Theoretical model for Rashba spin-orbit interaction in $d$ electrons

K. V. Shanavas, Z. S. Popović,† and S. Satpathy
Department of Physics, University of Missouri, Columbia, Missouri 65221, USA

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We show that the Rashba spin-orbit interaction in $d$ electron solids, which originates from the broken inversion symmetry at surfaces or interfaces, is strongly dependent on the orbital characters of the bands involved. This is studied by developing a tight-binding model in the presence of a uniform perpendicular electric field and spin-orbit coupling. We argue that for valence electrons, the spin-orbit coupling strength scales only as the square of the atomic number. The electric field distorts the $d$ orbitals through the admixture of $p$ and $f$ states and also introduces intersite overlap parameters. Expressions for Rashba coefficients for the bands are obtained in both weak and strong spin-orbit interaction limits and are shown to be orbital dependent. The results are compared with first-principles calculations for model systems, showing good agreement. Our study demonstrates the orbital-dependent gate control of the Rashba effect for the purposes of oxide electronics.

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I. INTRODUCTION

The recent discovery of the Rashba effect [1] in the two-dimensional electron gas (2DEG) systems such as perovskite surfaces and interfaces has led to the possibility of tuning its properties by external electric fields [2]. The study of the Rashba effect in 2DEGs is of interest not just from a fundamental point of view, but also due to potential applications in spintronics devices [3]. In contrast to their semiconductor counterparts, the perovskites are characterized by the presence of high-$Z$ elements and $d$ electrons with strong spin-orbit interaction.

For 2D electrons confined to the $x$-$y$ plane and subjected to an electric field along $z$, the Rashba splitting is commonly described by the Bychkov-Rashba Hamiltonian [4],

$$\mathcal{H}_R = \alpha_R (\vec{\sigma} \times \vec{k}) \cdot \vec{z} = \alpha_R (k_x \sigma_x - k_y \sigma_y),$$

where $\vec{k} = (k_x, k_y, 0)$ is the electron crystal momentum, $\vec{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ are the Pauli matrices, and $\alpha_R$ is the Rashba coefficient. The Rashba effect originates from a combination of the inversion symmetry breaking and spin-orbit interaction and has predominant contribution from the nuclear regions in the solid [5,6]. It has been observed in numerous condensed-matter systems including metal surfaces [7,8], topological insulators [9,10], interfaces of perovskite oxides [2,11–13], etc.

On the theoretical side, tight-binding (TB)-based model Hamiltonian approaches [14,15] have been successful in understanding the Rashba effect in solids. The basic idea is to incorporate the effect of broken inversion symmetry phenomenologically into atomic orbital overlap parameters. For example, in the case of $p$ orbitals on a plane, the coupling between in-plane $p_x$, $p_y$ orbitals and out-of-plane $p_z$ orbitals is zero. However, if the symmetry is broken by an external field, it leads to matrix elements between these orbitals [14] and, in conjunction with spin-orbit interaction, will result in effective couplings between spin-up and spin-down bands.

These ideas have been used to study the Rashba effect in several systems of current interest such as graphene [16–18] and polar complex oxides [6,19–21]. In the case of graphene, which is a $sp$-band system, model studies showed that in addition to the intersite coupling terms similar to the one proposed earlier, there also exist on-site terms that play an important role [18]. They arise from electric-field-induced couplings with orbitals that satisfy the selections rules $\Delta l = \pm 1$ and $\Delta m = 0$ at the same site, as these atomic wave functions are no longer orthogonal in the presence of external electric field.

At the complex oxides interfaces of LaAlO$_3$/SrTiO$_3$ and surfaces of KTaO$_3$, a 2DEG with transition-metal (Ti or Ta) $d$ orbital character develops. These systems have strong spin-orbit interaction and the structural inversion symmetry is broken at the interfaces/surfaces, making them good candidates for exhibiting a strong Rashba effect. In the case of the LaAlO$_3$/SrTiO$_3$ interface, it was shown that the magnitude of the splitting can be tuned by an applied gate voltage [2]. Tight-binding models [19,21] for the $t_{2g}$ states on a cubic lattice were found to agree well with first-principles calculations based on the density functional theory (DFT). It has also been suggested that the polar distortions of the metal ion oxygen bonds also play an important role in Rashba splitting [20]. From density functional calculations of KTaO$_3$, we showed earlier that the 2DEG can be manipulated by the electric field to go in and out of the surface, offering a method to tailor the magnitude of the Rashba splitting [6].

In this paper, we present detailed theoretical models to understand the dependence of the Rashba coefficient on the orbital character and spin-orbit (SO) coupling of the atomic states in the material. We obtain expressions for $\alpha_R$ in the weak and strong SO interaction limits. First-principles calculations are performed on model systems containing a single atomic layer of Ti or Ta on a square lattice, to make connection with the TB model.

This paper is organized as follows. In the next section, we discuss the orbital dependence of spin-orbit coupling strength, which is a crucial ingredient in the Rashba effect in solids. In Sec. III, we construct the tight-binding Hamiltonian for $d$ orbitals under a uniform electrostatic potential and discuss the origin of various contributions. The derivation of effective...
Finally, the results from the tight-binding model are compared to the calculated Fock method (colored lines) are compared to the hydrogenic expectation value using the Coulomb Hamiltonians for individual bands is discussed in Sec. IV. 


