Theoretical studies of oxide heterostructures

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Acknowledgements:
Prof. Paul J. Kelly;
Prof. Karsten Held
Bulk $\text{LaAlO}_3$ (LAO) and $\text{SrTiO}_3$ (STO)

- **Perovskite structure**
  - $\text{SrTiO}_3$ 3.905Å;
  - $\text{LaAlO}_3$ 3.789Å

- **Band insulator**
  - $\text{Sr}^{2+}$, $\text{Ti}^{4+}$, $(\text{O}^{2-})_3$  Gap: 3.2eV
  - $\text{La}^{3+}$, $\text{Al}^{3+}$, $(\text{O}^{2-})_3$  5.6eV

- **No-magnetic**

$\text{SrTiO}_3$ : non-polar $\text{SrO}^0$, $\text{TiO}_2^0$ (charge neutral)
$\text{LaAlO}_3$: polar  $\text{LaO}^+$, $\text{AlO}_2^-$
Two dimensional electron gas (2DEG) at LAO/STO

LaO\(^+\)/TiO\(_2\)\(^0\) interface:
critical thickness (\(N_{\text{LAO}} > 3\), conducting)
magnetic, superconducting, correlated,
spin-orbit coupling....

Semiconductor heterostructures
(GaAs/Al\(_x\)Ga\(_{1-x}\)As)

- Origins of the 2DEG?
  (i) polar catastrophe
  (ii) polarity induced oxygen vacancies

- Properties of the 2DEG?

Origins of 2DEG: (i) polar catastrophe

Charge transfer from surface $\text{AlO}_2^-$ to interface $\text{TiO}_2$
DFT calculation of bulk LAO and STO

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<thead>
<tr>
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Density of States of STO

DFT calculation of bulk LAO and STO

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Superlattice LAO/STO (4/4): unrelaxed

- A large internal electric field
Atomic relaxation will suppress the internal electric field
Assume:
Clean and abrupt interface
No oxygen vacancy
No surface reconstruction

Thickness dependent insulator-metal transition
Polar catastrophe seems to be reasonable
However, key evidence is missing......

The internal electric field is much smaller
DFT+ model demonstrate the internal electric field. But it is not observed in experiments.

- polar catastrophe (charge transfer)
- atomic relaxation (Ti-O buckling)
- atomic reconstruction (defects, oxygen vacancies)
Formation energy of oxygen vacancies in LAO/STO

\[ \Omega^{\text{Vac}} = E^{\text{Vac}}_{\text{SC}} - E_{\text{SC}} + \mu_O(T, p_{O_2}) \]

Asymmetric behavior of \( n \)- and \( p \)-type interfaces
Formation energy of oxygen vacancies

$E_{\text{LAO}} / \text{STO} < E_{\text{STO}}, E_{\text{LAO}}$

Thickness dependent formation energies

Oxygen vacancies are spontaneously created by polarity.
Origins of the 2DEG

- Polar catastrophe

- Polarity induced oxygen vacancies

Internal electric field
How to confirm?

\[ \Omega^\text{Vac} = E^\text{Vac}_{SC} - E_{SC} + \mu_O(T, p_{O_2}) \]

SrCuO\(_2\)  infinite layer structure
Parent compound of cuprate high-temperature superconductors
Stoichiometric SrCuO$_2$ thin films

Planar

Chain

SrO$^0$
TiO$_2^0$
SrO$^0$

CuO$_2^{2-}$/CuO$^0$

Sr$^{2+}$/SrO$^0$

TiO$_2^0$
SrO$^0$

SrO$^0$

Moving electrons or Oxygen ions?
Thickness dependence of structural transition

\[ \Delta E = -E_{\text{Planar}} + E_{\text{Chain}} \]
How to prove it?

