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I. INTRODUCTION

Very recently, Caviglia et al.\textsuperscript{1} and Ben Shalom et al.\textsuperscript{2} studied the magnetotransport properties of the high mobility two-dimensional electron gas (2DEG) at the interface between two insulating perovskite oxides, LaAlO$_3$ (LAO) and SrTiO$_3$ (STO).\textsuperscript{3} They found strong spin-orbit coupling (SOC) effects, whose magnitudes can even be tuned by gate voltages. This strong SOC has been the basis for many subsequent theoretical and experimental studies.\textsuperscript{4–9} Despite its increasing importance, a clear physical picture of the SOC effects in LAO/STO interfaces is still missing.

SOC generally originates from the relativistic correction $(\hbar^2/2m^*c^2)\xi(V \times \vec{p}) \cdot \vec{s}$ to the Schrödinger equation, with $m^*$ being the free electron mass and $V$ the potential in which the electrons move with momentum $\vec{p}$ and spin $\vec{s}$. If $V(\vec{r})$ has spherical symmetry like in atoms or approximately in solids, the form can be reduced to $\xi(\vec{r})\vec{I} \cdot \vec{s}$, where $\xi(\vec{r})$ denotes the strength of the atomic SOC, and $\vec{I}$ and $\vec{s}$ are the orbital and spin angular momenta of the electron. Thus SOC lifts orbital and spin degeneracies. For a cubic perovskite such as STO, the six angular momenta of the electron. Thus SOC lifts orbital and spin degeneracies.

This changes for a LAO/STO interface since the inversion symmetry is broken so that the SOC lifts the spin degeneracy of the 2DEG. This two-dimensional SOC effect is known as Rashba spin splitting, which has been widely studied in semiconductor heterostructures\textsuperscript{14,15} and metal surfaces.\textsuperscript{16} Assuming a nearly free 2DEG with effective mass $m^*$, its two spin components will be split by $\Delta_R = 2\alpha_R \vec{k}$, where the Rashba coefficient $\alpha_R = (\hbar/4m^*c^2)dV(z)/dz$ depends on the potential gradient in the $z$ direction (perpendicular to the interface). Naïvely, since an electric field gives rise to an electrostatic potential gradient, $\Delta_R$ seems to be simply proportional to the gate voltage. However, a typical electric field in experiments is $\sim 100$ V/mm yielding, according to the formula above, $\Delta_R \sim 10^{-9}$ meV,\textsuperscript{17} which is much smaller than the measured values of the order of meV.\textsuperscript{12} This is because the assumption of nearly free 2DEG, which ignores the region of ion cores and the asymmetric feature of the interface wave function, is too simple. In reality, the expression for $\Delta_R$ is much more complicated\textsuperscript{17–21} and usually treated as a fitting parameter in semiconductor heterostructures and metal surfaces.

The aim of this Rapid Communication is the theoretical description of SOC in oxide heterostructures and surfaces. From density-functional-theory (DFT) calculations we derive a tight-binding (TB) Hamiltonian for the low energy $t_{2g}$ orbitals and their spin splitting. In particular, we show that besides the standard $k$-linear Rashba spin splitting, there can be a $k$-cubic spin splitting around the $\Gamma$ point due to multiorbital effects. A much larger spin splitting occurs at the crossing point of the $xy$ and $yz$ (or $zx$) orbitals.

II. METHOD

Besides bulk STO, we calculate (i) LAO/STO (1.5/6.5 layers),\textsuperscript{22,23} which is symmetric with two $n$-type interfaces; (ii) LAO/STO (4/4) and (1/1), which is asymmetric with $n$- and $p$-type interfaces;\textsuperscript{24} (iii) vacuum/LAO/STO (3/1/4), which has a single $n$-type interface,\textsuperscript{25,26} and (iv) vacuum/STO (3/7/5) with a SrO terminated surface. We fix the in-plane lattice constant of the supercells to the calculated equilibrium value of STO, and optimize the internal coordinates. The DFT calculations have been done using the WIEN2K code with the generalized gradient approximation.\textsuperscript{27,28} The SOC is included as a perturbation using the scalar-relativistic eigenfunctions of the valence states. Through a projection onto maximally localized Wannier orbitals,\textsuperscript{29–31} we construct a realistic TB model, and in particular, we develop a way to describe the interface asymmetry.

