Synthetic routes to new physics

Ben Powell describes the exotic and poorly understood behaviours of organic charge transfer salts (which include unconventional superconductivity, metal-insulator transitions and ‘spin-liquids’), and how some old chemical ideas and synthetic chemistry may play a vital role in answering the many open questions in this field.

One can understand the behaviour of the electrons in many metals individually: it does not matter too much what the other electrons are doing. Technically, if the behaviour of one electron is essentially independent of the others, one says that the electrons are ‘uncorrelated’. In contrast, an accurate description of electronic correlations in molecules is often essential if one is to make usefully accurate predictions. However, electronic correlations in molecules do not, typically, cause qualitative changes in the behaviour of the material. This is not the case in solids, particularly if the electrons are confined to one or two dimensions. We will see below that, in organic charge transfer salts, electronic correlations cause behaviours that are qualitatively different from the predictions of uncorrelated theories. This makes these materials a key test for theories of strong electronic correlations.

Materials in which the electrons are strongly correlated display a fascinating range of behaviours and present many fundamental challenges to theory. However, because of the complications in understanding their behaviour, strongly correlated materials have not yet found widespread applications. This has led the US Department of Energy (DOE) to identify ‘understanding and controlling the remarkable properties of matter that emerge from complex correlations of atomic and electronic constituents’ as one of the most important problems in materials science for future technologies.

Summarising the DOE report co-chairs, Graham Fleming and Mark Ratner, wrote that:

If researchers could achieve for strongly correlated materials the same level of understanding, precise processing, and control that they routinely achieve for semiconductors, it would open up remarkable technological possibilities – for example, essentially lossless transmission of energy across the continents. The grand challenge of understanding and controlling collective phenomena and emergent properties will require the extension of existing theories to new regimes, the development of fundamentally new theories, and the building of new instruments to control directly the atomic-level dynamics.

Most strongly correlated materials are inorganic, and many are ceramics, e.g. the perovskites. The inherent tunability of organic chemistry makes the organic charge transfer salts a
particularly important class of strongly correlated material as they provide a set of model systems on which to hone our ability to control strongly correlated electrons.

Crystals of (BEDT-TTF)$_2X$ where $X$ is a monovalent anion, consist of alternating layers of organic cations and (often inorganic) anions, such as I$_3$ or Cu(NCS)$_2$ (Fig. 1). Hückel theory and density functional theory (DFT) predict that the radical cations (holes) in the layers of BEDT-TTF dimers are mobile, i.e. the organic layer is metallic, whereas the electrons are each localised on a particular anion. Further, holes find it extremely difficult to move between different BEDT-TTF layers. This means that the electrons are essentially confined in two dimensions. Thus the crystal is a stack of alternating insulating and metallic layers.

Within the organic layer, the BEDT-TTF molecules are dimerised (Fig. 2). The low-energy electronic structure of BEDT-TTF salts can be described in terms of a single orbital on each dimer (the antibonding combination of the two BEDT-TTF HOMOs; Fig. 2) with, on average, one hole per dimer. These holes move by 'hopping' from dimer to dimer, forming an 'anisotropic triangular lattice' within the BEDT-TTF layer (cf. Fig. 2). This model provides an important starting point for thinking about BEDT-TTF salts. However, both Hückel theory and DFT predict that the BEDT-TTF salts are metals - in contrast to the range of insulating, superconducting and metallic phases observed experimentally.

The 'Mott insulator' phase is of central importance in strongly correlated materials in general and organic charge transfer salts in particular. Further, the Mott insulator illustrates how electronic correlations can qualitative change the behaviour of a material, so we will now briefly discuss this phase. In the metallic state, some of the dimers are neutral, others are cationic and the rest are doubly cationic. Thus in the metal there is a dynamic equilibrium:

$$(\text{BEDT-TTF})_2^+ + (\text{BEDT-TTF})_2^{2+} \rightleftharpoons 2(\text{BEDT-TTF})_2^+$$

The effective Coulomb repulsion between two holes on the same dimer is the energy of this charge disproportionation reaction, and is usually called ‘the Hubbard U’. A Mott insulator occurs if U is large enough to prevent two holes from occupying the same dimer. This state is insulating as each dimer now has exactly one hole and none of the holes can move onto another dimer (as this would cause that dimer to have two holes).