- Enlarged lattice constant along $c \sim 0.5\text{Å}$
- Out of plane orbital character, $z^2$

Thickness dependent

Two experimental groups (Netherlands and Italy) find it
Cuprates heterostructures should be revisited

Orbital reconstruction at LCMO/YBCO
Properties of 2DEG: Rashba spin splitting

2D electron gas

\[ \varepsilon(k, \uparrow) = \varepsilon(-k, \uparrow) \quad \times \]

Time inversion symmetry \[ \varepsilon(k, \uparrow) = \varepsilon(-k, \downarrow) \]

(ii) Spin orbit coupling

\[ (\hbar/2m_e^2c^2)(\nabla V \times \vec{p}) \cdot \vec{s} \]

Free 2DEG:

\[ \Delta_R = 2\alpha_R k \quad \alpha_R = (\hbar/4m^2c^2)dV(z)/dz \]

\[ E \sim 100 \text{ Volt/mm} \quad \Delta_R \sim 10^{-8} \text{ meV} \]

\[ \Delta_R \sim \text{meV} \]

\[ 2\alpha k \text{ at LaAlO}_3/\text{SrTiO}_3 \text{ interface} \quad (\text{Caviglia et.al.; Ben Shalom et.al.}) \]

\[ 2\alpha k^3 \text{ at SrTiO}_3 \text{ surface} \quad (\text{Nakamura et.al.}) \]
Band structure of bulk SrTiO$_3$

- Three degenerate $t_{2g}$ orbitals
- Heavy carrier $yz$ (6.8$m_e$), two light carriers $xy$ and $xz$ (0.41$m_e$)
Spin-orbit coupling (SOC) effects on bulk STO

Γ₈⁺

Δ₀ = 29 meV

$\Gamma_7 \rightarrow \Gamma_8$

$\frac{1}{\sqrt{6}} (\pm i \ yz \ | \uparrow, \downarrow \rangle + zx \ | \uparrow, \downarrow \rangle + 2i \ xy \ | \downarrow, \uparrow \rangle)$

Hopping $t +$ atomic SOC $\xi \vec{l} \cdot \vec{s}$
Orbital splitting at LAO/STO interfaces and STO surfaces

Energy (eV)

LAO/STO (nn)  STO surface (SrO)  Model

\[ E \]

\[ \Delta_I \sim 300 \text{ meV} \]

\[ \Delta_O \sim 20 \text{ meV} \]

\[ t_{2g} \]

\[ \Delta_I \]

interface  atomic SOC

\[ yz, xz \]

\[ 0.72m_e \]

\[ 1.14m_e \]

\[ 0.48m_e \]
Model for Rashba spin splitting

\[ H_0^i + H_\xi + H_\gamma \]

Free: \(-2t_1 \cos k_x - 2t_1 \cos k_y - t_2 - 4t_3 \cos k_x \cos k_y\)

atomic SOC:

\[ \frac{\xi}{2} \begin{pmatrix} 
0 & 0 & i & 0 & 0 & -1 \\
0 & 0 & 0 & -i & 1 & 0 \\
-i & 0 & 0 & 0 & 0 & i \\
0 & i & 0 & 0 & i & 0 \\
0 & 1 & 0 & -i & 0 & 0 \\
-1 & 0 & -i & 0 & 0 & 0 
\end{pmatrix} \]

interface asymmetry: \(\gamma \begin{pmatrix} 
0 & 0 & 2i \sin k_x \\
0 & 0 & 2i \sin k_y \\
-2i \sin k_x & -2i \sin k_y & 0 
\end{pmatrix} \)

\[ \gamma = \langle xy | H | yz(R) \rangle \]

0.02eV, interface layer

\(s-p\) electrons of Au surfaces \(Lashell\ et\ al.(1996);\ Peterson\ et\ al.(2000)\)
Spin splitting

\[
\Delta R = 2\alpha_R k \\
\alpha_R = 2a\xi\gamma/\Delta_I \\
\Gamma, xy \text{ orbital: } 2\alpha_3 k^3 \\
\Gamma, yz/xz \text{ mixed orbitals: } 2\alpha_3 k^3 \\
xy-yz \text{ crossing point}
\]
Properties of 2DEG: Quantum Well states

