The Quantum World

I. Quantization

In classical physics it was presumed that, except for cases related to counting, physical quantities vary continuously. Ultimately this was based upon our experience. But that experience was so universal as to become ingrained in western thinking as a philosophical necessity!

How could an object move, for example, from A to B without touching all the points, P, *between* A and B along *some* path?! More generally, for any quantity, Q, that could, in principle, take on any value: how could Q possibly change from any value, q, to any other, different value, q', without passing through all the values between q and q'?

But this presumption led to the first paradox in classical physics which helped to produce the quantum revolution! To tell you that story I have to simplify it a bit. The historically accurate rendition is sufficiently convoluted, not to say incoherent at times, that presenting it in detail would seriously interfere with my pedagogical intention.

1. Thermal (Black Body) radiation: The problem was this. Suppose you had **electromagnetic waves** (What's that?) trapped in an oven. And you kept the temperature of the oven fixed at some value. It didn't really need to be hot. Any temperature above absolute zero would do (Absolute zero is roughly -273 degrees Celsius). So the enclosure didn't really need to be an oven. It just needed a fixed, non-zero, **absolute temperature** ($T \simeq T_C + 273^0$).

Now one would expect, and experience seemed to confirm, that if the waves inside had very little energy they would absorb some energy from the inside walls of the 'oven'. And if the waves had lots of energy they would give up some energy to the 'oven' walls. Eventually the give and take of energy would leave the waves with just the right energy to be in **thermal equilibrium** (What's that?) with the 'oven'.

But a straightforward (and non-controversial) calculation unequivocally led to the conclusion (late 19th century) that every **independent mode** (What's that?) of oscillation represented in the waves inside the 'oven' would carry,

when thermal equilibrium was reached, an average energy of kT (where k = 1.4 x 10^{-23} J/ ^{0}K , is called **Boltzman's constant**[1] and 1J = 1Ws ~ (1/4)cal. Is a unit of energy). For any range of **frequencies** (What's that?) of oscillation of the waves, any mode of oscillation with a frequency lying in the range would, on average, have energy equal to kT if it was in thermal equilibrium with the 'oven'. If it, momentarily, had less energy than that, it would absorb some from the 'oven'. If it had more than that, it would give some to the 'oven'. For ordinary temperatures, kT is a very small amount of energy!

The problem was that there would always be an *infinite* number of modes with various frequencies present in the 'oven'. But (infinity) times 3kT equals infinity. So the *total energy* carried by all the electromagnetic waves would be infinite at thermal equilibrium! Since an infinite amount of energy is hard to come by, *thermal equilibrium would never be reached!* The lower frequency modes would achieve their kT allotment first and then higher and higher frequency oscillations would just keep absorbing energy from the 'oven' indefinitely. But this was absurd and well known not to happen (**Fig. 1.1**)!
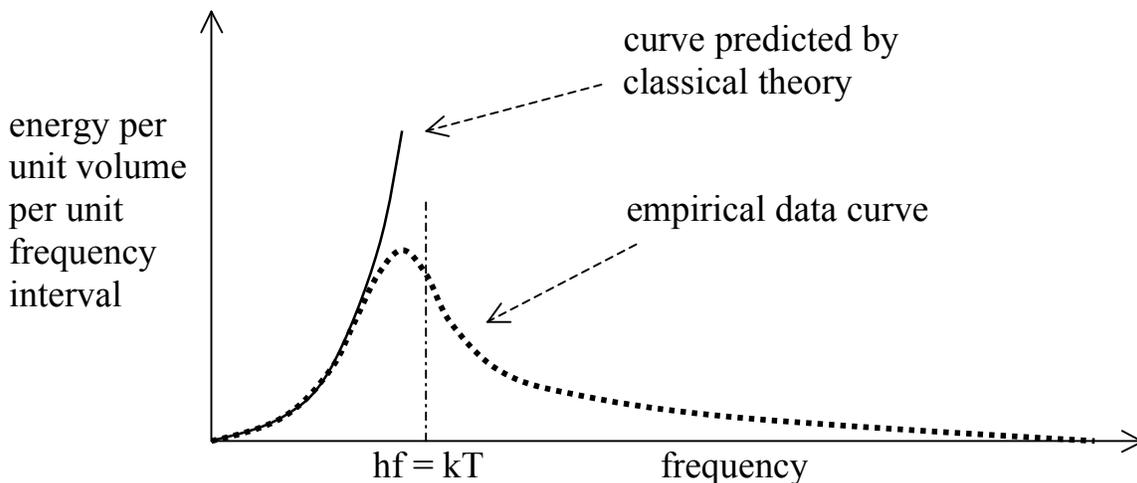

Fig. I.1: Thermal, 'Black Body' radiation curve. Classical theory versus experimental data for the distribution of energy with frequency for thermal radiation at a definite temperature. The total energy per unit volume is proportional to the area under the curve, finite for the experimental curve, infinite for classical theory. The classical, theoretical energy density per unit frequency interval grows with frequency because at higher frequencies there are more modes per frequency interval.

That 'straightforward', classical calculation required little more than the assumption that the energy carried by a wave of any frequency could, would and must *vary continuously*. In particular that it could change by arbitrarily small amounts.

By 1900 Max Planck[2] had been studying this kind of **thermal** (so-called **Black Body) radiation** for some time. And by using the best available data to get hints as to how one should try to modify the relevant equations he found equations that fit the data wonderfully if one fiddled with some parameters! But they made no sense when interpreted along the lines of the 'straightforward' calculation. So the problem was to find out what these new, empirically correct equations meant (**Math. Appendix 1**).

Eventually Planck realized that his new equations could be understood if one abandoned the assumption of continuous variation of energy. He saw that the empirical equations would hold if oven **molecules** (the smallest unit of a chemical substance) vibrating with frequency, f, could only exchange energy with the modes of EM radiation of the same frequency in amounts of hf, a **quantum** of energy, where h was a constant that Planck would evaluate by comparison with those earlier fiddled parameters (**Fig. I.2**). The energy values of vibration for the oven molecules were restricted to nhf, where n was 0, 1, 2, - - etc.

0   E   ∞
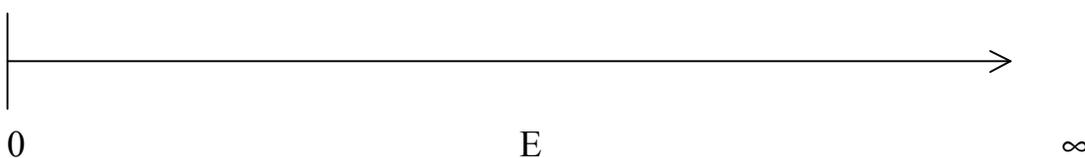
Continuous possible energy values for *classical* radiation modes of any frequency

0   hf   2hf   3hf   nhf

Fig. I.2: Planck's *quantized* possible energy values for radiation modes of frequency, f, due to restricted energy exchange with oven molecules.

