Band alignment and charge transfer in complex oxide interfaces

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The synthesis of transition metal heterostructures is currently one of the most vivid fields in the design of novel functional materials. In this paper we propose a simple scheme to predict band alignment and charge transfer in complex oxide interfaces. For semiconductor heterostructures band alignment rules like the well known Anderson or Schottky-Mott rule are based on comparison of the work function or electron affinity of the bulk components. This scheme breaks down for oxides due to the invalidity of a single workfunction approximation as recently shown (Phys. Rev. B 93, 235116; Adv. Funct. Mater. 26, 5471). Here we propose a new scheme which is built on a continuity condition of valence states originating in the compounds’ shared network of oxygen. It allows for the prediction of sign and relative amplitude of the intrinsic charge transfer, taking as input only information about the bulk properties of the components. We support our claims by numerical density functional theory simulations as well as (where available) experimental evidence. Specific applications include i) controlled doping of SrTiO$_3$ layers with the use of 4$d$ and 5$d$ transition metal oxides and ii) the control of magnetic ordering in manganites through tuned charge transfer.

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I. INTRODUCTION

Until today semiconductors present the most important class of functional materials for electronic applications. Their usage in electronic components and the continuous development of new devices keeps on pushing the limits of technology. In almost all such devices the key functionality originates not in the physics of the bulk, but in the peculiarities of interfaces [1]. Yet, semiconductor devices have intrinsic limitations: i) the characteristic length scales are relatively large so that further downscaling (current state of the art is 7nm technology) becomes very unlikely and Moore’s law is bound to end; ii) solely charge degrees of freedom are exploited. Transition metal oxides (TMO) on the other hand provide spin, orbital, charge and lattice degrees of freedom [2, 3] and are therefore viewed as one of the best candidates to replace semiconductors in future electronic device. Thanks to an immense progress of epitaxial growth techniques, TM oxides heterostructures can now be controlled on atomic length scales. Several novel physical phenomena have been discovered in recent years and potential multifunctional devices seem to be realizable [4-8].

In oxide electronics, one of the cornerstone mechanisms in complex heterostructures (in analogy to semiconductors) is the alignment of bands at a hetero interface and, driven by the resulting potential gradient, a charge transfer across the interface [9, 23]. This mechanism can be seen as intrinsic doping without undesired disorder induced by chemical doping. Consequently, controlling heterostructures with a wide variety and range of experimentally tunable parameters (e.g. strain, thickness, substrate choice, etc.) allows to engineer new phases which do not exist in bulk. It is, hence, obvious that predictive power for the direction and amplitude of charge transfer with rules that are as simple as possible is highly desirable.

A natural first attempt would be the usage of well established semiconductor rules, such as Anderson’s or the Schottky-Mott rule [26]. As schematically shown in Fig. 1(a) the vacuum energy levels of the two semiconductors on either side of the heterojunction should be aligned, which rely on the electron affinity (or work function) of semiconductors. However, those rules are not suitable for TM oxides, due to the fact that the reduction of the work function to a single value is an approximation that does not hold for TM oxides [27, 28]. Moreover, the characteristic length scales in oxides are one or two orders of magnitude smaller than in semiconductors, and hence certain approximations are no longer justified so that non-trivial microscopic terms need to be taken into account explicitly.

In this paper we propose a rule that is based on the continuity of states in the TMO’s oxygen matrix and which allows for qualitative prediction of band alignment and charge transfer in complex TMO heterostructures. The oxygen continuity boundary condition allows us to explain and predict the induced charge transfer between the constituents of the heterostructure starting only from energetics of the bulk compounds. In the first part of our report we sketch the underlying driving forces in TMO hetero compounds which are built from perovskites ABO$_3$ with A being the a cation (e.g. Sr or La) and B as a TM from strongly correlated 3$d$, 4$d$, or strongly spin-orbit coupled 5$d$ shell. We claim that bulk data for the oxygen 2$p$ energies $\varepsilon_p$ of the components can be used for predictions of ABO$_3$/AB’O$_3$ interfaces, and prove it by showing quantitative data for a wide range of materials. In the second part of the paper we provide selected examples as a proof of principle, and predictions for possible devices yet to be synthesized.
II. METHODS