SrTiO$_3$ surfaces

SrVO$_3$ ultrathin films

Diagram showing the energy levels and binding energy for different quantum well states as a function of the quantum number $N$. The states are labeled with $E_1(d_{xz/yz})$, $E_2(d_{xz/yz})$, and $E_1(d_{xy})$.
Properties of 2DEG: Quantum Well states along (110) is different

- Nearest neighbor hopping
  - $t_1 = -0.455 \text{eV}$
  - $t_2 = -0.040 \text{eV}$
Quantum Well states along (001)

- Orbital-selective quantum well states, with constant effective mass
- two light bands $xy, zx, \quad t_1$
- one heavy bands $yz, \quad t_2$

$\Gamma (0,0,0)$

$X (\pi/a,0,0)$

$M (\pi/a,\pi/a,0)$

$xy, zx$ and $yz$ bands are indicated in the diagrams.
Quantum Well states along (110) are different

- Effective mass: \[ \frac{2t_1 t_2}{(t_1 + t_2)} \cos \left( \frac{\pi n}{N + 1} \right) \]
- Anisotropic hopping
- Quantization
- Semi-heavy band, \( 2t_2 \), when \( N \gg n \)
SrTiO$_3$ (110) surface

(a) Side view of SrTiO$_3$ (110) surface with Ti, O, and Sr atoms. V$_0$ denotes a vacancy.

(b) Charge (e/Ti atom) vs. Layer index graph.

(c) Intensity (arb. units) vs. $E-E_F$ (eV) for clean and irradiated samples. $h\nu = 65$ eV, $T = 38K$.

(d) Energy level diagram showing the bandgap and states for SrTiO$_3$ and Titania.
“Semi-heavy” band is observed

\[ m_{xy} = 8.25 \]
\[ m_{yz} = 0.60 \]
\[ m_{yz} = 4.69 \]
\[ m_{xy} = 0.60 \]
Conclusion: origins and properties of the 2DEG at LaAlO$_3$/SrTiO$_3$

**Origin:** Polarity-induced oxygen vacancies

**Properties:**

- Spin-orbit coupling
- (110) is different
- Orbital polarized Mott insulator
Quantum well states in SVO thin film: Nearly Free Electron picture

$L = Na$

($N$ thickness of SVO; $a$ lattice constant)

$\psi(0) = \psi(L) = 0$

$$\frac{\hbar^2 k^2}{2m^*}$$

$$\frac{\hbar^2 \pi^2 n^2}{2m^* N^2 a^2}$$
Why not NFE?

\[ H_{\alpha\beta}(\vec{k}) = \sum_{\vec{R}} t_{\alpha\beta}(\vec{R}) e^{i\vec{k}\cdot\vec{R}} \]
Tight binding description of Geometric confinement

\[
\begin{pmatrix}
\varepsilon & t & 0 & 0 & 0 & 0 \\
 t & \varepsilon & t & 0 & 0 & 0 \\
 0 & t & \varepsilon & t & 0 & 0 \\
 0 & 0 & \ldots & \ldots & t & 0 \\
 0 & 0 & 0 & 0 & t & \varepsilon \\
 0 & 0 & 0 & 0 & 0 & t & \varepsilon
\end{pmatrix}
\]

\[
\frac{\hbar^2 \pi^2 n^2}{2m^* N^2 a^2} \quad \rightarrow \quad \varepsilon + 2t \cos\left(\frac{\pi n}{N+1}\right)
\]
SrVO₃ thin films: Quantum well states

<table>
<thead>
<tr>
<th></th>
<th>yz</th>
<th>xy</th>
<th>yz along z</th>
<th>yz along y</th>
<th>xy along y</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st V</td>
<td>0.508</td>
<td>0.436</td>
<td>0</td>
<td>-0.224</td>
<td>-0.260</td>
</tr>
<tr>
<td>2nd V</td>
<td>0.599</td>
<td>0.594</td>
<td>-0.242</td>
<td>-0.262</td>
<td>-0.259</td>
</tr>
<tr>
<td>3rd V</td>
<td>0.584</td>
<td>0.583</td>
<td>-0.255</td>
<td>-0.258</td>
<td>-0.259</td>
</tr>
</tbody>
</table>
SrVO$_3$ thin films: correlation $\rightarrow$ Z