For those frequencies for which hf $\ll$ kT, the energy quantum is too small to interfere with the random energy exchanges between the oven and the radiation of the classical argument. At such low frequencies the average energy per mode *was* kT. But at the higher frequencies, for which hf ~ kT, or greater, the larger quantum interferes with the energy transfer and the average energy per mode of the radiation decreases with f.

We call h **Planck's constant**. This quantization hadn't been noticed earlier because h was so small. In fact, h = 6.6 x 10^{-34} J-sec. But while *we* call it Planck's constant as an act of veneration, the earliest references to it were almost derisive! The idea of **quantized energy values** seemed so extreme no one took it seriously at first. The good fit was regarded as a fluke! Indeed, Planck, himself, initially regarded the idea as merely provisional.

Seven years later Einstein[3], recently famous for his **Special Theory of Relativity** (What's that?) and his explanation of the **photo-electric effect** (which we will discuss in part **II**), noted that Planck's idea, when applied to cold solids, could explain the fact that the colder a solid was, the less heat was required to raise its temperature by one degree Kelvin[4] (this required heat is called the **heat capacity** of the solid).

2. Heat capacity of solids: This was a puzzle for the same reason that the radiation in the 'oven' was 'required' to have infinite energy at thermal equilibrium.

The molecules comprising a solid would, just like the oven molecules above, oscillate like springs (see **Fig. A1 – 3** in **Appendix A**) about their average position in the solid as a consequence of thermal energy in the solid due to its temperature. If the solid was homogeneous and not too warm it was reasonable to expect that all the molecules would oscillate with the same frequency, f. Each molecule had 3 independent modes of oscillation in mutually perpendicular directions. Because of the classically presumed continuously variable energy of oscillation the same 'straightforward' calculation I mentioned before required the average energy of an oscillating molecule to be 3kT, and quite independently of the frequency of the oscillation. This didn't lead to infinite energy in the solid because there weren't an infinite number of molecules. But there was a *large* number; call it N. Then the total thermal energy in the solid would be 3NkT.

So to take the solid from temperature T_0 to the temperature $T_0 + 1^0K$ would require adding heat to the solid in the amount of $3Nk(1^0K)$, a value *independent of the temperature* at which one started. But this too was well known not to happen (**Fig. I.3**).

At *ordinary* temperatures the amount of heat that had to be added *was* independent of the temperature. This was known as the (experimental) **law of Dulong and Petit**. But when the temperature got very low, the amount of heat required to raise the temperature by 1^0K got lower and lower as well.
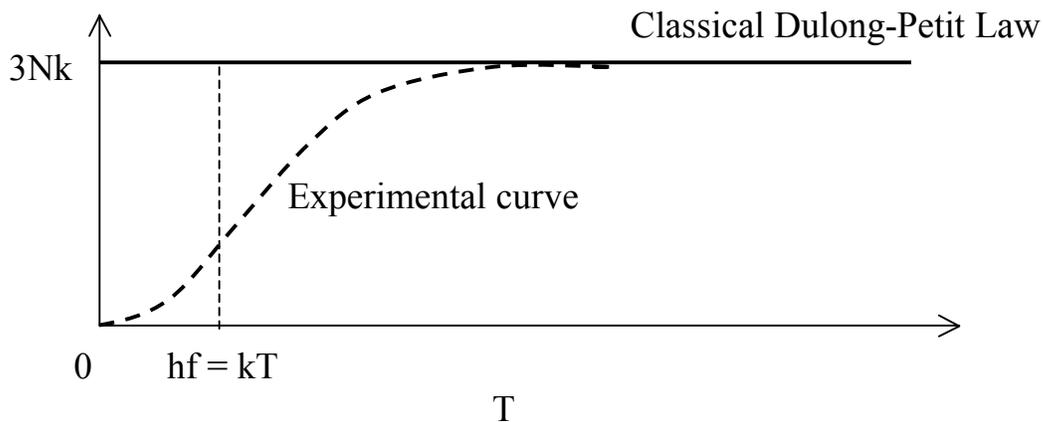

Fig. I.3: Deviation of heat capacity of solids from classical theory at low T.

By restricting the possible energy values of the molecular oscillators to Planck's conjectured nhf (**Fig. I.4**), Einstein showed that one could explain the decreasing heat capacity with decreasing cold temperature as well as the Dulong – Petit law at ordinary temperatures. When T was large enough so that kT >> hf, the gap presented no obstacle to random energy exchanges between molecules and the environment. The effect of the gap was indistinguishable from being zero in value. But when kT dropped to values of the order of hf or lower, the gap became more and more effective in obstructing energy exchanges and in lowering the average molecular energy below 3kT.

Now people started to take Planck's ideas seriously!