To reveal general material trends, we first study bulk complex transition metal oxides ABO$_3$ with a cubic perovskite structure (in the majority of cases A is taken as Sr but we also discuss other cases like Ca and La) with B being a 3d (Ti-Co), 4d (Zr-Rh) or 5d (Hf-Ir) transition metal element. The lattice constant is fixed at the optimized value of SrTiO$_3$, $a=3.945$ Å [69]. We then use SrRuO$_3$ as an example for effects of strain, cation A substitution, structural distortion, and magnetism. Most calculations were carried out for superlattices of (ABO$_3$)$_n$/((ABO$_3$)$_n$ with $n=5$ and $n=1$, in order to estimate possible quantum confinement effects for the latter. Moreover, in order to validate the assumption of clean interfaces we performed simulations of a rough interface with a 25% cation mixture (for details see appendix). It turns out that the observed changes are indeed small and will not affect our conclusions. For the study of magnetism in SrMnO$_3$ heterostructures, we take into account an on-site Coulomb interaction $U_{Mn}=2$ eV and a realistic GdFeO$_3$-type structural distortion which are considered to be important for a realistic description of the magnetism. In all calculations the atomic positions are fully relaxed.

Density functional theory (DFT) calculations were performed with the VASP (Vienna ab initio simulation package) code [29] using the generalized gradient approximation GGA-PBE functional [30] for electronic exchange and correlation. We consider that energy separation between transition metal $d$ states and oxygen $2p$ states is usually underestimated in the PBE potential, and use the MBJ potential [31], which is implemented in wien2k [32]. We perform Wannier projection [33,34] of the oxygen and TM states. We perform MBJ potential [31], which is implemented in wien2k [32].

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![FIG. 1: (a)Schematic figure of Anderson’s rule in semiconductor heterojunction: the vacuum energy levels of the two semiconductors on either side are aligned. (b) Schematic figure of a perovskite (001) interface ABO$_3$/ABO$_3$ emphasizing the common network of oxygen sites across the interface. (c) Alignment of oxygen states at the interface would generally yield mismatch in the heterostructure’s Fermi energy (see Eq. 1). This mismatch drives a charge transfer which itself alters interface and local potentials. The final equilibrium state is shown in (d) with indications (black arrows) of the three different contributions in the energy balance equation Eq. 2. $\varepsilon_p$ and $\varepsilon_d$ are the local energy levels of oxygen $p$ and TM $d$ states.](image)

In order to obtain quantitative estimates for the charge transfer we integrate the electron density below the Fermi level (down to the energy gap between $d$ and oxygen $p$ states) projected inside atomic spheres. The radius of the atomic spheres (and here is the mentioned ambiguity in the definition) were chosen to the default values of PAW potential in VASP, e.g. 1.2 Angstrom for a Vanadium atom in SrVO$_3$. In this way, the integrated electron density of Vanadium atom in bulk SrVO$_3$ is 0.75. Considering the formal valence of vanadium to be one $d$ electron, we then take 0.75 as renormalizing factor which we also apply to the interface case in order to obtain a quantitative value for the charge transfer. Moreover, in order to estimate the sensitivity of such values with respect to the choice of the radius of atomic spheres, we have checked that a 10% increase of the radius only induces approximately a 3% change of the charge transfer estimated in this way. Hence, the numbers for the charge transfer given in Tab. I have to be taken with some care. We stress that our conclusions do not rely on specific quantitative values, but on overall trends.
III. INTRINSIC CHARGE TRANSFER IN COMPLEX OXIDE INTERFACES

Let us start the discussion with the idea that motivated the study. For the sake of simplicity we restrict ourselves to perovskite ABO$_3$ heterostructures along the (001) direction. As common in such TM oxide compounds the most relevant states are i) the empty or partially filled TM $d$ states at the Fermi energy, which are split into $t_{2g}$ and $e_g$ states in cubic perovskites and ii) the oxygen $2p$ states residing at an energy $\varepsilon_p$ a few eV below the Fermi energy and forming more or less covalent bonds with the TM $d$ states. At an interface of two materials with different $\varepsilon_p$ we see a continuity of the oxygen states across the interface layers as a boundary condition.

One might start by visualizing the oxygen continuity condition with a very simple sketch we show in Fig. 1(b). For an ABO$_3$/AB'O$_3$ interface; later on we will extend our discussion to more general cases with different cations. In a hypothetical two step procedure the continuity condition would demand that at the interface the oxygen states need to be lined up which, for two materials with different $\varepsilon_p$, would result in a mismatch of the Fermi energy $E_F$ equivalent to

$$\Delta \varepsilon_p = \varepsilon_A BO_3 - \varepsilon_{AB'O_3}$$

, see Fig. 1(c). Since $E_F$ must, however, be constant all through the heterostructure in equilibrium, a charge transfer occurs between the layers which itself creates i) an electrostatic potential drop $\Delta\phi$ across the interface, ii) rigid band shifts we indicate by $\Delta \varepsilon_{\text{DOS}}$, and iii) a local electrostatic potential drop $\Delta \varepsilon_{dp}$ yielding relative shifts between TM $d$ and oxygen $p$. These three terms counter the original driving potential - see Fig. 1(d). As indicated in this last sketch we end up with a balance of potentials that has to be calculated self consistently. Before further formalization, let us support this hypothesis by numerical calculations starting with the easiest case of interfacing two band insulators which, in fact, has a one to one correspondence to the band alignment mechanism in semiconductor heterostructures.

