

Chapter 2

From Einstein to de Broglie

2.1 Photons

According to classical physics, the energy associated with a monochromatic electromagnetic wave is proportional to its intensity; the intensity can have any value above zero, and can therefore be varied with continuity. Furthermore this energy is distributed in space in a continuous way.

In order to explain the laws of photoelectric effect, in 1905 Einstein formulated an hypothesis in open contradiction with what we have reported above: an electromagnetic wave of frequency ν carries energy in ‘packets’ of energy E proportional to the frequency:

$$E = h\nu . \quad (2.1)$$

In other words, the energy associated to such a wave can only take the values $0, h\nu, 2h\nu, \dots, nh\nu, \dots$. That is to say that the energy of a wave of frequency ν is “quantized”. These energy packets, or “quanta”, or **photons**, are indivisible entities: the ‘half photon’ does not exist. For what regards the spatial and temporal distributions of such photons, Einstein makes no assumptions about their regularity: photons are randomly distributed.

The constant h had been introduced a few years before (1900) by M. Planck, whose name it brings, to interpret the spectrum of the radiation emitted by a black body. From Einstein relation (2.1) it appears that h has the dimensions of an action, namely an energy times a time, or equivalently of an angular momentum, or also of a linear momentum times a length: in general, of a coordinate times its canonically conjugate momentum. The numerical value of h taken from experiments is:

$$h = 6.6 \times 10^{-27} \text{ erg s} .$$

How much is the energy of a photon? Obviously this depends on the radiation one considers, namely on ν . Just to have an idea, let us consider radiation from the visible spectrum, i.e. with its wavelength satisfying

$$4000 \text{ \AA} \leq \lambda \leq 7000 \text{ \AA} \quad (\text{visible spectrum}).$$

Let us take for example $\lambda = 4000 \text{ \AA}$. Then ($1 \text{ eV} = 1.6 \times 10^{-12} \text{ erg}$):

$$E = h\nu = h \frac{c}{\lambda} = \frac{(6.6 \times 10^{-27}) \times (3 \times 10^{10})}{(4 \times 10^{-5}) \times (1.6 \times 10^{-12})} \text{ eV} \simeq 3 \text{ eV}$$

that is of the same order of the energies occurring in the photoelectric effect, e.g. the work function W .

Let us now see how the laws of photoelectric effect are explained by means of the Einstein hypothesis. According to the classical mechanism of interaction among charges and the electromagnetic field, the radiation can transfer an arbitrarily small quantity of energy to the electrons. Now, instead, according to the quantum hypothesis, an electron is allowed either not to absorb energy at all or to absorb an entire quantum (the probability it absorbs two or more quanta, we shall see, is extremely small, so we will neglect this possibility). Then it is clear that, if $h\nu < W$, no electron can jump out of the metal and that the minimum frequency for which the effect is observed is $\nu_0 = W/h$. If $\nu > \nu_0$, the electrons leave the metal with a maximum kinetic energy $E_k = h(\nu - \nu_0)$ (maximum because, in leaving the metal, the electrons may lose energy by collisions). So, incidentally, h can be determined by measuring the slope of the straight line in Fig. 1.5. Furthermore, for a fixed frequency, the intensity of the radiation is proportional to the number of photons that arrive on the metal per unit time and, therefore, to the number of extracted electrons.

Let us reconsider, in the light of this interpretation, the example of the bulb discussed at the end of Sect. 1.4. If we keep on accepting the somewhat optimistic assumptions that have led to (1.26) and if we suppose that the frequency of the radiation emitted by the bulb corresponds to photons with energy of the order of some eV, then (1.26) must be reinterpreted by saying that in a second there arrives, on the average, one photon every 10^2 atoms and, as a consequence, every second only one electron over a hundred receives the energy necessary to jump out of the metal (indeed much less than this, for part of the energy is taken by the lattice).

Thanks mainly to the assumptions made to arrive at (1.26), this discussion is somewhat superficial. What one wants to emphasize is the following: according to classical physics, owing to the fact that the energy of a monochromatic wave is uniformly distributed, the electrons share ‘democratically’ the incoming energy and each of them takes too little of it to be able to jump out of the metal; according to the quantum hypothesis, instead, some (a few) electrons take the incoming energy and most of them take nothing at all. These few electrons give rise to the photoelectric effect.

The example of the bulb also shows how unlikely it is that an electron may absorb two or more quanta of energy: the arrival of another photon should take place in the time interval one quantum is absorbed (10^{-8} s), but from (1.26) it follows that in 10^{-8} s there arrives one photon every 10^{10} atoms!

There are many phenomena that depend on the photoelectric effect and that, therefore, exhibit a threshold. One is in the old – i.e. pre-digital – pro-

cess of taking a photograph, particularly the formation of the latent image. The photographic plate is covered with a layer of AgBr crystals: the primary effect that (according to a mechanism we shall not describe) gives rise to the formation of the latent image exactly is the photoelectric effect triggered by the incident light. In this way one understands how it is that either infrared or red light does not impress the plate, whereas this happens with a light of lesser wavelength, even if of weak intensity.

It may be helpful to have at one's disposal a mnemonic rule to obtain quickly the photon energy associated to a given radiation and viceversa. If, as customary in atomic physics, we characterize radiation by means of its wavelength λ expressed in ångström and express energy in electronvolt, then it suffices to recall that $hc = 12400 \text{ eV} \times \text{Å}$, so that from $E = hc/\lambda$ one obtains:

$$E[\text{eV}] = \frac{12400}{\lambda[\text{Å}]} \quad (\text{photons}) . \quad (2.2)$$

Photoelectric effect does not prove that an electromagnetic wave carries energy in quanta, it rather proves that its energy is absorbed in quanta. It is natural to wonder what happens with emission, namely whether electromagnetic energy is emitted either in quanta or with continuity.

Let us consider the production of X-rays ($\lambda \simeq 1 \text{ Å}$): electrons emitted by means of thermionic effect are accelerated by a difference of potential about 10^4 V (Fig. 2.1) and then are let to hit a metal plate. Penetrating the metal, the electrons are suddenly decelerated and radiate. The spectrum of the emitted radiation – **bremsstrahlung** (deceleration radiation) spec-

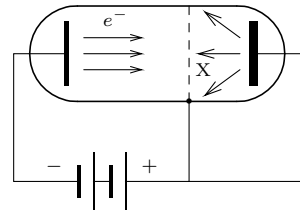


Fig. 2.1

trum – is a continuous spectrum on which some spectral lines are superposed, their position depending on the metal the plate is made of. The interesting thing is that, no matter what metal is used, the continuous spectrum has an upper limit at a certain frequency ν_0 , that depends only on the accelerating potential V , indeed it is proportional to it. The interpretation of this fact is straightforward, if one admits that also emission of electromagnetic radiation takes place by quanta: each electron loses the kinetic energy $E_k \leq e \times V$ by emitting one or more photons, whose frequencies are therefore such that $h\nu \leq e \times V$, namely $\nu \leq e \times V/h$ i.e. limited from above. The frequency $\nu_0 = e \times V/h$ is emitted when an electron loses all its energy by emitting only one photon. From the classical point of view, the spectrum should extend up to infinity, because the decelerated motion of the electron is not periodic.

