Design of electron correlation effects in interfaces and nanostructures

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Abstract We propose that one of the best grounds for the materials design from the viewpoint of electron correlation such as ferromagnetism, superconductivity is the atomically controlled nanostructures and heterointerfaces, as theoretically demonstrated here from three examples with first-principles calculations: (i) Band ferromagnetism in a purely organic polymer of five-membered rings, where the flat-band ferromagnetism due to the electron-electron repulsion is proposed. (ii) Metal-induced gap states (MIGS) of about one atomic monolayer thick at insulator/metal heterointerfaces, recently detected experimentally, for which an exciton-mechanism superconductivity is considered. (iii) Alkali-metal doped zeolite, a class of nanostructured host-guest systems, where ferromagnetism has been experimentally discovered, for which a picture of the “supercrystal” composed of “superatoms” is proposed and Mott-insulator properties are considered. These indicate that design of electron correlation is indeed a promising avenue for nanostructures and heterointerfaces.

1 Introduction

There is a growing realisation that the concept of materials design is becoming realistic, which is due to advances in fabricating tailor-made materials and in performing first-principles calculations. Now, one decisive direction in the condensed-matter physics in these decades is the physics of electron correlation, i.e., the high-Tc superconductivity as kicked off by the cuprates, ferromagnetism, Mott’s metal-insulator transition, etc. So we can ask a question: can we envisage materials design from the viewpoint of electron correlation[1]? Here we wish to advocate an idea that atomically controlled heterointerfaces and nanostructures, with their higher controllability than in the bulk, should be one of the best grounds to be explored. Specifically we present here proposals for one-, two- and three-dimensional systems, by combining the first-principles calculation with many-body studies:

(1D) We propose ferromagnetism in purely organic polymers for the first time, where we show, with a computer-aided design, that the ferromagnetism due to the electron-electron repulsion in systems having flat one-electron bands should be realised in a chain of five-membered rings[2, 3].

(2D) Second, we consider the metal-induced gap state (MIGS) at insulator/metal interfaces, which has been recently detected experimentally in LiCl/Cu,Ag for the first time[4]. Our first-principles calculation[4, 5] shows, despite the conventional wisdom, that the MIGS of about one atomic monolayer thick indeed exist. In the MIGS at insulator/metal interfaces the coupling of the carrier to excitons should be strong, which we envisage to work favourably for the exciton-mechanism superconductivity.

(3D) Third, we take the alkali-metal doped zeolite, a class of nanostructured host-guest systems, where ferromagnetism has been experimentally discovered. We propose to regard the system as a “supercrystal” composed of “superatoms” (i.e., clusters of loaded atoms), where the first-principles band structure is so surprisingly simple as to allow such a picture[6]. Mott-insulator properties can be understood as an effect of the electron correlation in the supercrystal.
2 Band ferromagnetism in an organic polymer

Introduction — The discovery of conducting organic polymers[7] has kicked off intensive studies, including optoelectronics[8]. In the viewpoint of the electron correlation, design of (purely-)organic[9], ferromagnetism is a challenging target, since, usually, ferromagnetism is specific to d or f electron systems. A theoretical proposal was made by Shima and the present author[10] for “superhoneycomb” networks of \(\pi\)-electrons, but this has to do with ferrimagnetism[11]. Here we propose a novel possibility of a band ferromagnetism in an organic polymer, which is a realisation of the flat-band ferromagnetism (Fig.1(a)) due to Mielke-Tasaki’s mechanism.[12]

Why the flat-band ferromagnetism? — We should first mention why we have to evoke a somewhat esoteric flat-band ferromagnetism. While the problem of ferromagnetism in repulsively interacting electron systems has a long history dating back to Gutzwiller, Kanamori and Hubbard in the 1960’s, we are still some way from a full understanding. In this context the flat-band ferromagnetism proposed by Lieb[11] and the subsequent flat-band ferromagnetism by Mielke and by Tasaki[12] are remarkable in that the magnetic ground state is proved rigorously for the repulsive Hubbard model when the one-electron band structure contains a flat band. The flat band considered here is not the usual narrow band limit (with a set of disjointed basis functions), but those satisfying a special property called the local connectivity condition. There, adjacent “Wannier” orbitals overlap (Fig.1(b)) no matter how they are chosen, which is why spins tend to align due to Pauli’s principle. When the (half-filled) flat band lies at the bottom of the band structure, the ferromagnetism is guaranteed for arbitrary strengths \((0 < U \leq \infty)\) of the electron-electron repulsion, while the ferromagnetism is expected for \(U < U_c\) when the flat band sits in between dispersive ones, as has been confirmed for a model atomic quantum wire.[13]

The connectivity condition is usually difficult to realise, but relatively easy for one-dimensional chain of molecules[13], which is why we have opted for organic polymers. Specifi-
cally, chains of five-membered rings should be promising, because we find it empirically easier to realise the flat bands for odd-membered rings, where the frustration tends to suppress antiferromagnetism in favour of ferromagnetism. The tight-binding model for the connected five-membered rings has indeed a flat band in appropriate, realistic conditions, where the eigenstates on the flat band satisfy the connectivity condition (Fig. 1(c)).