II. VARIATION OF SPIN-ORBIT COUPLING WITH ATOMIC NUMBER

It is well known that the spin-orbit interaction strength \( \lambda \) increases rapidly with the atomic number \( Z \). However, there is some confusion in the literature regarding just how rapid this increase is. We clarify this issue here and emphasize that the spin-orbit interaction strength for the outer electrons in the atom, i.e., the electrons that are relevant to the properties in the solid state, increases only as the Landau-Lifshitz scaling \( Z^2 \), while it increases much more rapidly within a certain series such as 3d, where it scales as \( Z^4 \) as suggested by the simple hydrogenic result. The Landau-Lifshitz scaling argument [22] is based on an estimate of the penetration of the outer electrons, rather than the electrons of a particular series, into the nuclear region where the bulk of the spin-orbit interaction originates.

The origin of the \( Z^4 \) dependence is well known. The spin-orbit interaction of an electron in a central field of potential \( V(r) \) is given by the expression

\[
\mathcal{H}_{SO}(r) = \frac{r^{-1}}{2m^2c^2} \frac{\partial V(r)}{\partial r} \vec{L} \cdot \vec{S} = \lambda(r) \vec{L} \cdot \vec{S}, \tag{2}
\]

and if we evaluate its expectation value using the Coulomb potential \( V(r) = -Ze^2/r \) and the hydrogenic wave functions \( R_{nl}(r) \) with energy \( E_{nl}^0 \), we get the well-known result for the perturbative correction due to the spin-orbit interaction, viz. [23],

\[
E_{nl} = E_{nl}^0 + \lambda_{nl} \times Z^2 (j(j+1) - l(l+1) - 3/4), \tag{3}
\]

where \( j \) and \( l \) are total and orbital angular momentum quantum numbers with

\[
\lambda_{nl} = \int_0^\infty R_{nl}^2 \lambda(r) r^3 dr = \frac{\alpha^2 Z^4}{n^3(l+1/2)(l+1)} \text{Ry}, \tag{4}
\]

which increases as \( Z^4 \), with \( \alpha \) being the fine-structure constant. To see how well this is obeyed in the actual atoms, we have taken the spin-orbit interaction strength \( \lambda_{nl} \), calculated by Herman and Skillman [24] using the Hartree-Fock method with the Slater exchange, and have plotted these in Fig. 1 along with the hydrogenic expression given by Eq. (4) for the 3d series. As seen from the figure, even though the \( Z^4 \) power dependence is not too bad for large \( Z \) for a particular series, the magnitude of \( \lambda_{nl} \) is nevertheless severely overestimated by Eq. (4). This is not surprising because the hydrogenic result neglected the screening of the nuclear potential by the innermost core electrons.

However, in the solid, the outer electrons are the relevant electrons, whose quantum numbers \( nl \) change with \( Z \). If one considers the outermost electrons for the atoms without worrying about \( nl \), then Landau and Lifshitz have argued that the spin-orbit interaction strength should scale more like \( Z^2 \), viz.,

\[
\lambda = A \alpha^2 Z^2 \text{Ry}, \tag{5}
\]

where \( A \) is of the order of one. We find that if we consider the outer electrons in the atom (shown by dots and the shaded area in Fig. 1), then \( \lambda_{nl} \) does roughly follow this \( Z^2 \) dependence with \( A \approx 0.1 \), as illustrated in Fig. 1. Note that the \( Z^2 \) dependence describes the rough overall systematic variation of the spin-orbit interaction strength and not the nonsystematic change from element to element. Thus the strength of the relevant spin-orbit interaction, viz., that for the outer electrons, does not increase nearly as fast as \( Z^4 \) as sometimes thought in the literature based on the hydrogenic expression given by Eq. (4). The spin-orbit interaction strengths for the atoms considered in this paper are listed in Table I.

![Image](image.png)

FIG. 1. (Color online) Dependence of the spin-orbit coupling strength \( \lambda_{nl} \) for atoms as a function of the atomic number \( Z \). The calculated results of Herman and Skillman [24] using the Hartree-Fock method (colored lines) are compared to the hydrogenic \( Z^4 \) dependence, which is computed from Eq. (4) for the 3d series (upper dashed line). For the outermost electrons (indicated by the circles and the shaded area), which are the relevant electrons in the solid, the quantum numbers \( nl \) change with \( Z \) and the spin-orbit interaction increases much more slowly, following roughly the Landau-Lifshitz \( Z^2 \) scaling [lower dashed line, calculated from Eq. (5) with \( A = 0.10 \)].

III. TIGHT-BINDING MODEL

To describe the Rashba spin-orbit interaction, the model Hamiltonian should have three terms: a band structure term \( \mathcal{H}_K \), a spin-orbit term \( \mathcal{H}_{SO} \), and the electric-field-induced inversion symmetry-breaking term \( \mathcal{H}_E \).

\[
\mathcal{H} = \mathcal{H}_K + \mathcal{H}_{SO} + \mathcal{H}_E. \tag{6}
\]

Table I. Spin-orbit coupling strength (in eV) for the outermost electrons in the atoms considered in this work as obtained from the hydrogenic expression [\( \lambda_{Hyd} \), Eq. (4)], the Landau-Lifshitz scaling [\( \lambda_{LL} \), Eq. (5)], and the Hartree-Fock calculations of Herman and Skillman [\( \lambda_{HF} \)]. The last column \( \lambda_{solid} \) lists the calculated values for the solid from the present DFT calculations. The atomic values differ from \( \lambda_{solid} \) because of the admixture of other orbitals and the delocalized nature of the outermost electrons in the solid as compared to the atom.