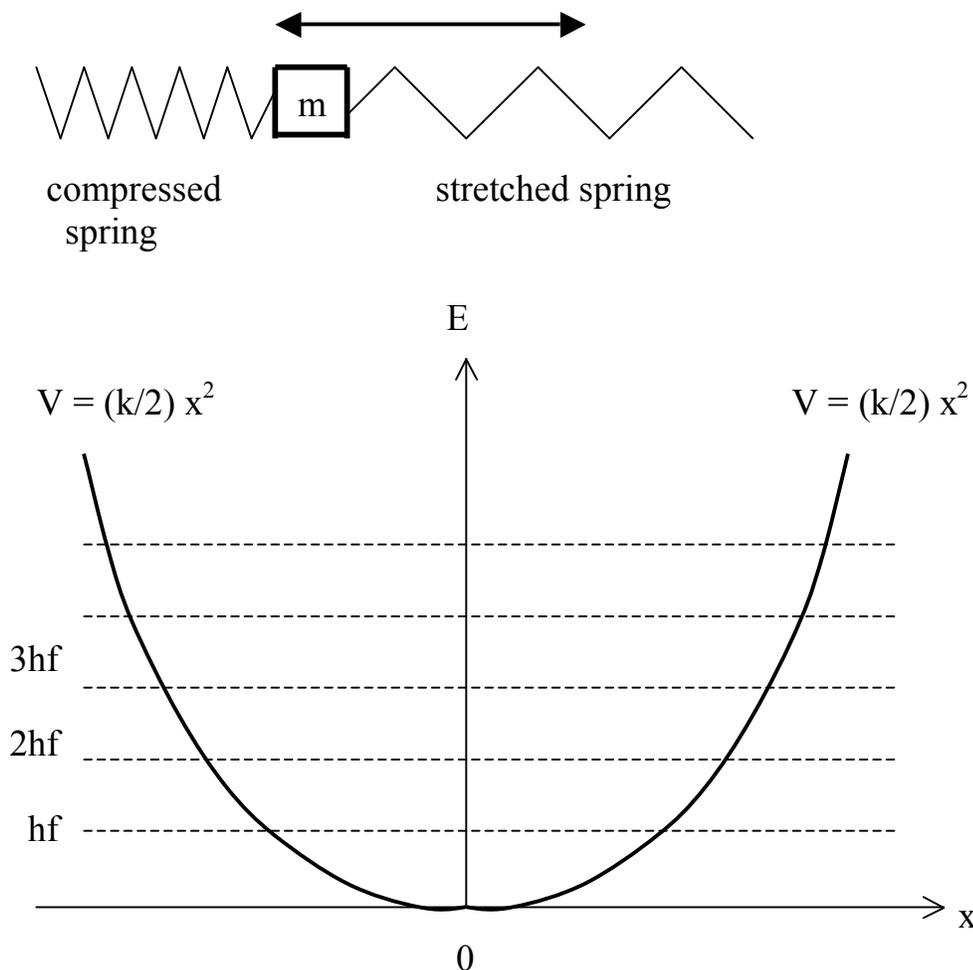The next step came with Bohr's[5] model for 'simple' **atoms** (the smallest unit of a chemical element).

Fig. I.4: Possible energy levels of a molecular oscillator. $f \propto \sqrt{(k/m)}$.

3. Atomic structure: By 1913 it seemed pretty clear that atoms consisted of two parts. First there was a tiny center, or **nucleus**, (discovered in 1911 by Rutherford[6]) that contained almost all the mass of the atom and a positive electric charge. Second, there was a collection of negatively charged **electrons** (discovered in 1897 by Thompson[7]) – just enough of them to balance the positive charge of the nucleus. These electrons, with very little mass, were, presumably, held in orbits around the nucleus by the electric attraction between the negative electrons and the positive nucleus (see **Fig. A4-6**). The orbits were thought to be enormous in size compared to the tiny nucleus but no one had a really good value for the exact size.

But there was a real problem with this picture! Orbiting electrons are *accelerating* electrons. And accelerating charged particles should, according

to classical physics, continuously radiate away electromagnetic energy in the form of waves, (as electrons do when they are accelerating back and forth in a radio transmission antenna). As the electrons radiate energy away their orbits should spiral into the nucleus and the atoms should quickly collapse. Furthermore, while they're doing this, the escaping radiation should display a continuous range of frequencies.

Clearly this was not happening. Atoms were rather stable systems (lucky for us!), they did not undergo this spiraling collapse. And while they did radiate electromagnetic waves under certain conditions (when heated, for instance) the radiation always contained only very specific separated frequencies, characteristic of the type of atom in question, i.e. **Hydrogen, Helium**, etc.

Bohr discovered that the peculiar frequencies emitted by Hydrogen atoms, with one orbiting electron, and those emitted by other atoms in which one outermost electron was doing almost all the radiating (so-called **Hydrogenic atoms**), could be understood if one assumed two bizarre things.

(1) That the electron in question was only permitted circular orbits in which the **angular momentum** (What's that?) of the electron had one of the values, $nh/2\pi$, where n was a non-zero integer. (2) That the electrons only radiated when they *jumped* from one allowed orbit to a lower energy orbit and then the frequency, f, of the emitted radiation was given by the change in energy,

$$hf = \text{minus the change in electron energy} = E_i - E_f.$$

The success of this idea was really strange since, among other things, it meant that the connection between the frequency of the emitted radiation and the orbital frequency of the orbiting electron was very tenuous.

Nevertheless, it gave the Hydrogen atom energy values as ε_0/n^2, where n was an integer, n = 1, 2, 3, - - - , and $\varepsilon_0 = -13.6$ ev, the *ground state energy*, and these values accounted for the observed frequencies of electromagnetic radiation emitted from Hydrogen (**Fig. I.5**). The model also gave definite values for the orbital radii of the electron and the radius for the ground state (the other radii are larger), was $a_0 \sim 10^{-10}$ m $\underline{=}$ 1 **Ångstrom**, the 'size' of the atom (See **Math. Appendix 2**).

In the next years the restriction to circular orbits was relaxed to allow for elliptical orbits that, via a solar system analogy, the **inverse square force** (What's that?) would lead one to expect. This change improved agreement with some experiments. Later, in the mid twenties, the whole idea of precise orbits
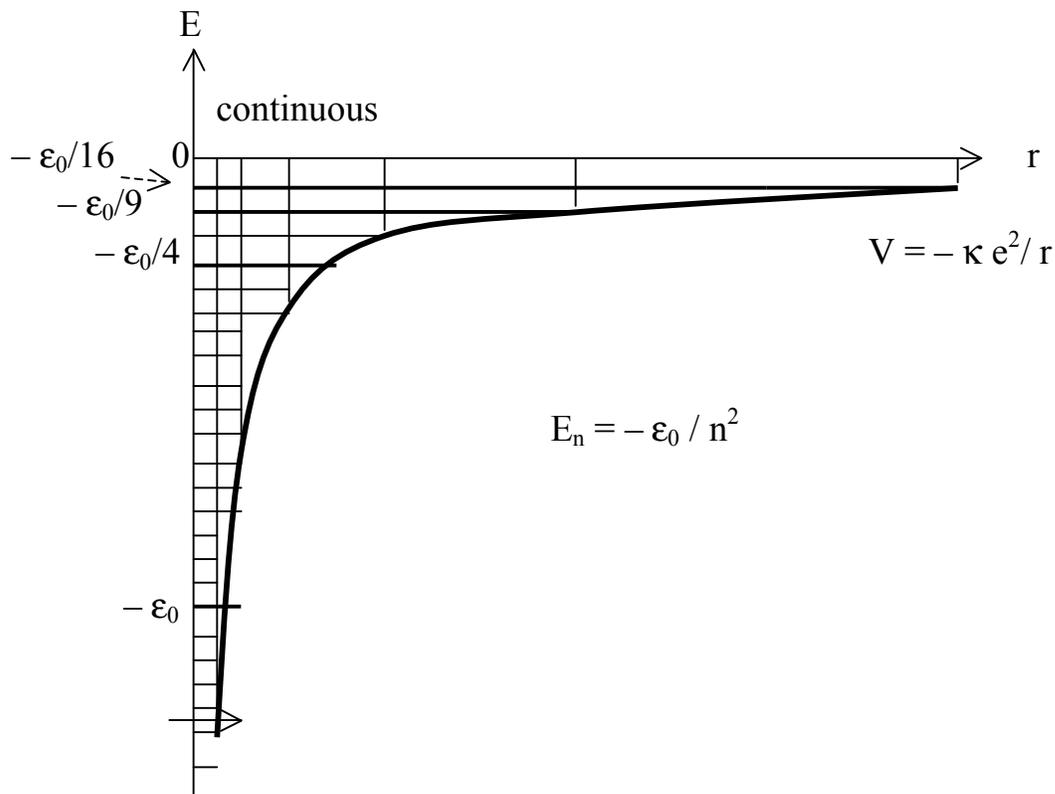