2.2 Compton Effect

It is known that, in classical physics, an electromagnetic wave carries linear momentum, according to the relationship $p = E/c$. Since we now know that energy is carried by photons, it is natural to wonder whether these photons bring a linear momentum $p = E/c = h\nu/c$. This conclusion can be reached

by analyzing the Compton effect: if a beam of “hard” X-rays (wavelength $\lambda_0 \leq 1 \text{ \AA}$) is shot against whatever substance, one observes that X-rays scattered at an angle θ with respect to the direction of the incident radiation are endowed with a wavelength $\lambda(\theta)$ slightly higher than λ_0 . The variation of the wavelength is independent of the particular substance off which X-rays are scattered and depends on θ according to:

$$\lambda(\theta) - \lambda_0 = 0.024 (1 - \cos \theta) \text{ \AA} . \quad (2.3)$$

Compton effect can be easily explained by attributing it to the interaction between radiation and electrons and by interpreting this interaction as the collision process between a photon, of energy $h\nu$ and momentum $h\nu/c$, and a free electron (the binding energy of electrons, at least the outer ones, is of the order of some eV, whereas that of photons is $\simeq 10^5 \text{ eV}$). In the photon-electron collision total linear momentum and total energy are conserved, so it is clear that the larger the angle θ by which the photon is scattered, the higher the momentum and the energy transferred to the electron, and the larger the wavelength $\lambda(\theta)$ of the photon itself. Indeed, let $\vec{k}_0$ be the momentum of the incident photon and $\vec{k}$ and $\vec{p}$ respectively those of the photon and the electron after the collision (the initial momentum of the electron $\simeq \sqrt{2m E_k}$ is neglected, since typically it is two orders of magnitude smaller than that of the photon), one has:

$$\begin{aligned} \begin{cases} c k_0 + m_e c^2 = c k + \sqrt{m_e^2 c^4 + c^2 p^2} \\ \vec{k}_0 - \vec{k} = \vec{p} \end{cases} &\Rightarrow p^2 = k_0^2 + k^2 - 2k_0 k \cos \theta \\ (k_0 - k + m_e c)^2 = m_e^2 c^2 + p^2 = m_e^2 c^2 + k_0^2 + k^2 - 2k_0 k \cos \theta &\Rightarrow \\ m_e c (k_0 - k) = k_0 k (1 - \cos \theta) &\Rightarrow \frac{1}{k} - \frac{1}{k_0} = \frac{1}{m_e c} (1 - \cos \theta) \end{aligned}$$

and, if $k = h\nu/c \equiv h/\lambda$, one finally obtains:

$$\lambda(\theta) - \lambda_0 = \frac{h}{m_e c} (1 - \cos \theta) . \quad (2.4)$$

The quantity $\lambda_C \equiv h/m_e c$ (that has the dimension of a length) is called the electron **Compton wavelength** and its numerical value is about $0.024 \text{ \AA}$, in agreement with (2.3). We can then conclude that photons behave as corpuscles of energy $h\nu$ and momentum $h\nu/c$. According to special relativity, the relationship $p = E/c$ is typical of massless particles: photons are therefore corpuscles of vanishing mass.

2.3 General Features of Spectra. Bohr Hypotheses

Any substance can absorb and emit only electromagnetic radiations of well defined frequencies, typical of the substance itself. The frequencies a substance can absorb give rise to its **absorption spectrum**, those it can emit give rise

to its **emission spectrum**. We shall mainly be concerned with the spectra of gaseous substances and vapours.

A device suitable to obtain absorption and emission spectra of a substance is schematized in Fig. 2.2: white light hits a cell containing the gas or vapour one is interested in; a spectrograph, schematized as the prism P_1 , breaks the light transmitted by the gas up into its monochromatic components before they impress the photographic plate L_1 : a uniform illumination (due to the continuous spectrum transmitted by the gas) will appear on L_1 , with the exception of some dark lines in correspondence with the frequencies absorbed by the gas. These dark lines make up the absorption spectrum. In order to obtain the emission spectrum it is necessary to provide energy to the gas: this energy will be re-emitted as electromagnetic radiation. This can be done in several ways, for example either by heating the gas by a flame, or provoking an electric (arc) discharge, or even sending light on the substance, as in Fig. 2.2.

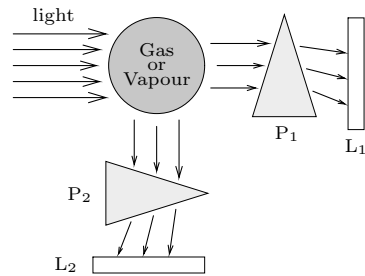


Fig. 2.2

on L_1 , with the exception of some dark lines in correspondence with the frequencies absorbed by the gas. These dark lines make up the absorption spectrum. In order to obtain the emission spectrum it is necessary to provide energy to the gas: this energy will be re-emitted as electromagnetic radiation. This can be done in several ways, for example either by heating the gas by a flame, or provoking an electric (arc) discharge, or even sending light on the substance, as in Fig. 2.2.

For the sake of simplicity, we shall refer to the last method of excitation of the gas or vapour. If one wants to analyze the emission spectrum of the substance, one will observe the light emitted in a direction orthogonal to the direction of the incident light: in this way the latter will not disturb the observation. The prism P_2 separates the monochromatic components that impress the plate L_2 . On L_2 , on a dark background, there will appear some bright lines in correspondence with the frequencies emitted by the gas. These lines make up the emission spectrum. The first thing one notes is that the emission and absorption spectra of a substance are different from each other: the emission spectrum is richer than the absorption one, with all the absorption lines appearing in the emission spectrum. If, in addition, the incident radiation has a spectrum consisting of frequencies ν higher than a given $\bar{\nu}$, in the emission spectrum of the gas there appear also lines corresponding to frequencies smaller than $\bar{\nu}$.

In order to explain emission and absorption spectra, in 1913 N. Bohr put forward some hypotheses that, as Einstein hypothesis, are in contrast with classical physics which, by the way, is unable to explain spectra.

1-st Bohr Hypothesis: For any atom only a discrete set of energies, starting from a minimum value on, $E_0 < E_1 < \dots < E_n < \dots$, are allowed.

These energies are called **energy levels** of the atom. Note that, from the classical point of view, the allowed energies for a system *always* make up a continuous set.

The first hypothesis concerns the **bound states** of an atom, namely those states that correspond to orbits limited in space (think e.g. of ellipses or circles in the hydrogen atom). For unbounded – or ionization – states, all the

classically possible energies are allowed. The state of a system corresponding to the minimum allowed energy is called the **ground-state** of the system.

2-nd Bohr Hypothesis: *When the system is in one of the above mentioned energy states, it does not radiate; either emission or absorption of electromagnetic radiation only takes place in the transition from a state with energy E_n to a state with energy E_m and the frequency of the radiation is:*

$$\nu_{nm} = \frac{|E_n - E_m|}{h}. \quad (2.5)$$

If the transition is from a state with higher energy to a state with lower energy, there occurs emission; in the contrary case one has absorption.

In the next section we will enunciate the third Bohr hypothesis that allows one to calculate the allowed energies $E_0 < E_1 < \dots < E_n < \dots$ in simple cases. Let us now examine the consequences of the first two Bohr hypotheses. This discussion mainly concerns the hydrogen atom.