<table>
<thead>
<tr>
<th>Element</th>
<th>Z</th>
<th>( \lambda_{Hyd} )</th>
<th>( \lambda_{LL} )</th>
<th>( \lambda_{HF} )</th>
<th>( \lambda_{solid} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti 3d</td>
<td>22</td>
<td>0.42</td>
<td>0.035</td>
<td>0.023</td>
<td>0.02</td>
</tr>
<tr>
<td>Ta 5d</td>
<td>73</td>
<td>11</td>
<td>0.39</td>
<td>0.30</td>
<td>0.18</td>
</tr>
</tbody>
</table>

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To model the 2DEG at the perovskite structures, we would like to use a linear combination of atomic orbitals as basis functions denoted by |φ\(_{\alpha R}\rangle\), where α is the combined orbital and spin index and R is the lattice vector, which points to atoms on a square lattice, as shown in Fig. 2. Note that in actual systems, the d orbitals are interconnected through oxygen p states. Since spin-orbit interaction (SOI) in oxygen is quite small, we can incorporate their effect as an effective d-d coupling.

The electrostatic potential \(\mathcal{H}_E\) breaks the spherical symmetry around the atoms and distorts the atomic orbitals. But it is much weaker than the nuclear potential, hence, we can treat \(\mathcal{H}_E\) as a perturbation and write

\[
\mathcal{H} = \mathcal{H}_0 + \zeta \mathcal{H}_E,
\]

(7)

where \(\mathcal{H}_0 = \mathcal{H}_k + \mathcal{H}_\text{SO}\) and \(\zeta\) is a dimensionless parameter (\(\zeta = 1\)). With \(|\phi\_\alpha R\rangle\) as the first-order corrections to the atomic orbitals, we can write the matrix elements of \(\mathcal{H}\) as

\[
\langle \phi\_a | \mathcal{H}_k | \phi\_b \rangle + \zeta \langle \phi\_a | \mathcal{H}_\text{SO} | \phi\_b \rangle + \zeta \langle \phi\_a | \mathcal{H}_E | \phi\_b \rangle + \zeta^2 \langle \phi\_a | \mathcal{H}_0 | \phi\_b \rangle + O(\zeta^2)
\]

\[= T_k + T_\text{SO} + T_E + T_1,
\]

(8)

where \(T_k, T_\text{SO}, \text{ and } T_E\) are matrix elements with the unperturbed orbitals and \(T_1\) are the matrix elements introduced by the perturbation. We ignore terms quadratic in \(\zeta\). Note that we have taken into account the fact that not only does the changed Hamiltonian modify the hopping integral between the original basis orbitals, but in addition the basis orbitals themselves become modified via the admixture of other atomic orbitals at the same site, viz., the \(p\) and the \(f\) orbitals. In other words, the Hilbert space axes become modified as well. We discuss the individual terms in detail below.

A. Kinetic-energy terms \(T_k\)

The periodic nature of the lattice helps us construct the matrix elements \(|\phi\_a | \mathcal{H}_k | \phi\_b \rangle\) in the reciprocal space by writing the atomic orbitals as a Bloch sum,

\[
|\chi_{\alpha R}\rangle = \frac{1}{\sqrt{N}} \sum_{R} e^{i \vec{k} \cdot \vec{R}} |\phi_{\alpha R}\rangle.
\]

(9)

Therefore,

\[
T_k(\vec{k}) = \epsilon_a \delta_{a\beta} + \sum_{\vec{R}} e^{i \vec{k} \cdot \vec{R}} T_k(\vec{R}).
\]

(10)

The sum runs over the nearest-neighbor lattice sites except the central site, \(\vec{R} = 0\), which produces the first term, with \(\epsilon_a\) being the on-site energies. For the atomic orbitals in the order \(\phi_a = \{|d_{x^2-y^2}, d_{x^3}, d_{x}, d_{y}, d_{z}\}\}, \) the \(\vec{R}\) matrix can be written with the help of Slater-Koster tables \([25,26]\),

\[
\hat{T}_k = \begin{pmatrix}
    h_1 & h_{12} & 0 & 0 & 0 \\
    h_{12} & h_2 & 0 & 0 & 0 \\
    0 & 0 & h_3 & 0 & 0 \\
    0 & 0 & 0 & h_4 & 0 \\
    0 & 0 & 0 & 0 & h_5
\end{pmatrix},
\]

(11)

where

\[
\begin{align*}
    h_1 &= \epsilon_1 + (V_\sigma / 2 + 3 V_\delta / 2)(\cos k_x a + \cos k_y a), \\
    h_2 &= \epsilon_2 + (3 V_\sigma / 2 + V_\delta / 2)(\cos k_x a + \cos k_y a), \\
    h_{12} &= (\sqrt{3} V_\delta / 2 - \sqrt{3} V_\sigma / 2)(\cos k_x a - \cos k_y a), \\
    h_3 &= \epsilon_3 + 2 V_\sigma (\cos k_y a + \cos k_x a), \\
    h_4 &= \epsilon_4 + 2 (V_\sigma \cos k_y a + V_\delta \cos k_x a), \\
    h_5 &= \epsilon_5 + 2 (V_\pi \cos k_y a + V_\delta \cos k_x a),
\end{align*}
\]

(12)

\(V_\sigma, V_\delta, \text{ and } V_\pi\) are the Slater-Koster parameters for \(d-d\) overlap, \(\epsilon_i\) are the on-site energies, and \(a\) is the nearest-neighbor distance.