In Fig. 2 we show the layer dependent density of states for the interface of SrTiO$_3$ and SrZrO$_3$ simulated in a
5/5 superlattice. The chemical potential, which is basically free to move inside the gap, is indicated by the dashed black line while the center of mass (i.e. the on-site energy) of the oxygen 2p states (dark gray DOS) is shown as a black solid line. In the plots, we show ZrO₂ and TiO₂ layers directly at the interface as well as the TiO₂ bulk-like layer two unit cells further away from the interface. As can be seen, the alignment of oxygen states across the interface and even in the next TiO₂ layer is practically perfect due to the absence of any charge transfer between the insulating layers. This observation is a first indication of the validity of the backbone hypothesis of the oxygen states continuity. We note in passing that we have an advantage compared to semiconductor heterostructures where obvious structural and electronic continuity is absent\[39\]. In such semiconducting heterojunctions one might try to employ the Anderson’s (or Schottky-Mott) rules in order to estimate the band mismatch by the difference of the components electron affinity (or work function) \[26\]. It turns out, however, that in realistic cases this rules often fails to predict band offsets. Furthermore, a direct extrapolation of this rule to oxides is rather questionable due to the fact that the concept of a compound’s work function is invalid as well known and understood in semiconducting \[27,28\] which strongly depend on details of the surface orientation and termination. In contrast, the workfunctions\[27, 28\] which strongly depend on details of the concept of a compound’s work function is invalid as the oxygen 2p- states with a sign equal to that of $\Delta n_e$ and ii) from the specific structure of density of states $\Delta \varepsilon_{\text{DOS}}$. In summary we can write

$$\Delta \varepsilon_p = \Delta \phi + \Delta \varepsilon_{\text{DOS}} + \Delta \varepsilon_{\text{dp}} \quad (2)$$

The terms on the right hand side depend on the transferred charge $\Delta n_e$ and we may try to linearize them. For the first term $\Delta \phi$ we can assume a plate capacitor model which would yield a potential drop per unit cell of $\Delta \phi = \Delta n_e \cdot d/\epsilon$ with $d$ being the effective distance of charge transfer across the interface and $\epsilon$ the dielectric permittivity \[42,43\]. The second term can be simplified by assuming an approximately constant density of states around Fermi level $E_F$ to be $\Delta n_e \cdot D$, where $D = 1/D_B + 1/D_B'$, $D_B$ and $D_B'$ the local density of states for B and B’ sites. This contribution D can be seen from Fig. 5 to be of the order of up to 1eV. The last term indicates the change of $\varepsilon_{\text{dp}}$ induced by the charge transfer that modifies the valence of transition metal. The argument for the linearity in $\Delta n_e$ of the last term is easily understood by considering a Hartree type self energy ($\propto n_e$) so we can assume $\Delta \varepsilon_{\text{dp}} \approx \Delta n_e \cdot U_H$. $U_H$ reflects the change of the energy due to the static single particle mean-field energy that comes from electronic Coulomb interaction. Using virtual crystal approximation for SrVO₃ allows us to roughly estimate this contribution to be also of the order of 1eV. Hence, assuming the charge transfer of the order of $\Delta n_e = 1$ will lead, different to semiconductors, to non-negligible contributions of D and $U_H$, since the first term $d/\epsilon$, i.e. the typical length scale, is much smaller in our oxide heterostructures than in semiconductors. We arrive eventually at a simplified linear relation between $\Delta n_e$ and $\varepsilon_p$:

$$\Delta n_e \approx - \frac{1}{(d/\epsilon + D + U_H)} \cdot \Delta \varepsilon_p \quad (3)$$

While also the simplified equation is hardly solvable in a closed form it allows for a remarkable insight and confirmation of our initial idea: The sign and strength of the charge transfer at an interface between two materials, which turns out to be much larger than in semiconductor devices, should be determined by the difference of the respective bulk oxygen 2p energies with respect to their Fermi level $\varepsilon_p$ \[71\].
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Before we turn to the discussion of how these num-
bers can be used for predictions we need to address the
fact that the results shown in Fig. 4 are all obtained
for undistorted cubic unit cells. The energy scale of the
listed material trends is of the order of a few eV and it
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scales that are non-negligible compared to our reference
data. Therefore we have performed calculations for spe-
cific cases studying the influence of strain, orthorhom-
bic distortions, and magnetism (in Tab. IV in the ap-
pendix we provide the numerical data for these bench-
mark cases).