**Search for the right polymer** — So we start with a search for the case of flat bands by scanning various five-membered polymers, i.e., polypyrrole, polythiophene, etc. The band structure is obtained with first principles calculations within the framework of the generalised gradient approximation based on the density functional theory (GGA-DFT).[14] The atomic configuration is optimised to minimise the total energy with the conjugate gradient scheme[15]. The flat band has turned out to be rather hard to realise even for five-membered chains (not a sufficient condition) even after various functional groups are attached to the rings, but we have succeeded in finding the right polymer, polyaminotriazole (PAT for short; see inset of Fig. 2). Figure 2(a) shows that the top valence band (with two branches corresponding to the band folding due to a dimerisation) has little dispersion ($\sim O(0.1eV)$).

We have then carried out the GGA calculation with the spin density functional theory (GGA-SDFT)[14] for the doped PAT with the half-filled flat band. The doping for the single chain is realised by increasing the number of electrons with a uniform positive background for charge neutrality. The optimised state is polarised as shown in Fig. 2(b) with the splitting between the majority and minority-spin bands being $\sim 1$ eV, which is similar to the exchange

![Figure 2: The band structure of the undoped (a) and doped (b) PAT obtained by the GGA-SDFT. The solid (dashed) lines represent bands with $\pi$ ($\sigma$) character. The inset shows the (optimised) atomic configuration.](image)
splitting estimated in [16] for the atomic quantum wire.[13] The ferromagnetic state has a total energy lower than that of the antiferromagnetic state by $\sim 50$ meV. We have also shown that the Peierls distortion, to which 1D systems are prone, is negligibly small in the present system, which is because $\sigma$-electrons provide rigid enough backbone of the structure[17].

**Electron correlation mechanism relevant** — We can confirm that the ferromagnetism obtained in the band calculation is identified as the flat band ferromagnetism for the Hubbard model a l´a Mielka-Tasaki. To do so we have first mapped the $\pi$-electron system to a tight-binding model to examine whether the ground state is spin-polarised in the presence of the Hubbard repulsion, $U$. The phase diagram (Fig.3), drawn on a realistic parameter region, has a wide ferromagnetic region, to which PAT should belong (unless $U$ is unusually large ($> 4$ eV)).

**Discussions** — The flat-band ferromagnetism should work not only for long polymers but for oligomers as well, for which we should end up with high-spin state oligomers. Second, the one-electron dispersion does not have to be exactly flat[18, 19], nor does the band filling exactly half-filled[20] to realise the ferromagnetism. Also, electron-electron interactions can extend beyond the on-site[21]. Even when a single chain becomes ferromagnetic, whether the magnetism remains in the bulk, i.e., in a three-dimensional crystal of polymers, is an important question. We have studied this by means of the spin density functional calculation for the crystal[3] (Fig. 4) to find that the ferromagnetism is robust against crystallisation, where the chemical dopant HF$_2$ puts the system close to the bulk ferromagnetism, so stronger anions such as BF$_4$ or PF$_6$ should be promising.

### 3 Insulator/metal heterointerfaces — metal-induced gap states

**Why insulator/metal interfaces?** — While there are mounting interests in the nature of heterointerfaces, insulator/metal interfaces are especially intriguing for their fascinating possibilities such as metal-insulator transition[22, 23], band gap narrowing [24] and superconductivity[25] as well as technological ones such as catalysis, magnetic tunnelling junctions, etc. Despite the interest, insulator/metal interfaces have not been studied satisfactorily, for good reasons: well-defined interfaces are hard to prepare due to the different nature of chemical bonds.
Figure 4: The optimised atomic configuration of the crystallised polyaminotriazole doped with HF$_2$ (top), along with the band structure for the ferromagnetic solution with black (green) lines representing the majority (minority) spin.
A specific interest is the metal-induced gap states (MIGS), which were first introduced for semiconductor/metal junctions in discussing the Schottky barrier at the interface[26], and subsequently applied to insulator/metal interfaces[27]. Roughly, MIGS are evanescent states of the metal electrons that (exponentially) penetrate into the insulating side of the interface, with the penetration depth $\propto 1/E_G$. Recently, Muller et al. reported an observation of MIGS in MgO/Cu interfaces on fine particles [28]. However, the interface studied there is polar (hence metallic presumably) and not well-defined atomically either, so there was some ambiguity. Kiguchi et al.[4] have then made a clear-cut observation: they have employed atomically well-defined insulator/metal interfaces,[29] which are alkali halides grown epitaxially on metal substrates (LiCl on Cu(001) or Ag(001)). The near edge x-ray absorption fine structure (NEXAFS) has provided a clear evidence for the MIGS that are about one monolayer(ML) thick.

