Theory of t_{2g} electron-gas Rashba interactions

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Using qualitative considerations based on a two-center approximation for tight-binding-model matrix elements, we demonstrate that Rashba interactions in complex-oxide two-dimensional electron gases are due primarily to changes in metal-oxygen-metal bond angles at surfaces and interfaces. We verify this conclusion by comparing our picture with illustrative *ab initio* electronic structure calculations.

The perovskite crystal structure supports most of the Periodic Table and hosts a variety of appealing material characteristics, including ferroelectricity, magnetism, and superconductivity.[1] High quality perovskite oxides can be grown epitaxially, using molecular beam epitaxy or pulsed laser deposition to achieve artificially tailored heterostructures.[2,3] Moreover, it has also been shown that epitaxial growth of the perovskite lattice can be achieved on silicon—a necessary condition for integration with current technologies.[4,5] These considerations have motivated strong interest in perovskite surfaces and interfaces.[6] Unlike conventional semiconductors in which the effective mass is a fraction of the bare electron mass, perovskite semiconductors can have band masses up to ten times the bare electron mass. This distinction is expected to lead to strong correlation effects in perovskite two-dimensional electron systems (2DESs). In addition recent experimental studies of 2DESs involving SrTiO₃ (Refs. 7–12) and KTaO₃ (Refs. 13 and 14) have found evidence of strong spin-orbit interactions (SOI) which could be valuable in spintronics. These experiments have been interpreted using established ideas which apply to conventional semiconductors. In this study we present a theory that applies directly to strong SOI induced spin splitting in 2DESs formed at t_{2g} perovskite surfaces and heterojunctions and establishes some essential differences. In particular we find that interaction spin-splitting magnitudes are controlled by changes in metal-oxygen-metal bond angles and by atomic spin-orbit interaction strengths.

The spin degeneracy of Bloch bands in a crystal can be lifted[15,16] when SO coupling is present and inversion symmetry is absent. In a 2DES spin degeneracy is lifted by Rashba interaction[17,18] terms—symmetry invariant Hamiltonian contributions that are scalar products of spin and orbital axial vectors. Rashba interactions are symmetry allowed whenever a 2DES is not invariant under reflections through the plane it occupies. In this Rapid Communication, we use a tight-binding model informed by *ab initio* electronic structure calculations to develop a theory of Rashba splitting in the t_{2g} bands of the two-dimensional electron systems[19–23] formed at cubic perovskite crystal surfaces and interfaces. We find that Rashba splitting in these systems is due to atomiclike on-site SO interactions combined with processes in which t_{2g} electrons change orbital character when they hop between metal sites. These processes are absent in a cubic environment and are due primarily to polar lattice distortions which alter the metal-oxygen-metal bond angle.

Bulk cubic perovskites have chemical formula ABO_3 and the crystal structure illustrated in Fig. 1(a). The 2DESs in which we are interested are formed from conduction band B-site transition-metal d orbitals. Because the B site, at the cubic cell center, has octahedral coordination[24] with neighboring oxygen atoms, located at the centers of the cubic cell faces, oxygen-metal bonding partially lifts the degeneracy of the d orbitals, pushing the $e_g = \{x^2 - y^2, 3z^2 - r^2\}$ orbitals up in energy relative to the $t_{2g} = \{yz, zx, xy\}$ orbitals [Fig. 1(b)]. In the simplest model of the bulk electronic structure,[25] the bonding networks of the three t_{2g} bands are decoupled; an xy orbital on one B site, for example, can hop only along the y or x direction through an intermediate p_x or p_y orbital to an xy orbital on the B site of a neighboring cubic cell. In perovskite 2DESs, the t_{2g} bands are reconstructed[26,27] into two-dimensional (2D) subbands whose detailed form depends on the bulk band parameters,[28] the surface or interface confinement mechanism, and the dielectric response of the material. A polar displacement of A and B atoms relative to the oxygen octahedra occurs in response to the confinement electric field; this is the same response that is responsible in some materials (including, in particular, SrTiO₃) for extremely large bulk dielectric constants.[26,29] At the same time atomiclike SO splitting interactions hybridize the three t_{2g} orbitals, which are split in the 2DES by differences in their confinement energies. [For ⟨001⟩ 2DESs (assumed below) xy orbitals, which have weak bonding along the z direction, have the lowest confinement energy.] We explain below how these two effects combine to produce a Rashba interaction.