Starting with strain, we see for the example of SrRuO
3, that 1% compressive strain will decrease the $\varepsilon_p$ of clearly
non-negligible 0.2eV and realize that this effect can actu-
ally be additionally exploited to tune the energetics for
the desired effect [14]. Next, we turn to orthorhom-
bic distortions [22] in the same material for which we also
observe a change of $\varepsilon_p$ of the order of 0.3eV compared to
the cubic case which is less but still important for a re-
liable prediction. Finally, let us address the influence of
magnetic order for ferromagnetic SrRuO
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split between up and down states not only in the Ru 4d
states but also in the associated oxygen states of 0.7eV.
We remark that this issue does not occur in antiferromag-
netic ordered structures and also for temperatures higher
than the Curie temperature. In the FM ordered phase a
prediction of the charge transfer by our simplified scheme
is not straight forward and becomes questionable if the

corresponding energy scales are equal or larger than the
$\Delta \varepsilon_p$ in question.

After these remarks, however, we will now show that
for many cases the numerical data for the bulk materials
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With this insight we generate DFT reference data for a
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Within the intra 3$d$, 4$d$, and 5$d$ series we observe a
monotonous and almost linear increase of $\varepsilon_p$ of
about 2 – 3eV within each period.

Within one group we have a monotonous drop in
$\varepsilon_p$ for a given configuration of about $\geq 3$ eV from
3$d$ to 5$d$ compounds.

Changing Sr to La, i.e. decreasing the oxidation
number of the transition metal leads to a decrease of
$\varepsilon_p$ up to two eV. This change is actually closely
related to $\Delta \varepsilon_{valence}$ in Eq. 2 and represents in some
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appendix.
order to make general predictions:

- Given the monotonous trends within early materials of the same period in the SrBO$_3$ series we conclude that electron transfer will be only possible from lighter to heavier B compounds. This is somewhat counter intuitive: For instance, $d^1$ SrVO$_3$ will transfer its electron to $d^2$ SrCrO$_3$ but not to the empty Ti $3d$ states of SrTiO$_3$. As it turns out, this is in agreement with experiment and other numerical simulations for a variety of interfaces including LaMnO$_3$/LaNiO$_3$[17, 18, 19], LaTiO$_3$/LaFeO$_3$[19, 20, 22], LaTiO$_3$/LaNiO$_3$[18, 22], and SrVO$_3$/SrMnO$_3$[44, 45].

- Given the monotonous behaviour of $\varepsilon_p$ within one group over different periods we can state that here electron will be transferred from the heavier to the lighter B element. e.g. SrNbO$_3$ will electron dope SrVO$_3$.

- For the more general case of ABO$_3$/AB’O$_3$ one has to consider precise values to make predictions. For instance, SrIrO$_3$ should be able to intrinsically dope SrMnO$_3$ at an interface, while SrRuO$_3$ cannot dope SrTiO$_3$.

In order to strengthen the first claim of this list we extend our simulations with a calculation of a SrTiO$_3$/SrVO$_3$ interface for which we have a $\Delta \varepsilon_p = -0.37$eV. Indeed, consistent with our arguments we see from Fig. 5 that practically no charge transfer occurs. The layer resolved partial density of states shows that basically all $d$ electron remains in the SrVO$_3$ slab and the oxygen $2p$ states are rather well aligned.

At this point it might be asked if our analysis can be extended to the lighter B element. e.g. SrNbO$_3$ taken from Fig. 5 is also listed. [22] Remarkably, we find that in all cases the charge transfer can be anticipated in direction and relative amplitude with the data from Fig. 5. This is remarkable since it is not a prior clear that a qualitative argument made for the interface between two bulk materials still holds for a periodic stack with strong quantum confinement effects and lattice relaxations at the interfaces. They are fully taken into account in the heterostructure calculations but do not spoil the predictive capabilities from bulk calculations neither. Looking closer at the values in Tab. I reveals a remarkable consistency between $\Delta \varepsilon_p$ and $\Delta n_e$. We have already seen in the example of the SrTiO$_3$/SrVO$_3$ interface that in order to dope electron into Ti or V $3d$ states, $4d$ or $5d$ TM components have to be considered since a positive $\Delta \varepsilon_p$ is needed and, as we can see from the stacks in the first four rows $\Delta n_e$ grows monotonously with $\Delta \varepsilon_p$. The same is true for the opposite case (reported in the lower four rows) where an increased negative $\Delta \varepsilon_p$ drives an increased transfer from the vanadium $3d$ states to heavier elements like Cr, Mn, Fe, and Co in the $3d$ series. Moreover, we can learn from the observation $\Delta \varepsilon_p > \varepsilon_p(B) - \varepsilon_p(B')$, that for the energy balance (Eq. 2) besides $\Delta \phi$, $\Delta \varepsilon_{\text{DOS}}$ and $\Delta \varepsilon_{\text{valence}}$ contribute significantly.

