, as discussed in Sec. II. The overlap integrals are treated as fitting parameters. Due to the shorter distance between the atoms the largest contribution to hopping is expected to come from the first-nearest

neighbors Fe-As and Fe-Fe overlap integrals. As shown in the text it is possible to reproduce the most important features of the band structure, including its orbital content and dependence on  $\alpha$ , neglecting all the contributions beyond these ones:  $pd\sigma$ ,  $pd\pi$ ,  $(dd\sigma)_1$ ,  $(dd\pi)_1$ , and  $(dd\delta)_1$ . From the above fitting we see that while the inclusion of direct hopping between Fe nearest neighbors is crucial to reproduce the band structure, direct hopping to second Fe neighbors can be neglected. Giving all the energies, including  $d$ - $d$  orbital overlap integrals, in units of  $(pd\sigma)^2/|\epsilon_d - \epsilon_p|$ , and except  $p$ - $d$  overlap integrals, which are given in units of  $pd\sigma$ , the determination of the hopping amplitudes reduces to the computation of just four fitting parameters  $pd\pi$ ,  $(dd\sigma)_1$ ,  $(dd\pi)_1$ , and  $(dd\delta)_1$ .

The formalism used here allows to study how the band structure depends on changes in the lattice. Indirect hopping between Fe atoms via As induces a dependence of the hopping amplitudes in the angle  $\alpha$  formed between the Fe-As bonds and the Fe-Fe plane. This dependence is plotted in Fig. 2. All hopping terms show angle dependence with the only exception of  $t_{x^2-y^2,x^2-y^2}$  which does not have any indirect contribution. On the other hand the amplitudes which couple orbitals  $yz, zx$  with  $xy, 3z^2-r^2, x^2-y^2$  vanish for  $\alpha=0$  when the arsenic atoms are in the Fe plane.

## APPENDIX B: HAMILTONIAN IN MOMENTUM SPACE

In the ten-orbital reduced Brillouin zone  $-\frac{\pi}{2} < k'_x, k'_y < \frac{\pi}{2}$  the Hamiltonian is a  $10 \times 10$  matrix. Only the terms which mix orbitals  $zx, yz$  with  $xy, 3z^2-r^2, x^2-y^2$  feel the unit-cell doubling and couple states with momentum  $\mathbf{k}'$  with other with momentum  $\mathbf{k}' + \mathbf{Q}$  with  $\mathbf{Q} = (\pi, \pi)$ . Choosing the orbital basis  $d_{\mathbf{k}';\alpha,\sigma}, d_{\mathbf{k}'+\mathbf{Q};\alpha,\sigma}$  in a convenient order:

$$\begin{aligned} \{ & d_{\mathbf{k}';yz,\sigma}, d_{\mathbf{k}';zx,\sigma}, d_{\mathbf{k}'+\mathbf{Q};xy,\sigma}, d_{\mathbf{k}'+\mathbf{Q};3z^2-r^2,\sigma}, d_{\mathbf{k}'+\mathbf{Q};x^2-y^2,\sigma}, \\ & d_{\mathbf{k}'+\mathbf{Q};yz,\sigma}, d_{\mathbf{k}'+\mathbf{Q};zx,\sigma}, d_{\mathbf{k}';xy,\sigma}, d_{\mathbf{k}';3z^2-r^2,\sigma}, d_{\mathbf{k}';x^2-y^2,\sigma} \} \end{aligned}$$

the  $10 \times 10$  Hamiltonian can be written as block diagonal

$$\begin{pmatrix} H_{5 \times 5}(\mathbf{k}') & 0 \\ 0 & H_{5 \times 5}(\mathbf{k}' + \mathbf{Q}) \end{pmatrix}$$

with

$$H_{5 \times 5}(\mathbf{k}') = \begin{pmatrix} H_{2 \times 2}(\mathbf{k}') & H_{2 \times 3}(\mathbf{k}') \\ H_{3 \times 2}(\mathbf{k}') & H_{3 \times 3}(\mathbf{k}' + \mathbf{Q}) \end{pmatrix} - (\mu - \epsilon_\gamma) \mathbb{I}.$$

