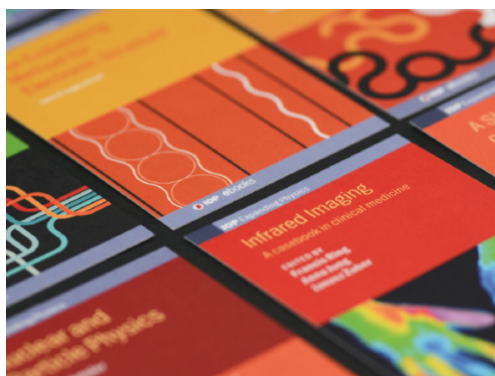# Excitons

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Excitons

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An exciton is a quantum of electronic excitation energy travelling in the periodic structure of a crystal; it is electrically neutral and hence its movement through the crystal gives rise to the transportation of energy but not charge. This is a concise description of the *ideal* exciton. We now try to give a more physical picture, to show some of the interesting properties, their observation and the importance of the concept of excitons in relation to metals and insulators. In the imperfect world of crystalline solids, we will also find excitons taking part in a number of optical effects such as luminescence, photographic process, photoconductivity, and so on.

The concept of excitons was first introduced by Frenkel in 1931 and Peierls in 1932 as the 'excitation waves' when light energy is absorbed and subsequently transformed into heat in solids. Frenkel considered simple solids in which the interaction between electrons from neighbouring atoms or ions is small compared with the forces holding the electrons within individual atoms. Solid xenon (inert gas) and sodium chloride (ionic compound) are examples of this type of solid. The electronic shells within each atom are always full, and the electrons are little affected by the presence of other atoms so long as they remain in the closed shells. These give rise to the property of almost complete inability to conduct current – an insulator. Let one of the atoms in the solid be excited, or more precisely let one of the electrons be given sufficient energy to come out of its closed shell by absorbing a quantum of light, then the minimum energy required for this excitation is that which results in a stable bound state of the electron and its parent atom (ion). The electron is moving in the space influenced by the positive charge field created by its own absence from the closed shell. In solid state physics, the latter is called a 'hole'; it is treated as though it has all the properties of an electron except for its positive charge. Quantum theory will show that there is not just one but a series of bound stationary states, leading up to a series limit. The energy corresponding to the series limit is simply that required to produce a free electron and a hole in the solid. These energies of excitation, in the form of the bound stationary states of an electron–hole pair are not bound to any particular ion, but are capable of passing from one ion to the next and thence to the next and so on through the crystal, constituting what Frenkel called 'excitation waves' or excitons. It can also be seen that since the electron–hole pair moves bodily through the crystal, there is no net flow of charge. The existence of bound stationary states follows from the fact that the electron is attracted to the hole by the Coulomb potential energy $-e^2/\varepsilon r$ where r is the distance between them and ε the appropriate dielectric constant. ε determines the screening effect on the potential energy of the background, which consists of all the atoms and any free electrons present, and ε plays an important role in the properties of excitons. We know that for a hydrogen atom ε is unity (in free space); but in a solid ε may be quite large, of the order of 10 for a semiconductor and about 2 for an ionic crystal. The potential energy is therefore correspondingly reduced. When the electron–hole distance which we shall call the exciton 'radius' is large and covers many atomic sites, an average effect of other atoms can be represented by the high frequency value of ε. However, in the insulating solids that Frenkel considered, the radius of the lowest energy exciton is often comparable or less than the interatomic distance; clearly a different and smaller value of ε should be used. Consequently, we have a relatively large potential and a somewhat localized excitation. It also means that an additional large amount of energy will be required in order to ionize the exciton to produce a free electron and hole. We will see this more clearly later. The excitons we have so far considered are those in which the electron and the hole are tightly bound and localized. These form a class known as 'Frenkel' excitons.