Ab-initio calculation — So it is intriguing what an ab-initio calculation can tell us for the MIGS with a thickness $\sim$ 1 ML, since a simple model for the interface (e.g., tight-binding insulator/jellium) would predict a negligible ($\ll$ 1 ML) penetration for the gap $E_G \sim O(10)$ eV. This is where the first-principles calculation based on the local density functional theory (LDF) comes in. Figure 5 (a) shows the band structure of 1 ML LiCl/Cu(001). When the 1 ML LiCl is put on Cu(001), new bands appear in the gap. In the LDF wavefunctions (Fig. 5(c)) for the three bands just above $E_F$ at $\Gamma$ point, two in-gap states closest to $E_F$ indeed have, on top of the exponential decay, appreciable amplitudes on the interfacial Cl atoms with a $p_z$-like structure, in agreement with the polarisation dependence in NEXAFS. MIGS with one ML thickness persist when we replace LiCl with LiF or LiI.

It is well-known that the LDF generally underestimates the band gap, while GW approximation improves this. However, while the band-gap underestimation may be amended via the self-energy correction (i.e., without any corrections for LDF wavefunctions), the shape of the wavefunctions should be reliable even in LDF, hence the present calculation for the local density of states is expected to be a good approximation.

We have also performed an LDF calculation for 3 ML LiCl put on a jellium to confirm the appearance of the MIGS is not specific to Cu (transition metal) substrate (Fig. 6). When we change the density of electrons in the metal by varying $r_s$ (the sole parameter characterising the jellium) the MIGS are found to be only weakly dependent on $r_s$ (Fig. 6). This accounts for the experimental result that MIGS are observed for both Cu(with $r_s$ = 2.7) and Ag($r_s$ = 3.0) substrates.

Electron correlation effects at the heterointerface — So what electron-correlation effects can we expect specifically in such insulator/metal interfaces? A fascinating possibility should be the exciton-mediated superconductivity. The exciton mechanism has been originally proposed by Little[30] for quasi-one dimensional electrons to which polarisable molecules are attached, and subsequently two-dimensional version of this has been proposed for metal/semiconductor interfaces by Ginzburg[25, 31, 32]. However, a difficulty was subsequently pointed out by Inkson[33] that the presence of excitons requires a wide-gap insulator, while this in turn prevents the metallic carriers to penetrate into the insulator and makes the coupling of electrons to excitons too weak.

In the present insulator/metal interfaces, by contrast, we do have a built-in coexistence (in real space) of carriers and excitations (associated with the wide band gap ($\simeq 9$ eV for LiCl) of the insulator), since the MIGS penetrate into the insulator side. So the carrier-exciton interaction should be strong (Fig. 7). A theoretical estimate[5] shows that the exciton contribution on top of the phonon mechanism can significantly enhance the superconductivity, where LiI on Al, for example, should make $T_c$ 1.6 times greater than that in the bulk Al.
Figure 5: (a) The band structure of 1 ML LiCl/Cu(001) as compared with that for an isolated 1 ML LiCl (right panel), along with the contours of the absolute value of the LDF wavefunctions for the in-gap states (MIGS in red). (b) Atomic configuration. (c) The charge distribution.
Figure 6: Configuration (a) and the band structure (b) of 1ML (left) or 3ML (centre) LiCl/jellium with $r_s = 2.5$. The right panel is for $r_s = 6.0$.

Figure 7: Strong electron-exciton coupling schematically shown.
4 Electronic properties of alkali-metal loaded zeolites

Why zeolites? — Materials design we have described so far is done by manipulating molecular or crystal structures. As an alternative way, we may envisage introducing guest atoms into host materials that are open-structured on nanometer scale. Doped zeolites are exactly such systems, and they are unique in that the host itself appears in a rich variety of crystal structures, on top of rich possibilities for the species and the number of guest atoms[34].

The nanometer scale implies that the Coulomb interaction energy, which only decreases inversely with the size, can remain large (∼ eV) for the cluster doped in the cage. Indeed, experimental results by Nozue et al have established that some zeolites (Fig. 8) loaded with ≃ five potassium atoms per cage are ferromagnetic for $T < 8K$[35], despite all the ingredients being non-magnetic elements[36].