The Rashba interaction couples an orbital axial vector that is odd under $z \rightarrow -z$ to spin, and must therefore arise from hopping processes that are odd under inversion in the x-y plane. We therefore begin by considering a single plane [see Fig. 1(c)] of metal atoms and identify the relevant process by using a tight-binding model[30] for p-d hybridization, assigning a hopping amplitude t_{pd} to the process discussed above. Because of the difference in parity between p and d orbitals, t_{pd} changes sign when the hopping direction changes (Fig. 2). To leading order in t_{pd} virtual hopping via oxygen sites, the Hamiltonian is diagonal in the t_{2g} space with eigenenergies:

$$\epsilon_{yz} = 4t_1 - 2t_1 \cos(k_y a),$$
$$\epsilon_{zx} = 4t_1 - 2t_1 \cos(k_x a), \qquad (1)$$
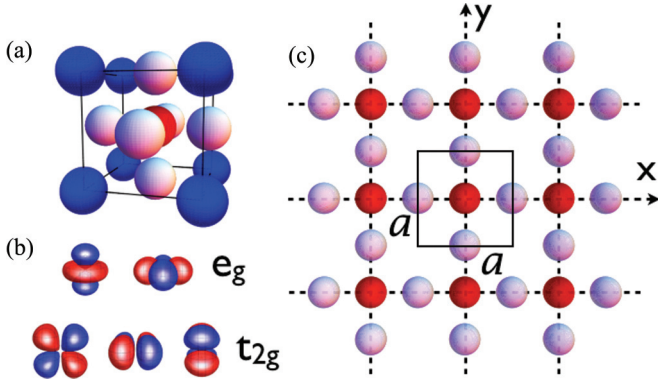$$\epsilon_{xy} = 4t_2 - 2t_2 \cos(k_x a) - 2t_2 \cos(k_y a).$$

FIG. 1. (Color online) Perovskite crystal structure. (a) Bulk cubic unit cell with the A atom in blue, B atom in red, and the oxygen atom in white. (b) Splitting of atomic d orbitals into e_g and t_{2g} manifolds. (c) Single BO_2 plane with one unit cell, with area a^2, in the boxed region.

Here $t_{1,2} = t_{pd}^2 / \Delta_{pd}$, where Δ_{pd} is the splitting between the oxygen p and metal t_{2g} energy levels and the subscripts acknowledge a symmetry allowed difference, ignored below, between xy and $\{yz, zx\}$ hopping amplitudes in the planar environment. Note that the xy band is twice as wide as the $\{yz, zx\}$ bands, and lower in energy at the 2D Γ point. Level repulsion from apical oxygens contributes $2t_1$ to $\epsilon_{yz,zx}$. Even when combined with on-site SO terms, this effective metal-to-metal hopping does not produce a Rashba effect. This is because the metal-to-metal hopping amplitude is independent of direction. In order to explain the Rashba effect, we must look more deeply into how the bonding network is altered in an electric field.

Rashba interactions are caused by broken mirror symmetry and, in particular, by the associated electric field E perpendicular to the 2DES plane. For t_{2g} 2DESs, this field both polarizes the atomic orbitals and induces a polar lattice displacement. These effects open new covalency channels in the metal-oxygen network. In particular, there is no hopping in the unperturbed system between a metal zx orbital and an oxygen x orbital separated along the y direction. This
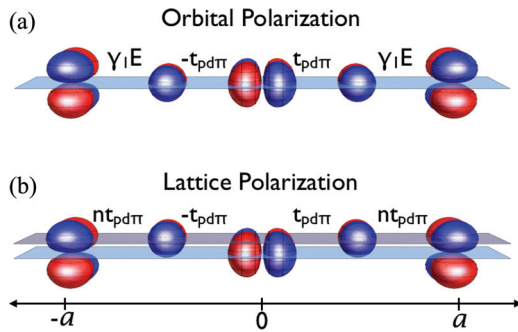

FIG. 2. (Color online) Bonding network along the y axis with an electric field. (a) Orbital polarization. Bonding between zx and xy on neighboring metal atoms through p_x orbitals. The positive and negative lobes of the orbital functions are represented in blue and red, respectively. (b) Lattice polarization. Displacement of the metal (light blue plane) and oxygen (light purple plane) sublattices in an electric field.

