

Electrons in Condensed Matter

T V Ramakrishnan

Introduction

A hundred years ago, J J Thomson tore light negatively charged particles out of many different kinds of atoms by subjecting them to strong electric fields in discharge tubes. He showed that the same particle (with identical charge e and charge to mass ratio (e/m)) came out of different atoms. This established the electron as a basic ingredient of atoms and molecules, which constitute all common forms of matter.

In dilute gases of atoms and molecules, electrons lead stable, private lives; an electron is confined to its atom, or is shared between the atoms of a molecule. The electron is attracted and bound to the positively charged nucleus, and the resulting atom or molecule is stable and is electrically neutral. This is a reason why it took so long to free and know electrons.

As atoms or molecules are brought close to each other, i.e as matter condenses to a liquid or a solid, atoms exert strong forces on each other. This often frees outer electrons from bondage to individual atoms or molecules; they are free to move around the entire liquid or solid. The variety of electronic behaviour which then results is astonishingly diverse and stretches our imagination to its limits. It is influenced by the spatial arrangement of atoms, by the atomic heritage of the electrons, by the fact of their being identical and together and by the interactions between them. In this and two other articles, one by D N Bose on *Transistors – From Point Contact to Single Electron* and another by A K Raychaudhuri on *Seeing with Electrons*, we briefly celebrate a century of this continuing journey of exploration and discovery. What electrons do in condensed matter is not only surprising and interesting; it is also a large part of physics and materials



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based technology which is continuing to transform the world. This will also be brought out wherever possible.

I will start with a brief account of early discoveries and ideas pointing to some roles electrons play in condensed matter. It was however only with the development of quantum mechanics (that is, the correct laws of motion of electrons and other material objects) in the 1920's, that some basic patterns in the electronic properties of condensed matter could be rationalized. Finally, some examples illustrating the unusual diversity of electronic behaviour in condensed matter, eg. ferromagnetism, superconductivity, metal to insulator transitions and quantized Hall effect will be described.

Perhaps the most important for us here is the free electron theory of metals, developed by P Drude in 1900, within three years of the discovery of the electron. The theory is simple and has many consequences some of which agree very well with experiment, and others which conflict equally spectacularly!

Beginnings: The Drude Free Electron Theory of Metals

As the idea that the electron is a constituent of atoms gained ground, a number of implications became clear. Perhaps the most important for us here is the free electron theory of metals, developed by P Drude in 1900, within three years of the discovery of the electron. The theory is simple and has many consequences some of which agree very well with experiment, and others which conflict equally spectacularly! However, with relatively minor changes (which take into account properties of the electron discovered later) this picture is still an accurate approximation to the properties of many metals.

Suppose atoms in metals are so close that electrons from different atoms 'run into' each other, lose their atomic identity, and move about freely in the solid. These *free* electrons help conduct electrical current, as described below, and the high electrical conductivity of metals such as aluminium is ascribed to their having a high density of free, mobile electrons. One problem with this explanation is that some other equally dense solids, eg diamond, are insulators! We return to this later.



Is there any experimental way one can see that there are free electrons in metals? How many are there? One answer is the following: consider a free electron in an oscillatory electric field $\vec{E}(t) = \vec{E}_0 e^{-i\omega t}$ such as could be due to an electromagnetic wave of angular frequency ω . The electron experiences a force $e\vec{E}(t)$ and is forced to oscillate in tune. If the electron position is $\vec{r}(t)$, we have

$$e\vec{E}(t) = m\ddot{\vec{r}}(t) = -m\omega^2\vec{r}(t). \quad (1)$$

since $\vec{r}(t)$ oscillates with frequency ω . Thus the electron has an induced electric dipole moment $e\vec{r}(t)$, and if there are n free electrons per unit volume, the induced dipole moment per unit volume is $ne\vec{r}(t) = -(ne^2/m\omega^2)\vec{E}(t)$. This induces an electric field $\vec{E}_i = -(4\pi ne^2/m\omega^2)\vec{E}$ so that the dielectric constant κ of the free electron gas is

$$\kappa(\omega) = 1 - (4\pi ne^2/m\omega^2). \quad (2)$$

From this, we infer a frequency dependent refractive index

$$n(\omega) \sqrt{\kappa(\omega)} = \sqrt{1 - (4\pi ne^2/m\omega^2)} \quad (3)$$

We notice that for $\omega < \omega_p = (4\pi ne^2/m)^{1/2}$, the refractive index is pure imaginary; light does not go through the metal, but decays exponentially into it starting from the surface. The incident energy is reflected back.¹

In the calculation so far there is no absorption of electromagnetic energy, hence it is all reflected.

