

STRONGLY CORRELATED ELECTRONS IN SOLIDS

Most emergent properties of the materials discovered since the 1980s are related to the existence of electron-electron interactions which are large with respect to the kinetic energies and could not be thoroughly studied before. The occurrence of **metal insulator transitions**, of **exotic magnetic and/or superconducting** properties in many new compounds have stimulated a large series of experimental and theoretical developments to grasp their physical significance. We present here a simple introduction to the elementary aspects of the physics of electron-electron interactions, which could be a starting point for typical undergraduate students.

Introduction

The study of the electronic properties of solids, done within an independent electron approximation since World War II, has been essential for the understanding of the occurrence of semi-conductors. This understanding was at the origin of the information technologies which expanded rapidly after the war. But during that period, a myriad of new materials with increasing [complexity](#) have been discovered as well. These materials were found to display unexpected novel electronic properties. Many such properties are not explained by the independent electron approximations, require new conceptual developments, and will certainly lead in the future to specific promising applications. Most of these emergent properties are linked with magnetic responses due to the strong electron-electron interactions in these complex new materials.

We will briefly discuss how these electronic interactions yield original states of electronic matter. A variety of experimental and theoretical techniques have been developed which permit a detailed investigation of their unexpected properties.

This article will be organised as follows. Electronic properties of solids were, in the first half of the twentieth century, considered mostly in the frame of an independent electron approximation with spin degeneracy. The resulting electronic band structure of metals which will be briefly recalled in **section 2** is such that each electronic level could be doubly occupied. In such an approach one expects metals or insulators with no significant magnetic properties.

In order to explain that some solids display magnetic properties one must reassess the underlying approximations that led to the band theory, and especially the [averaging](#) approach to the Coulomb interactions between electrons. In **section 3** we shall show that one has to take into account the strong local coulomb repulsion on atomic orbitals, which permits magnetic atomic states and magnetic insulators in the solid state.

We shall then specifically mention in **section 4** the superconducting state which is an original correlated electronic state which occurs in most metals at low temperature. This is a macroscopic quantum electronic state which results from an indirect electron-electron attractive interaction induced by the interplay of electronic and atomic vibrations in classical metals in which the electron states do not interact at high temperatures.

We shall then consider in **section 5** how electronic correlations yield materials with properties which are in an intermediate regime between independent, delocalised electrons and local states. Those intermediate electronic states are at the basis of the correlated electron physics. They often display exotic superconducting states with unexpectedly high transition temperatures, can undergo charge ordering or metal insulator transitions as well as exotic magnetic states considered as spin liquids. Such original states, which are far from being fully understood at this time, will be introduced in dedicated [Scholarpedia](#) articles.

The basics of the electronic band structure of solids

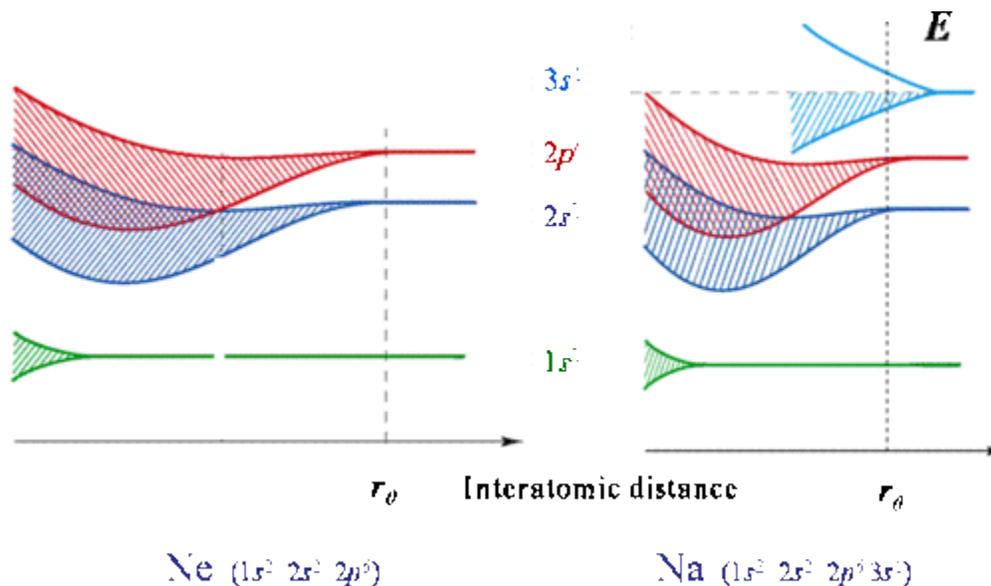


Figure 1: Band structures of Ne and Na. Here the calculated energy bands are plotted versus a fictitious distance between atomic orbitals and r_0 represents the [equilibrium](#) distance at ambient temperature. Ne only displays filled or empty bands and is an insulator, while Na has its higher energy band only filled with one electron per atom and is a metal.