III. DFT RESULTS FOR STO

Bulk SrTiO$_3$ is a band insulator with an energy gap between occupied O$_{2g}$ bands and unoccupied Ti$_{3d}$ $t_{2g}$ ($yz, zx, xy$) bands. The $t_{2g}$ band structure calculated by DFT is shown in Fig. 1(a). In the absence of SOC, the three $t_{2g}$ orbitals are degenerate at $\Gamma(0,0,0)$ due to an octahedral $O_h$ crystal field around the Ti atoms in a perfect perovskite structure. Around $\Gamma$ the bands can be fit by a parabolic function of the form $\hbar^2k^2/2m^*$ where the effective mass $m^*$ depends on the orbital and the direction.
We set \( \Delta_{1O} \) in this Rapid Communication. In the absence of spin-orbit coupling, the sixfold-degenerate orbitals into \( \Gamma_1 \) and \( \Gamma_5 \) states separated by \( \Delta_{O} = 29 \text{ meV} \).

Along the \( \Gamma-X(\pi,0,0) \) direction (here in units of \( 1/a \) with \( a = 3.92 \text{ Å} \) being the calculated lattice constant of STO), the \( yz \) band has a small energy dispersion corresponding to a heavy mass of \( 6.8 m_e \). In contrast, the \( xz \) and \( xy \) orbitals have the same, large energy dispersion and a light effective mass of \( 0.41 m_e \). Including the SOC, the sixfold-degenerate orbitals are split into a doubly and a fourfold-degenerate level with an orbital splitting of \( \Delta_{O} = 29 \text{ meV} \) (Ref. 13) (see Fig. 1). The energy dispersion of the resulting orbitals is now considerably different from the initial orbitals. Consequently, the corresponding effective masses around \( \Gamma \) are changed to 1.39, 0.41, and 0.53\( m_e \), respectively.

### IV. TB HAMILTONIAN FOR STO

To understand the DFT results, we use a Wannier projection to obtain the local energy and hopping terms of the \( t_{2g} \) orbitals. Without SOC, the constructed three-band TB Hamiltonian of bulk STO \( H^b_0 \) can be expressed in the \( t_{2g} \) basis in a matrix form:

One of the diagonal terms is \( \langle \mathbf{xy} | H^b_0 | \mathbf{xy} \rangle = \epsilon^b_0 = -2t_1 \cos k_x - 2t_2 \cos k_y - 4t_3 \cos k_z \cos k_x; \) the other two follow by exchanging the \( x,y,z \) indices. The local energy term is \( \epsilon_0 = 3.31 \text{ eV} \) for all three orbitals. The large hopping \( t_1 = 0.277 \text{ eV} \) stems from the large \( xy \) intraorbital hopping integral along the \( x \) and \( y \) directions; it is due to two lobes of \( xy \) orbitals at the nearest-neighbor sites pointing to each other along the two directions. In contrast, \( t_2 = 0.031 \text{ eV} \) and \( t_3 = 0.076 \text{ eV} \) indicate a much smaller hopping integral along the \( z \) and \( (1,1,0) \) directions, respectively. We find all orbital-off-diagonal (interorbital hopping) terms to be negligible. The TB energy dispersion for the three orbitals is plotted in Fig. 1(b), showing good agreement with the DFT results.

We include SOC at the atomic level as \( H_\xi = \xi \hat{\mathbf{r}} \cdot \hat{s} \), where \( \xi \) is the atomic SOC strength and depends on atomic numbers. Under the \( O_h \) crystal field, the six spinful \( t_{2g} \) orbitals break into a doublet \( | \Gamma^+_7, \pm \frac{1}{2} \rangle \equiv \frac{1}{\sqrt{2}} (i yz | \uparrow \rangle \mp z x | \downarrow \rangle \mp x y | \uparrow \rangle \pm z x | \downarrow \rangle \mp i y z | \uparrow \rangle ) \), and a quartet \( | \Gamma^+_5, \pm \frac{1}{2} \rangle \equiv \frac{1}{\sqrt{2}} ( i y z | \uparrow \rangle \mp z x | \downarrow \rangle \mp 2 x y | \uparrow \rangle + i y z | \downarrow \rangle ), \), \( | \Gamma^+_8, \pm \frac{1}{2} \rangle \equiv \frac{1}{\sqrt{2}} ( i y z | \uparrow \rangle \mp z x | \downarrow \rangle + 2 x y | \uparrow \rangle + i y z | \downarrow \rangle ) \).