Fig. I.5: Energy relationships and Coulomb potential energy for the Bohr model of the Hydrogen atom. ε_0 = 13.6 ev

was completely abandoned (as we will see later) but the quantization of both the energy values and the orbital angular momentum was retained in an improved form.

Finally, in this first account of the march towards quantization of previously continuous physical quantities, we find Wolfgang Pauli[8], trying to improve the account of the basic regularities of the **Periodic Table of the Chemical Elements** (What's that?)(These regularities had come to be regarded as determined by the orbital behaviour of the 'outer' electrons in an atom).

Pauli succeeded by first attributing a "mysterious two valuedness" to electrons and then declaring that no two electrons are ever permitted to be in exactly the same situation, or *physical state* in an atom. This assertion was called the **Pauli Exclusion Principle** and the "two valuedness" was soon interpreted as due to two possible directions of an intrinsic or *spin* angular momentum of the electron.

4. The conditions for quantization: In standard quantum theory there is no quantization of position or velocity or momentum. These quantities can acquire any value in a continuous range from negative infinity to positive infinity just as they could in classical physics. So why angular momentum and energy?! What's so special about them? At the deepest level, of course, we just have to say - - that's the way nature is, live with it. But there is a unifying notion that may be helpful.

First we note that *angular momentum is always quantized*, and, in a precise sense (to be made clear below), always the same way. In contrast, energy values are not *always* quantized: the energy of a free particle is not quantized. Even if a system is not free but is subjected to forces, if those forces allow the system to roam arbitrarily far from its starting place, the energy of the system is not quantized. But if the system is constrained to remain, at least most of the time, within some finite volume by the forces, then the energy is quantized.

Secondly, we note that angular momentum describes the quantity of rotational motion a system possesses. But rotational motion, by itself, never takes one arbitrarily far away. Any part of a purely rotating system always returns to its starting place and never goes too far away. That's the unifying key – confined motion!

The *otherwise familiar quantities* that become quantized in the quantum world are only those that have a close relationship to confined motion.

5. Angular momentum and a paradox of quantization: As mentioned above, the quantization rules for angular momentum are universal. All angular momenta are restricted to values that can be relatively simply characterized. Within the restriction there are three subclasses that we will discuss in later parts of this course. For now we will consider only the general characterization.

Like velocity, angular momentum is a quantity having both magnitude and direction, a so-called *vector* that can be represented by an arrow. The direction is usually parallel to the axis of the rotational motion being described and points along the stretched thumb of the right hand with the fingers of the right hand curling in the direction of the rotational motion (**Fig. I.6**).
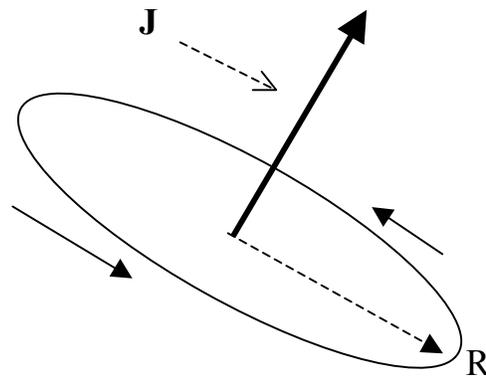
Fig. 1.6: Angular momentum

For the simple case of a material circular rim of mass, M, and radius, R, rotating, with rim speed, V, about its central axis once every time interval, T, the magnitude of the angular momentum is given by,

$$J = M R V = M R (2\pi R / T) = 2\pi M R^2 / T.$$

Like all vectors, angular momenta have *components* relative to specified directions (**Fig. I.7**). A component is determined by passing a line in the specified direction through the origin of the vector and then dropping a perpendicular from the end of the vector to the new line. The component is
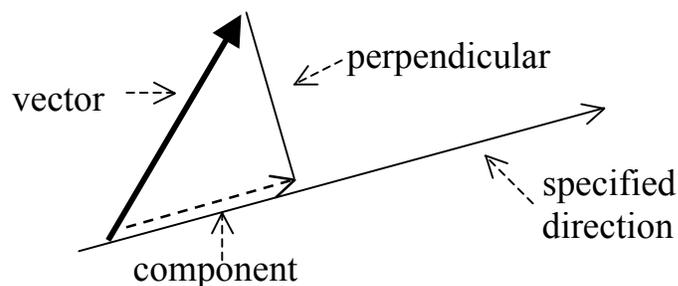
Fig. I.7: Component of a vector relative to a direction

the magnitude of the directed interval from the origin of the vector to the intersection of the new lines. Notice that if the vector in **Fig. I.7** was leaning enough to the left instead of the right, the component would point opposite to the specified direction. In such a case we append to the component a negative algebraic sign.

It is a consequence of the *Pythagorean theorem* (What's that?) that if x, y and z denote any three, mutually perpendicular directions, then for any vector, **V**, with magnitude, V, and component values, V_x, V_y and V_z in the given directions, we have,

$$V^2 = V_x{}^2 + V_y{}^2 + V_z{}^2.$$

But applying this theorem to *quantized* angular momentum gives rise to an apparent paradox, the first of several in the quantum world.

The quantization rules for angular momentum are:

(1.) The only precise values the squared magnitude, J^2, can ever have are,

$$(h/2\pi)^2 \, j(j + 1) \quad \text{where} \quad j = 0, 1/2, 1, 3/2, 2, \text{ - - -}$$

(For comparison, the angular momentum of *anything* you've ever come across that you *noticed* was rotating, had a *very* high value of j!).