1. It is clear that spectra are made out of lines whose frequencies are given by (2.5) with all possible E_n and E_m . Any substance may also exhibit a continuous spectrum that corresponds to transitions from a bound state to an ionization state (the latter are also called **continuum states** since for them the hypothesis of discrete energies does not apply).
2. Bohr hypotheses are compatible with Einstein hypothesis. Rather it is probably more correct to state that Bohr was led to the formulation of his hypotheses as a consequence of Einstein's. Indeed, if an atom radiates quanta, when it either emits or absorbs a photon of frequency ν , its energy varies by $h\nu$. As it was known that an atom either emits or absorbs only certain frequencies, it looks reasonable to assume that only certain energies are allowed for the atom, i.e. those for which the observed frequencies are given by (2.5).
3. One can understand why emission spectra are richer than absorption spectra. Indeed (we shall come back to this point) at room temperature the great majority of the atoms are in their ground state. As a consequence, only the lines with frequencies $\nu_{0n} = (E_n - E_0)/h$ are observed in absorption: the latter correspond to the transitions from the lowest energy level E_0 to a generic level E_n . After the atom has been excited to the level E_n , in a very short time ($10^{-7} \div 10^{-9}$ s) it re-emits radiation effecting one or more transitions to lower energy levels until the ground state is reached. In this way one observes in emission the entire spectrum given by (2.5).
4. It follows from the above discussion that all the frequencies of the emission spectrum are obtained by making all the possible differences of the frequencies of the absorption spectrum:

$$|\nu_{0n} - \nu_{0m}| = \left| \frac{E_n - E_0}{h} - \frac{E_m - E_0}{h} \right| = \frac{|E_n - E_m|}{h} = \nu_{nm}$$

This fact was already known as Ritz **combination principle**.

5. Bohr explanation of Ritz combination principle is consequence also of the fact that the energies E_n can be derived from the knowledge of the absorption spectrum. Indeed, Planck constant h being known, the absorption spectrum enables one to determine $E_1 - E_0, E_2 - E_0, \dots, E_n - E_0 \rightarrow E_\infty - E_0$ i.e. all the energies up to the constant E_0 . If we set to zero the energy corresponding to the ionization threshold, namely to the limiting value E_∞ , one obtains $E_0 = -h\nu_\infty$, where ν_∞ is the limiting frequency of the spectrum of lines: for higher frequencies one has a continuous spectrum, corresponding to the ionization of the atom.
6. The above discussion suggests an experimental verification of Bohr hypothesis. Indeed $|E_0|$, measured by the absorption spectrum, is the ionization energy E_I of the atom. But the atom can be ionized by collisions with electrons or other atoms, instead of absorption of light. One can then measure the energy necessary to ionize an atom by collisions and compare the result with the value measured (or predicted) by spectroscopic way.
7. Spectroscopists had succeeded in grouping the lines of a spectrum in **series**, in such a way that the frequencies, or better the **wavenumbers** $1/\lambda = \nu/c$ corresponding to the lines of a spectrum could be expressed as differences between **spectroscopic terms**: $1/\lambda = \nu/c = T(n) - T(m)$ (n, m integers ≥ 0), and each series is identified by the value of n . So, for example, the first series, that is the absorption series, corresponds to the wavenumbers:

$$1/\lambda_m = T(0) - T(m), \quad m \geq 1.$$

Now, according to Bohr, the spectroscopic terms $T(n)$ are nothing but the energy levels divided by hc : $T(n) = -E_n/(hc)$ and each series corresponds to the transitions that (in emission) have in common the arrival level; the different series are identified by the arrival energy level.

2.4 Hydrogen Energy Levels According to Bohr

The problem that has been left open is that of determining the energy levels of a system. In this section we will limit our discussion to the case of hydrogen and hydrogen-like atoms. Hydrogen-like atoms are atoms ionized one or more times in such a way that only one electron is left, for example He^+ , Li^{++} , Be^{+++} etc. In all such cases one deals with systems with only one electron in the field of a nucleus of charge Ze , where Z is the atomic number.

In general the orbits are ellipses (bound states!), and it is known from classical physics that energy only depends on the major axis of the ellipse. So, stating that only some energies are allowed is the same as saying that only certain orbits are allowed: the problem is to calculate which ones. Let us limit ourselves, as Bohr did, to circular orbits.

The relationship between the energy and the radius of the orbit is (see (1.4) and (1.8))

$$E = \frac{1}{2} V = -\frac{1}{2} \frac{Z e^2}{r}. \quad (2.6)$$

In order to determine the allowed energies, i.e. radii, Bohr put forward the following hypothesis:

3-rd Bohr Hypothesis: *The allowed orbits are those for which the angular momentum is an integer multiple of $\hbar/2\pi$.*

This rule can be enunciated in a more general (Bohr-Sommerfeld) form in the following way:

$$\int_{\text{orbit}} p dq = n \hbar, \quad n = 1, 2, \dots \quad (2.7)$$

where q and p are canonically conjugate variables and the integral is to be taken along one orbit. In any event, for circular orbits, the third Bohr hypothesis requires that:

$$\mu_e v r = n \hbar \quad (2.8)$$

where $\mu_e = m_e M / (m_e + M)$ is the reduced mass of the electron-nucleus two-body system. As it is customary in quantum mechanics, we have set:

$$\hbar \equiv \frac{h}{2\pi} = 1.05 \times 10^{-27} \text{ erg s}.$$

Squaring (2.8) and recalling that $E_k = \frac{1}{2}\mu_e v^2 = -\frac{1}{2}V$, one obtains

$$\frac{1}{2}\mu_e v^2 = \frac{n^2 \hbar^2}{2\mu_e r^2} = \frac{Z e^2}{2r} \quad (2.9)$$

whence:

$$r_n = \frac{n^2 \hbar^2}{\mu_e Z e^2} = \frac{n^2}{Z} (m_e / \mu_e) a_B, \quad a_B \equiv \frac{\hbar^2}{m_e e^2}. \quad (2.10)$$

where a_B is the **Bohr radius**. Equation (2.10) says which are the allowed orbits, according to Bohr. By inserting (2.10) into (2.6) one finally obtains the allowed energies:

$$E_n = -\frac{1}{2} \frac{Z^2 e^2 (m_e / \mu_e)}{n^2 a_B}, \quad n = 1, 2, \dots \quad (2.11)$$

Putting:

$$R = \frac{e^2 (m_e / \mu_e)}{2a_B \hbar c} = \frac{\mu_e e^4}{4\pi \hbar^3 c} \quad (2.12)$$

one can write:

$$E_n = -Z^2 \frac{R \hbar c}{n^2}. \quad (2.13)$$

The reason why we have written (2.11) in the form (2.13) is in the fact that spectroscopists had already experimentally determined the spectroscopic terms of hydrogen and had found $T(n) = R_H / n^2$ with $R_H = 109677.6 \text{ cm}^{-1}$ (**Rydberg constant** for hydrogen). The fact that R_H was known with seven

significant digits is due to the high precision by which spectroscopic experiments were made even in that time. Presently Rydberg constant is known with a precision higher than one part over 10^{11} : if R_∞ stands for Rydberg constant with $M = \infty$ ($\mu_e = m_e$), one has $R_\infty = 109737.31568508(65) \text{ cm}^{-1}$ (“2014 CODATA recommended values”).

It is worth calculating the value of R_H predicted by (2.12) to realize the excellent agreement with the experimental value: we leave this exercise to the reader. We can conclude that the spectroscopic terms deduced from Bohr theory are in very good agreement with the corresponding experimental values.

Let us now examine in detail the consequences of the obtained results. Let us start with

Hydrogen: $Z = 1$

If the difference between reduced mass and electron mass is neglected ($m_e/M_H \simeq 0.5 \times 10^{-3}$), one has:

$$r_n = n^2 a_B, \quad a_B = \frac{\hbar^2}{m_e e^2} = 0.53 \text{ \AA}, \quad E_n = -\frac{1}{2} \frac{e^2}{n^2 a_B} \quad (2.14)$$

where a_B is the radius of the first allowed orbit for the atom in its ground state. The value of a_B is satisfactory because it is in agreement with the value expected for atomic size. Note that now, having at one’s disposal the Planck constant, it is possible to form a length with the right order of magnitude. Furthermore, the atom in its first orbit cannot collapse, exactly because it is in the state of minimum energy.