These facts are close to what we know from experience. More interestingly, for $\omega > \omega_p$, $n(\omega)$ is real, and the metal is transparent! This transparency of metals for high frequency light was observed by Wood in 1930 or so. In addition to confirming the free electron picture, it allows us to estimate n from a measurement of the transparency frequency ω_p (known as the plasma frequency). For example for Na, $\hbar\omega_p = 5.8$ eV.



This leads to an n of $2.6 \times 10^{22}/\text{cm}^3$, which is about one electron per sodium atom. This is reassuring, since the Na atom does have one loosely bound electron outside the closed shell.

Suppose the electron collides with random obstacles (vibrating ions, ions out of place, other electrons) so that the momentum gained by it (in an electric field say) is lost at a rate τ^{-1} (τ is called collision or relaxation time). This damping force is included in the force equation (1) as a term $-(m \ddot{r})/\tau$ on the left hand side. (This is very much like the Stokes viscous force on a ball falling through a fluid, which goes as $-6\pi\eta \dot{r}$). One can again find the dielectric function and the electrical conductivity σ , which is seen to be of the form

$$\sigma(\omega) = (ne^2\tau/m)(1-i\omega\tau)^{-1} = \sigma_0(1-i\omega\tau)^{-1} \quad (4)$$

This phenomenon is called *the skin effect*, and is well known in ac circuits, and is one of the reasons why connecting wires for high frequency circuits especially, have many strands (much more skin!)

This is the famous Drude formula for complex conductivity which can be checked by measuring σ at different frequencies. It relates the dc conductivity σ_0 to electron density and the relaxation time τ . It does describe the an ac conductivity of metals well. It can also be used to show that ac electric field does not penetrate the metal uniformly, but is exponentially damped out inside, starting from the surface, with a characteristic distance $\lambda = \sqrt{c / \sigma_0 \omega}$, called the skin depth. This phenomenon is called *the skin effect*, and is well known in ac circuits, and is one of the reasons why connecting wires for high frequency circuits especially, have many strands (much more skin!) The earlier dielectric function formula (2) is obtained from (4) in the limit $\omega\tau \gg 1$. So, here we have a simple, detailed and successful description of electrical (dc and ac) *and* optical properties of metals in a classical free electron picture.

Is anything wrong? Well, yes, as Drude and others realized very early. As mentioned above, this picture does not explain why some solids are metals with free electrons, while others, nearly equally dense, are not. Secondly, if there are so many



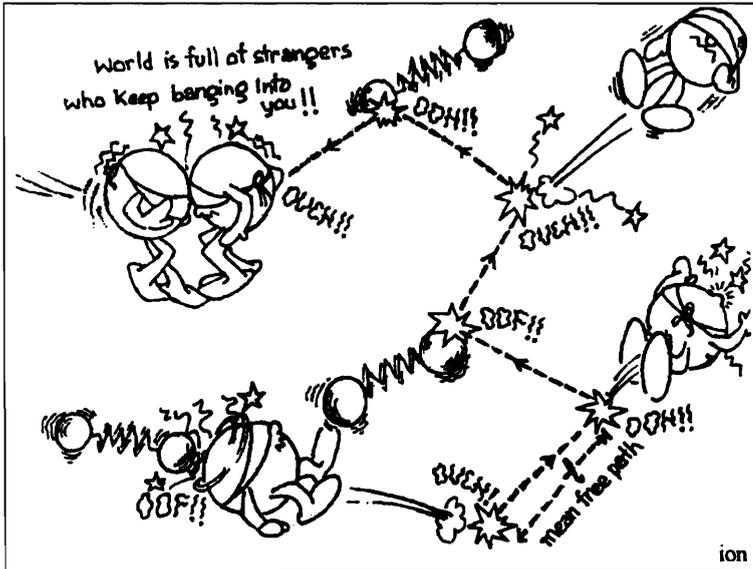


Figure 1. The world of Drude electrons.

free electrons, they ought to contribute to the specific heat. For example, aluminium has three free outer electrons per atom. Its specific heat² ought to be $(3k_B + 3 \times 3 k_B/2)$ per atom, $3k_B$ for the vibrating atom, and $3 \times (3 k_B/2)$ for the three freely moving electrons. The value at room temperature is $3.1 k_B$; the electronic specific heat is missing! The next stage in the electronic theory of solids clears up these two puzzles, as we see now.