Isolated atoms display discrete, narrow electronic levels. In the solid state, the electron can delocalise between sites due to the overlap of the electronic orbitals of neighboring atoms. The transfer integrals t between orbitals of neighboring atoms lead to a broadening of the atomic levels into electronic bands which characterize the actual band structure of a given material. The width of these energy bands is typically determined by zt where z is the number of neighboring atoms surrounding a given site. In such an independent electron approach the available electrons in the material fill the energy levels in increasing energy order. This yields

insulators when filled and empty bands are separated by finite gaps, and metals if there are partially filled energy bands up to an energy level which defines the Fermi energy, as shown in Fig.1. In such an approach, solids with an odd number of electrons per unit cell are expected to be metals as they should necessarily display partially filled bands in which delocalisation of electrons can be done at moderate energy cost. One distinguishes then among the insulators the cases where the energy gap is small compared to the thermal energy kBT . In that case electrons can be excited thermally at temperature $\sim T$ into the first empty band (conduction band) and leave empty holes in the last occupied band (the valence band), this being the case of semiconductors. Among those, graphene has been highlighted recently, as in that case the gap vanishes and the conduction and valence band touch each other at a single energy point, the Dirac point which corresponds in that case to the Fermi energy.

In those cases the band theory for the electronic states applies rather well and explains most of the electronic properties of these metals, insulators, semiconductors or Dirac point metals. In all those cases the independent electrons approach yields a weak paramagnetism as all these descriptions do not lift the spin degeneracy of the electronic states. This Band theory describes these materials well as the k space construction lifts the site degeneracy of the atomic state by building Bloch states which have different energies and well defined properties under translation.

The origin of Atomic [magnetism](#) and Mott insulators

If t is small, then one expects very narrow bands and localized electronic states, as the case $t=0$ corresponds to strictly isolated atomic states. In that case electronic interactions can no longer be treated as an average as done in band theories and do give rise to local moment and magnetism, as we shall see hereafter.

Mott insulators

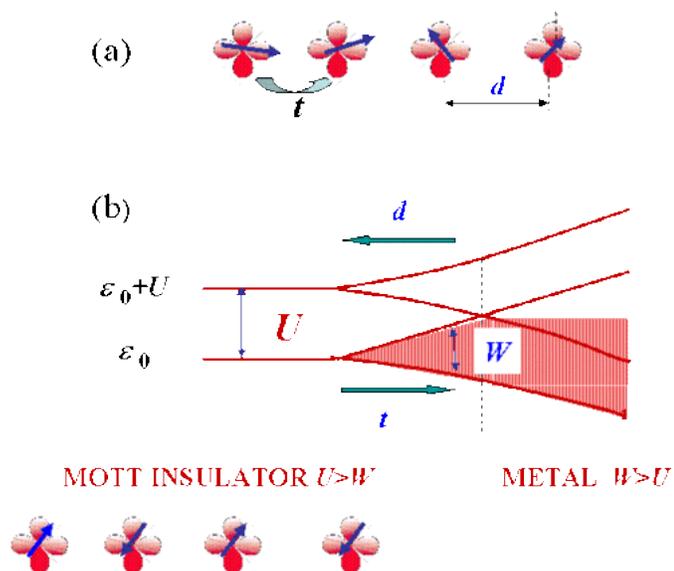


Figure 2: The Mott–Hubbard model. (a) The atomic orbitals on atomic sites at a distance d , with the transfer integrals t between neighboring sites. (b) The levels for the Hubbard model as a function of t or d . On the left: Isolated atom with energy levels ϵ_0 and ϵ_0+U . Center: Mott–Hubbard insulator obtained for a small hopping integral $W < U$. Right: Metallic situation corresponding to $W > U$. This very simple approach goes by the name of the Hubbard model.