The energy levels given by (2.14) are negative and decrease, in absolute value, towards 0: the position of these level is illustrated in Fig. 2.3 (in scale). The energy E_1 of the ground state is, apart from

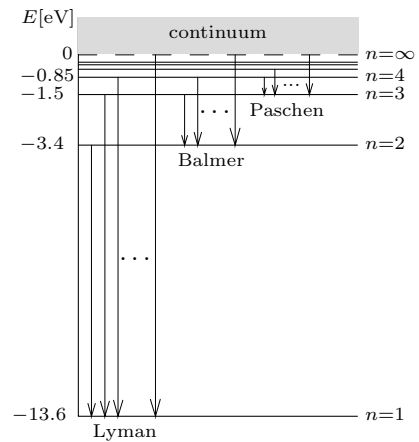


Fig. 2.3

its sign, the ionization energy of the atom (since the minimum value of the **quantum number** n is in the present case 1, we prefer to call E_1 instead of E_0 the energy of the ground state). One has $E_1 = -e^2/2a_B = -13.6 \text{ eV}$. The energies of the different levels, expressed in eV, are therefore:

$$E_n[\text{eV}] = -\frac{13.6}{n^2}. \quad (2.15)$$

So $E_2 = -3.4$, $E_3 = -1.5$, $\dots$.

How does the hydrogen spectrum look like?

The first series (**Lyman series**) is that consisting of all transitions to level $n = 1$ (Fig. 2.3): the lines get denser and denser in the neighborhood of a

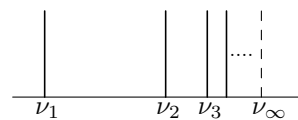


Fig. 2.4

limiting line (Fig. 2.4). The first line corresponds to a transition with $\Delta E = E_2 - E_1 = 10.2 \text{ eV}$ and has therefore a wavelength $\lambda_1 = 12400/10.2 \simeq 1200 \text{ \AA}$; the limiting line corresponds to $\Delta E = 13.6 \text{ eV}$ and $\lambda_\infty \simeq 900 \text{ \AA}$: both λ_1 and λ_∞ are in the ultraviolet, and so is all the series. Since this is the series that is observed in absorption, one understands why hydrogen is transparent: it does not absorb in the visible part of the electromagnetic spectrum.

The second series (**Balmer series**) corresponds to all transitions from levels with $n > 2$ to the first *excited level* ($n = 2$) (Fig. 2.3). The structure of this series still is of the type reported in Fig. 2.4, but in comparison with Lyman series it is shifted towards lower frequencies. Indeed:

$$\lambda_1 = \frac{12400}{1.9} \simeq 6500 \text{ \AA}, \quad \lambda_\infty = \frac{12400}{3.4} \simeq 3700 \text{ \AA}$$

namely λ_1 is in the orange and λ_∞ is in the near ultraviolet so that almost all the series is in the visible. As for the third series (**Paschen series**), it all lies in the infrared.

Let us now consider the case of

Hydrogen-like atoms: $Z > 1$

The most remarkable effects are

- (i) the size of the orbits decreases with increasing Z , due to the $1/Z$ factor in (2.10);
- (ii) the energies increase, in absolute value, like Z^2 .

So, for example, the ionization energy of He^+ (also called **second-ionization** energy of He) is $4 \times 13.6 = 54 \text{ eV}$. As a consequence also all the energetic jumps increase by a factor Z^2 with respect to H and all the spectral lines are shifted toward higher frequencies. Note that the factor Z^2 has a twofold origin: a factor Z in the potential energy – and, as a consequence of (2.6), in the energy – and a factor Z^{-1} in the allowed radii.

Another, less conspicuous but important, effect is due to the fact that the nuclei of hydrogen-like atoms have different masses: this entails differences, although small, in the reduced masses of the systems upon which the Rydberg constant (2.12) and, in the very end, the energy levels (2.13) depend.

As $m_e \ll M$, one can write $\mu_e = m_e/(1 + m_e/M) \simeq m_e(1 - m_e/M)$. The term m_e/M , that for hydrogen is about $1/2000$, for deuterium is half such value (deuterium D is an isotope of hydrogen: the nucleus of deuterium consists of a proton and a neutron), for He is four times smaller.

Thus we see that the Rydberg constant slightly varies for the different atoms we have considered:

$$\begin{aligned} R_{\text{H}} &= 109677 \text{ cm}^{-1} \\ R_{\text{D}} &= 109707 \text{ cm}^{-1} \\ R_{\text{He}^+} &= 109722 \text{ cm}^{-1} \\ R_{\text{Li}^{++}} &= 109728 \text{ cm}^{-1} \\ R_{\infty} &= 109737 \text{ cm}^{-1} \end{aligned}$$

with differences smaller than 0.5% with respect to R_∞ (the limiting case of nucleus with infinite mass), as had to be expected. No matter how small, the variation of the Rydberg constant is well detectable, given the precision of spectroscopic measurements.

However the most important fact is that the dependence of R – and therefore of the spectrum – on the nuclear mass allows one to distinguish the different isotopes of a single element. As well known, one calls *isotopes* those elements that have the same atomic number Z but different atomic weight A , due to the different number of neutrons in the nucleus, as is the case of hydrogen and deuterium.

So, for example, if one analyzes a mixture of hydrogen H ($Z = 1$, $A = 1$) and deuterium D ($Z = 1$, $A = 2$), or He^3 and He^4 ($Z = 2$, $A = 3, 4$ respectively), one finds a spectrum of doubled lines, as in Fig. 2.5. In the case of H and D the res-

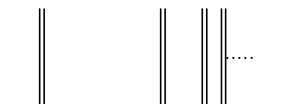


Fig. 2.5

olution $\Delta\nu/\nu = \Delta\lambda/\lambda$ necessary to distinguish the lines of the doublets is $\Delta\mu/\mu \simeq 2.8 \times 10^{-4}$. The relative intensity of the spectral lines enables one to find the composition of the mixture (for example, the percentage of heavy water D_2O in a sample of water).

Such effect is known as *isotopic effect* and, therefore, allows one to establish either the presence or the absence of an isotope in a given substance.

The fact that the energy levels of even order in the spectrum of He^+ coincide, up to corrections of reduced mass, with the levels of H had induced the interpretation of the spectrum of some stellar radiations as due to hydrogen: only thanks to Bohr theory it was correctly attributed to He^+ .

In conclusion Bohr theory had explained several questions left unsolved by the Rutherford atomic model: stability of atomic sizes, emission of line spectra, absence of radiative collapse. All this made it possible that the theory had been very favourably welcome since, by postulating something new, provided the explanation of many facts.

We shall see in the forthcoming sections that the solution of other problems and further experimental verifications reinforce even more the validity of this theory, even if (not only) from a conceptual point of view there still remain many open problems.

2.5 Energy Levels for an Oscillator and for a Particle in a Segment

After the successful application of the Bohr quantization condition to the hydrogen atom, we feel encouraged to apply it to other systems and to explore its consequences. Both for its simplicity and, mainly, for the interest it has in almost all the fields of physics, we shall now apply the quantization condition to the harmonic oscillator. In order to emphasize the importance this system has in physics, we recall that we have already considered harmonic oscillators with regard to the heat capacities of both solids and diatomic gases.