\( H_\xi \) lifts their degeneracy at the \( \Gamma \) point and is diagonal in the \( \Gamma^+_7, \Gamma^+_5, \Gamma^+_8 \) basis with eigenvalues of \( \xi \) and \( -\xi/2 \), respectively. We set \( \xi = 2 \Delta_{O}/3 = 19.3 \text{ meV} \), which leads to the same orbital splitting as the DFT results. In the original \( t_{2g} \) basis (yz | \uparrow \rangle, yz | \downarrow \rangle, zx | \uparrow \rangle, zx | \downarrow \rangle, xy | \uparrow \rangle, xy | \downarrow \rangle ), \( H_\xi \) has off-diagonal terms and reads

\[
\begin{pmatrix}
0 & 0 & i & 0 & 0 & -1 \\
0 & 0 & 0 & -i & 1 & 0 \\
-i & 0 & 0 & 0 & 0 & i \\
i & 0 & 0 & 0 & i & 0 \\
0 & 1 & 0 & -i & 0 & 0 \\
-1 & 0 & -i & 0 & 0 & 0 \\
\end{pmatrix}
\]

\( H^b_0 + H_\xi \) is the TB Hamiltonian of bulk STO including SOC. Its band structure is shown as a solid line in Fig. 1(b) and agrees well with the DFT results. This model allows for a deeper understanding of the SOC effects: The SOC eigenstates are admixtures of the \( yz, zx \), and \( xy \) orbitals, which explains the significant changes of the effective masses.

### V. DFT RESULTS FOR INTERFACES

The band structure of LAO/STO (1.5/6.5) calculated by DFT is shown in Fig. 2(a). Without SOC, similar to bulk STO, all bands exhibit a paraboliclike behavior. In the \( x \) direction, the \( yz \) band is the flattest (heaviest); at \( \Gamma \), it is degenerate with the \( zx \). Due to the interface, the \( xy \) band is \( \Delta_y = 250 \text{ meV} \) lower in energy at \( \Gamma \) than the degenerate \( yz \) and \( zx \) bands. The splitting \( \Delta_r \) is the most notable feature of the heterostructure,22,23,26 It is not mainly a crystal field effect, but originates from the vanishing of the hopping from the interface Ti \( \text{yz} \) to LAO along the \( z \) direction.31 Consistently, a similar behavior is expected in a SrO terminated STO surface, and indeed we obtain it.
with $\Delta_I = 320$ meV [see Fig. 2(b)]. Our calculated splittings are qualitatively consistent with the ARPES measurements of STO surfaces.

Including SOC does not influence the $xy$ band very much. It splits the degenerate $yz$ and $zx$ orbitals with $\Delta_O = 19$ meV at $\Gamma$ [see Fig. 2(a)]. The \textit{ab initio} calculated $\Delta_O$ is qualitatively consistent with experiment, albeit smaller than its experimental value. $\Delta_O = 60$ meV. Around $\Gamma$, the effective masses for $xy$ and the resulting two states are 0.48, 1.14, and 0.72$m_e$, respectively. For the asymmetric case Fig. 2(c) the SOC also results in a spin splitting which is most noticeable at the $xy$-$yz$ crossing region where it is up to 18 meV [see Figs. 2(d) and 2(e)]. This spin splitting is a multiorbital effect, very different from the standard Rashba spin splitting of single orbital. For a better understanding, we now construct a TB Hamiltonian.

VI. SPIN SPLITTING AT THE INTERFACE LAYER

Without SOC, a model Hamiltonian $H_0^I$ can describe the interface hopping and the induced splitting $\Delta_I$. In contrast to $H_0^I$, the hopping terms of $H_0^I$ in direction $z$ essentially vanish. The diagonal term for $xy$ is hence $\epsilon^{xy} - 2t_1 \cos k_x - 2t_1 \cos k_y$, while that for the $yz$ (and $zx$) orbital is $\epsilon^{yz} - 2t_2 \cos k_x - 2t_1 \cos k_y - t_1 - 2t_2 \cos k_y$. The local energy terms $\epsilon^{yz/yz}$ will be influenced by the interface crystal field, electron filling, and confinement.