- Quantum confinement in perovskite oxide heterostructures:
  - Tight binding instead of a nearly free electron picture

- Correlation effect: DFT+ Dynamical Mean Field Theory (DMFT)
Insulating state in SVO thin films ($N=2$) grown on STO substrate

- $yz$ orbital is narrowed, but the energy of $xy$ is lower.
- Competition: bandwidth $\sim$ orbital splitting
- Surface(Second) layer, strong(weak) orbital polarization.
The lower Hubbard band of the surface layer: enhanced, shifted, and orbital polarized.
$\Delta_R = 2\alpha_R k$

$\alpha_R = 0.76 \times 10^{-2} \text{eVÅ} \quad \Delta_I = 0.4 \text{eV}$

$6.0 \times 10^{-2} \text{eVÅ} \quad \Delta_I = 0.0 \text{eV}$

$1 - 5 \times 10^{-2} \text{eVÅ} \quad \Delta_I = 0.0 \text{eV}$ (exp)

$\Delta_R = 2\alpha_3 k^3$

$\alpha_3 = 4 \text{eVÅ}^3$

$1 - 2 \text{eVÅ}^3 \quad \Delta_I = 0.0 \text{eV}$ (exp)

Anisotropic spin splitting $\rightarrow$ AMR (exp)
Comparison: semiconductor and oxide heterostructures

GaAs/Al$_x$Ga$_{1-x}$As $\rightarrow$ 10nm 2DEG $\rightarrow$ 1nm

LAO/STO

- single orbital Rashba
- nearly free electron

- fitting parameter or $kp$ method
- multi-orbital
- magnetic, superconducting, correlated, and spin-orbit coupling

First principle tight-binding

Spin splitting at LAO/STO interfaces and STO surfaces

Asymmetric structure

Energy (eV)

- X/2  Γ  X/2

0.25X  0.35X  0.4X  0.5X

--- without SOC

spin up  Spin splitting ~10meV at xy-yz crossing region?
spin down
DFT studies of Bulk properties of ACuO$_2$ (A=Ca, Sr, Ba)

<table>
<thead>
<tr>
<th></th>
<th>$a_{\text{LDA}}$</th>
<th>$c_{\text{LDA}}$</th>
<th>$a_{\text{GGA}}$</th>
<th>$c_{\text{GGA}}$</th>
<th>$a_{\text{exp}}$</th>
<th>$c_{\text{exp}}$</th>
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<tr>
<td>SrTiO$_3$</td>
<td>3.87</td>
<td>3.87</td>
<td>3.95</td>
<td>3.95</td>
<td>3.905</td>
<td>3.905</td>
</tr>
<tr>
<td>CaCuO$_2$</td>
<td>3.77</td>
<td>3.08</td>
<td>3.87</td>
<td>3.20</td>
<td>3.853$^a$</td>
<td>3.177$^a$</td>
</tr>
<tr>
<td>SrCuO$_2$</td>
<td>3.84</td>
<td>3.38</td>
<td>3.95</td>
<td>3.47</td>
<td>3.926$^b$</td>
<td>3.432$^b$</td>
</tr>
<tr>
<td>BaCuO$_2$</td>
<td>3.92</td>
<td>3.68</td>
<td>4.03</td>
<td>3.84</td>
<td></td>
<td></td>
</tr>
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</table>

- Lattice constant $c$ is 10% smaller than $a$;
- $dx^2-y^2$ orbital

DOS (states/eV)