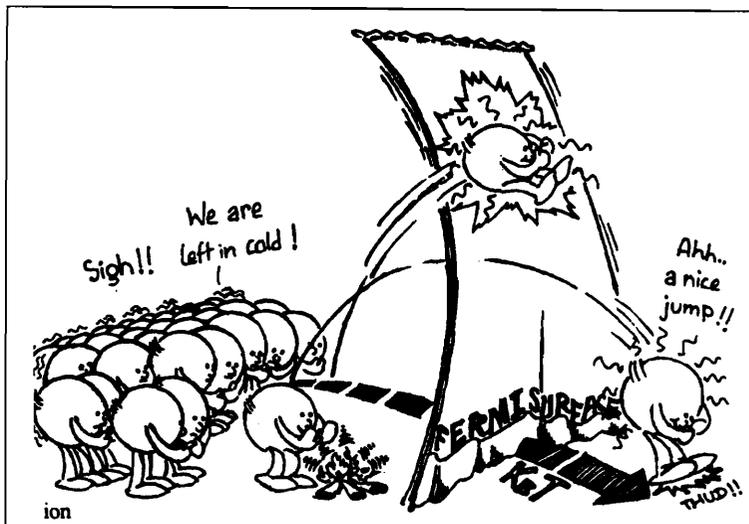
Electron Waves in Solids

In the 1920's, it became clear that electrons are waves (this is discussed in other articles in this issue). Electron waves of different wavelengths inhabit the solid, much like a string fixed at both ends supports different modes. In a large system, these modes are very closely spaced; the energy spacing between two successive modes goes inversely as the volume of the system. Now a given mode or wavelength state can be occupied by only two electrons, these differing in their intrinsic spin or magnetic moment orientation; this is the Pauli exclusion principle. So, at zero temperature, the lowest energy states are occupied one by one, up to a maximum depending on the number of electrons.

² k_B is Boltzmann's constant $\approx 1.38 \times 10^{-23}$ Joules per degree Kelvin. According to simple kinetic theory, a free particle has energy $3k_B T/2$ and a bound particle (like the aluminium ion) $3k_B T$. The specific heat is just the coefficient of proportionality between energy and T in this simple model.



Figure 2. Thermal energy can excite only a small fraction of the total electrons.



This maximum, called Fermi energy ϵ_F , is about 30,000 to 60,000 K in temperature units. (If we write $\epsilon_F = k_B T_F$, where k_B is the Boltzmann constant, then T_F is between 3×10^4 to 6×10^4 K. Suppose we heat this solid to a temperature T , i.e. give each electron an energy $k_B T$. The only ones which can actually increase their energy are the small fraction $(k_B T / \epsilon_F)$ situated near the Fermi energy. For the others, the states to which they could go on gaining an energy $k_B T$ are fully occupied! Thus the energy gained by a gas of N electrons is approximately $N k_B T (k_B T / \epsilon_F)$. The specific heat is the temperature derivative of this energy, and is $2N k_B (k_B T / \epsilon_F)$. The factor in brackets is the reduction with respect to a classical gas value due to the wave nature of the electron and the Pauli exclusion principle; it is only 1% or so at room temperature. So electrons cannot contribute much to the specific heat of metals at room temperature. Both this, and the linear temperature dependence (easily measured at low temperatures) are indeed in agreement with experiment.

Now consider the wavelength of the highest occupied electronic state. If this is the same as the lattice spacing, there is resonance; the electron is repeatedly scattered back and forth by the periodically arranged lattice of ions, the scattered and original waves have a definite phase relationship and there is interference.



This resonant interference lowers or increases the energy of the state by a discrete amount, called the *energy gap*. Thus when certain numbers of electrons (even numbers per unit cell) fill the solid, the next possible propagating state is separated from the highest occupied state by an energy gap. (The closely spaced occupied states form a ‘band’, called the *valence band*; the unoccupied or partially occupied states are part of the *conduction band*.)