is because the x orbital is even and the zx orbital is odd under reflection in the xy plane passing through the metal-oxygen bond. When $E \neq 0$, the Hamiltonian is no longer invariant under this reflection and the hopping process is allowed. If, for example, we think about the perturbation as arising from an additional potential $-eEz$, we can write the induced hopping amplitude approximately as $E\gamma_1$, where $\gamma_1 = \langle zx, \vec{R} = 0 | -ez | x, \vec{R} = a/2\hat{y} \rangle$ [Fig. 2(a)]. At the same time, the electric field will produce forces of opposite sign on metal cations and oxygen anions. The induced polarization will change the metal-oxygen bond angle introducing a nonzero $\hat{z}$-component direction cosine n in the bond axis direction. In a two-center approximation, this change also gives a nonzero amplitude $n t_{pd}$ for zx to x hopping along the y direction. Similar considerations imply an identical yz to y hopping amplitude along x [see Fig. 2(b)]. Including these weak effects, which at leading order act only once in the two-step metal-oxygen-metal hopping process, we obtain an additional effective metal-to-metal hopping amplitude that changes sign with hopping direction and therefore produces a Rashba effect. The (yz, zx, xy)-representation Rashba Hamiltonian is

$$H_E^{t_{2g}} = \begin{pmatrix} 0 & 0 & -2it_R \sin(k_x a) \\ 0 & 0 & -2it_R \sin(k_y a) \\ 2it_R \sin(k_x a) & 2it_R \sin(k_y a) & 0 \end{pmatrix},$$
(2)

where the Rashba interaction strength parameter $t_R = (\gamma_1 t_{pd} E)/\Delta_{pd} + (n t_{pd}^2)/\Delta_{pd}$. When combined with the an atomiclike bulk SO interaction,[26,28]

$$H_{SO} = \frac{\Delta_{SO}}{3} \begin{pmatrix} 0 & i & 0 & 0 & 0 & -1 \\ -i & 0 & 0 & 0 & 0 & i \\ 0 & 0 & 0 & 1 & -i & 0 \\ 0 & 0 & 1 & 0 & -i & 0 \\ 0 & 0 & i & i & 0 & 0 \\ -1 & -i & 0 & 0 & 0 & 0 \end{pmatrix}.$$
(3)

$H_E^{t_{2g}}$ leads to Rashba spin splitting in the t_{2g} bands. We note that broken mirror plane symmetry also introduces other covalent bonding channels, but these do not contribute to the Rashba effect.[31] We also note that, a surface metal atom in a BO_2 terminated perovskite is not octahedrally coordinated. This absence of local inversion symmetry and the decrease in level repulsion with neighboring oxygen atoms mixes e_g and t_{2g} orbitals at the surface. When this mixing is strong, a more elaborate theory of Rashba SO coupling is required.

In general, t_{2g} 2DESs will be spread over many coupled metal layers, and the Rashba Hamiltonian $H_E^{t_{2g}}$ will act within each layer with a layer-dependent coupling constant t_R. For the extreme case of a single-layer t_{2g} 2DES, the xy band will be pulled below the $\{yz, zx\}$ bands by differential confinement effects. In this case we can derive a simple effective Rashba Hamiltonian which acts within the xy subspace. To do so, we define δ as the energy scale which splits the xy and $\{yz, zx\}$ bands at the Γ point. Allowing virtual transitions to the $\{yz, zx\}$ manifold due to orbital/lattice polarization ($H_E^{t_{2g}}$), and bulk SO effects (H_{SO}), we find the part of the Hamiltonian linear in electric field is given at small k by

$$H_R^{xy} = \epsilon_{xy}(\vec{k}) - \alpha \, \vec{\sigma} \cdot (\vec{k} \times \hat{z}),$$
(4)

where $\alpha = 4\Delta_{SO}t_R a/(3\delta)$. This expression, valid for small k and for the xy band only, has the conventional Rashba Hamiltonian form. In this single-orbital limit the Rashba interaction is equivalent to an effective magnetic field. Away from the 2D Brillouin zone center the direction of the Rashba field is no longer perpendicular to $\vec{k}$.

Analogies between Rashba interactions in oxide 2DEGs and Rashba interactions in conventional semiconductor 2DESs are very limited. t_{2g} 2DESs are in general composed of subbands of $\{yx, zx, xy\}$ character and as such, Eqs. (1)–(3) need to be coupled and solved in the presence of a confining potential in order to achieve a minimal model of the electronic structure.[26,27]

To support our theory of the Rashba effect we have carried out an *ab initio* study of a typical t_{2g} 2DES. The first-principles calculations were based on density functional theory and carried out using the Vienna *Ab Initio* Simulation Package.[32] To simplify the comparison we examined the case of a single