Here  $\mathbb{I}$  is the unit matrix and  $\gamma$  the orbital index in the order given above. The subindices in the matrix name serve to label the matrices and indicate their dimension,

$$H_{2 \times 2}(\mathbf{k}') = \begin{pmatrix} 2t_{yz,yz}^y \cos k'_y + 2t_{yz,yz}^x \cos k'_x + 4\tilde{t}_{yz,yz} \cos k'_x \cos k'_y & -4\tilde{t}_{yz,zx} \sin k'_x \sin k'_y \\ -4\tilde{t}_{yz,zx} \sin k'_x \sin k'_y & 2t_{zx,zx}^y \cos k'_y + 2t_{zx,zx}^x \cos k'_x + 4\tilde{t}_{zx,zx} \cos k'_x \cos k'_y \end{pmatrix},$$



$$H_{3 \times 3}(\mathbf{k}') = \begin{pmatrix} 2t_{xy,xy}^x(\cos k'_x + \cos k'_y) & -4\tilde{t}_{xy,3z^2-r^2} \sin k'_x \sin k'_y & 0 \\ +4\tilde{t}_{xy,xy} \cos k'_x \cos k'_y & & \\ -4\tilde{t}_{xy,3z^2-r^2} \sin k'_x \sin k'_y & 2t_{3z^2-r^2,3z^2-r^2}^x(\cos k'_x + \cos k'_y) & 2t_{x^2-y^2,3z^2-r^2}^x(\cos k'_x - \cos k'_y) \\ +4\tilde{t}_{3z^2-r^2,3z^2-r^2} \cos k'_x \cos k'_y & & \\ 0 & 2t_{x^2-y^2,3z^2-r^2}^x(\cos k'_x - \cos k'_y) & 2t_{x^2-y^2,x^2-y^2}^x(\cos k'_x + \cos k'_y) \\ & & +4\tilde{t}_{x^2-y^2,x^2-y^2} \cos k'_x \cos k'_y \end{pmatrix}$$

and  $H_{3 \times 2} = [H_{2 \times 3}^*]^T$  with  $H_{2 \times 3}(\mathbf{k}')$  equal to

$$\begin{pmatrix} 2i \sin k'_y (t_{yz,xy}^y - 2\tilde{t}_{yz,xy} \cos k'_x) & 2i \sin k'_x (t_{yz,3z^2-r^2}^x - 2\tilde{t}_{yz,3z^2-r^2} \cos k'_y) & 2i \sin k'_x (t_{yz,x^2-y^2}^x - 2\tilde{t}_{yz,x^2-y^2} \cos k'_y) \\ 2i \sin k'_x (t_{zx,xy}^x - 2\tilde{t}_{zx,xy} \cos k'_y) & 2i \sin k'_y (t_{zx,3z^2-r^2}^y - 2\tilde{t}_{zx,3z^2-r^2} \cos k'_x) & 2i \sin k'_y (t_{zx,x^2-y^2}^y - 2\tilde{t}_{zx,x^2-y^2} \cos k'_x) \end{pmatrix}.$$

In the above-mentioned basis order, the block-diagonal form given provides a natural way<sup>35,40</sup> to unfold the Brillouin zone (see Fig. 1), that is, to define  $\mathbf{k}=\mathbf{k}'$  for orbitals  $yz$  and  $zx$  and  $\mathbf{k}=\mathbf{k}'+\mathbf{Q}$  for  $xy, 3z^2-r^2$  and  $x^2-y^2$ . In this extended Brillouin zone  $-\pi < k_x, k_y < \pi$  the Hamiltonian is given by  $H_{5 \times 5}(\mathbf{k})$ . All the figures and expressions in the main text are given in the unfolded  $k$  space.