In order to determine the energy levels of a harmonic oscillator, we shall use the Bohr-Sommerfeld condition (2.7). Recalling that $p = m\dot{q}$ and $dq = \dot{q}dt$,

(2.7) becomes:

$$\int_{\text{period}} m \dot{q}^2 dt = n h \quad (2.16)$$

the integral being taken over a period $\tau = 2\pi/\omega$. It is known (and the verification is straightforward) that for the harmonic oscillator the average (over one period) of the kinetic energy equals a half of the total energy E (virial theorem), so from (2.16) one obtains:

$$\int_{\text{period}} m \dot{q}^2 dt = \frac{2\pi}{\omega} E \quad \Rightarrow$$

$$E_n = n \hbar \omega, \quad n \geq 0 \quad (\text{harmonic oscillator}) \quad (2.17)$$

so the energy levels of a harmonic oscillator are equidistant and their distance is $\hbar \omega$.

One can ask why in this case n may also be 0, whereas for the hydrogen atom this is not the case: indeed, on this point Bohr theory provides no answer. In this particular case starting from either $n = 0$ or $n = 1$ makes no difference because, the energy levels being equidistant, it is the same as shifting them all by the additive constant $\hbar \omega$ (it is however the case to anticipate that the result provided by quantum mechanics will be $E_n = \hbar \omega (n + \frac{1}{2})$, $n \geq 0$).

If the oscillator carries an electric charge, it can either emit or absorb radiation. Due to the second Bohr hypothesis, the frequency of the either emitted or absorbed radiation equals the frequency ν_0 of the oscillator, provided the transition takes place between two adjacent energy levels; otherwise it will be an integer multiple of ν_0 , namely it will correspond to a higher harmonic. Also according to classical physics an oscillator emits all the frequencies that are integer multiples of the fundamental frequency, however – when the dipole approximation holds (velocity of the oscillator $v(t) \ll c$) – higher harmonics are much less intense. One of the flaws of Bohr theory just is its incapability at predicting the intensity of the radiation emitted in the various transitions.

Let us examine one more example of application of the quantization rule (2.7).

Consider a particle constrained to move in a segment of length a (in three dimensions this would be the problem of a particle constrained within a box). From a physical point of view such a problem is encountered when considering the motion of a particle subject to a potential $V(x)$ that can be approximated

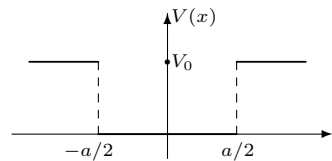


Fig. 2.6

by a constant in a region of size a and rapidly grows to another constant of higher value out of the considered region: in such cases the potential is schematized as a **potential well**, as shown in Fig. 2.6. There are several examples: the molecules of a (perfect) gas within a box; a free electron within a metal; a free electron within a crystal cell (size: a few ångström) that makes up an impurity in a given material (colour centers); ...

In this case (2.7) gives

$$n h = \oint p dq = 2 a p \quad \Rightarrow \quad p = n \frac{h}{2a}$$

and, since $E = p^2/2m$, one obtains the following energy levels:

$$E_n = \frac{h^2 n^2}{8m a^2} \quad n \geq 0 (?) \quad (\text{potential well}) \quad (2.18)$$

(in the present case, according to quantum mechanics, $n \geq 1$).

We will complete the present section with a few observations.

1. The dependence on n of the energy levels is different for each system ($\propto n^{-2}$ for the hydrogen atom, $\propto n$ for the oscillator, $\propto n^2$ for the particle in the potential well);
2. the quantization condition has been applied, and can be applied, only if the orbit is finite; consider, for example, the case of the particle in a segment: if $a \rightarrow \infty$, the integral $\oint p dq$ diverges and therefore, in this case, there is no quantization condition. A different way to look upon the same thing is the following: the distances among the energy levels given by (2.18) are proportional to a^{-2} ; if $a \rightarrow \infty$ they tend to 0, i.e. one finds the continuum of energies from 0 to ∞ of classical physics. Therefore, for example, in the case of a potential such as that of Fig. 2.6, the result expressed by (2.18) holds only for $E_n < V_0$, whereas for energies higher than V_0 all the values are admissible (much as for the ionization states of the hydrogen atom).
3. Thanks to Stokes' theorem the integral on the left hand side of (2.7) equals the area enclosed by the orbit of energy E_n , therefore (2.7) means that the number of states (i.e. energy levels) in a (two-dimensional) volume Ω of the phase-space is given by Ω/h . In general, if $2f$ is the dimension of the phase-space, the quantization condition implies that h^f is the phase-space volume per state.

2.6 Einstein and Debye Theories for the Heat Capacities of Solids

If one accepts Bohr hypothesis about the existence of discrete energy levels, there are several things that must be re-examined from this point of view: first of all, the theory of heat capacities. Indeed, the theory of heat capacities was based on the calculation of the average energy (theorem of equipartition of energy) that is obtained from the expression $\int E(q, p) dn(q, p)$ by integrating over all the phase space, i.e. over all the classically admitted states. Now, according to the first Bohr hypothesis, only some states with energies E_n are allowed and, as a consequence and in the first place, the very Boltzmann distribution (1.13)

$$dn(q, p) = B e^{-\beta E(q, p)} dq dp$$

is meaningless and needs to be reformulated. Instead of asking oneself which is the (most probable) number of subsystems with coordinates and momenta

between q and $q + dq$, and p and $p + dp$, one must ask which is the (most probable) number n_i of subsystems with energy E_i , where the E_i are the allowed energies. This problem is solved by the same reasoning that has led to (1.13), so a formally analogue result will obtain

$$n_i = B e^{-\beta E_i}$$

where again B can be found by requiring $\sum n_i = N$. Finally:

$$n_i = N \frac{e^{-\beta E_i}}{\sum_j e^{-\beta E_j}} \quad (2.19)$$

namely Boltzmann distribution still applies to the number of subsystems in the energy level E_i (the n_i are also called **populations** of the levels E_i). Indeed, (2.19) is not quite correct, it must be modified according to

$$n_i = N g_i \frac{e^{-\beta E_i}}{\sum_j g_j e^{-\beta E_j}} \quad (2.20)$$

where the g_i are integer numbers (normally of the order of a few units), called **degree of degeneracy** of the level E_i , whose origin is not easy to explain now: they represent the number of states corresponding to the level E_i ; we shall clarify in the sequel the exact meaning of this statement. They can be ignored in the discussion of the forthcoming sections.

Before proceeding any further, we wish to briefly discuss (2.19), from which it follows that, for a given temperature, the average number of systems that are in the energy level E_i decreases exponentially with the increase of the energy. It follows that, if $E_r < E_s$, always one has $n_r > n_s$, so the higher the level the lower the population. It is interesting to evaluate the ratio of the populations relative to two energy levels E_r and E_s : for temperature T and putting $\Delta E = E_r - E_s$, one has:

$$\frac{n_r}{n_s} = \frac{B e^{-E_r/k_B T}}{B e^{-E_s/k_B T}} = e^{-\Delta E/k_B T} . \quad (2.21)$$

Let us evaluate, for example, the ratio n_2/n_1 between the populations of the first excited and the lowest energy level for an atomic system. The energy differences are of the order of some eV (an exception is provided by hydrogen, for which $E_2 - E_1 \simeq 10$ eV): this is proven by the fact that, normally, the absorption spectrum lies in the visible region ($1.5 \div 4$ eV). Now for such differences of energy one realizes that, at room temperature, the excited level practically is unpopulated. Indeed, for $T_0 \simeq 300$ K, one has:

$$k_B T_0 = \frac{(1.38 \times 10^{-16}) \times 300}{1.6 \times 10^{-12}} \simeq \frac{1}{40} \text{ eV} . \quad (2.22)$$

Both this relationship and the equivalent:

$$k_{\text{B}}T = 1 \text{ eV} \quad \Rightarrow \quad T \simeq 12000 \text{ K} \quad (2.23)$$

are very useful as they allow for a quick evaluation of $k_{\text{B}}T$ for any temperature.