B. Spin-orbit terms \(T_\text{SO}\)

From Eq. (2), we can construct matrix elements of SOI for \(d\) states,

\[
T_{\text{SO}} = \frac{i \lambda}{2} \begin{pmatrix}
    0 & 0 & 0 & \sqrt{3} \sigma_x & \sqrt{3} \sigma_z \\
    0 & 2 \sigma_z & 0 & -\sigma_x & \sigma_y \\
    2 \sigma_x & 0 & -\sigma_z & \sigma_y & \sigma_z \\
    -3 \sigma_y & -\sigma_x & 0 & -\sigma_z & \sigma_z \\
    -3 \sigma_x & -\sigma_y & 0 & -\sigma_z & \sigma_z
\end{pmatrix},
\]

(13)

where \(\sigma_x, \sigma_y, \sigma_z\) are the \(2 \times 2\) Pauli spin matrices. SOI has only on-site terms and no \(k\) dependence. To understand the effect of \(\lambda\) on Rashba splitting, we consider two limits. (1) The first limit is a weak SOI, with \(\lambda \ll V\), where \(V\) is the electron hopping parameter. In the first-principles calculations (Sec. V), this case is simulated using 3d ion Ti with \(Z = 22\). (2) The second limit is a strong SOI, with \(\lambda \gg V\), which is simulated by the 5d element Ta with \(Z = 73\). The values of \(\lambda\) obtained for these two cases using the methods discussed above are summarized in Table I.

C. Perturbative terms \(T_1\)

To evaluate the matrix elements \(T_1\), we first write down the expression for the first-order correction from perturbation theory,

\[
|\phi^{1}_{\alpha R}\rangle = \sum_{\beta \neq a} \frac{\langle \phi_{\beta R} | \mathcal{H}_E | \phi_{\alpha R}\rangle}{\epsilon_a - \epsilon_\beta} |\phi_{\beta R}\rangle,
\]

(14)
where the index $\alpha$ runs over the five $d$ orbitals of interest here, and $\beta$ runs over all other atomic orbitals at the same site. The perturbation $H_{\text{E}}$ may originate from an external electric field or proximity of an atom to a surface, which also breaks the inversion symmetry. In the simplest form, it can be written in terms of the effective electric field $\eta_e$,

$$H_{\text{E}} = \eta z,$$ (15)

which may be different from the applied electric field due to electronic and ionic screening [6].

Now, we can write $\phi_{\alpha \beta} = R_{\alpha}(r)[\vec{r} - \vec{R})]Y_{\alpha}(\theta, \phi)$ and $z = (4\pi/3)^{1/2}rY_{10}$. The cubic harmonics $\tilde{Y}_{\alpha}$ can be expressed in terms of the spherical harmonics $Y_{lm}$ so the matrix elements in Eq. (14) boil down to a product of an integral over $r$ and an angular integral over the product of three spherical harmonics. The angular part of the integral can be solved with the help of the Gaunt coefficients $C_{lm,l'm',m''}$ defined as [27,28]

$$C_{lm,l'm',m''} = \int Y_{lm}(\theta, \phi)Y_{l'm'}^{*}(\theta, \phi)Y_{m''}(\theta, \phi) \; d\Omega = \left( \frac{2l' + 1}{4\pi} \right)^{1/2} e^{i1 \langle l' m'; l m \rangle}.$$ (16)

The coefficients $e_{l'}(l' m'; l m)$ vanish unless $m'' = m' - m$ and $l'' = |l' - l|, |l' + l| + 2, \ldots, (l + l')$ [23]. The second condition couples the $d$ orbitals only to the $p$ and $f$ orbitals ($\Delta l = \pm 1$) and the first condition requires $\Delta m = m'' - m' = 0$.

Following the above procedure to evaluate Eq. (14), we find that the first-order correction to the $d$ orbitals contains just a few terms, viz.,

$$|d_{z^2}^{\pm}\rangle = \frac{2\eta_p}{\sqrt{5}}|p_z\rangle + \frac{3\eta_f}{\sqrt{15}}|f_{z^2}\rangle,$$

$$|d_{x^2-y^2}^{\pm}\rangle = \frac{\eta_f}{\sqrt{5}}|f_{x^2-y^2}\rangle,$$

$$|d_{xy}^{\pm}\rangle = \frac{\eta_f}{\sqrt{5}}|f_{xy}\rangle,$$

$$|d_{xz}^{\pm}\rangle = \frac{2\eta_f}{\sqrt{5}}|p_x\rangle + \frac{2\sqrt{2}\eta_f}{\sqrt{35}}|f_{xz}\rangle,$$

$$|d_{yz}^{\pm}\rangle = \frac{\eta_f}{\sqrt{5}}|p_y\rangle + \frac{2\sqrt{2}\eta_f}{\sqrt{35}}|f_{yz}\rangle,$$

where

$$\eta_p = \frac{\eta}{\epsilon_d - \epsilon_p} \int dr R_p(r) r R_d(r),$$

which is a dimensionless parameter that depends on the energy separation and radial spread of the orbitals. Figure 3 shows the asymmetric $d_{z^2}$ orbital because of the admixture with the other orbitals at the same site.

Thus, $T_1$ includes $p-d$ and $d-f$ hopping parameters due to the admixture of $d$ orbitals with these orbitals. The only contribution towards $T_1$ comes from $H_{\text{K}}$ with $R \neq 0$, since $H_{\text{SO}}$ does not couple different angular momentum and since on-site terms of $H_{\text{K}}$ between different orbitals are zero. Evaluating all the matrix elements for nearest neighbors, we get

$$T_0 = \begin{pmatrix}
0 & 0 & 0 & h_{14} & h_{15} \\
0 & 0 & 0 & h_{24} & h_{25} \\
0 & 0 & 0 & h_{34} & h_{35} \\
\end{pmatrix},$$ (18)

where

$$h_{14} = 2i\gamma_1 \sin k_x, \quad h_{15} = 2i\gamma_1 \sin k_x,$$

$$h_{24} = 2i\gamma_2 \sin k_x, \quad h_{25} = 2i\gamma_2 \sin k_x,$$

$$h_{34} = 2i\gamma_3 \sin k_x, \quad h_{35} = 2i\gamma_3 \sin k_x,$$

the electric-field-dependent parameters $\gamma_1, \gamma_2$, and $\gamma_3$ are

$$\gamma_1 = \eta_p \left[ \frac{V_{pd\sigma}}{2\sqrt{5}} + \frac{2V_{pd\pi}}{2\sqrt{15}} \right] + \eta_f \left[ \frac{\sqrt{3}V_{df\pi}}{2\sqrt{35}} + \frac{3\sqrt{3}V_{df\pi}}{2\sqrt{70}} \right],$$

