Electron-Hole Liquids in Transition Metal Oxide Heterostructures

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Appropriately designed transition metal oxide heterostructures involving small band gap Mott insulators are argued to support spatially separated electron and hole gasses at equilibrium. Spatial separations and carrier densities favoring the formation of excitonic states are achievable. The excitonic states may exhibit potentially novel properties. Energetic estimates are given, candidate material systems are discussed, and the possibility of large photovoltaic effects is mentioned.

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Electron-hole bound states are a topic of longstanding importance in condensed matter physics and play a crucial role in solar energy conversion. Excitons dynamically generated by incident photons dominate the optical response of many materials including organic compounds such as carbon nanotubes\textsuperscript{1–3} and transition metal oxides\textsuperscript{4} such as $\text{Cu}_2\text{O}$. A dense gas of excitons may bore condense or form a Wigner crystal\textsuperscript{5,6}. Excitonic condensed states are of interest because the excitons may be spin singlet or triplet, or have more complicated properties in the presence of spin orbit coupling\textsuperscript{7} and in a topological insulators\textsuperscript{8}, and also couple via dipolar interactions\textsuperscript{9}.

Considerable effort has been invested over the years in optically generated electron-hole liquids,\textsuperscript{4,10,11} but creating and manipulating a sufficiently high-density optically excited particle-hole gas while preventing it from recombing has proven challenging. An alternative route, proposed by Zhu et. al.\textsuperscript{12} is to construct a double quantum well system in which one quantum well contains holes and the other contains electrons. The spatial separation prevents recombination while if the quantum wells are close enough the electrons and holes may interact.

Double quantum wells can be fabricated in semiconductor systems such as $\text{(Al,Ga)}\text{As}$ but perhaps because of the large bandgap it has not been possible to bias these systems strongly enough to create significant equilibrium electron and hole populations. Eisenstein and co-workers have created double-well systems in which each well was tuned to the $\nu = 1/2$ quantized Hall state, thereby producing a hole condensate with highly unusual and still incompletely understood properties including nearly dissipationless transport characterized by counterflowing currents in the two layers.\textsuperscript{13,14} Recent theoretical papers have raised the possibility of similar effects occurring in graphene bilayers.\textsuperscript{15,16} Excitonic instabilities have also been considered in intrinsically compensated materials with coexisting electron and hole bands,\textsuperscript{17} including high-$T_c$ cuprates.\textsuperscript{18}

In this paper we propose a different route to the formation of proximal electron and hole liquids. The basic idea is sketched in the middle panel of Fig. 1: an oxide heterostructure involving a thin layer of narrow gap correlated (‘Mott’) insulator (labelled as $B$ in the figure) sandwiched between two possibly different wide-bandgap insulators (labelled as $A$ and $C$ in the figure). If the $AB$ and $AC$ interfaces are polar, then in the absence of charge reconstruction,\textsuperscript{20,21} an internal electric field will be generated, leading to a potential drop which scales linearly with the thickness of the correlated material (top panel of Fig 1). The potential drop causes band-bending (shown in the lower panel of Fig. 1) which, if large enough, pushes the conduction band below the Fermi level on one side of the structure and the valence band above the Fermi level on the other side, leading to electron and hole accumulation respectively. If the band gap of the inner material (‘$B$’) is smaller than the band gaps of the outer materials (‘$A$’ and ‘$C$’) and the heterojunctions have type I band offsets then the electron and hole gasses will...
remain within layer B.

The idea is a variant of the proposal of Ref [12]. The importance of polar-discontinuity fields and the possibility of exciton formation was previously noted in the context of the non-Mott LaAlO$_3$/SrTiO$_3$ interface by Bristowe, Artacho and Littlewood [22]. However, several features, apparently not previously noted, make the ‘tricolor’ oxide heterostructures involving Mott insulators particularly attractive candidates. First, Mott insulators often have relatively small gaps $\Delta \sim 0.3 - 2 eV$ so that the electric fields required to produce the needed band-bending need not be prohibitively large. Second, the physics of correlated materials is local: the relevant length scales for charge phenomena are of the order of local interactions and estimating $d \approx 4Å$ and estimating $\epsilon \sim 10$ from previous analyses of oxide heterostructures and from calculations of the screening of local interactions we obtain $E_c \approx 0.15 eV$. For simplicity we neglect the energy cost of the dipole layer needed to remove the potential step shown in the left panel of Fig [2]: including it would increase the densities of the electron and hole gasses. We also assume that the transferred layer is one unit cell thick, so that $x$ electrons per unit cell are transferred from the correlated electron layer nearest the interface on one side of the structure to the correlated electron layer nearest the interface on the other side. We determine $x$ by minimizing the sum of the electronic charging energy cost to add electrons or holes to the correlated insulator and the volume integral of the electric field energy density $E^2/(8\pi \epsilon)$. We express the field energy in terms of the basic scale $E_c = \epsilon a^2/2$ with $a$ the in-plane lattice constant, $\epsilon$ the dielectric constant and $d$ the distance between the charge blocks shown in Fig [2]: in the situations considered here $d \approx a/2$. Using $a \approx 4Å$ and estimating $\epsilon \sim 10$ from previous analyses of oxide heterostructure and from calculations of the screening of local interactions we obtain $E_c \approx 0.15 eV$. For simplicity we neglect the energy cost of the dipole layer needed to remove the potential step shown in the left panel of Fig [2]: including it would increase the densities of the electron and hole gasses. We also assume that the transferred layer is one unit cell thick, so that $x$ electrons per unit cell are transferred from the correlated electron layer nearest the interface on one side of the structure to the correlated electron layer nearest the interface on the other side. We find