In conclusion, for $\Delta E \simeq 1 \text{ eV}$ and $T \simeq 300 \text{ K}$, the ratio between the populations, according to (2.21), is

$$e^{-\Delta E/k_{\text{B}}T} = e^{-40} \simeq 10^{-16} \quad (e^x \simeq 10^{0.4x}) .$$

In order to have an appreciable population also for the excited levels, $k_{\text{B}}T \simeq \Delta E$ will be needed. As $\exp(-\Delta E/k_{\text{B}}T) \rightarrow 1$ for $T \rightarrow \infty$, one can say that only at very high temperatures the energy levels tend to become all equally (un)populated.

The fact that, at room temperature, practically all the atoms are in the ground state explains why the atoms of the same type all have the same size, whatever their past history (stability of atomic sizes), and also explains the fact that in the absorption spectrum of a substance (in normal conditions) only the first series is observed, namely only the transitions that start from the ground state.

It should be said that (2.19) applies to systems that only possess discrete energy levels (as the harmonic oscillator); for the systems that also possess a continuum of energies (as atoms, molecules ...), no quantization condition existing for them, (1.13) still holds. So we shall have:

$$\begin{cases} n_i = B e^{-\beta E_i} & (\text{discrete levels}) \\ dn(q, p) = B e^{-\beta E(q, p)} dq dp / h^f & (\text{continuous levels}) \end{cases} \quad (2.24)$$

where

$$B = N \left(\sum_j e^{-\beta E_j} + \int e^{-\beta E(q, p)} dq dp / h^f \right)^{-1}$$

the factor h^f dividing $dq dp$ is there because, as discussed at the end of Sect. 2.5, $dq dp / h^f$ is the number of quantum states in the cell $dq dp$.

Equation (2.24) may be useful, for example, in the calculation of the degree of ionization of a gas in the condition of thermal equilibrium: indeed, observe that, even if the population fast decreases as E increases, the degree of ionization can nonetheless be appreciable, owing to the great number of continuum states.

Let us now go back to the problem of the heat capacities. Having now (2.19) at one's disposal, the expression for the average energy of a subsystem (with only discrete levels) is

$$\overline{E} = \frac{\sum_i E_i n_i}{\sum_j n_j} = \frac{\sum_i E_i e^{-\beta E_i}}{\sum_j e^{-\beta E_j}} = -\frac{\partial}{\partial \beta} \ln Z(\beta) \quad (2.25)$$

where

$$Z(\beta) = \sum_i e^{-\beta E_i} .$$

Not always the series that defines the partition function can be explicitly summed.

In the case of the harmonic oscillator, as $E_n = n \hbar \omega$, the thing is simple since one is dealing with a geometric series

$$Z(\beta) = \sum_{n=0}^{\infty} e^{-\beta E_n} = \sum_{n=0}^{\infty} (e^{-\beta \hbar \omega})^n = \frac{1}{1 - e^{-\beta \hbar \omega}}$$

so, by use of (2.25), the average energy for a quantum oscillator reads:

$$\overline{E} = \frac{\hbar \omega}{e^{\hbar \omega / k_B T} - 1} . \quad (2.26)$$

In Fig. 2.7 both $\overline{E}$ as the function of T given by (2.26) and (dashed line) the graph of the classical expression ($\overline{E}_{cl} = k_B T$) are reported; we have put $T_c \equiv \hbar \omega / k_B$ (T_c is called **characteristic temperature**). Note that, contrary to the classical result, the average energy $\overline{E}$ depends on the frequency of the oscillator: now the quantum theory is able to distinguish ‘harder’ oscillators from the less ‘hard’ ones; at high temperatures, (2.26) is well approximated by the classical value, up to an irrelevant additive constant. This happens when $k_B T \gg \hbar \omega$: indeed, in such a case, one can expand in series (2.26) and obtain:

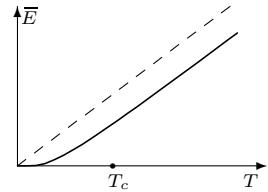


Fig. 2.7

$$\overline{E} = \frac{\hbar \omega}{1 + \hbar \omega / k_B T + \dots - 1} \simeq k_B T \quad (T \gg T_c)$$

(if the next term in the expansion of the exponential is kept, also the constant term is recovered: $\overline{E} \simeq k_B T - \frac{1}{2} \hbar \omega$).

The result could have been predicted, indeed $\hbar \omega$ is the jump between two adjacent energy levels of the oscillator: saying that $k_B T \gg \hbar \omega$ is the same as saying that the levels are very close to one another (with respect to thermal energy scale $k_B T$) and the quantization does not show up; the result is therefore the same one has classically (it could also be said that for $\hbar \omega \ll k_B T$ the series in (2.25) can be approximated by integrals and one is back to the classical case).

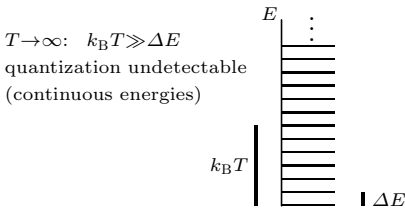


Fig. 2.8a

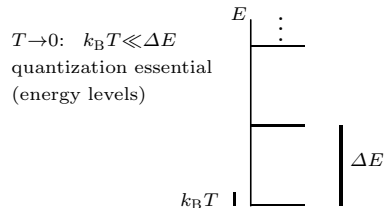


Fig. 2.8b

For $T \rightarrow 0$, (2.26) becomes $\overline{E} = \hbar \omega \exp(-\hbar \omega / k_B T)$ that tends very fast to 0, as is seen in Fig. 2.7. The two limiting cases ($T \gg T_c$ and $T \ll T_c$) are

shown in Figs. 2.8a and 2.8b. Let us now see the consequences of the above discussion for what concerns the heat capacities of solids.

As we have already seen in Sect. 1.3, according to the Einstein model, a solid (for the sake of simplicity we shall deal with a monatomic solid) is made out of many identical oscillators, with frequency ν and non-interacting with one another ('ideal gas of oscillators'). As the oscillators are three-dimensional, the internal energy of a gram-atom of substance is given by $\mathcal{U} = 3N_A \bar{E}$, with $\bar{E}$ given by (2.26). The atomic heat capacity is therefore:

$$C_V = \frac{\partial \mathcal{U}}{\partial T} = 3N_A k_B \left(\frac{\hbar \omega}{k_B T} \right)^2 \frac{e^{\hbar \omega / k_B T}}{(e^{\hbar \omega / k_B T} - 1)^2}. \quad (2.27)$$

It is easy to verify that, for $T \rightarrow 0$, $C_V \rightarrow 0$ whereas, for $T \rightarrow \infty$, $C_V \rightarrow 3R$. In Fig. 2.9 we have reported the graph of C_V as a function of the temperature: the figure shows that C_V reaches its classical value – up to less than 10% – already for $T = T_c \equiv \hbar \omega / k_B$, while at temperatures one order of magnitude smaller, $T \simeq T_c/10$, C_V is practically vanishing.

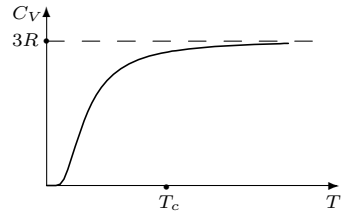


Fig. 2.9

Furthermore, we can examine how things change if we consider different solids, i.e. solids made out of oscillators with different frequencies. First of all, note that the C_V given by (2.27) is a universal function of the ratio T/T_c , where only $T_c = \hbar \omega / k_B$ depends on the considered solid (through $\omega = 2\pi \nu$), so that for different solids the curve is the same, apart from the scale of abscissae.