(2.) *For a given value* of j, the only precise values the components, J_x, J_y, J_z, can have take the form, $(h/2\pi) \, m_{x, y, z}$, where $m_{x, y, z}$ each, have one or another of the $2j + 1$ values,

$$m_{x, y, z} = -j, -j + 1, -j + 2, \text{ - - - }, j - 2, j - 1, j,$$

independently.

From Pythagoras we have $J^2 = J_x{}^2 + J_y{}^2 + J_z{}^2$. Now consider the low j values.

For j = 0, we have $m_{x, y, z} = 0$ and Pythagoras asserts $0 = 0 + 0 + 0$. OK!

For j = ½, we have $m_{x, y, z} = \pm \, ½$ and Pythagoras asserts

$$1/2 \text{ x } 3/2 = (1/4) + (1/4) + (1/4) . \qquad\qquad \text{OK!}$$

For $j = 1$, we have $m_{x, y, z} = 0, \pm 1$ and Pythagoras asserts

$$1 \times 2 = (0 \text{ or } 1) + (0 \text{ or } 1) + (0 \text{ or } 1) . \quad \text{Just barely, but OK!}$$

For $j = 3/2$, we have $m_{x, y, z} = \pm 1/2, \pm 3/2$, and Pythagoras asserts

$$3/2 \times 5/2 = (1/4 \text{ or } 9/4) + (1/4 \text{ or } 9/4) + (1/4 \text{ or } 9/4) . \quad \text{No way!}$$

Apparently the square of the magnitude of an angular momentum can sometimes have a precise value that can not possibly be the sum of the squares of any allowed precise values of its Cartesian components! That *seems* paradoxical. Many other examples like this exist.

The reason these restricted possible values for the total magnitude and the components of angular momenta seem to lead to paradoxical contradictions is that we quite naturally assume that any quantitative property of a physical system *always possesses* one or another of the precise values that it is allowed to possess. But how could it be otherwise?! We shall see.

Footnotes:

1: Ludwig Boltzmann (1844 – 1906)
2: Max Planck (1858 – 1947)
3: Albert Einstein (1879 – 1955)
4: Kelvin, or absolute, temperature, T, is related to Celsius, or centigrade, temperature, T_C, by $T = T_C + 273^{\circ}$.
5: Niels Bohr (1885 – 1962)
6: Ernest Rutherford (1871 – 1937)
7: Joseph J. Thompson (1856 – 1940)
8: Wolfgang Pauli (1900 – 1958)

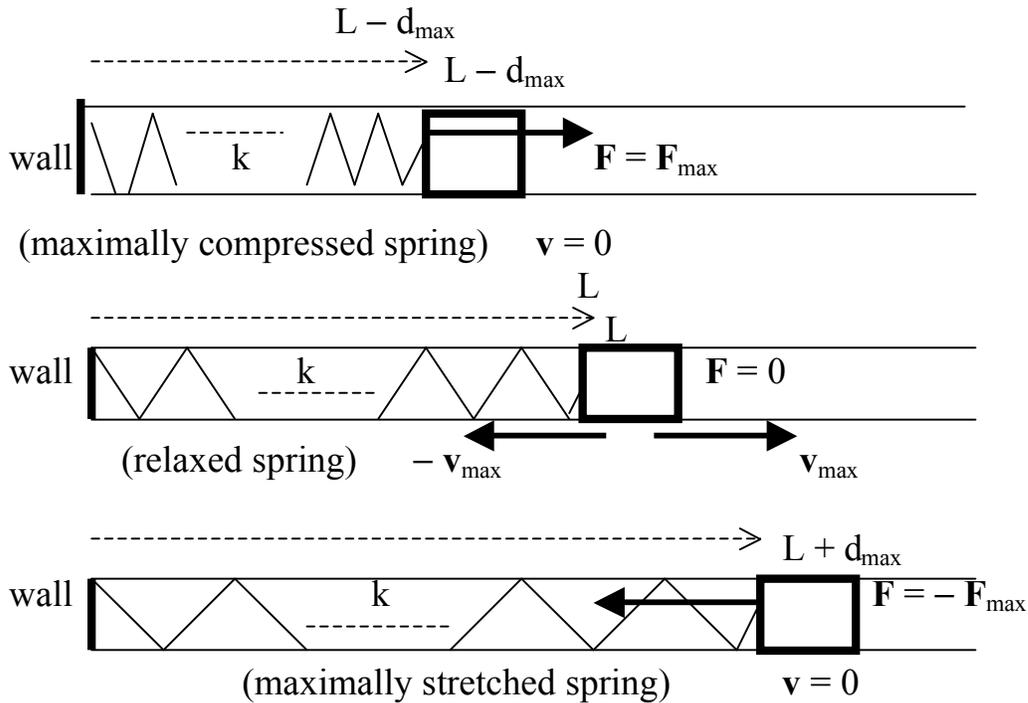## Appendix A: Harmonic oscillators and Coulomb potentials

Fig. A1: Three stages in the oscillating motion of a mass, m, attached to spring, k, sliding in groove.

$$d = d_{max} \cos (2\pi t / T) , \qquad v = - v_{max} \sin (2\pi t / T) , \qquad (A1)$$
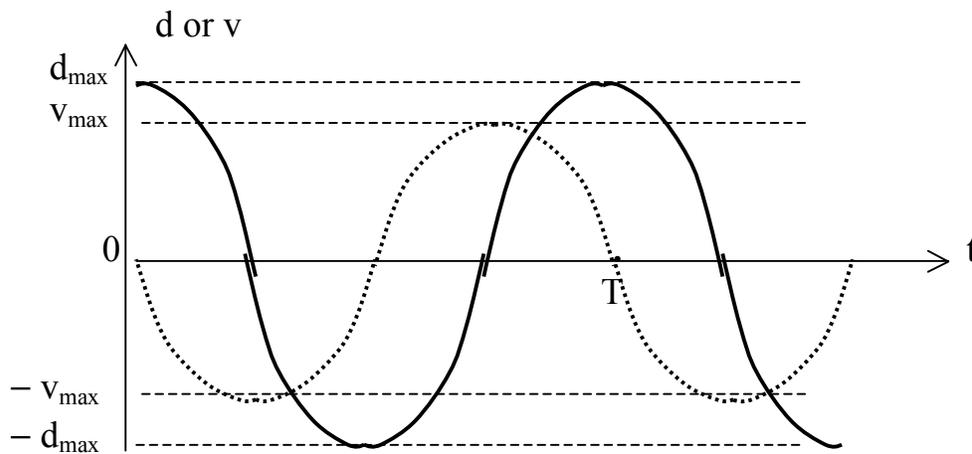
$$v_{max} = 2\pi d_{max} / T \qquad (A2)$$