In the BEDT-TTF salts one can tune U/t, the relative strength of the Coulomb repulsion between two holes on the same dimer (U) and the bandwidth for an electron to hop from one dimer to another (t, defined in Fig. 2), by varying the separation between dimers. This can be achieved either by hydrostatic pressure, by chemical pressure (changing the lattice spacing by the size of anion, $\lambda$), or even by deuterating the BEDT-TTF molecule. These variations cause a material (or family of materials) to change from a Mott insulator to a superconducting state. The superconducting state in the BEDT-TTF salts is now known to be very different from those in 'conventional' superconductors, such as Nb or Sn.

In conventional superconductors, the electrons are bound together into pairs because of the effective attraction between electrons due to their coupling to phonons (quantised lattice vibrations).
Sketch of (a) a valence bond insulator and (b) an RVB superconductor. Bars represent singlet valence bonds formed between sites (i.e. BEDT-TTF dimers; circles). In the valence bond insulator there is exactly one electron per site (dimer) and therefore the material is a Mott insulator. In the RVB superconductor some double occupation is allowed (indicated by one site with two electrons (arrows) and another with no electrons). The valence bonds can now move (dissipationlessly) giving rise to superconductivity.

Figure 3. Sketch of (a) a valence bond insulator and (b) an RVB superconductor. Bars represent singlet valence bonds formed between sites (i.e. BEDT-TTF dimers; circles). In the valence bond insulator there is exactly one electron per site (dimer) and therefore the material is a Mott insulator. In the RVB superconductor some double occupation is allowed (indicated by one site with two electrons (arrows) and another with no electrons). The valence bonds can now move (dissipationlessly) giving rise to superconductivity.

Geometrical frustration. (a) On a 4-site cluster (or a square lattice), it is straightforward to arrange spins antiferromagnetically (i.e. with each spin pointing in the opposite direction to its nearest neighbour). (b) On a 3-site cluster (or a triangular lattice), it is impossible to arrange the spins antiferromagnetically.

Figure 4. Geometrical frustration. (a) On a 4-site cluster (or a square lattice), it is straightforward to arrange spins antiferromagnetically (i.e. with each spin pointing in the opposite direction to its nearest neighbour). (b) On a 3-site cluster (or a triangular lattice), it is impossible to arrange the spins antiferromagnetically.

vibrations). These ‘Cooper’ pairs were discovered to move dissipationlessly through the superconductor by Bardeen, Cooper and Schrieffer (BCS), for which they shared the Nobel Prize. But, in BEDT-TTF salts phonons do not cause the superconductivity and it is not described by BCS theory. Recently, several researchers (including the present author) have argued that the superconductivity is described by the ‘resonating valence bond’ (RVB) theory, which is highly analogous to Pauling’s valence bond theory. A remarkable feature of the RVB theory is that it suggests that Mott insulators are almost the same thing as superconductors!

To understand this seemingly bizarre claim let us consider two holes on neighbouring lattice sites (dimers) in a Mott insulator. Classically, the exchange interaction wants the spins of the two holes to point in opposite directions, a phenomenon known as antiferromagnetism. But, quantum mechanically the lowest energy state is for the holes to form a singlet ‘valence bond’, an object very much like a chemical bond, but localised between two dimers rather than two atoms. In three dimensions antiferromagnetism has a lower energy (because the spin of the hole can align with many neighbours in a crystal but a hole cannot form a valence bond with more than one neighbour). However, if one restricts the holes to less than three dimensions, there are fewer neighbours and so a valence bond state may be stabilised. If U/t is decreased by hydrostatic or chemical pressure, the valence bond state ceases to be a Mott insulator, and the valence bonds become mobile and, like Cooper pairs, able to move dissipationlessly through the crystal (see Fig. 3).