$$\gamma_2 = -\sqrt{3}\eta_p \frac{V_{pd\sigma}}{2\sqrt{5}} - \eta_f \left[ \frac{3V_{df\sigma}}{2\sqrt{35}} + \frac{5V_{df\pi}}{2\sqrt{14}} \right],$$ (20)

$$\gamma_3 = -\eta_p \frac{V_{pd\pi}}{\sqrt{70}},$$

and $V_{pd\sigma}$ ($V_{df\pi}$) and $V_{pd\pi}$ ($V_{df\sigma}$) are $\sigma$ and $\pi$ hopping between $p$ ($f$) and $d$ orbitals on neighboring sites. We can make an approximate estimate of the parameters $\gamma$ by using the analytical expressions for $p-d$ hopping [26],

$$V_{pd(\sigma/\pi)} = \eta_p \frac{\hbar^2 r_a^{3/2}}{ma^{3/2}},$$ (21)

where $a$ is the nearest-neighbor distance. For typical values of $p-d$ hopping parameters, $\eta_p = -3.14$, $\eta_f = 1.36$, $\hbar^2/m = 7.62 \text{ eV} \text{ Å}^2$, and $r_a = 1.08 \text{ Å}$. Variations of the $\gamma$’s as a function of neighbor distance are shown in Fig. 4. Close to the origin, $\gamma_2$ and $\gamma_3$ diverge and the empirical expressions for hopping given in Eq. (21) are valid only for larger distances. Due to symmetry, the two terms involving $V_{dp\sigma}$ and $V_{dp\pi}$ in the expression for $\gamma_1$ cancel each other exactly.

**D. Electrostatic potential terms $T_{\text{E}}$**

The matrix elements $T_0 = \langle \phi_{\alpha \beta} | \eta z | \phi_{\alpha \beta} \rangle$ represent coupling between $d$ orbitals on different sites due to the electrostatic potential. The integral is too complicated to solve analytically, so we evaluate it numerically assuming hydrogenic functions
with a screened nuclear charge $Z_e$ for the radial part of the wave functions,

$$ R_a(r) = \left( \frac{2Z_e}{na_0} \right)^{\frac{3}{2}} (n - l - 1)! e^{\rho l} L_{n-l-1}^l(\rho), \quad (22) $$

where $\rho = (2Z_e/na_0)r$, $a_0$ is the Bohr radius, and $L(\rho)$ is the associated Laguerre polynomials. We find there are three nonzero coupling parameters, viz.,

$$ \gamma'_1 = \eta(d_{2z}\hat{\sigma}d_{2z},a\hat{x}) = \eta(d_{2z}\hat{\sigma}d_{2z},a\hat{y}), $$

$$ \gamma'_2 = \eta(d_{2z}\hat{\sigma}d_{2z},a\hat{x}) = \eta(d_{2z}\hat{\sigma}d_{2z},a\hat{y}), $$

$$ \gamma'_3 = \eta(d_{2y}\hat{\sigma}d_{2z},a\hat{y}) = \eta(d_{2y}\hat{\sigma}d_{2z},a\hat{y}). $$

(23)

Here, the orbital on the left side of the inner product is at the origin, while the one on the right is located on a neighboring atom shifted by the lattice constant $a$ along the indicated direction.

The coupling parameters, shown in Fig. 5, become negligible for distances beyond 5 Å. For a typical 3$d$ element such as Ti, the covalent radius is about 1.5 Å, so $d$-$d$ distances are of the order of a few angstroms. In this range, the strongest contribution comes from $\gamma'_2$, followed by $\gamma'_1$ and $\gamma'_3$, which is understandable since $d_{2z}$ and $d_{xy}$ have the largest spread in the $xy$ plane. However, for shorter distances, $\gamma'_1$ is the largest, as the electronic field has the strongest effect on $d_{2z}$ since it lies along the $z$ axis. Figure 5 shows that the relative magnitudes of the electric-field-induced couplings between orbitals can be tuned by changing the lattice spacing, and therefore also the Rashba effect with applied pressure.

Finally, collecting all the terms, viz., Eqs. (11), (13), (18), and (24), the $10 \times 10$ TB Hamiltonian in the orbital-spin space can be written as

$$ \mathcal{H} = \mathcal{H}_K + \mathcal{H}_T \otimes \mathcal{1} + \mathcal{H}_{SO}, $$

(25)

where $\mathcal{1}$ is the identity matrix in the spin-$1/2$ space. After taking the five on-site energies $\varepsilon_i$ to be zero for simplicity, we have seven other TB parameters: $V_a, V_b, V_c, \lambda, \gamma_1, \gamma_2$, and $\gamma_3$. They depend on specific systems, and in Sec. V we discuss typical values derived from DFT calculations on Ti and Ta systems.

**IV. EFFECTIVE HAMILTONIAN**

By diagonalizing the full Hamiltonian in Eq. (25) at different $k$ points with appropriate parameter values, we can study the energy levels in the system. For the 2DEG in perovskite materials, the important region in the reciprocal space is around the zone center. At the $\Gamma$ point, the $d$ states are split into five doubly degenerate states by electron hopping and spin-orbit coupling. The levels are spin degenerate when $k = 0$, since the effect of the electric field is zero. As long as the states are well separated, we can describe the effect of momentum-dependent spin splitting around the $\Gamma$ point for each band by a $2 \times 2$ Rashba Hamiltonian. The effect of the remaining eight-dimensional subspace is folded via renormalization of the parameters. To illustrate this, we consider two limits of parameter values, when spin orbit is weak compared to electron coupling, and vice versa. The energy levels at the $\Gamma$ point in both cases are shown in Fig. 6.