One advantage of the present tight-binding model is the possibility to understand many features of the band structure. In particular, exactly at  $\Gamma$  and  $M$  none of the five bands show orbital mixing and simple expressions follow for their energies,

$$E_\gamma = \pm 2t_{\gamma,\gamma}^y \pm 2t_{\gamma,\gamma}^x + 4\tilde{t}_{\gamma,\gamma} + \epsilon_\gamma - \mu \quad (\text{B1})$$

with  $\gamma=yz, zx$ . Plus (minus) sign applies at  $\Gamma$  ( $M$ ),

$$E_\gamma = \mp 4t_{\gamma,\gamma}^x + 4\tilde{t}_{\gamma,\gamma} + \epsilon_\gamma - \mu \quad (\text{B2})$$

for  $\gamma=xy, 3z^2-r^2$ , and  $x^2-y^2$ . Minus (plus) sign applies at  $\Gamma$  ( $M$ ). From Eqs. (B1) and (B2) the degeneracy of  $yz$  and  $zx$  bands at  $\Gamma$  and  $M$  follows. This twofold degeneracy is clearly seen at the top of the hole bands which cross the Fermi level in  $\Gamma$  and in the two highest in energy bands at  $M$ . As discussed in the text the dependence of  $E_{xy}(M)$  on  $\alpha$  originates in the sensitivity of  $\tilde{t}_{xy,xy}$  to changes in the angle. The same dependence is present in  $E_{xy}(\Gamma)$  which shifts with  $\alpha$  in the same way as  $E_{xy}(M)$  does, namely, decreases as the angle is squashed, keeping  $E_{xy}(\Gamma) - E_{xy}(M) = -8t_{xy,xy}^x$  almost unchanged. On the contrary, due to the combined dependence of first- and second-nearest neighbors in  $\alpha$  both  $E_{3z^2-r^2}(M)$  and  $E_{3z^2-r^2}(\Gamma) - E_{3z^2-r^2}(M)$  decrease when the angle is elongated, the latter becoming eventually negative. Dependence of the hopping parameters on  $\alpha$  are plotted in Fig. 2.

At  $X$  and  $Y$  only  $3z^2-r^2$  and  $x^2-y^2$  mix, the energies of the other orbitals can be expressed in the simple form

$$E_\gamma(X, Y) = \pm 2t_{\gamma,\gamma}^y \mp 2t_{\gamma,\gamma}^x - 4\tilde{t}_{\gamma,\gamma} + \epsilon_\gamma - \mu \quad (\text{B3})$$

for  $yz$  and  $zx$ . First sign applies for  $X$  and second for  $Y$ . The degeneracy found in  $\Gamma$  and  $M$  is broken but their energies are related by symmetry  $E_{yz,yz}(X) = E_{zx,zx}(Y)$  and  $E_{yz,yz}(Y) = E_{zx,zx}(X)$ . Due to the sign which precedes  $\tilde{t}_{xy,xy}$  in the expression for the energy corresponding to the  $xy$  orbital in  $X$  and  $Y$ ,  $E_{xy}(X, Y) = -4\tilde{t}_{xy,xy} + \epsilon_{xy} - \mu$ , the shift of  $E_{xy}(X, Y)$  with  $\alpha$  is opposite to that found at  $\Gamma$  and  $M$ .

In the present paper we have neglected the dependence of the crystal-field splitting on the angle  $\alpha$  but, due to the simplicity of the expressions for the energy at the symmetry points, guessing its effect in the band structure is straightforward. In particular, a possible change in crystal field of  $xy$  with  $\alpha$  would shift  $E_{xy}$  in the same amount in  $\Gamma, M, X$ , and  $Y$ , contrary to the effect produced by the angle-dependent hopping parameters.

Another interesting feature regards the mixing between orbitals along the high-symmetry lines  $\Gamma Y, \Gamma X, MX$ , and  $MY$ . Along  $\Gamma Y$  and  $MX$   $xy/yz$  bands cross  $zx/x^2-y^2/3z^2-r^2$  bands without hybridization resulting in Dirac points. These Dirac points can be observed in Figs. 3 and 4. Along  $MX$  there are crossings between the two upmost bands and between the second and third bands (the later crossing being only present for  $\alpha^{\text{squashed}}$  in Fig. 4). Along  $\Gamma Y$  such crossings appear between the two upmost bands and between the two lower ones, the former crossing being absent in the case of  $\alpha^{\text{squashed}}$ . Along this direction a Dirac point close to the Fermi level is also found at the crossing between  $zx$  and  $xy$  derived bands, as discussed in the main text and mentioned previously by other authors.<sup>10,25</sup> The same physics appears along  $\Gamma X$  and  $MY$  with the interchange of  $yz$  for  $zx$ .

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