Thus whether a crystalline solid is a metal or not depends on the number of outer electrons per unit cell of the crystal. If the number is odd, as in Cu where it is one, the solid is a metal. If the number is even, as in diamond or silicon where it is four, the solid can be an insulator. We say ‘can be’, because in a solid, the wavelength for resonance depends on the direction of propagation of the wave. Thus the energy after reduction (or increase) by the gap depends on direction; the highest occupied states may not then be separated by a gap from the lowest unoccupied states! So, for example, lead with four electrons per unit cell is a metal.

(Whether a solid is called a semiconductor or an insulator depends on the size of the band gap. If the band gap is about an

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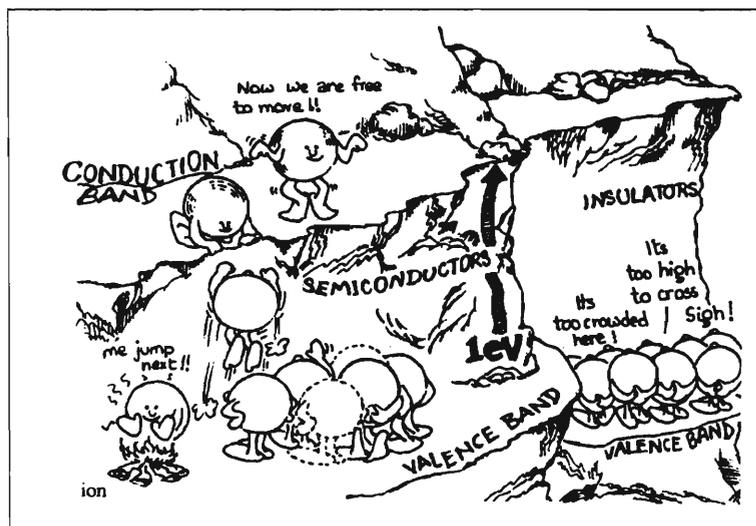


Figure 3. About semiconductors and insulators...

eV or less, sufficient electrons can be thermally excited across the energy gap so that the conductivity is 0.1 to 1 ($\text{ohm cm})^{-1}$ at room temperatures. Such substances are called semiconductors; those with a larger gap or lower room temperature conductivity are called insulators).

There are two spectacular ways in which this picture also fails; both are subjects of continuing attention, needing new ideas. One is the insulating nature of nonperiodic or glassy solids; some of the best insulators are glassy, even liquid!

The above basic classification of solids, depending on the periodicity of the solid, and on the wave nature of the electron, holds up generally, and is substantiated by detailed calculations of the energies of various modes, called *band structure*. There are two spectacular ways in which this picture also fails; both are subjects of continuing attention, needing new ideas. One is the insulating nature of nonperiodic or glassy solids; some of the best insulators are glassy, even liquid! The notion of band gaps mentioned above is tied to waves in a periodic structure, interference, electron count etc.. A new general idea, called localization of states in a random medium, is needed and has been developed to rationalize some properties of *nonperiodic* electronic systems. The other is the insulating nature of some periodic solids with *odd* numbers of electrons per unit cell; these ought to be metallic. For example, La_2CuO_4 has, in its square planar unit cell, one Cu^{++} O^{--} 'molecule'. O^{--} has a filled shell configuration, while Cu^{++} has nine d electrons in the outermost shell. It ought to be a metal, but is an insulator. What is the reason for the existence of such 'Mott' insulators? On replacing some La with Sr in La_2CuO_4 a *high temperature* superconductor $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($0.1 < x < 0.2$) is obtained, with unusual normal state properties. Does this have something to do with the parent compound being a Mott insulator? We do not know yet; questions of this sort are very much at the heart of modern condensed matter physics.

Unusual Lives of Interacting Electrons

We have pretended so far that electrons move freely in solids, or at best that they are aware only of the periodic arrangement of atoms which diffract them. This is surprisingly useful fiction.