For simplicity, we approximate these by the bulk value $\epsilon_0$. Thus, $\Delta_I = t_1 - t_2 + 2t_1 = 0.4$ eV, which is comparable to the DFT results. At the interface the $O_h$ symmetry breaks down to $C_{4v}$, and we can use the same atomic SOC $H_\ell^I$ matrix as before, since under $C_{4v}$ the $\Gamma^+_y$ doublet does not break, whereas the $\Gamma^+_z$ quartet breaks into $\Gamma^+_0 \oplus \Gamma^+_y$, with the same set of basis functions as given previously. The $H_0^I + H_\ell^I$ Hamiltonian gives an atomic SOC induced orbital splitting about $\Delta_\ell = \sqrt{5}eV/2$ at $\Gamma$ similar to Figs. 2(a)–2(c). However $H_0^I + H_\ell^I$ does not contain any terms breaking the interface inversion symmetry, and hence it does not include the Rashba spin splitting.

To this end, we introduce a term $H_\gamma$ to describe the broken inversion symmetry at the interface, a key component for Rashba spin splitting. The essential physics of this term was analyzed by Lashell et al., and then introduced by Petersen et al. to construct a TB model for the Rashba effects of s-p orbitals in metal surfaces. To our knowledge, there and in other publications, $H_\gamma$ was always treated as a parameter and hence its utility and importance are strongly limited. In this study, we project the DFT results above onto maximally localized Wannier orbitals and then directly extract the spin independent hopping term $H_\gamma$, 

$$
\gamma \begin{pmatrix}
0 & 0 & 2i \sin k_x \\
0 & 0 & 2i \sin k_y \\
-2i \sin k_x & -2i \sin k_y & 0
\end{pmatrix}
$$

describing interorbital hopping terms due to the interface asymmetry. The key hopping term is $\gamma = \langle xy \rangle \langle H \rangle_{yz}(R)$, where $R$ is the nearest neighbor in the $x$ direction. As shown in the schematic Fig. 3(a), $\gamma$ is an antisymmetric hopping between $xy$ and $yz$ orbitals along the $x$ direction. Its origin is the interface asymmetry deforming the orbital lobes of the interface layer. We find $\gamma \sim 20$ meV at the $n$-type interface for all geometries, and hence take this value in the model. Let us note $\gamma$ drops quickly in the second and further layers towards its bulk value $\gamma = 0$.

The combined model Hamiltonian $H_\gamma^I + H_\ell^I + H_\gamma$, including Rashba effects, is expressed in the $t_{2g}$ basis by a $6 \times 6$ matrix, where $H_\gamma^I$ describes the interface hopping and splitting $\Delta_I$, $H_\ell^I$ includes the atomic SOC and accounts for the orbital splitting of $\Delta_O$, and $H_\gamma$ describes the interface asymmetry. The first effect is a standard Rashba type of spin splitting in the single $xy$ band. It splits a single parabola around the minimum at $\Gamma$ into two parabolas with opposite spin [see Fig. 3(d)]. By downfolding the matrix onto an effective Hamiltonian for the $xy$ band, we obtain an analytical expression for the spin splitting $\Delta_\gamma = 2\alpha_\ell k_x$, with $\alpha_\ell = 2\alpha_\ell \xi / \Delta_I = 0.76 \times 10^{-2}$ eV Å for $\Delta_I = 0.4$ eV, $\xi = 19.3$ meV, and $\gamma = 20$ meV. Note that $\Delta_\gamma$ depends strongly on the details of the interface and
VII. CONCLUSION

We performed first-principle calculations and developed a realistic three-band (\(xy,yz,\) and \(zx\)) model for SOC effects at LAO/STO interfaces and STO surfaces. The key ingredients to the spin splitting are the atomic SOC and the interface asymmetry, which enters via asymmetric \(t_{eg}\) orbital lobes. The \(xy\) orbital around \(\Gamma\) exhibits the standard Rashba spin splitting \(2\alpha_R k \times G\sim 2\alpha_R G/\Delta_1 \sim 10^{-2} \text{ eV A}^{-1}\); in contrast, for negative \(\Delta_1\) there is instead a \(k\)-cubic dependence spin splitting in the lowest band around \(\Gamma\). As \(\Delta_1\) depends on the particular surface or interface, this solves the experimental controversy regarding linear or cubic Rashba splitting. Even more importantly, we find an unusually large spin splitting 18 meV at the crossing point of \(xy\) and \(yz/\sigma_{xx}\) orbitals. Our results indicate that LAO/STO has peculiar SOC properties arising from the multiorbital character which are absent in the standard single-band description as for the nearly free 2DEG in semiconductor heterostructures.

Note added. The same tight-binding model and physical results have also been presented in Ref. 47.

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If the antisymmetric hopping $H_y$ is included, we obtain the same behavior as for the dashed line of Figs. 2(c)–2(e).