Before the end of this section where we have focused mostly on interfaces of the form SrBO$_3$/SrB’O$_3$,

| B/B’ | $\varepsilon_p’$(BO$_2$) | $\varepsilon_p’$(AO) | $\varepsilon_p’$(B’O$_2$) | $\Delta n_e$ | $\Delta \varepsilon_p$ |
|------|-----------------|-----------------|-----------------|-------|--------|
| Ti/Nb | -4.67 | -4.93 | -5.22 | 0.36 | 2.03 |
| Ti/Ta | -5.07 | -5.46 | -5.89 | 0.63 | 3.18 |
| V/Nb | -4.26 | -4.50 | -4.89 | 0.49 | 2.38 |
| V/Ta | -4.62 | -4.92 | -5.62 | 0.71 | 3.56 |
| V/Fe | -3.72 | -3.61 | -3.60 | -0.27 | -0.64 |
| V/Ta | -3.40 | -3.18 | -3.07 | -0.30 | -1.34 |
| V/Mn | -3.02 | -2.77 | -2.31 | -0.49 | -2.02 |
| V/Co | -2.65 | -2.42 | -1.38 | -0.57 | -2.43 |

FIG. 5: Same plot as in Figs. 2 and 3 for a SrTiO$_3$/SrVO$_3$ heterostructure. In this case alignment of oxygen bands will not drive electron transfer and (as expected from Fig. 5) SrVO$_3$ is a bad candidate for doping SrTiO$_3$.
let us make some remarks about the generalization to ABO$_3$/A’BO$_3$ and the most general ABO$_3$/A’B’O$_3$ interfaces. In Fig. 4 we have already shown data for LaBO$_3$ in comparison to the SrBO$_3$ series. If we consider the same element on the B site our scheme is directly applicable as before. More specifically, $\varepsilon_p$ of a LaBO$_3$ perovskite is always lower than in the corresponding SrBO$_3$ so that at a LaBO$_3$/SrBO$_3$ interface the electron is always transferred from LaBO$_3$ to SrBO$_3$ which is consistent with experiments, e.g. for the case of LaTiO$_3$/SrTiO$_3$ [3, 52] or LaMnO$_3$/SrMnO$_3$ [13, 14].

Additional complications arise in the most general ABO$_3$/A’B’O$_3$ setup where we have two qualitatively different interface configurations which might be either AO-B’O’ or BO$_2$-A’O. We might actually consider the realistic case of a SrTiO$_3$/LaMnO$_3$ interface [11, 15, 24, 53]. Starting with the interface TiO$_2$-LaO we assume to have a unit of LaTiO$_3$ linked with SrTiO$_3$ on the one side and LaMnO$_3$ on the other - so we have broken the problem down to a SrTiO$_3$/LaTiO$_3$ and a LaTiO$_3$/LaMnO$_3$ interface which we know how to handle. As a result, by considering our reference data, we would arrive at a prediction of charge transfer at the interface from the Ti states of the central LaTiO$_3$ part to its neighbors. The opposite is true for the other possible interface SrO-MnO$_2$, and in this case a decomposition as before would yield the conclusion that no charge transfer will occur. This line of argument is in agreement with experiments on SrTiO$_3$/LaMnO$_3$ where electron transferred has been observed for the LaO-TiO$_2$ terminated interface [15]. According to our claim, the other interface structure, SrO-MnO$_3$, which experimentally can be realized by inserting a monolayer of SrMnO$_3$, should not allow for such charge transfer. Please note we did not consider the contribution from polar discontinuity [12, 54], which might induce complexity such as oxygen vacancies and other defects.

We conclude our first main section with the claim that charge transfer at the interfaces of perovskite heterostructures can be qualitatively predicted by comparison of bulk qualities. It is not even necessary to perform a numerical simulation of the interface in order to anticipate the direction and relative magnitudes of charge transfer.

IV. APPLICATIONS AND PREDICTIONS

In the second part of our paper we highlight two applications of our prediction scheme starting with the controlled doping of SrTiO$_3$ (see IV.A) drawing also a parallel to heterogeneous semiconductor devices. We then turn to magnetic transitions in manganite heterostructures triggered by controlled charge transfer (see IV.B) explaining past theoretical and experimental results in the context of our unifying concept which we then complement by predictions on how to improve external control of such transitions.