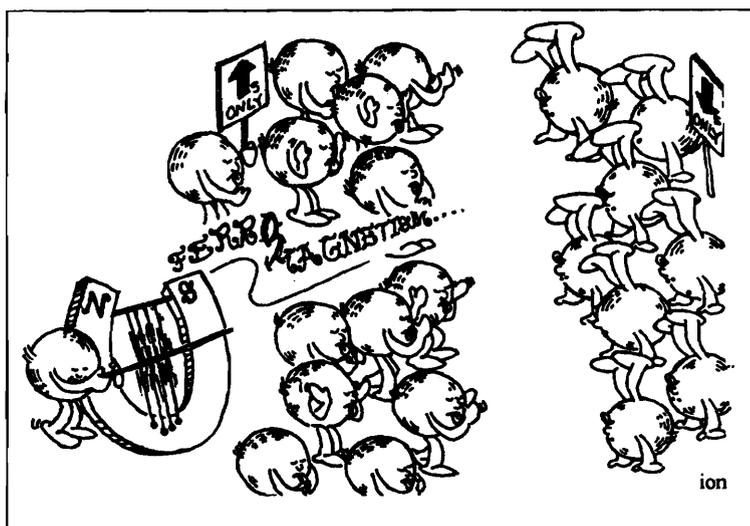


But there is an amazing variety of phenomena, possible only because electrons exert forces on each other; a small selection of these is presented here, with very sketchy explanations. The idea is to convey a flavour of the possibilities.

Ferromagnetism: Iron and many other metals, intermetallic compounds, alloys, and insulators, are magnetized below a certain temperature. The magnetic moments of the outer electrons spontaneously align themselves parallel to each other, at temperatures as high as a thousand degrees (1043 K for Fe). A little thought shows that this has to be due to interactions between electrons. First consider an atom. If the outer electronic shell is incompletely filled, the atom will have a magnetic moment. In solids this is mainly due to the intrinsic or spin magnetic moment of the electrons; the orbital moment is 'quenched' by the low local symmetry of the solid. So, each atom has a spin magnetic moment. Or does it? If electrons can move in and out of atoms in a solid, what is to preserve the magnetic integrity of each atom, its magnetic moment? Can there be magnetic moments in metals? It turns out there can be, but these are objects mixed with their surroundings, nonintegral in general and often disappearing at low temperatures. It is clear that the question of their ordering involves electrons being exchanged from one moment to the other. One can imagine two limits. The atomic limit is one where the intermoment electron mixing is weak. The energy of purely *magnetic* interaction between near neighbour moments (dipole-dipole interaction) is of the order of a few degrees Kelvin : ordering temperatures are more than a hundred times higher. So magnetic order has to involve exchange of electrons. The opposite is the itinerant limit, where the 'up' spin electrons and the 'down' spin electrons freely and separately (independently) move in the solid, forming bands. If they are truly independent, they will occupy the same energy levels one by one (Pauli exclusion principle) and there will be no net magnetization. There has to be repulsive interaction between up and down spin electrons; this gives *maximum repulsive* energy when their numbers are equal, and thus favours ferromagnetism

Can there be magnetic moments in metals? It turns out there can be, but these are objects mixed with their surroundings, nonintegral in general and often disappearing at low temperatures.

Figure 4. Repulsive interaction between UP and DOWN spins favours ferromagnetism.



(in which the numbers become unequal). So we see that ferromagnetism in metals requires exchange and interaction, and raises questions about the nature of moments in metals. These questions are not fully answered yet, even for iron.

Superconductivity: In 1908, Kamerlingh Onnes succeeded in liquefying helium at 4K or so. In the succeeding years, in his laboratory at Leiden, many solids were cooled in liquid helium, and their properties were studied. One aim was to check if as predicted by Drude, resistivity of pure metals continues to decrease as atomic vibrations are chilled out. This indeed happens; but mercury suddenly seemed to lose *all* electrical resistance below 4.2K or so. The resistivity of a mercury sample was observed to decrease from 40Ω at room temperature to about 0.08Ω at 4.3 K, and to then plummet suddenly to unmeasurably low values, below $3 \times 10^{-6}\Omega$! This new state of superconductivity (see R Srinivasan in Suggested Reading), discovered in 1911, took about fifty years to be fully understood. It occurs not just in mercury, but in many metals and alloys at low temperatures.