Let us compare, for example, lead and diamond; their physical features (e.g. the melting points) lead us to think that the oscillators the diamond consists of are harder (namely have an elastic constant with a higher value) than those of Pb: it follows that $\nu_{\text{Pb}} < \nu_{\text{C}}$ and consequently $T_c^{\text{Pb}} < T_c^{\text{C}}$. But we have seen that for $T = T_c$ the atomic heat capacity is practically equal to the classical Dulong–Petit value, so the curve relative to Pb should reach the value $3R$ at a lower temperature than that of diamond: this is exactly what happens experimentally (see Fig. 1.1).

In conclusion, the Einstein model – together with the quantization of the energy levels of the harmonic oscillator – accounts fairly well for the heat capacities of solids. Fairly well but not quite, because while (2.27) predicts that, for $T \rightarrow 0$,

$$C_V = 3R \left(\frac{\hbar \nu}{k_B T} \right)^2 e^{-\hbar \nu / k_B T} \quad (2.28)$$

(recall that $\hbar \omega = \hbar \nu$), namely that $C_V \rightarrow 0$ with all its derivatives, the curves relative to experimental data indicate that $C_V \rightarrow 0$ only as T^3 . This depends on the fact that the schematization of the solid, typical of the Einstein model, is rather inaccurate. Indeed, as we have said, Einstein identifies the solid with a collection of identical and independent oscillators. One should instead think that the interactions among the oscillators are not negligible: it

is sufficient to recall that hitting a metal gives rise to a sound, which proves the propagation of the perturbation along the whole piece of metal, i.e. the existence of elastic waves and, in turn, the existence of interactions among the oscillators.

It was P. Debye who proposed a model more complicated, but more plausible, assuming that the oscillators are not independent, but elastically bound to each other: this amounts to considering the small vibrations of the lattice ions around their equilibrium positions. Let $V(x_1, \dots, x_{3N})$ the potential energy of the system consisting of N ions ($3N$ degrees of freedom). By expanding V in Taylor series around the equilibrium positions x_i^0 and keeping only the first significant terms of the expansion (namely restricting to small vibrations) one has:

$$V(x_1, \dots, x_{3N}) = \frac{1}{2} \sum_{i,j=1}^{3N} \frac{\partial^2 V}{\partial x_i \partial x_j} \Big|_{x_i^0, x_j^0} (x_i - x_i^0)(x_j - x_j^0) + \dots \quad (2.29)$$

that is the potential energy of a system of N *coupled* oscillators. Since the right hand side of (2.29) is a quadratic form, there always exists a suitable change of variables that takes such a system to a system of $3N$ one-dimensional *independent* oscillators, whose frequencies we shall denote by ν_i , $i = 1, \dots, 3N$.

As an example, consider the system consisting of only two coupled oscillators (Fig. 2.10a): it is straightforward to realize that the possible motions of such a system are linear combinations of two fundamental harmonic motions, in which the oscillators vibrate either with the same phase (Fig. 2.10b) or with opposite phases (Fig. 2.10c), with different frequencies ν_1 and ν_2 . It is in this sense that one says that two identical, elastically bound oscillators are equivalent to a system consisting of two independent, but different (i.e. different frequencies) oscillators.

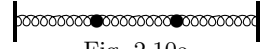


Fig. 2.10a

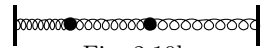


Fig. 2.10b

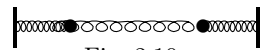


Fig. 2.10c

In the case at hand, one is dealing with many interacting oscillators that, similarly, are equivalent to as many independent oscillators with different frequencies that start from a certain minimum $\nu_{\min}$ up to a maximum $\nu_{\max}$. The frequencies ν_i are no longer frequencies relative to the single ions: they rather are collective oscillations (as in the case of Fig. 2.10), i.e. they are frequencies (***characteristic frequencies***) of the crystal as a whole. One understands that $\nu_{\min}$ must be of the order of magnitude of acoustic vibrations, i.e. $\simeq 10^3 \text{ s}^{-1}$.

From the point of view of classical theory, since $\overline{E}$ does not depend on ν , there is no difference between Einstein and Debye models. Instead, applying the quantization condition to the oscillators, the Debye model leads to a different result.

Indeed, the average energy of the i -th oscillators is given by (2.26):

$$\overline{E}_i = \frac{h \nu_i}{e^{h \nu_i / k_B T} - 1}$$

and the total energy is $\mathcal{U} = \sum_{i=1}^{3N} \overline{E}_i$ (sum over all the oscillators).

For a fixed temperature T , put $\nu_T \equiv k_B T / h$

and assume that $\nu_{\min} < \nu_T < \nu_{\max}$: the oscillators whose frequency is $\nu_i < \nu_T$ – given that for them $h\nu_i < k_B T$ – contribute to the total energy with $\overline{E}_i \simeq k_B T$ (the classical value). For this reason such oscillators are

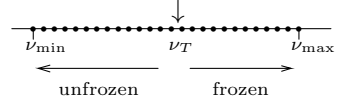


Fig. 2.11

said ‘unfrozen’ (Fig. 2.11). On the contrary, the oscillators for which $\nu_i > \nu_T$, having $h\nu_i > k_B T$, give a contribution to the energy – and to the heat capacity – that tends to 0 as ν increases: they are said ‘frozen’. It follows that, by increasing T , and therefore ν_T , all the oscillators tend to unfreeze until the classical value $3R$ for the atomic heat capacity is obtained. Instead, by decreasing T , more and more oscillators become frozen and $C_V \rightarrow 0$. The temperature such that all the oscillators are unfrozen, called **Debye characteristic temperature** and denoted by Θ , is defined by:

$$\Theta \stackrel{\text{def}}{=} \frac{h \nu_{\max}}{k_B} \quad (2.30)$$

and gives an indication of the temperature at which the specific heat reaches the classical value of the Dulong–Petit law.

So, at a certain temperature T , the solids for which $T > \Theta$ certainly will follow the Dulong–Petit law, those for which instead $T \ll \Theta$ will still be far away from the classical behaviour. Experimentally one has:

$$\Theta_{\text{Fe}} = 450 \text{ K}, \quad \Theta_{\text{Cu}} = 315 \text{ K}, \quad \Theta_{\text{Pb}} = 90 \text{ K}, \quad \Theta_{\text{C}} = 2000 \text{ K}$$

(the last datum refers to diamond carbon).

The values given above for Θ and (2.30) enable one to obtain that $\nu_{\max}$ is of the order of 10^{14} s^{-1} .

It is interesting to note that $\nu_{\max}$ depends on the velocity v of the sound in the solid, according to the following relationship:

$$\nu_{\max} \simeq v \sqrt[3]{\frac{N}{V}} \quad (2.31)$$

where N is the number of atoms contained in the volume V . The origin of (2.31) lies in the fact that, since a solid is not a continuous medium, the minimum wavelength admissible for the vibrations of the solid is of the order of magnitude of the interatomic distance, i.e. $(V/N)^{1/3}$, and $\nu_{\max} \simeq v/\lambda_{\min}$. Also (2.31) leads, for $\nu_{\max}$, to values of the order of $10^{13} \div 10^{14} \text{ s}^{-1}$.