Formulation and the result: an array of “superatoms” — First question we want to ask is: can such host-guest systems (where the number of atoms in a unit cell is as large as 84) have simple electronic structures? So we start with the undoped aluminosilicate zeolite having a simple-cubic array of cages (Fig. 8), where each cage (called α) is an Archimedes polyhedron. The region surrounded by eight α cages forms another cage called β. The material used in most experiments[35] is K(potassium)-form zeolite A (abbreviated as LTA) with a chemical formula $K_{12}Al_{12}Si_{12}O_{48}$. The crystal structure obtained from a recent neutron powder diffraction study by Ikeda et al[37] is adopted.

We have then performed an LDF calculation with the all-electron full-potential linear muffin-tin orbitals (FP-LMTO)[38]. In fact ours is the first reliable band structure calculation for zeolites[39]. The result for the band structure for the undoped LTA shows that the undoped zeolite has the conduction bands whose wavefunctions primarily reside within the α cage or within β. The dispersion of the bands around the energy gap can be excellently fitted by the dispersion of tight-binding bands on the simple cubic lattice, and we can identify the band as tight-binding bands of s- or p-like orbitals.

When three K atoms per unit cell are doped ($K_3$LTA, which belongs experimentally to the magnetic regime), three bands around $E_F$ can be identified as $p_x$, $p_y$, and $p_z$ bands, respectively, as shown in Fig.9. The fit of the dispersions to the tight-binding model is again
excellent, where the hopping integrals are almost an order of magnitude greater than those for \( K_1 \)LTA, as expected from the larger cluster size. In passing we note the doped zeolites are rather distinct from the doped solid fullerene: The latter, while a nanostructured crystal as well, has the relevant orbitals that are basically LUMO/HOMO of the cage (buckyball) rather than those of dopants even after doped with alkali metals[40].

The good fit to a simple tight-binding model is highly nontrivial, since the ionic host, \((K^+)_{12}(Al^{3+})_{12}(Si^{4+})_{12}O^{2-}\)\(_{48}\), should possess a wildly varying potential well. Chemically, this should be because the cage has a low electron affinity so that the electrons stay well away from the wall, as confirmed here. The surprisingly simple band structure around \( E_F \) enables us to regard each cluster in the cage a “superatom” with well-defined \( s \) and \( p \) orbits, and regard the whole system as a “supercrystal” (i.e., an array of superatoms). The result explains why the experimentally obtained optical spectrum can be assignment to those between \( s \) and \( p \) orbitals in a simple well[41].

**Electron correlation properties** — Now we come to the question of whether the system is strongly correlated. The largest Coulomb matrix element is the intra-orbital Coulomb interaction \( U \), which is estimated here to be \( U \approx 4.5 \) eV for the \( s \) band in \( K_1 \)LTA, and \( \approx 4.0 \) eV for the \( p_x \) band in \( K_3 \)LTA. Given that \( U/W \approx 10 \gg 1 \), where \( W \approx 0.4 \) eV is the band width, we can expect that these materials are Mott insulators. However, since the relevant \( p \) bands are significantly anisotropic, we have to be careful in estimating the critical \( U_c \). Here we have employed the dynamical mean-field theory[42] with the maximum entropy method[43] to estimate the transition point for a typically anisotropic (\( t_x : t_y : t_z = 5:1:1 \)) single-band Hubbard model. The result shows that the system becomes a Mott insulator (as indicated by
Figure 10: Spectral function, $\rho(\omega)$, for various values of $U/W$ obtained with the dynamical mean-field theory for the Hubbard model on an anisotropic cubic lattice ($t_x : t_y : t_z = 5:1:1$).

A gap in the spectral function) for $U/W > 2$ in the anisotropic case (Fig.10). So we conclude that the K-doped zeolite is well on the Mott-insulator side. This resolves a puzzle that the band calculation predicts that the system is a metal, while an infrared experiment indicates an insulator.[44] As for magnetic properties, the system is mapped to multi-band (triply-degenerate p-band) systems, which are in general favourable for ferromagnetism since the inter-orbital kinetic-exchange coupling is ferromagnetic. We can discuss magnetic properties in terms of the magnetic phase diagram obtained in the literature[45, 46].

In the context of materials design, we expect that the electron correlation in zeolites can be controllable through control of $U/W$. For example, faujasite becomes metallic when metal-doped[47], where this form of zeolite has a significantly wider (7 Å against 5 Å for LTA) window between the cages, which should result in a smaller $U/W$.

5 Concluding remarks

The message obtained from the above examples is that the design of electron correlation can indeed be a promising avenue for atomically controlled nanostructures and heterointerfaces. There are a lot of theoretical works to be done, among which is the problem of how to estimate “U”. Kusakabe, for instance, has shown that a kind of electron correlation Hamiltonian can be constructed by modifying the Kohn-Sham theory[48]. Another way will be an elaboration of the LDF + dynamical mean-field theory.[49]

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