The superconductor is not just a perfect conductor with no electric fields \vec{E} inside it; it is also a perfect diamagnet with $\vec{B} = 0$! No magnetic field is admitted, as discovered by Meissner

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and Ochsenfeld in 1933. The perfect conductivity raises the following question: How is it that electrons that were being randomly scattered by various objects, causing electrical resistance, are no longer affected by the same objects at an infinitesimally lower temperature? The crude answer is that the entire collection of electrons in the superconductor goes into a single coherent state, which pervades the solid and is rigid against local deformations. What is the nature of this 'macroscopic quantum coherent' state? Bardeen, Cooper and Schrieffer, in their successful microscopic theory proposed in 1957, argued that electrons condense in pairs, and that these pairs are in phase with each other. Now, pairing of electrons seems unlikely; they *repel* each other electrically, and because of the Pauli exclusion principle, cannot be in the same state. Bardeen, Cooper and Schrieffer proposed an unusual mechanism of attraction. An electron whizzes past the lattice of ions, deforming it in some place. The ionic deformation being heavy, moves slowly. Another electron travelling in the opposite direction comes by later, and experiences the attraction due to this still present lattice deformation (caused by an electron no longer there!). The retarded (i.e. delayed) attraction mediated by lattice deformation (phonons) can overcome the instantaneous repulsion, and causes pairing of

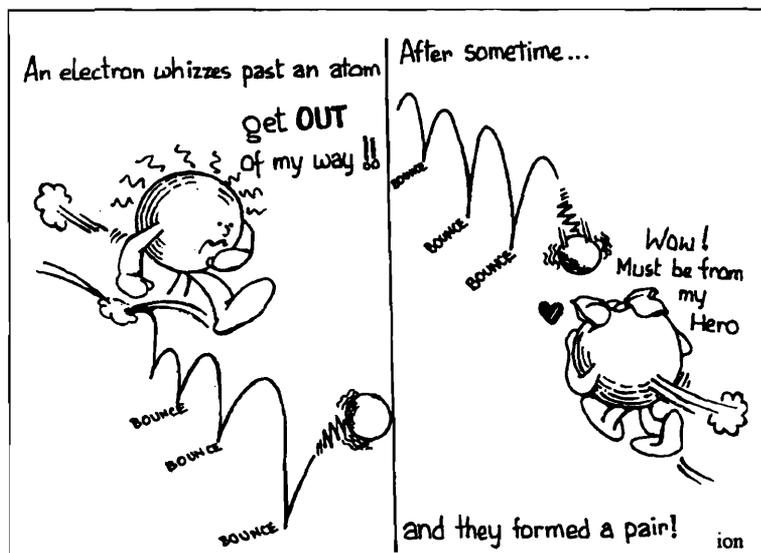


Figure 5. Pairing of electrons via lattice vibrations.

electrons with zero total momentum (and total spin). This mechanism seems to be the right one for many superconductors.

The recently discovered high T_c or cuprate superconductors, eg. $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, $\text{Ba}_2\text{Cu}_3\text{O}_7$ almost certainly become superconducting due to some other causes. Their metallic state above the superconducting transition temperature T_c is in detail unlike that of any metal we know. For example, the cuprates are metallic in the plane containing the Cu^{++} ions, but behave like an unusual kind of *insulator* perpendicular to the plane, and become bulk three dimensional superconductors below T_c . As mentioned earlier, the parent compound La_2CuO_4 is a Mott insulator (which orders antiferromagnetically at about 200 K). The Sr doped compound $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ is an unusual metal that becomes a high T_c superconductor. How does this transformation take place? We do not understand these mysteries yet; hopefully it will take less than fifty years.

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One very bizarre consequence of macroscopic quantum coherence is the effect theoretically predicted by Josephson in 1961 (he was a Ph D student at Cambridge then). If two superconductors are separated by a very thin insulating layer, a steady dc voltage difference, say V , can be maintained between them. When this is done, an ac signal, of angular frequency $\omega = (2eV/\hbar)$ is generated! The two superconductors are in single quantum states with precisely defined phases. The applied voltage changes the phase difference at a steady rate: $\dot{\phi} = (2eV/\hbar)$. The factor two is a giveaway; the phase is of charged electron *pairs*. Indeed the *ac Josephson effect* is observed, and is used among other things as a quantum voltage standard.

Metal - Insulator Transitions: One idea basic to our thinking of electrons in condensed matter, is the distinction between metals and insulators. In the former, occupied and unoccupied states near the Fermi energy are extended in space, and can carry current. In the latter, there is either a gap between extended occupied states and unoccupied states, or these states are local-



ized and unable to carry current. These seem fundamentally distinct phases electronically. Surprisingly, many systems undergo a transition from one to the other as some parameter is varied. One well known example is V_2O_3 , which on cooling suddenly becomes an insulator, with a millionfold increase in resistivity. How is it that electrons which were there (moving about, spread around) are no longer there?