A slightly different approach was formulated by Mott and Wannier in 1936 for those excitons with large radius, and in solids where the valence electrons are no longer identifiable with any atom. Many semiconductors, particularly the so called covalent solids such as germanium, silicon, gallium arsenide and cuprous oxide and so on, are of this type. In these solids, the interaction between neighbouring atoms has significantly increased, and the valence electrons

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are usually shared by a number of atoms to form bonds. The electrons have gained the spatial volume in which to move, they are, however, still not free to contribute to an electric current when the solid is subject to ordinary electric field. The valence electrons occupy states which complete an energy band known as the valence band. The next allowed states for the electrons are in the conduction band and are separated by an energy gap from the top of the valence band. It can be shown that as the interaction between neighbouring atoms increases, so will the extent of the valence electrons in space and the width of the valance band, accompanied by a reduction in the energy gap. The ionic solids discussed earlier are therefore merely a limiting case, having a narrow valence band and a large energy gap. If now a photon is absorbed by such a semiconductor, one of the valence electrons will be excited, leaving a vacant state in the valence band – a positive hole. This will attract the electron to form an exciton. The potential energy which binds the electron and hole together is much weaker than that for the ionic crystal. The radius of the exciton is large, covering many tens or hundreds of atomic sites. We are now justified in using a single dielectric constant, and with Bohr's quantum theory to derive a formula for the energy E_n of the exciton series, we have

$$E_n = E_\infty - \frac{R}{n^2},$$

where $n = 1, 2, \ldots$ and $R = m^* e^4 / 2 h^2 \varepsilon^2$.

This formula is essentially similar to that first derived to account for the spectral lines in a hydrogen gas discharge. E_∞ is the series limit (a constant), n is a quantum number, and R the binding energy (known in atomic physics as the Rydberg constant), R represents the energy required to ionize an exciton in its lowest energy state, that is, the energy separation between the lowest bound state ($n = 1$) and the series limit, and is very much smaller than that for a hydrogen atom. This is clearly shown to be due to the introduction of the dielectric constant ε, and to a lesser extent, a smaller value of the reduced effective mass m^* of the electron–hole system. For a typical covalent semiconductor, $\varepsilon \approx 10$ and $m^* \approx 0.2 m_e$ ($m_e =$ free electron mass). Accordingly, R for the exciton is about 500 times smaller than that for a hydrogen atom, that is approximately $13.6 \times 1/500 \approx 4.806 \times 10^{-21}$ J. The observation of a series of absorption lines, leading up to a continuum in many substances such as cuprous oxide and cadmium sulphide, is in agreement with the hydrogen-like formula (figure 1); and this verifies the existence of the weakly bound excitons in which the electron–hole separation is large compared with the interatomic distance. This type of exciton is more

commonly known as a 'Mott–Wannier' exciton. If we take the values of ε and m^* for the ionic solids, we find that for a 'Frenkel' exciton R is about 1.6×10^{-19} J, a very different magnitude indeed!

So far we have not considered the effect of the lattice vibrations on excitons, but assumed an ideal situation in which all the atoms in the solid are stationary and arranged in a perfectly periodic manner. In a real crystal, however, every atom is vibrating about its equilibrium position, even at the absolute zero (zero point energy). The energy of an exciton, instead of being uniquely defined by E_n as given by the hydrogen-like formula, is modified by the vibrational motion of the atoms, to spread over a band of allowed values. The extent of this broadening increases with temperature and the effect can be seen in the width of the exciton absorption line in spectra taken at different temperatures. Lattice vibrational energy is measured as kT, where k is the Boltzmann constant and T the temperature in kelvin. For example, at room temperature $T = 295$ K, kT is approximately 4×10^{-21} J. In comparing this figure with the binding energies of excitons, we find that the absorption line of a 'Mott–Wannier' exciton at room temperature will be too broad to be observed, while that of a 'Frenkel' exciton will only be slightly affected. Therefore in order to study the exciton series, experiments are usually performed at very low temperatures, often at the temperature of liquid helium (4.2 K).
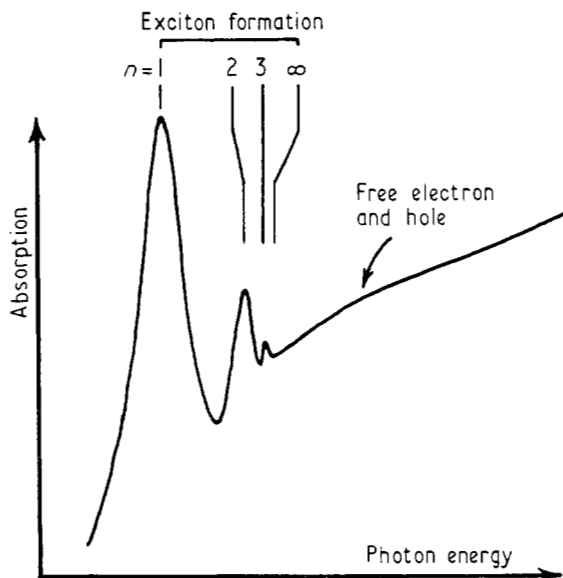