Fig. A2: Graphs of the position vs time and velocity vs time of the object attached to the spring. T = period. f = 1 / T = frequency.
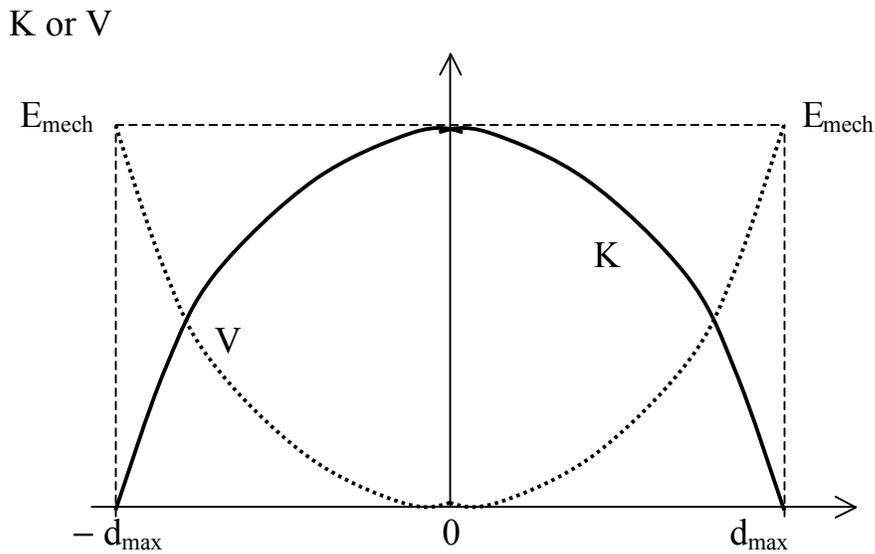
K or V

Fig. A3: Graphs of K and V vs d for the sliding object attached to a spring.

$$E_{mech} = K + V = (1/2)mv^2 + (1/2)kd^2 \qquad (A3)$$

$$F_{12} = F_{21} = k\,|q_1\,q_2|\,/\,(d_{12})^2 \qquad (A4)$$

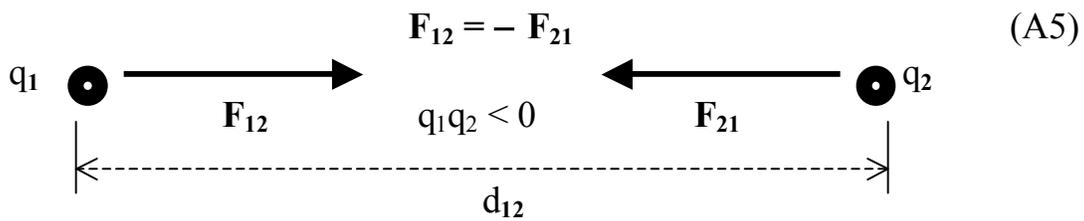$$\mathbf{F_{12}} = -\,\mathbf{F_{21}} \qquad (A5)$$

Fig. A4: Forces of mutual electrostatic attraction between unlike
Charges

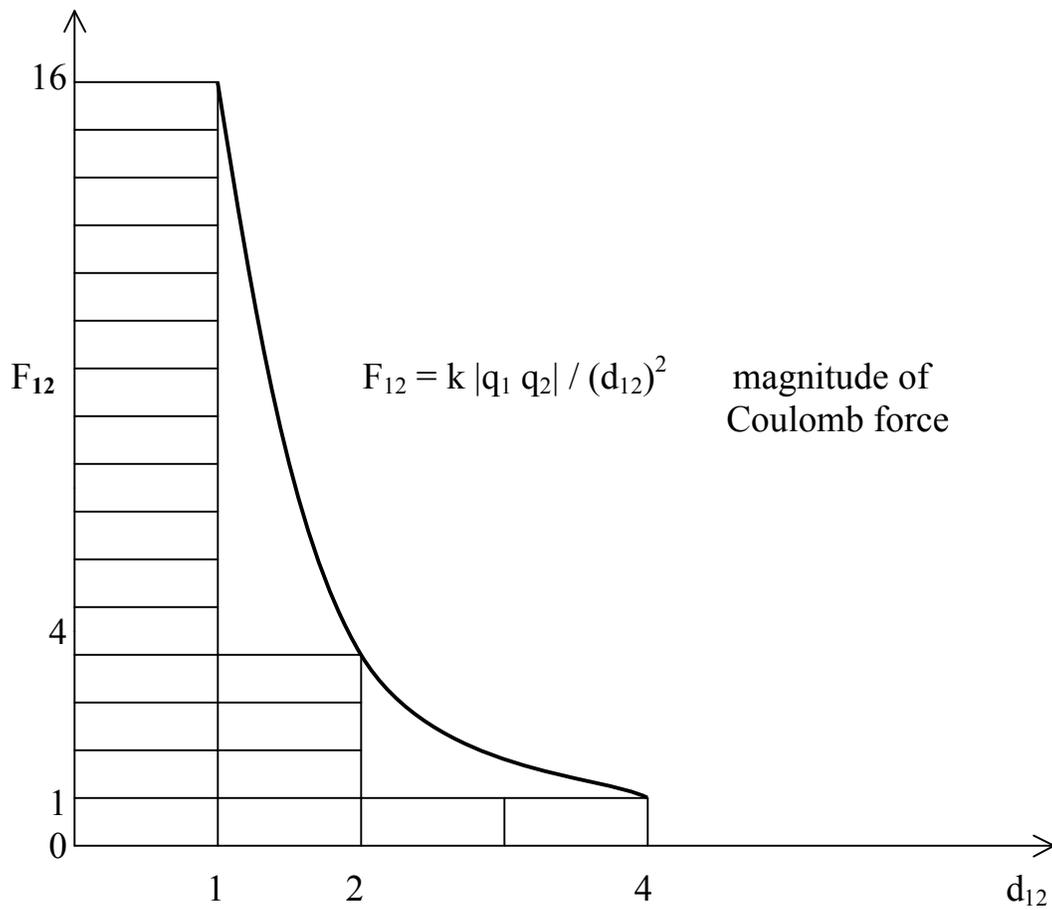**Fig. A5:** Variation of the magnitude of electrostatic force between charged particles with the distance between them.
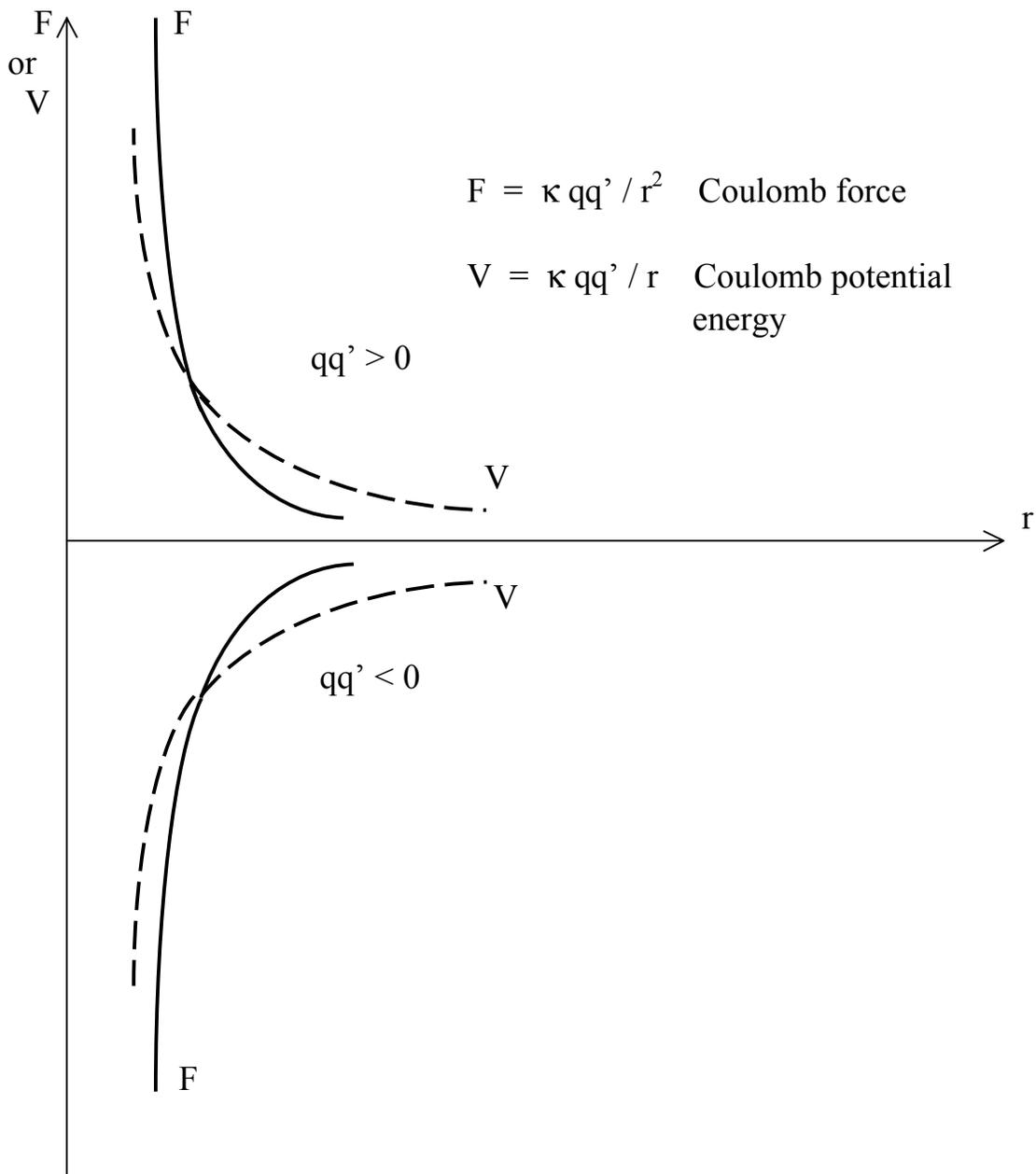
F
or
V