In the last few years, another family of oxides eg $La_{2-x}Ca_xMnO_3$, has been extensively explored all over the world, including a group in Bangalore (C N R Rao and A K Raychaudhuri). These manganites show a transition from a high temperature paramagnetic insulating phase to a low temperature ferromagnetic metallic phase. The transition occurs at a temperature of about 230 K. Near the transition, a relatively small magnetic field of order a Tesla or so, can change the electrical resistivity by factors of two or more! This colossal magnetoresistance is astonishing because the energy scale associated with the magnetic field is $\mu_B H \cong 2$ K for 1 T. This is a hundred times smaller than the energy scale $k_B T_c$ of the transition, and ten thousand times smaller than electronic energies which are of order 10^4 K in temperature units. How can such a small change in magnetic energy make such a large change in physical properties? Can a small tail wag a big dog? We do not know the reasons yet. As it turns out for many fundamentally interesting phenomena, colossal magnetoresistance may also find applications, this time in magnetic recording.

Quantized Hall Effect: We conclude our selection of unusual doings of electrons in solids with a beautiful quantum effect discovered by von Klitzing in 1980. He was investigating anomalies in resistance and magnetoresistance of a gas of electrons confined to move in a plane. (This is achieved by a semiconductor arrangement called an inversion layer). A large magnetic field, of ten Tesla or more, is applied perpendicular to the plane, and the inversion layer is at a low temperature, of order a degree or so. Under these conditions von Klitzing found

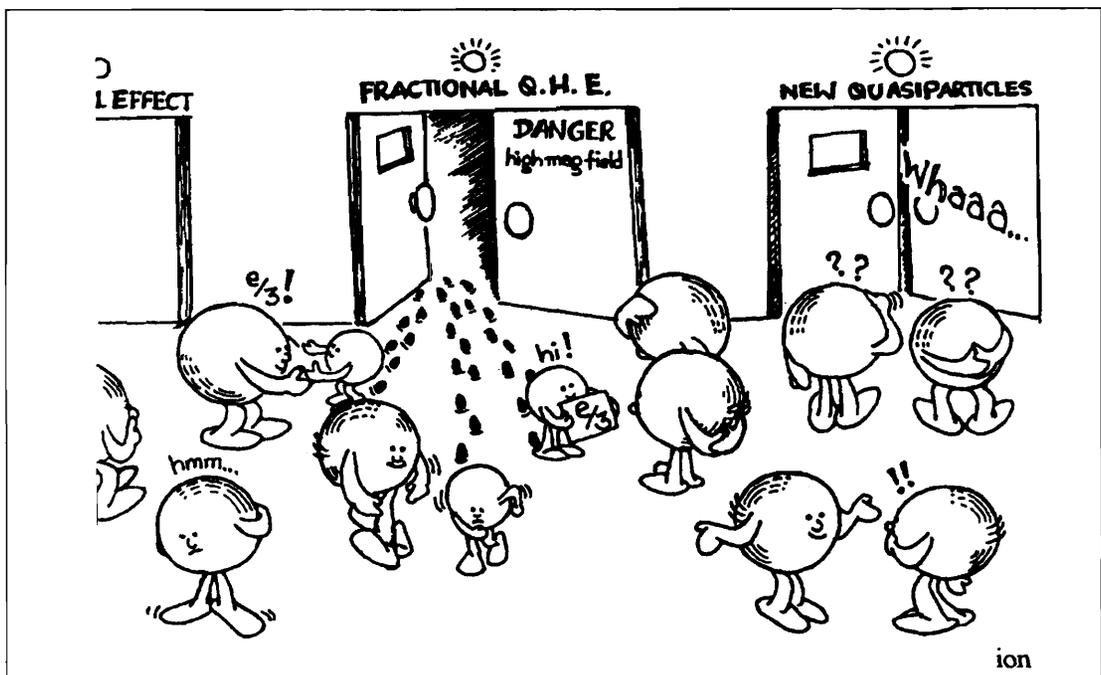


The quantized Hall effect is accurate and reproducible to a few parts in 10^8 ; there is a quantum resistance standard $(h/e^2) = 25812.80 \text{ W}$.