We noted above that BEDT-TTF dimers form a triangular lattice within the plane. One cannot arrange spins antiferromagnetically on a triangular lattice; or even on a single triangle (Fig. 4). This property of the triangular lattice is known as frustration. Frustration, like reduced dimensionality, decreases the stability of the magnetically ordered phases. Therefore frustrated systems are excellent places to look for exotic quantum phenomena. The most frustrated of the BEDT-TTF salts is κ-(BEDT-TTF)$_2$Cu(CN)$_3$, which forms an isotropic triangular lattice ($t' = t$, cf. Fig. 2). Recent experiments have found that there is no magnetic order down to the lowest temperatures studied (~30 mK), despite exchange interactions that are large enough for one to expect magnetic order at tens or hundreds of kelvin! It is therefore believed that κ-(BEDT-TTF)$_2$Cu(CN)$_3$ is a spin liquid: an exotic quantum state of matter in which there are localised radical cations, ‘spins’, on every lattice site, but there is no long-range magnetic ordering of these spins. This is exciting because in systems with localised spins there is usually magnetic order at low temperatures and because spin liquids appear to be ideal model systems to study exotic quantum phenomena such as ‘deconfinement’ or ‘fractionalisation’, which we will now discuss.

On the energy scales relevant to chemistry one does not need to worry about the fact that protons and neutrons are made up of smaller particles (quarks). This is because the quarks are ‘confined’ within the proton/neutron. Similarly, in a normal magnet it does not matter that the material is made up of spin 1/2 particles (electrons). On the energy scales relevant to magnets the spins are confined into spin one particles called magnons. These magnons can be directly observed in inelastic neutron scattering experiments. Importantly, magnons can be described in terms of two spin 1/2 ‘spinons’, which are confined inside the magnon. However, a number of theories suggest that in a spin liquid the spinons are ‘deconfined’, i.e. the spinons can move independently of one another (cf. Fig. 5). As the magnon is a composite particle ‘made’ from two spinons, this is often referred to as fractionalisation.
In order to observe the putative deconfined spinons, some heroic synthetic chemistry will be required. Up until now, synthetic chemists in this field have focused (incredibly successfully) on producing new materials with ever more exotic properties. But, if further progress is to be made in understanding and controlling the exotic phenomena seen in these materials, what the field is crying out for now is not just new materials but higher quality crystals of the materials that have already been synthesised. For example, in order to directly observe deconfined spinons (cf. Fig. 5) one needs to perform inelastic neutron scattering experiments. Such experiments would require single crystals that are ~1 cm³ in volume, much larger than those yet grown. Producing large high-quality single crystals is a daunting challenge, but one that is likely to lead to significant new physics.

REFERENCES

*This classic physics paper relies heavily on chemical arguments. Mott argues that the wavefunction of a metal is analogous to the molecular orbital wavefunction for H₂, whereas the wavefunction of a Mott insulator is the lattice analogue of the Heitler–London wavefunction for H₂. While in H₂ these are just two approximations to the exact wavefunction, in a crystal these two wavefunctions correspond to different thermodynamic phases.

Ben Powell is an Australian Research Council (ARC) Queen Elizabeth II Fellow in the Centre for Organic Photonics and Electronics at the University of Queensland. Funding by the ARC (project DP0878523) and the UQ Foundation (Research Excellence Award) is gratefully acknowledged.

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Figure 5. Spinons in a 1D spin chain. (a) Local antiferromagnetic correlations. (b) A neutron scattering off the chain causes one spin (circled) to flip. (c, d) Spontaneous flips of adjacent pairs of spins due to quantum fluctuations allow the spinons (circled) to propagate independently. A key question is: ‘Can this free propagation occur in 2D, or do interactions confine the spinons?’ This might be tested experimentally by looking for spinons in inelastic neutron-scattering experiments on the spin liquid phase of κ-(BEDT-TTF)₂Cu₂(CN)₃ if sufficiently large single crystals could be grown.