A. Electron doping in SrTiO$_3$ heterostructure

As a first application we chose to highlight how to control doping of one of the most widely spread and used TM oxide compounds SrTiO$_3$. So far SrTiO$_3$ has been doped by various 3d TM oxides e.g. LaAlO$_3$ [10] and LaTiO$_3$ [9] to produce a two dimensional electron gas but there is no known SrBO$_3$ with B from the 3d series. With the data from Fig. 4 we have already given the reason why this is not surprising and, in fact, impossible. The very naive guess that electron from a more filled 3d element like, e.g. vanadium would spill into the empty Ti 3d states is prohibited by the energy balance that originates in the oxygen states continuity condition (see Fig. 5). So, SrVO$_3$ is identified as a bad candidate for doping SrTiO$_3$. Instead we have seen in Fig. 8 that SrNbO$_3$ is a much more promising component for that purpose. In (SrTiO$_3$)$_{3/5}$(SrNbO$_3$)$_{2/5}$ the continuity of oxygen 2p states drives a sizable charge transfer. What we have not discussed yet, however, is the question if microscopic details of orbital degrees of freedom at the interface, which are not included in our scheme, are equally or even more important for the charge transfer than the considered energetics. In order to shed light on this issue we extend our calculations with the inclusion of an insulating buffer
layer which will allow for a spatial separation of Ti and Nb $d$-states. The choice of a perovskite buffer layer is actually quite straightforward in the light of our reference data and we chose SrZrO$_3$ for this purpose which will remain band insulating in the three component heterostructure. In Fig. 5 we show the result for a symmetric (SrTiO$_3$)$_5$/(SrZrO$_3$)$_2$/(SrNbO$_3$)$_1$/(SrZrO$_3$)$_2$ superlattice which is experimentally realizable $^{[21, 55–57]}$.

Here we see another confirmation of our simple argument: while the buffer layer remains band insulating we still observe a transfer of electron from Nb to Ti $d$-states even though they are spatially separated. At this point we might refer to an analogous technique in semiconductor setups where the doping impurities are spatially separated from the charge carriers. A concept which is commonly known as “modulation doping” and widely applied in so-called MODFET setups $^{[58, 59]}$. Besides the shown results we have checked the dependence of the charge transfer amplitude as a function of the thickness of the buffer layer but were unable to find significant trends up to supercells that include buffers of 5 bulk unit cells. In fact modulation doped oxides recently started to attract some theoretical $^{[43]}$ and experimental $^{[21, 53, 57]}$ researchers.

**B. AFM to FM transition in SrMnO$_3$ heterostructures**

After having exemplified how our oxygen energetics argument can be used to anticipate charge transfer in the case of SrTiO$_3$ based heterostructures we now take one step further by considering manganite heterostructures. Here the goal is similar yet more ambitious since a provoked charge transfer in SrMnO$_3$ setups should have a sensitive impact on magnetic transitions. Starting point for us is bulk SrMnO$_3$ which is found to have a G-type antiferromagnetic ground state. Our goal is to find an appropriate heterostructure in which doping into Mn $d$-states triggers a transition to a ferromagnetic ground state - see review papers $^{[46, 62]}$ and references therein. From our reference data we see that it should actually be rather easy to provoke electron transfer into Mn $d$-states considering the comparatively large value of $\varepsilon_p$ for Mn. Indeed it turns out that by employing our predictive scheme we can confirm experimentally known routes to charge-transfer induced magnetic transition and classify possible heterostructure components to tune more or less charge transfer.

We carried out calculations for 1/1 and 2/2 layered superlattice (SrMnO$_3$)$_1$/SrBO$_3$)$_1$ (considering also a GdFeO$_3$ structural distortion since magnetism can be strongly coupled to the lattice) for four different species of B site elements. The results are summarized in Tab. II where we report the size of the magnetic moment on the B and the Mn site of the respective compound. We have sorted the table with ascending electron transfer. As anticipated choosing SrIrO$_3$ as interfacing partner will result in a little electron transfer and, in the 2/2 structure the antiferromagnetic order with a moment of 3.05 $\mu_B$ remains. In the case of the 1/1 structure we observe a somewhat larger electron transfer which is already sufficient to trigger a magnetic transition to a ferromagnetic ground state $^{[22]}$ with ordered Mn moments of 3.24 $\mu_B$. The next component we consider is SrVO$_3$ - here the data from Fig. 2 tells us to expect similar to the Ir compound only a small amount of transferred electron which we see confirmed in our numerical results. Interestingly, both 1/1 and 2/2 compounds seem to be intermediate between antiferromagnetic and ferromagnetic phase yielding a ferrimagnetic ground state $^{[44, 45]}$. We can further predict which components would yield a much more significant electron transfer: Candidates are easily nominated from Fig. 4 and to this end we select SrNbO$_3$, which is recently grown experimentally $^{[40]}$, as well as SrTaO$_3$ - our most potent electron donor for oxide heterostructures. The selected components perform as predicted in the numerical simulations and we observe a large charge transfer pushing the (SrMnO$_3$)$_{1.2}$/(SrNbO$_3$)$_{1.2}$ and (SrMnO$_3$)$_{1.2}$/(SrTaO$_3$)$_{1.2}$ into a ferromagnetic metallic ground state with ordered Mn moments up to 3.74 $\mu_B$. $^{[74]}$