that the Hall resistance showed well defined plateaus as a function of magnetic field. The Hall resistance is the ratio of the in plane voltage developed across the sample, and the current flowing perpendicular to it in the plane. (The magnetic field is perpendicular to both). The surprising thing was the value of the resistance; it is (h/e^2i) where h is Planck's constant, e the electron charge, and i is an integer. Why is the Hall resistance quantized in terms of fundamental constants? How accurately is it quantized? We cannot here discuss the explanation, which finally has to do with the effect of a magnetic field on the phase of the electron wave, but the second question is easier to answer. So far as we can tell, the relation is exact. It is accurate and reproducible to a few parts in 10^8 ; there is a quantum resistance standard $(h/e^2) = 25812.80 \Omega$.

A few years after this discovery, in 1982, Tsui, Störmer and Gossard discovered the *fractional* quantum Hall effect, in which the conductance is not $i(e^2/h)$, but $\nu(e^2/h)$ where ν is an odd denominator fraction, e.g. $\nu = 1/3, 2/5 \dots$. An explanation of this

Figure 6. New quasi particles and an exciting future.





required completely new ideas, due to Laughlin (who also provided the general framework for understanding the integral quantum Hall effect). Strong magnetic fields, low temperature electron interactions and some disorder are essential to the observation of these unique quantum phenomena. Laughlin predicted that the lowest stable excited particle state for a $\nu = 1/3$ fractional quantum Hall state has a charge ($e/3$); its statistics is also fractional (it is neither a fermion nor a boson). Indeed such ($e/3$) charge excitations have been *directly* observed in electrical noise experiments at very low temperatures. So, as a consequence of interactions and magnetic field, new quasi particles are generated with fractional quantum numbers; they actually exist.

As the first century of our acquaintance with the electron nears its end, this most fundamental and stable of all particles seems to be coming apart, assuming unexpected forms. In systems containing many electrons that interact strongly with each other, the collection settles to some 'ground' state as disorderly thermal motions cease (i.e. as temperature $T \rightarrow 0$). Particle excitations out of this ground state, or excited 'quasi' particles can be quite unlike electrons in their basic properties. This is clear in several one and two dimensional systems. For example, in one dimension, for an interacting many electron system, there are excitations carrying spin but no charge, moving with a different speed from excitations carrying charge but no spin! (This is called spin-charge separation). In polyacetylene, namely $(\text{CH})_x$ (where x is very large, of order a thousand or more) there are alternating single and double carbon-carbon bonds; the molecule forms a long chain. One can have defects such as two double bonds or two single bonds adjacent to each other. It turns out that such defects are mobile, and have a charge ($e/2$) for the former and ($-e/2$) for the latter. We have already mentioned above the fact that if a collection of electrons moving in a plane is subjected to very high magnetic fields, for some density of electrons, the quasi-particle excitations have charge exactly ($e/3$). These examples illustrate strikingly the fact that the effective low excitation



energy degrees of freedom of a background interacting electron fluid can be qualitatively different from electrons. (This of course raises again the question: what is an electron? Is this charged magnetic clump of matter, the lightest member of a family, an excitation out of some more basic ground stuff?).

Considering the slow and sedate beginnings of our century old journey into the realm of electrons and their unexpected doings in condensed matter that we have come to know of in the last few decades, the next century promises to unfold wonderful new worlds.

Suggested Reading

- ◆ W Hume Rothery. *Electrons, Atoms, Metals and Alloys*. 3rd Edn. Dover Publication. New York, 1963. A book in the form of a dialogue between an older metallurgist and a younger scientist on the relevance of quantum behaviour of electrons to metallurgical phenomena.
- ◆ T V Ramakrishnan and C N R Rao. *Superconductivity Today*. Wiley Eastern. New Delhi. 1992. An elementary introduction.
- ◆ C Kittel. *Introduction to Solid State Physics*. Seventh Edition. (Wiley, New York. 1994. A standard text notable for its attention to phenomena and physical explanation.
- ◆ P W Anderson. *Physics Today*. October 1997. A stimulating essay on the unusual ways of electrons in condensed matter, by a master.
- ◆ R Srinivasan, *Resonance*, Vol.1. No.12, Vol.2. No.2, No.6, No.10.

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In science the credit goes to the man who convinces the world, not to the man to whom the idea first occurs.

Sir William Osler