Let us begin by considering the case of an isolated atom (on the left in **Fig. 2**). In this context, in band theory it is assumed that the energy brought to the system by an extra electron would be ϵ_0 , and that a second electron on the same atom would also bring ϵ_0 , so that the total energy would be $2\epsilon_0$ for a doubly negatively charged ion. But this is obviously not very realistic, owing to Coulomb repulsion. Apart from its 'orbital' energy ϵ_0 , the second electron will also be subject to the Coulomb repulsion of the first electron, and its energy will thus be higher than ϵ_0 by an amount usually denoted by U , which represents the Coulomb repulsion between the first and second electrons added to an initially neutral atom. The total energy of the doubly negative ion is thus $2\epsilon_0+U$. Note that U can vary considerably depending on the atom (from about 1 eV to more than 10 eV). If we now consider this ion in a crystal, the hopping integrals between nearest neighbors will broaden the discrete atomic levels into bands of width $W=zt$. To begin, we consider the limiting case of small hopping integral compared with U . We find ourselves in a situation corresponding to the middle of **Fig. 2**. There are two allowed energy bands called the upper and lower Hubbard bands, separated by a band gap. This gives the impression that we have a typical insulator (or semiconductor). But this is not in fact correct. There is one additional one-electron state per atom, so that, in a solid comprising N_n atoms, the lower band of the middle column can contain up to N_n electrons, rather than up to $2N_n$ electrons, as is the case in the context of the independent electron band theory. In particular, if there is now one electron per atom (or more generally an odd number of electrons per primitive cell), the lower band will be completely filled and the upper band completely empty. We will thus have an insulator with an odd number of electrons per primitive cell, as a consequence of the interactions U between electrons. The very existence of such an insulator (usually called a Mott-Hubbard insulator in recognition of the two British scientists who first studied them in the 1960s) is thus a consequence of the Coulomb interaction between electrons. As we shall see later, important examples of Mott-Hubbard insulators are undoped cuprates in which the Cu^{2+} ions are in a $3d^9$ state.

Magnetism of Mott Insulators

While usual band insulators should be nonmagnetic (or more precisely, slightly diamagnetic), very different expectations occur for a Mott-Hubbard insulator. If we begin by considering the limiting case of very small hopping integrals, we end up with isolated atoms. The electron in the level ϵ_0 can then have spin up or spin down, behaving like an isolated spin $1/2$. In the solid, these spins taken together will give rise to Curie paramagnetism with a spin susceptibility $\sim 1/T$, that is, a paramagnetic insulator susceptibility that contradicts band theory. If one takes into account the finite value of the hopping integral t , it can be shown that, at low

enough temperatures, the spins on neighboring atomic sites will like to arrange themselves in opposite directions, that is, antiferromagnetic coupling dominates.

The main conclusion which can be taken here is that going beyond the possibilities offered by band theory (paramagnetic metals and diamagnetic insulators), the presence of Coulomb interactions between electrons, if they are strong enough, can give rise to an insulating state with a variety of magnetic properties, such as Curie paramagnetism, antiferromagnetism (but also ferromagnetism), and so on as will be shown later on.

The Hubbard model, which replaces the true Coulomb potential $V(r) \sim 1/r$ by a repulsion which only acts if the two electrons are located on the same atom, is clearly a drastic simplification of the actual physical situation. However, it is rather naturally justified in the context of the theory of magnetic phenomena. Experiments show that there are not only magnetic insulators of spin 1/2 (in fact these are in the minority), but that in most cases the spin per atom is much higher. This is due to the fact that, in almost all cases, the atomic orbitals involved are not *s* levels (hence non-degenerate), but *d*- or *f*-type (hence five- or seven-fold degenerate).

In such a situation one has to take in more detail the local repulsive Coulomb interaction between electrons on the orbitals of such poly-electronic atoms. Though the Coulomb interaction is purely electrostatic, it differentiates the energy levels of the atomic orbitals, depending of their orbital symmetry and disfavors then double occupancy of some of them. These electronic interactions when combined with the Pauli principle are responsible for the local moment magnetism of isolated atoms. In this situation, the angular momentum of each atom in the Mott-Hubbard insulating state is determined by the electronic filling of the atomic levels through specific rules named Hund's rules.

The interactions between those local moments in ordered solids are responsible for the various long range ordered magnetic states (ferromagnetic or antiferromagnetic) or their absence thereof in the case where ordering is prohibited by geometric frustration effects, as will be illustrated later on.

Source : http://www.scholarpedia.org/article/Strongly_Correlated_Electrons_in_Solids