**TABLE II: Magnetic ground states of (SrBO$_3$)$_n$/(SrMnO$_3$)$_n$ with $n=1.2$. B = Ir, V, Nb, and Ta. The magnetic moments localized on TM B and Mn sites are also listed.**

|  | 1/1 | 2/2 |
|---|---|---|
| B ($\mu_B$) | Mn($\mu_B$) | M | B($\mu_B$) | Mn($\mu_B$) | M |
| SrIrO$_3$ | 0.0 | 3.24 | Ferro | 0.0 | 3.05 | AFM |
| SrVO$_3$ | -0.19 | 3.2 | Ferri | -0.36 | 3.16 | Ferri |
| SrNbO$_3$ | 0.05 | 3.66 | Ferro | 0.02 | 3.56 | Ferro |
| SrTaO$_3$ | 0.03 | 3.74 | Ferro | 0.0 | 3.67 | Ferro |

In order to underline the data given in Tab. II we plot the resolved single particle density of states in Fig. 7 - this time, however, for magnetic DFT calculations. In the upper panels of the figure we start as a reference with the bulk results for the doped antiferromagnetic DOS of SrMnO$_3$ and metallic and paramagnetic SrTaO$_3$. In the lower two panels one can nicely observe how in the (SrMnO$_3$)$_{1.2}$/(SrTaO$_3$)$_{1.2}$ heterostructure almost all Ta $d$ electron is depleted in the MnO$_2$ layers yielding a metallic ferromagnetic ground state with significant filling of the Mn 3$d$-$e_g$ states.

**V. SUMMARY AND OUTLOOK**

In summary we have presented a simple prediction scheme for the tuning of charge transfer in oxide heterostructures. By employing arguments based on the requirement that the $p$ states of the oxygen network in a heterostructure need to be continuous, we were able to utilize reference data from bulk calculations in Fig. 4 to predict the direction and relative amplitude of charge
transfer between layers in oxide heterostructures. Remarkably this scheme remains in tact even for layered compounds down to a 1/1 geometry. As a proof of principle we provided simulations for electron doping of SrTiO$_3$ in heterogeneous arrays simultaneously confirming experimentally known trends and offering suggestions to material growers which are the most promising components to control the low energy electronic structure. In a second application part we have exemplified, with the help of SrMnO$_3$ based heterostructures, how controlled charge transfer can be systematically exploited in order to trigger magnetic phase transitions. The shown examples are only a taste of what can be predicted with the unifying concepts we presented and we hope that experimental colleagues will be inspired by our work to create new materials and devices. This includes specifically also the possibility to couple/entangle - via charge transfer - physics of 3d and 5d TM oxides which, on their own, are governed by very different energy scales. One might try, for instance, to induce spin-orbit coupling effects in 3d systems, e.g. in the case of SrMnO$_3$ /SrTaO$_3$ where one might find a large magnetic anisotropy energy and antisymmetric exchange on the magnetic Mn sites. One might even target the realization of yet more exotic skyrmion, spin-spiral, and topological phases. On the computational side we already started a hunt for the best possible candidates to be manipulated towards exciting new ground states.

In order to give an outlook for future theory and computational development we state once more that for certain cases the application of our scheme is not straightforward and needs to be extended. One of these cases is the interfacing of compounds that are ferromagnetic ordered in bulk. Another issue that should be mentioned is the change of $\varepsilon_p$ due to correlation effects: Given that the relevant effects we discussed have a characteristic energy scale of a few eV, shifts due to single particle self energies might have to be included instead of the simplified $\Delta\varepsilon_{dp}$ contribution in Eq. 2. A very clear example where this will be the case is the usage of charge transfer insulators, typically found in late 3d TM oxides e.g. cuprates. An extension to include such correlation effects is very desirable since the sensitivity of correlated electron systems would add even more possibilities to generate novel functionality like, e.g. the recently suggested Mott transistor [65]. Moreover, focusing more on material trends the presented initial study did not extensively discuss how to use the thickness of periodic stacks or buffer layers to quantitatively tune charge transfer and how to interface non-perovskite oxides. The oxygen continuity condition, or adaptations thereof, should be valid not only in the complex oxides with perovskite structures, but also in other lattice structures like anatase, pyrochlores, spinel, Ruddlesden-Popper and double perovskites [66 - 68] which are structurally equal to the 1/1 interfaces along a (111) direction.