F

$F = \kappa\, qq' / r^2$ Coulomb force

$V = \kappa\, qq' / r$ Coulomb potential
energy

qq' > 0

V

r

V

qq' < 0

F

Fig. A6: Comparing the variation with distance, r, of electrostatic force, F, and potential energy, V, between point charges.

Appendix B: Conductors, Non-conductors and Semi-conductors

Although the molecular level distinction between conductors (mostly metals), non-conductors (mostly ceramics and plastics) and semi-conductors was not understood until much more was known about the quantum world than we have yet discussed, there is a basic aspect of that distinction that involves only the concept of quantized energy levels and can be explained at this point.

If two atoms of the same kind are brought close together, i.e., separated by only a few Angstroms (1 $A^0 = 10^{-8}$cm), the identical energy levels of their outermost electrons, which they normally possess individually, will each change into two slightly different levels possessed by the pair of atoms.. If three such atoms are brought close together, their identical energy levels for the outermost electrons will usually change to three slightly distinct energy levels for the 3-atom system. These shifts in energy levels are due to the forces the atoms exert on each other; repulsions between the electrons of the different atoms and repulsions between the nuclei and attractions between the electrons of one atom and the nuclei of another.
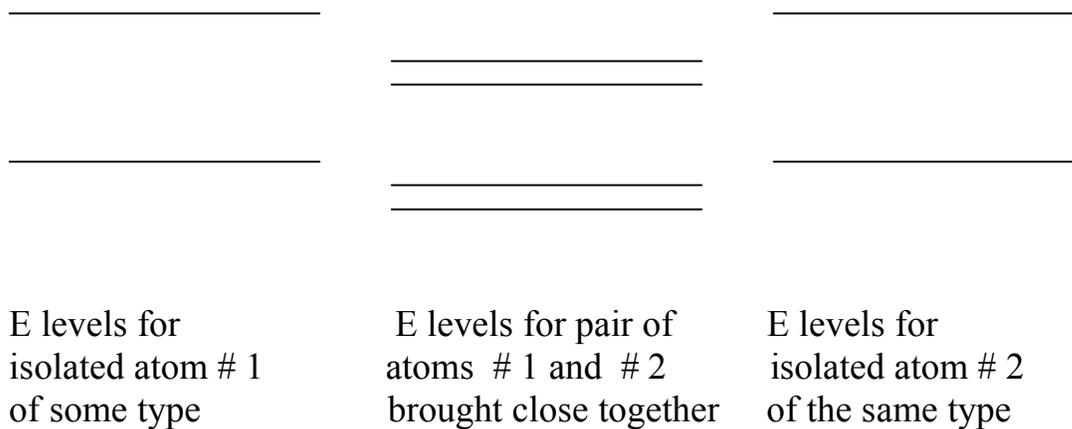
E levels for	E levels for pair of	E levels for
isolated atom # 1	atoms # 1 and # 2	isolated atom # 2
of some type	brought close together	of the same type

Fig. B1: Shifting of energy levels (E levels) of atoms upon being brought into close proximity. The details vary from one type of atom to another.