$$E^P_{\text{field}} = 4\pi(N-1)E_c \left(1 - 2x + 2x^2\right) \quad (1)$$

$$E^{NP}_{\text{field}} = 4\pi(N-1)E_c \left(11/4 - 3x + 3x^2\right) \quad (2)$$

The electronic charging energy is the sum of the gap energy $\Delta_{e=\text{el, hole}}$ and the 'compressibility' energy $\kappa^{-2} = \partial\mu/\partial n$. Defining $\kappa^{-2} = (\kappa_{e}^{-2} + \kappa_{h}^{-2})/2$ and gap $2\Delta = \Delta_{e} + \Delta_{h}$ we get

$$E_a = 2\Delta x + \kappa^{-2}x^2$$

$\kappa^{-2}$ is expected to be enhanced in correlated materials relative to its band theory value $\sim 0.7 eV/(\text{unit-cell})$; an

![FIG. 2: Electrostatics of electron-hole liquid formation. Upper panel: $N = 3$ layers of polar correlated insulator such as LaTiO$_3$, LaVO$_3$ or LaCoO$_3$ inserted in hypothetical wide bandgap non-polar insulating host (here CaZrO$_3$), with sheet charge density (in carriers per unit cell) indicated in the ionic picture, along with the induced electric field and the electrostatic potential (in units of the energy $E_c$ defined in the main text. Also shown is the surface dipole required for electrostatic equilibrium, Lower panel: $N = 3$ layers of a non-polar correlated insulator such as an infinite-layer cuprate inserted in a polar host, with electric field and potential drop indicated. The final surface dipole layer is not shown.](image-url)
The Mott insulating channel material is most likely to exhibit excitonic binding. The Coulombic binding energy. One sees that 2 or 3 empty bands. A detailed analysis requires a full many-body treatment of the interplay of binding and many-body physics which is not yet available. Here we argue that the ’kinetic energy’ associated with the ’Drude’ (zero-frequency-centered) component of the optical conductivity gives the delocalization energy of the doped holes or electrons. For high-$T_c$ materials the Drude kinetic energy per dopant has been determined. Using this information and our computed electron densities we can model the momentum that each electron experiences when it is excited by light at frequencies of order the Mott gap will lead to spin transport without charge transport.

The next question is whether excitonic binding may occur. For weakly correlated systems binding occurs if the interparticle distance in one plane is greater than to the spacing between planes, or alternatively if the binding energy is larger than the Fermi energy. The issue is more subtle in the doped Mott insulator case, because one must address the question whether one counts carriers with respect to the half filled insulator or the full and empty bands. A detailed analysis requires a full many-body treatment of the interplay of binding and many-body physics which is not yet available. Here we argue that the ’kinetic energy’ associated with the ’Drude’ (zero-frequency-centered) component of the optical conductivity gives the delocalization energy of the doped holes or electrons. For high-$T_c$ materials the Drude kinetic energy per dopant has been determined. Using this information and our computed electron densities we can model the momentum that each electron experiences when it is excited by light at frequencies of order the Mott gap will lead to spin transport without charge transport.

Even if excitonic binding does not occur, the properties may be of interest. The slow rise to saturation of the transferred charge shown in Fig. 3 implies that a typical structure will have a non-negligible internal electric field. In a structure of thickness $N > 2$ the intermediate layers will be in the insulating configuration. Absorption of incident light at frequencies of order the Mott gap will produce particle-hole pairs which will be rapidly dissociated by the internal field, leading (if the electron or hole layers are mobile) to a large photocurrent. If the Mott insulator is magnetic, then the electron and hole currents will each be spin polarized.

Significant difficulties are likely to arise in attempts to put into practice the ideas proposed here. The most serious is that while a number of reports have appeared of electron conduction at oxide interfaces, hole conduction seems to be very difficult to achieve in the $A BO_3$ perovskite systems which have been the prime focus of study so far. Systems based on $CuO_2$ layers may be more appropriate choices. High-$T_c$ cuprate materials exist in both electron and hole-doped forms. While most most crystal structures support either electron or hole liquids, both $n$ type and $p$-type superconductivity have been observed.
been reported in the infinite-layer material. These systems also exhibit very weak interlayer coupling which is important for the spatial segregation of the electron and hole gasses. Further, the results in this paper are based on the assumption that the polar discontinuity fields are resolved by electronic reconstruction; of course in practice ionic and chemical effects such as interdiffusion and vacancy formation are likely to be important. Finally, the subject of excitonic pairing in a strongly correlated background is in its infancy. Theoretical investigation of this issue is warranted.

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