Figure 1 *Absorption curve of a semiconductor at low temperature, showing strong absorption peaks due to 'Mott–Wannier' exciton series ($n = 1, 2, \ldots \infty$) and the 'continuum' absorption due to 'free electrons and holes' at higher energies.*

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There is yet a third type of exciton known as the 'Davydov' exciton. It is found in organic substances having units of rings such as benzene or anthracene. The ring as a whole may be excited by the absorption of light, and the energy of excitation can also be passed on from one ring to another. Since the interaction between neighbouring rings is small compared with the interatomic forces within the ring, 'Davydov' excitons are localized and resemble the 'Frenkel' exciton.

We have seen how lattice vibrations affect the width of the exciton absorption line. When the thermal energy kT is comparable with the binding energy of the exciton, the exciton can be ionized to produce a free electron and hole which are then current carriers. Thus if light is absorbed under this condition, the conductivity of the crystal will increase. The increase in conductivity following the absorption of light is known as photoconductivity. There are other ways too, by which an exciton can be ionized. A crystal normally has a large number of imperfections such as vacancies, interstitial defects, dislocations, foreign atoms and even the surfaces of the crystal; all contribute towards destroying the perfect periodicity of the lattice. When an exciton meets one of these irregularities, ionization can take place and photoconductivity will be observed. The collision of two excitons can also cause ionization but the probability of this happening is relatively small unless we use laser beams. Next we come to the photographic process, that is, the darkening of silver halides under the action of light. This in many ways is similar to photoconductivity. When an emulsion plate of say silver bromide is exposed to light corresponding to the exciton energy, excitons are formed and are subsequently ionized by the various mechanisms described above. The free electrons in particular will be reunited with the positive silver ions to form neutral atoms, whose concentration increases with the intensity of light. Of course, both photoconductivity and photographic processes are also observed at light energies greater than the exciton continuum.

Once an exciton is created in a solid, the energy of excitation can be dissipated in three ways: by conversion into heat energy through collisions with the lattice, by ionizing to give free electron and hole, and by returning to the ground state accompanied by the emission of light. The last mechanism is known as luminescence, and it has many industrial applications such as solid state light panels and solid state lasers. It is essential that an exciton in luminescence should be stationary about a given site in the crystal and this is known as 'trapping'. Lattice imperfections or lattice vibrations can provide the trapping centres. In the latter case, the nuclei of the atoms round the excited atom can be seen to take up positions of lower energy. Consequently, the energy of excitons if it is re-emitted as light will be observed as quanta of lower energy.

We have seen that the Coulomb potential energy in a semiconductor is modified by the dielectric constant ε. In a solid where free electrons are present, the Coulomb potential is severely screened and the potential is more appropriately represented by

$$-\frac{e^2}{r}\exp\left(-\frac{r}{\lambda}\right),$$

where λ is the screening length which defines the distance beyond which the potential rapidly approaches zero. λ is related to the density of the free electrons such that λ is small for a large density. In the field of the screened Coulomb potential, the formation of bound electron–hole pair states depends on the screening length or the density of free electrons present. Therefore, depending on whether excitons are observed, a solid is said to be a semiconductor (with excitons) or a semimetal (without excitons). The density of free electrons in a semiconductor can be controlled by various artificial means such as the introduction of suitable impurities, application of pressure or changes of temperature. This controlled condition can bring about a transition between a semiconductor and a semimetal in the same solid.

It should be emphasized finally that the understanding of excitons was made possible only after the discovery of quantum theory. An exciton is a quantum of excitation and hence a psuedoparticle. There are many other forms of excitation which are also quantized. Among them, lattice vibrations have the greatest influence on excitons. In some ionic solids, these two forms of excitation may be coupled and give rise to a new pseudoparticle known as the 'exciton–phonon complex'.

In addition to the topics already considered, excitons could play a part in superconductivity and in the transport of energy in biological systems.

Praeceptor