$\langle 001 \rangle$ BO_2 plane and studied the influences of z-direction external electric fields and oxygen-metal sublattice relative displacements separately. Because we expect Rashba splitting to be proportional to Δ_{SO} we use the $5d$ transition metal halfnium (Hf) as the B atom. To minimize the mixing between t_{2g} and e_g bands, approximate octahedral coupling has been maintained by including apical oxygens. In our calculations we used projector-augmented wave pseudopotentials and the generalized gradient approximation exchange-correlation functional of Perdew, Burke, and Ernzerhof.[33] The supercell contained a three atom HfO_2 layer with two oxygen atoms located directly above and below the Hf atom. The molecular layers with 4.054 Å lattice constant were separated by a 20 Å vacuum, the plane-wave energy cutoff was set to 500 eV, and we employed $8 \times 8 \times 2$ k-point sampling to achieve electronic convergence. Figure 3(a) shows the band structure of a Hf perovskite plane with ideal atomic positions in the absence of an applied external electric field when spin-orbit interactions are neglected. At the zone center, the xy band has lower energy
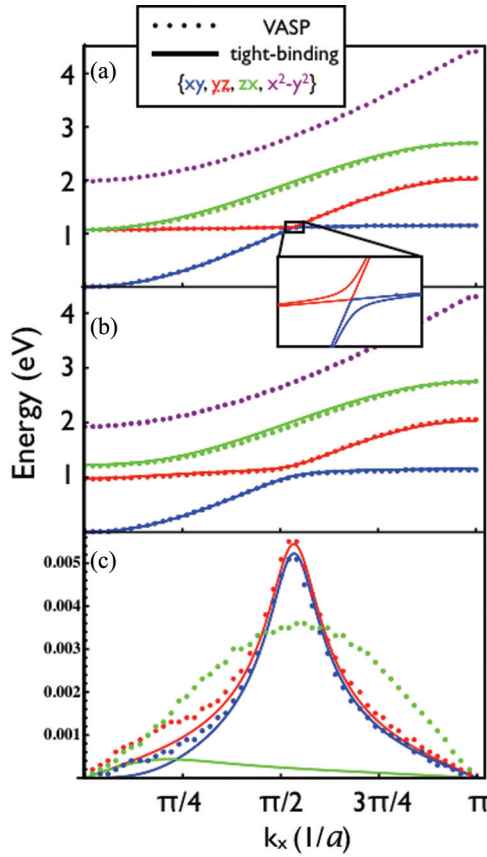

FIG. 3. (Color online) Orbital polarization changes to t_{2g} band structure. (a) t_{2g} band structure in the absence of an electric field and SO coupling. The results of our model are shown as solid lines, while the simulation is shown as dotted lines. The color coding in the figure [xy (blue), yz (red), zx (green), and x^2-y^2 (purple)] represents the orbital character of the band near Γ in the absence of SO coupling. When SO coupling is included, the dominant character is still xy (blue) for the lowest band (due to confinement), while the yz (red) and zx (green) will be significantly hybridized. The inset shows the onset of an avoided crossing in the presence of an electric field. (b) t_{2g} band structure with SO coupling and orbital polarization. (c) Comparison of the orbital polarization part of the Rashba splitting in the t_{2g} space.
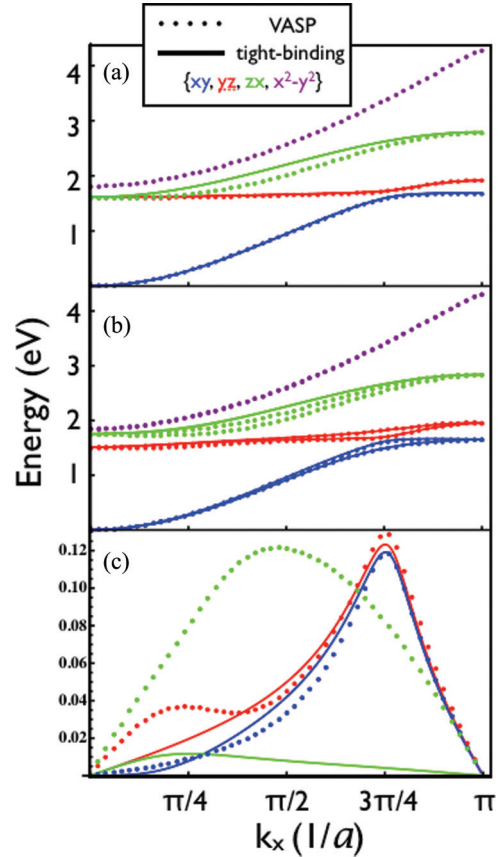
FIG. 4. (Color online) Lattice polarization changes to t_{2g} band structure. (a) t_{2g} band structure with lattice displacement and no SO coupling. The results of our model are shown as solid lines, while the simulation is shown as dotted lines. The color coding in the figure [xy (blue), yz (red), zx (green), and x^2-y^2 (purple)] represents the orbital character of the band near Γ in the absence of SO coupling. When SO coupling is included, the dominant character is still xy (blue) for the lowest band (due to confinement), while the yz (red) and zx (green) will be significantly hybridized. (b) t_{2g} band structure with SO coupling and lattice displacement. (c) Comparison of the lattice mediated Rashba splitting in the t_{2g} space.