![Fig. 5. (Color online) Electric-field-induced overlap parameters due to the intersite contribution term $T_i$ obtained from Eqs. (22) and (23) and numerical integration for 3d wave functions with parameter values $n = 3, l = 2, Z_e = 4$, and $\eta = 1$ eV/Å.](image)

![Fig. 6. Energy splitting for a square lattice at the $\Gamma$ point in the presence of (a) weak and (b) strong spin-orbit interaction compared to the electron hopping parameters $V_a, V_b$.](image)
TABLE II. Energy- and orbital-dependent Rashba coefficients in the weak and strong spin-orbit interaction limits. The Rashba coefficients \( \alpha_g/a \) (in meV) obtained from the TB expressions are compared with numerical results from the DFT and TB calculations. For simplicity, \( V_1 \) is neglected as compared to \( V_6 \) and \( V_9 \) in the TB expressions. DFT calculations are for the square lattice of Ti and Ta for cases of weak and strong SOI, respectively. The TB expressions given here are correct to the lowest order; omitted terms are \( O(\lambda^2) \) for the weak SOI case and \( O(\gamma/\lambda) \) or \( O(\gamma/V) \) for the strong SOI case.

<table>
<thead>
<tr>
<th>Sym</th>
<th>Energy at ( \Gamma )</th>
<th>TB ( \alpha_g/a ) (downfolding)</th>
<th>DFT ( \alpha_g/a ) (full ( H ))</th>
<th>DFT Orbital character</th>
<th>DFT ( \alpha_g/a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Gamma_1 )</td>
<td>( 3V_6 )</td>
<td>( 2\gamma y/(2\lambda y V_6) )</td>
<td>( -0.62 )</td>
<td>( 0.73 )</td>
<td>( x^2-y^2 )</td>
</tr>
<tr>
<td>( \Gamma_1 )</td>
<td>( V_6 )</td>
<td>( 2\sqrt{3}\gamma y/(\lambda y V_6) )</td>
<td>( -0.64 )</td>
<td>( 4.13 )</td>
<td>( z^2 )</td>
</tr>
<tr>
<td>Weak SOI (( \lambda \ll V_6, V_9 ))</td>
<td>( \Gamma_6 )</td>
<td>( 2V_6 - \lambda/2 )</td>
<td>( -2\sqrt{3}\lambda y/(\lambda y V_6) )</td>
<td>( 5.64 )</td>
<td>( 4.25 )</td>
</tr>
<tr>
<td></td>
<td>( \Gamma_7 )</td>
<td>( 2V_6 + \lambda/2 )</td>
<td>( 2\lambda y/(\lambda y V_6) + \gamma y V_6 )</td>
<td>( 0.93 )</td>
<td>( 1.02 )</td>
</tr>
<tr>
<td></td>
<td>( \Gamma_6 )</td>
<td>( 2V_6 )</td>
<td>( -\lambda y V_6 )</td>
<td>( -0.57 )</td>
<td>( 0.30 )</td>
</tr>
<tr>
<td>Strong SOI (( \lambda \gg V_6, V_9 ))</td>
<td>( \Gamma_7 )</td>
<td>( -3\lambda/2 + 6V_6/3 + 5V_9 )</td>
<td>( 4(y_2 - y_1)/5 )</td>
<td>( 13.60 )</td>
<td>( 9.78 )</td>
</tr>
<tr>
<td></td>
<td>( \Gamma_7 )</td>
<td>( -3\lambda/2 + 6V_6/3 + 5V_9 )</td>
<td>( -4\sqrt{3}y_1/5 )</td>
<td>( -0.90 )</td>
<td>( 6.88 )</td>
</tr>
<tr>
<td></td>
<td>( \Gamma_7 )</td>
<td>( \lambda + 9V_6/5 + 4V_6/3 )</td>
<td>( -4/5y_2 + 6/15y_3 )</td>
<td>( -14.9 )</td>
<td>( 13.2 )</td>
</tr>
<tr>
<td></td>
<td>( \Gamma_7 )</td>
<td>( \lambda + 3V_6/5 + 4V_6/3 )</td>
<td>( 4\sqrt{3}y_1/5 )</td>
<td>( 9.00 )</td>
<td>( 6.88 )</td>
</tr>
<tr>
<td></td>
<td>( \Gamma_7 )</td>
<td>( \lambda + 8V_6/3 )</td>
<td>( 4y_3/3 )</td>
<td>( 1.33 )</td>
<td>( 3.50 )</td>
</tr>
</tbody>
</table>

A. Weak SOI (\( \lambda \ll V \))

The energy levels at the \( \Gamma \) point, obtained from the full tight-binding Hamiltonian, are given in Fig. 6(a). Bond formations split the states into four, where \( d_{xz} \) and \( d_{yz} \) are degenerate due to symmetry. The symmetry is further lifted by SOI. The character of the bands at these energies is given below,

\[
\begin{align*}
\Gamma_1' &= \{d_{x^2-y^2}\uparrow, d_{xy}\uparrow, d_{xy}\downarrow, d_{x^2-y^2}\downarrow\}, \\
\Gamma_7' &= \{\frac{1}{\sqrt{2}}(d_{x^2-z^2} - id_{xz})\uparrow, \frac{1}{\sqrt{2}}(d_{xz} + id_{x^2-z^2})\downarrow\}, \\
\Gamma_7'' &= \{d_{xy}\uparrow, d_{xy}\downarrow\}, \\
\Gamma_7''' &= \{d_{x^2-z^2}\uparrow, d_{xz}\downarrow\},
\end{align*}
\]