U=7.5 eV
J=1.0 eV
**Oxide Interfaces—An Opportunity for Electronics**

J. Mannhart* and D. G. Schlom*

<table>
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<tr>
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<th>GaAs - Al$<em>x$Ga$</em>{1-x}$As</th>
<th>LaAlO$_3$ - SrTiO$_3$</th>
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<tbody>
<tr>
<td><strong>Carrier density $n$ (without gate field)</strong></td>
<td>several $10^{10}$ - several $10^{11}$/cm$^2$</td>
<td>several $10^{13}$/cm$^2$</td>
</tr>
<tr>
<td><strong>Sheet resistance $\rho (H=0)$</strong></td>
<td>order of 10-100 $\Omega$/$\square$ (low $T$, samples with high-$\mu$)</td>
<td>$\sim 200$ $\Omega$/$\square$ (4.2 K) $\sim 20$ k$\Omega$/$\square$ (300 K)</td>
</tr>
<tr>
<td><strong>Thickness $d$</strong></td>
<td>order of 10 nm</td>
<td>$\sim 10$ nm (4.2 K) $\leq 4$ nm, possibly 0.4 nm (300 K)</td>
</tr>
<tr>
<td><strong>Equivalent volume carrier concentration</strong></td>
<td>order of $10^{17}$/cm$^3$</td>
<td>order of $10^{20}$/cm$^3$</td>
</tr>
<tr>
<td><strong>Typical thicknesses of the host layers in heterojunctions (e.g., cap layers)</strong></td>
<td>tens of nanometer</td>
<td>$\geq 1.6$ nm LaAlO$_3$ (4 unit cells)</td>
</tr>
<tr>
<td><strong>Hall mobility $\mu$</strong></td>
<td>$\geq 10^7$ cm$^2$/Vs (4.2 K)</td>
<td>$\leq 1000$ cm$^2$/Vs (4.2 K) $\leq 10$ cm$^2$/Vs (300 K)</td>
</tr>
<tr>
<td><strong>Effective mass $m$ of carriers at interface</strong></td>
<td>$m_e \sim 0.07 \ m_e$</td>
<td>$m_e \sim 3 \ m_e$</td>
</tr>
<tr>
<td><strong>Mean scattering time $\tau$, mean free path</strong></td>
<td>100 psec, order of 100 $\mu$m</td>
<td>psec, tens of nm (4.2 K)</td>
</tr>
<tr>
<td>$v_F$</td>
<td>$\sim 3 \times 10^7$ cm/s</td>
<td>several $10^6$ cm/s</td>
</tr>
<tr>
<td><strong>Magnetic flux density inducing quantum Hall filling factor $\nu = 1$</strong></td>
<td>order of 10 T</td>
<td>order of 1000 T</td>
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<td><strong>Energy dependence of density of states $N(E)$</strong></td>
<td>step function of 2-DEG (ideal case)</td>
<td>complex function reflecting the $N(E)$-dependence of the Ti-, La-, and O-ions</td>
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<td>GaAs - Al\textsubscript{x}Ga\textsubscript{1-x}As</td>
<td>LaAlO\textsubscript{3} - SrTiO\textsubscript{3}</td>
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<tr>
<td>• two-dimensional electron gas (2-DEG);</td>
<td>• two-dimensional electronic liquid (2-DEL);</td>
<td></td>
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<tr>
<td>• quantum well induced by band bending;</td>
<td>• metal-insulator transition at a few $10^{12}$ /cm$^2$;</td>
<td></td>
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<tr>
<td>• 2D-subbands of nominally free electrons</td>
<td>• quantum well structure as shown in Fig. 4;</td>
<td></td>
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<td>• 2D-subbands composed of ionic orbital states</td>
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<td></td>
<td>with local character (e.g., Ti 3$d$, La 5$d$, O 2$p$);</td>
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<td>• 2D-superconducting ground state;</td>
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<td>• strong spin-orbit coupling.</td>
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\[ H_{yz}(k_z, k_M) = -4t_1 - 2t_2 + 2t_1 \cos(k_z a) - 2(t_1^2 + t_2^2 + 2t_1 t_2 \cos(k_M \sqrt{2} a))^{1/2} \cos\left(\frac{\pi n}{N + 1}\right) \]

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