than the $\{yz, zx\}$ bands as expected in t_{2g} 2DESs. The strength of the Rashba hopping processes can be read off the band structure by identifying the avoided crossing which occurs between an xz or yz band. We find that even for an extremely large electric field, 0.1 eV/Å, the level repulsion [Eq. (2)] at the crossing is very small. Figure 3(b) shows the band structure changes when SO coupling is included. Note the expected confinement-induced t_{2g} manifold degeneracy lifting at the Γ point. On the scale of this figure, the Rashba splitting is too small to be visible. Figure 3(c) plots the spin splitting as a function of k, which is largest near the band crossing and reaches a maximum value of ~ 5 meV. The calculated splitting agrees well with the splitting predicted by our model with the value of t_R fit to the *ab initio* bands calculated in the absence of spin-orbit coupling.[31]

Figure 4 reports the corresponding results obtained for the case of a polar lattice displacement. Figure 4(a) shows the band structure for a Hf perovskite plane with a displacement of 0.2 Å. The Hf atom displacement was chosen to emulate the interface atomic configuration. According to earlier first-principles calculations for LaTiO$_3$/SrTiO$_3$ interfaces,[34] Ti atoms at the interface are displaced out of the TiO$_2$ plane by $\sim 4\%$ of the lattice constant. For illustrative purposes we report results for a similar Hf atom displacement of $\sim 5\%$ of a lattice constant.

The yz, xz-xy avoided crossing is now easily visible. After SO coupling is included, a clear Rashba splitting is visible [Figs. 4(b) and 4(c)] that is an order of magnitude larger than for the orbital polarization case. Note that our t_{2g} only model underestimates the zx band splitting in both cases, particularly close to the band center. We ascribe this to the proximity of the lower e_g level that is visible in the band plots and neglected in our theory. For the xy band in the Hf case, we find $\alpha = 51.6$ meV Å. Because SrTiO$_3$ is the most experimentally studied system we estimate α in that case. Assuming the yz, zx-xy splitting is comparable, we can scale this value by the SO splitting (18 meV)[26] and lattice constant (3.904 Å) to

find $\alpha_{\mathrm{SrTiO}_3} \propto 2.6$ meV Å. The Rashba interaction strength has recently been estimated experimentally[7–9,11] by using theory valid for conventional semiconductor two-dimensional systems to interpret weak-antilocalization effects apparent in low-temperature transport data. We emphasize that t_{2g} 2DESs differ greatly from conventional semiconductor 2DESs. Our theory provides a starting point for a more quantitative interpretation of low-temperature transport data.

Our theory of Rashba interactions in t_{2g} 2DESs is consistent with the qualitative experimental evidence for strong spin-orbit interactions at interfaces between polar and nonpolar perovskites,[7–9,11] for example, the SrTiO$_3$/LaAlO$_3$ interface, and in surface 2DESs induced by the very strong electric fields applied by ionic liquid gates. It also suggests that Rashba interactions will tend to be stronger in materials which are more easily polarized. In this sense SrTiO$_3$ has a potential for relatively strong spin-orbit interactions even though Ti is a light transition metal. Our theory implies that magnetotransport properties in these 2DES conductors will be strongly sensitive to local lattice polarization at the surface or interface. We believe that this work can provide a starting point for the interpretation of heretofore unexplained magnetotransport phenomena,[10,12] and that it suggests new strategies for designing two-dimensional electron systems with strong spin-orbit interactions, including systems that have superconducting or magnetic[35] order.

Recently, we learned of a related paper[36] which identifies the same hopping process as being responsible for the oxide two-dimensional electron gas Rashba interaction. The present paper identifies the dominant role of changes in the metal-oxygen-metal bond angles at surfaces and interfaces.

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