The full Hamiltonian in Eq. (25) can be transformed into the basis set for weak SOI given in Eq. (26) by a unitary transformation \( U^\dagger H U \),

\[
H_U = \begin{pmatrix}
\frac{V_6}{\lambda} & 0 & 0 & 0 & 0 & \frac{\sqrt{2}}{\sqrt{2}} & 0 & -i\sqrt{2} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\frac{\sqrt{2}}{\sqrt{2}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\frac{\sqrt{2}}{\sqrt{2}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
i\lambda & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
-i\lambda & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\end{pmatrix},
\]

where the two blocks are well separated in energy. The effective Hamiltonian in the subspace \( h \) can be written as

\[
h' = h + b(\gamma I - c)^{-1}b^\dagger,
\]

which, however, involves the eigenvalue \( E \) of the full Hamiltonian and needs to be solved iteratively. In the limit that the states in \( h \) and \( c \) are well separated and the coupling \( b \) is small, we can substitute \( E \) by the eigenvalues of matrix \( h \). Also, it can be shown that an iterative solution of Eq. (29) produces Brillouin-Wigner perturbation series, which to the lowest order
yields
\[ h'_{ij} = h_{ij} + \sum_k b_{ik}b^*_{kj} E - c_{kk}. \tag{30} \]

If \( |b_{ik}| \ll |h_{ii} - c_{kk}| \), the eigenvalues \( E \) can be replaced by the diagonal elements \( h_{ii} \). Following this procedure, the effective Hamiltonian within each 2D subspace can be obtained. For example, for the \( \Gamma_6' \) state, we get
\[ \mathcal{H}_R = \left( \epsilon \mathbf{1} + \alpha_R (k_y \sigma_x - k_x \sigma_y) / \epsilon \right), \tag{31} \]

which can be written in the Rashba form \( \mathcal{H}_R = \epsilon + \alpha_R (k_y \sigma_x - k_x \sigma_y) / \epsilon \), with \( \epsilon = -\lambda/2 \) and the Rashba coefficient \( \alpha_R = -2\sqrt{3}\lambda\gamma_1 / V_r \) from Eq. (27). Complete expressions for all states are given in Table II.

We see that both the spin-orbit coupling and the electric field are necessary to produce the Rashba term. Note that \( \sigma \) represents not the real spin, but rather the spin-orbital entangled pseudospin, which for the present example of the \( \Gamma_6' \) case as seen from Eq. (26) is
\[ |\uparrow\rangle = \frac{1}{\sqrt{2}} (d_{xz\uparrow} + i d_{yz\uparrow}), \]
\[ |\downarrow\rangle = \frac{1}{\sqrt{2}} (d_{xz\downarrow} - i d_{yz\downarrow}). \tag{32} \]

Finally, here we assumed that the field-induced parameters are smaller than spin-orbit coupling, i.e., \( \gamma_1 \ll \lambda \). However, if they are comparable, the off-diagonal elements in the subspace of \( \Gamma_6' \), \( \Gamma_7' \) become as strong as the on-site terms and the downfolding method breaks down. In such cases, one must either use degenerate perturbation theory to change the basis such that the off-diagonal matrix elements vanish or work with the full \( 4 \times 4 \) Hamiltonian in the combined subspace [6].

B. Strong SOI (\( \lambda \gg V \))

For the opposite limit, when spin-orbit is much stronger, the energy levels are shown in Fig. 6(b). The angular momentum states \( j = 5/2 \) and \( 3/2 \) with energies \( \lambda \) and \( -3\lambda/2 \) split further due to the electron hopping. The characters of the bands are approximately the eigenfunctions of the spin-orbit Hamiltonian \( H_{SO} \), which preserve the symmetry of the lattice,
\[ \Gamma_7' = \left\{ \begin{array}{l}
\frac{1}{\sqrt{15}} (2d_{xz\downarrow} + 2id_{yz\downarrow} - d_{xz\uparrow} + id_{yz\uparrow}) \\
\frac{1}{\sqrt{10}} (2d_{xz\downarrow} - 2id_{yz\downarrow} + d_{xz\uparrow} + id_{yz\uparrow}) \end{array} \right\}, \]
\[ \Gamma_7'' = \left\{ \begin{array}{l}
\frac{1}{\sqrt{15}} (3d_{xz\downarrow} - 2d_{yz\downarrow} + id_{xz\uparrow} + id_{yz\uparrow}) \\
\frac{1}{\sqrt{10}} (3d_{xz\downarrow} - 2id_{yz\downarrow} + d_{xz\uparrow} + id_{yz\uparrow}) \end{array} \right\}, \tag{33} \]
\[ \Gamma_6' = \left\{ \begin{array}{l}
\frac{1}{\sqrt{3}} (d_{xz\downarrow} + id_{yz\downarrow} + d_{yz\downarrow}) \\
\frac{1}{\sqrt{3}} (-d_{xz\uparrow} - id_{yz\uparrow} + d_{yz\uparrow}) \end{array} \right\}, \]
\[ \Gamma_6'' = \left\{ \begin{array}{l}
\frac{1}{\sqrt{10}} (2d_{xz\downarrow} + \sqrt{3}d_{xz\uparrow} + \sqrt{3}id_{yz\downarrow}) \\
\frac{1}{\sqrt{10}} (2d_{xz\downarrow} - \sqrt{3}d_{xz\uparrow} + \sqrt{3}id_{yz\downarrow}) \end{array} \right\}, \]
\[ \Gamma_6''' = \left\{ \begin{array}{l}
\frac{1}{\sqrt{3}} (\sqrt{3}d_{xz\downarrow} - d_{xz\uparrow} - id_{yz\uparrow}) \\
\frac{1}{\sqrt{3}} (\sqrt{3}d_{xz\downarrow} + d_{xz\uparrow} - id_{yz\uparrow}) \end{array} \right\}. \]