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Appendix A: Simulation of a rough surface

To test the effect of cation mixing we have performed benchmark calculations with up to 25% mixing. To this end we employ a 2×2 supercell with a layered structure as -BO$_2$-AO-B$_0$.75B$_{0.25}$O$_2$-AO-B$_0$.25B$_{0.75}$O$_2$-AO-B’O$_2$. The comparison between the density of states for clean and rough interfaces with (and without) charge transfer is shown in Fig. 8. Our main conclusion remains, hence, unchanged, and effects like cation mixing can indeed be regarded as a secondary effect.

Appendix B: Numerical data

In Tab. III we provide the numerical data plotted in Fig. 2. Moreover, in Tab. IV we report values of $\varepsilon_p$.
FIG. 8: Projected Density of TM $t_{2g}$ states of the BO$_2$ layer with two layers away from interface. Red indicates a clean interface, while blue indicates a rough interface with 25% cation intermixing.

for benchmark calculations including effects of cation exchange, orthorhombic distortion, strain, and ferromagnetic ordering.
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[73] The DFT-GGA optimized lattice constant for SrTiO$_3$ is $a=3.945\,\text{Å}$, which is about 1% larger than the experimental one. Our estimates of effects from strain show that such effects are negligible for the conclusions we draw.

[74] In band insulating materials such as SrTiO$_3$, it turns out (from several DFT simulations of the material) that the assumption of a slight $n$-type doping ($E_F$ at the bottom of the conduction band) is the appropriate choice.

[75] Let us, finally, remark that this relation also holds for the case of band insulating interfaces (i.e. vanishing density of states at $E_F$) where D will diverge and, hence, an infinitesimal $\Delta n_e$ leads to finite $\Delta \varepsilon_F$.

[76] The change of $E_F$ within the series is quite small, e.g $E_F$(SrVO$_3$)=5.20eV, $E_F$(SrMnO$_3$)=5.13eV.

[77] At a closer look one should note a very small amount of charge at the interface TiO$_2$ (concomitant with a non-perfect oxygen alignment) layer which one might attribute to a covalent hybridization of Ti and V d-states directly at the interface. However, as we will see in the next step, this effect is very small compared to the charge transfer one can obtain by replacing SrVO$_3$ with another compound.

[78] Let us remark once more that, due to additional confinement effects, the 1/1 compounds are the materials “furthest away” from a single interface situation so that some exceptions to the trends are quite expected - it is actually rather remarkable how well most of the predictions from bulk energetics still work!
| 3d   | 4d   | 5d   |
|------|------|------|
| SrTiO$_3$ | -4.00 | SrZrO$_3$ | -6.23 |
| SrVO$_3$ | -3.63 | SrNbO$_3$ | -6.03 |
| SrCrO$_3$ | -2.99 | SrMoO$_3$ | -5.31 |
| SrMnO$_3$ | -2.28 | SrTeO$_3$ | -4.41 |
| SrFeO$_3$ | -1.60 | SrRuO$_3$ | -3.40 |
| SrCoO$_3$ | -1.19 | SrRhO$_3$ | -2.47 |

TABLE IV: Reference data for $\varepsilon_p$ of manganites and ruthenates depending on cation exchange, orthorhombic distortion, compressive strain and ferromagnetic ordering. The unit is eV

| Manganites                  | $\varepsilon_p$ | Ruthenates $\varepsilon_p$ |
|-----------------------------|-----------------|----------------------------|
| KMnO$_3$                    | -1.47           | KRuO$_3$                  | -2.48 |
| CaMnO$_3$                   | -2.30           | CaRuO$_3$                 | -3.44 |
| BaMnO$_3$                   | -2.22           | BaRuO$_3$                 | -3.29 |
| LaMnO$_3$                   | -3.57           | LaRuO$_3$                 | -4.56 |
| SrMnO$_3$                   | -2.28           | SrRuO$_3$                 | -3.40 |
| 1% compressive SrMnO$_3$    | -2.42           | SrRuO$_3$                 | -3.60 |
| distorted CaMnO$_3$         | -2.70           | SrRuO$_3$                 | -3.72 |
| FM SrMnO$_3$                | -2.25/-2.75     | SrRuO$_3$                 | -3.46/-4.17 |