Now consider a very large number of atoms or molecules of a given type that are brought into close proximity as in a typical crystal structure (not every pair of the atoms are close, but each one has several nearest neighbors and a larger number of next-nearest neighbors and so on). Then the identical

energy levels of the outermost electrons of each of the atoms or molecules when isolated are shifted into collections of very many, very close energy levels for the entire system. For many practical purposes, these collections appear as practically continuous **energy level bands**. Sometimes these energy level bands overlap and sometimes there are gaps between them. The two most important bands of energy levels are called the **valence band** and the **conduction band**. Most of the outer electrons lie in the valence band which is filled or very nearly so and are not free to move easily from atom to atom in the crystal. The electrons in the conduction band can easily move through the crytal under the influence of any external electric force applied to the crystal and these electrons make up the current the external force generates.

A **conductor** is a crystal in which the bottom portion of the conduction band overlaps the top portion of the valence band and there are always plenty of electrons in the conduction band free to move under external influences.
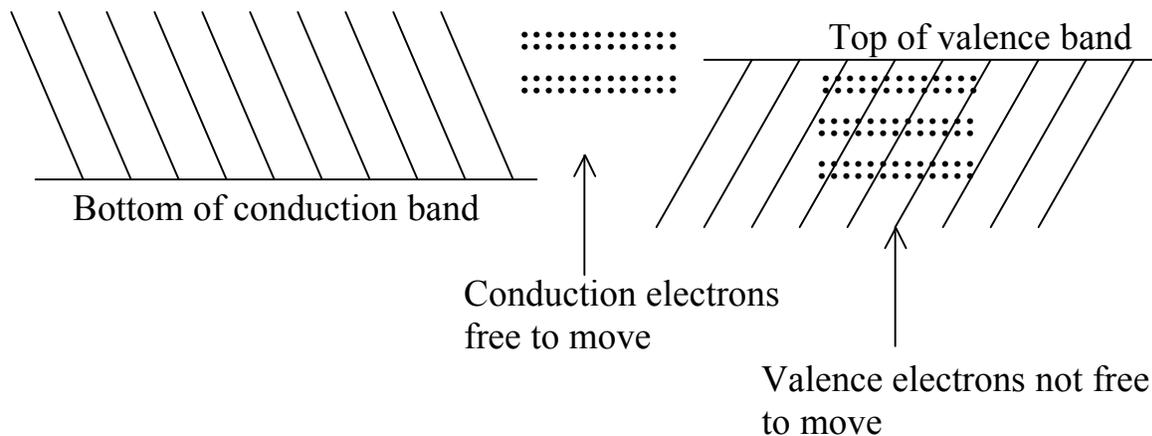

Fig. B2: Energy band structure for conductors which always have electrons in the conduction band.

For **non-conductors** or insulators the bottom of the conduction band is significantly higher than the top of the valence band (~ 5 ev) and very few electrons ever make the transition into the conduction band, even under the influence of strong, external electric forces.

For **semi-conductors** the bottom of the conduction band is again higher than the top of the valence band, *but not by much* (~ 1 ev). In particular, for any temperature above absolute zero, some of the outer electrons, which otherwise would completely fill the valence band, will be lifted into the conduction band just from the kinetic energy associated with random atomic / molecular vibrations. This makes the current – voltage characteristics of semi-conductors very temperature dependent.
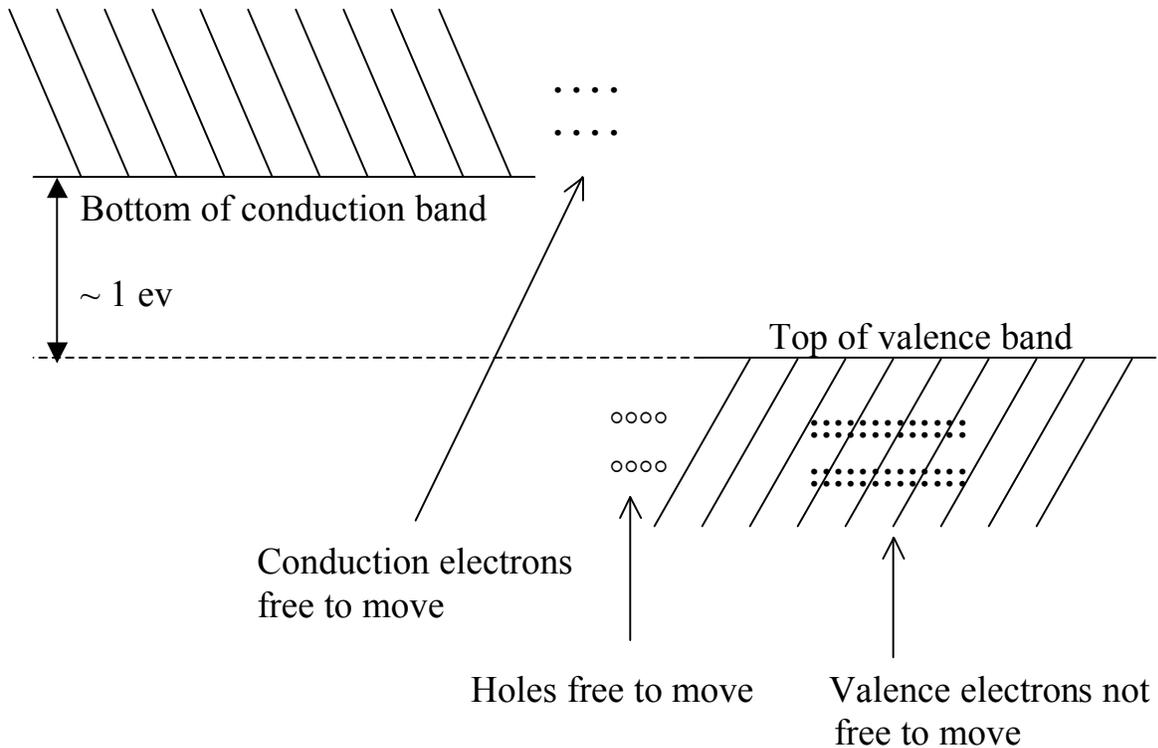

Bottom of conduction band

~ 1 ev

Top of valence band

Conduction electrons
free to move

Holes free to move

Valence electrons not
free to move

Fig. B3: Energy band structure for semi-conductors which have a temperature increasing number of mobile electrons in the conduction band and an equal number of mobile 'holes' in the valence band.

Furthermore, when electrons move into the conduction band they leave behind 'holes' in the valence band which can also move easily and behave like positively charged particles.