In this basis, the spin-orbit part of the Hamiltonian is diagonal. But, since the basis set is spin mixed, the electric field now has off-diagonal matrix elements within each 2D subspace. This is unlike the weak SOI case, where the basis set was spin pure [see Eq. (26)], and therefore the electric field did not contain an off-diagonal term within each 2D subspace. Taking the example of the \( \Gamma_6' \) doublet, we find the \( 2 \times 2 \) TB matrix within this subspace has the same form as Eq. (31) with \( \epsilon = -3\lambda/2 + (2V_r + 6V_s)/5 \) and, again, the matrix has the Rashba form with \( \alpha_R = \frac{-4\sqrt{3}\lambda\gamma_1 / 5} {\sqrt{\gamma_1}} \). The Löwdin downfolding that takes into account the effects of the other eight orbitals will produce higher-order terms \( O(\gamma/\lambda) \) or \( O(\gamma/V) \) because of the energy denominator. These terms are small compared to the leading terms listed in Table II because the electric field is assumed to be small leading to \( \gamma \to 0 \).

V. COMPARISON WITH DFT

To gauge the accuracy of our model, we compare the results with that of first-principles calculations using DFT. The simulation cell is as shown in Fig. 2. The weak and strong SOI cases are simulated using Ti and Ta atoms. The DFT calculations were carried out using the Vienna \textit{ab initio} simulation package (VASP) [30], within the projector augmented wave method. We used the local density approximation including the spin-orbit interactions with a plane-wave energy cutoff of 350 eV and \( k \)-space sampling on a \( 9 \times 9 \times 1 \) Monkhorst-Pack grid. We considered a single layer of atoms (Ti or Ta) on a square lattice, shown in Fig. 2. The unit cell was 10 Å long along the \( c \) axis, so that the large vacuum layer avoids any interaction with periodic images. The effect of the electric field is added via a sawtoothlike potential and using dipole corrections to help the energy convergence.

The parameters used in the calculations are given in Table III and the resulting band structures for the two cases are shown in Fig. 7. The bands are plotted along \( k \) which lie in the \( xy \) plane around the \( \Gamma \) point. The TB parameters in Table III are chosen such that there is good agreement between the DFT and TB bands, as seen from Fig. 7. The Rashba coefficients are obtained from the slope of the Rashba band splitting \( \Delta_R = 2\alpha_R k_{||} \), as shown in Fig. 8(b). The results are shown in Table II. The numerical values obtained from the TB expressions more

\begin{table}[ht]
\centering
\begin{tabular}{|c|c|c|}
\hline
 & DFT & TB fitting parameters \\
\hline
\textbf{DFT} & & \\
\hline
\textbf{Weak SOI} & & \\
\hline
Atom: Ti & & \\
\( a = b = 4 \) Å & & \( V_r = -0.02 \) eV, \( V_s = 0.02 \) eV, \\
\( c = 10 \) Å & & \( \gamma_1 = 25 \) meV, \( \gamma_2 = 10 \) meV, \\
\textbf{Strong SOI} & & \\
\hline
Atom: Ta & & \\
\( a = b = 5 \) Å & & \( V_r = -0.1 \) eV, \( V_s = 0.05 \) eV, \\
\( c = 10 \) Å & & \( \gamma_1 = 2 \) meV, \( \gamma_2 = 0.18 \) eV, \\
\( E = 0.5 \) eV/Å & & \\
\textbf{DFT} & & TB fitting parameters \\
\hline
\textbf{DFT} & & \\
\textbf{Weak SOI} & & \\
\hline
Atom: Ti & & \\
\( a = b = 4 \) Å & & \( V_r = -0.17 \) eV, \( V_s = 0.07 \) eV, \\
\( c = 10 \) Å & & \( \gamma_1 = 25 \) meV, \( \gamma_2 = 10 \) meV, \\
\textbf{Strong SOI} & & \\
Atom: Ta & & \\
\( a = b = 5 \) Å & & \( V_r = -0.1 \) eV, \( V_s = 0.05 \) eV, \\
\( c = 10 \) Å & & \( \gamma_1 = 6.5 \) meV, \( \gamma_2 = 18 \) meV, \\
\end{tabular}
\end{table}
or less agree with the full calculations (TB or DFT); there are some disagreements in the magnitudes, however, because the weak and strong SOI limits \((\lambda \rightarrow 0 \text{ or } \infty)\) are not fully satisfied in the realistic systems. Nevertheless, it is clear that the Rashba coefficients are quite strongly orbital dependent.

VI. SUMMARY

In summary, we studied the Rashba effect in the \(d\) electron systems and showed that the effect depends strongly on the orbitals involved in a particular band. This was illustrated by density functional studies for selected systems in the limit of both weak and strong SOI. The symmetry-breaking electric field introduces matrix elements in two distinct ways, viz., via mixing of the atomic orbitals on the same site and by introducing intersite hopping terms within the tight-binding description, both of which we examined in studying the Rashba effect. Using the tight-binding model, we derived the expressions for the Rashba coefficients in both limits of weak and strong SOI. The \(d\) electron systems offer a rich system for manipulating the Rashba effect, not only because the magnitude of the effect can be strong owing to the large atomic numbers \(Z\), but also because the orbital characters and the band energies are sensitive to external forces such as strain, which can be used for tailoring the effect for potential applications in oxide electronics.

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