The difference between Einstein model and Debye’s is therefore in the fact that, while for the first all the oscillators – being identical – either freeze or unfreeze all together (this is the reason why $C_V \rightarrow 0$ too fast for $T \rightarrow 0$), in the second model the oscillators freeze gradually when $T \rightarrow 0$, which entails a vanishing of C_V slower ($\propto T^3$) than in the former case.

2.7 Heat Capacities of Gases

In this section we shall examine in which way the hypothesis of discrete energy levels allows one to overcome the difficulties associated with the heat capacities of gases, discussed in Sect. 1.3.

Monatomic Gases

In this case we had found no discrepancy between classical theory and experimental data. Indeed, the atoms of the gas – schematized as pointlike particles – are free particles and therefore Bohr quantization condition does not apply: the classical treatment needs no modification. One could object that the gas is closed in a vessel and the atoms are bound to move within precise limits, so that also in this case one will have energy levels.

To provide an answer to this objection, it is convenient to have a glance at the situation from a quantitative point of view. Let us take, for the sake of simplicity, the energy levels of a particle in a segment, given by (2.18). By choosing a (size of the vessel) = 1 cm and $m = 10^{-24}$ g, one has:

$$E_n = n^2 E_1 ; \quad E_1 = \frac{h^2}{8ma^2} \simeq 10^{-18} \text{ eV} . \quad (2.32)$$

We must now ask what is the relationship between $k_B T$ and the distance among the energy levels. However this time, contrary to the case of harmonic oscillators, the distance between the energy levels is not constant but grows with n ; indeed, for $n \gg 1$:

$$E_{n+1} - E_n \simeq 2n E_1 . \quad (2.33)$$

Of course we are interested in comparing $k_B T$ with the distances among the levels that are appreciably populated, namely those levels for which $E_n \lesssim k_B T$. Equation (2.32) implies that this happens for $n \lesssim \sqrt{k_B T / E_1}$. Thanks to (2.33), the energy distances we are interested in are of the order of

$$\Delta E \lesssim \sqrt{E_1 k_B T} .$$

The conditions $\Delta E \ll k_B T$ or $\Delta E \gg k_B T$ take respectively the form:

$$\sqrt{E_1} \ll \sqrt{k_B T} \quad \text{or} \quad \sqrt{E_1} \gg \sqrt{k_B T} . \quad (2.34)$$

Recalling now that, for example, for $T = 1$ K, $k_B T = 1/12000$ eV, (2.32) implies that *for any temperature* $\sqrt{k_B T / E_1} \gg 1$ (e.g. He becomes liquid at about 4 K), and therefore quantization is undetectable and the atomic heat capacity C_V always is $\frac{3}{2}R$.

Diatomic Gases

In the discussion of Sect. 1.3 we had, initially, schematized the molecule as made out of two (pointlike) atoms at a fixed distance d . The Hamiltonian is given by (1.22): it can be written as

$$H = H_{\text{tr}} + H_{\text{rot}}$$

namely the sum of the first term that represents the translational motion of the center-of-mass, and of the second term that represents the energy associated with rotations.

The discussion made about monatomic gases teaches us that, as for the part relative to the translational degrees of freedom, quantization does not show up and, as a consequence, H_{tr} contributes $\frac{3}{2}R$ to the molar heat capacity C_V . Let us now examine the contribution of H_{rot} to C_V .

In order to determine the energy levels associated to the rotational degrees of freedom, it is convenient to recall the physical meaning of H_{rot} . For the sake of simplicity we shall restrict to the case of identical atoms: one has

$$H_{\text{rot}} = \frac{1}{2}m v_1^2 + \frac{1}{2}m v_2^2.$$

In the center-of-mass frame, however, $v_1 = v_2$ so that

$$H_{\text{rot}} = m v^2 = \frac{(m v d)^2}{m d^2} = \frac{L^2}{2I}$$

where L is the angular momentum of the system and I is the moment of inertia with respect to an axis passing through the center of mass and orthogonal to the segment joining the two atoms.

Thanks to the Bohr quantization condition $L = n \hbar$ already used for the hydrogen atom (see (2.8)), one finds:

$$E_n = \frac{\hbar^2 n^2}{2I} \quad (\text{rigid rotator}) \quad (2.35)$$

(actually, the energy levels we shall find later by quantum mechanics are given by $E_n = (\hbar^2/2I) n(n+1)$; the difference with the levels given by (2.35) decreases with the increase of the quantum number n).

To discover under which conditions the effect of quantization is detectable – recall the discussion made for monatomic gases (note that also in that case $E_n \propto n^2$) that has led to (2.34) – we must compare $k_B T$ with $\hbar^2/2I$. In other words we can, for every gas, define a characteristic temperature $T_c^{\text{rot}} \equiv \hbar^2/(2I k_B)$: for $T \gg T_c^{\text{rot}}$ we expect to find again the classical value R as contribution to C_V by the two rotational degrees of freedom, while for $T \ll T_c^{\text{rot}}$ we expect that the effect of quantization shows up with a $C_V^{(\text{rot})}$ tending to 0 for $T \rightarrow 0$. Indeed, in order to calculate $\mathcal{U}$, and therefore C_V , at low temperatures for *whatever* system endowed with discrete energy levels, we may limit ourselves to consider only the first two levels (in the case the third is not too close to the second): the lower the temperature, the lesser the contributions to the average energy of the excited levels.

So, putting $\Delta E = E_2 - E_1$, one has

$$\mathcal{U} = N \frac{E_1 e^{-\beta E_1} + E_2 e^{-\beta E_2}}{e^{-\beta E_1} + e^{-\beta E_2}} = N E_1 + N \Delta E \frac{e^{-\beta \Delta E}}{1 + e^{-\beta \Delta E}}$$

whence:

$$C_V = R \left(\frac{\Delta E}{k_B T} \right)^2 e^{-\Delta E/k_B T}, \quad T \ll \Delta E/k_B \quad (2.36)$$

(as a confirmation of the generality of this result, note that (2.36) coincides with (2.27) derived directly from (2.26)).

Let us now give the values of T_C^{rot} for some gases:

$$\text{H}_2 : 85 \text{ K}, \quad \text{N}_2 : 3 \text{ K}, \quad \text{O}_2 : 2 \text{ K}, \quad \text{NaCl} : 15 \text{ K}$$

and it appears from these data that the effect of quantization, in practice, is detectable only for H_2 : in this case $\Delta E = \hbar^2/2I \simeq 10^{-2} \text{ eV}$, whereas for the other gases ΔE is smaller by a factor $10 \div 100$.

In the present case, contrary to the case of oscillators, it is not possible to calculate $\mathcal{U}(T)$ analytically, and the same is true for $C_V(T)$; the numerical calculation is however possible. The solid curve in Fig. 2.12 has been obtained by making use of the correct quantum expression for the energy levels, including the degeneracy factors g_n that, in this case, are $g_n = 2n + 1$; only five levels have been taken into consideration (the lowest and the first four excited energy levels) and we have verified that, at least for $T \leq 2T_C^{\text{rot}}$, and up to 1%, the curve is not modified by the inclusion of 20 further levels: as it is evident, for $T \geq 0.5 T_C^{\text{rot}}$, $C_V \simeq R$.

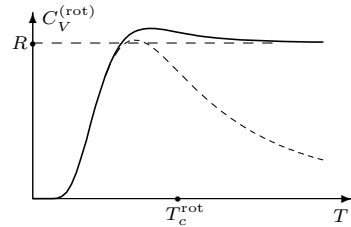


Fig. 2.12

The dashed curve is the one obtained by taking into consideration only the first two levels: in agreement with (2.36) the curve reproduces very well the behaviour of C_V at low temperatures, whereas for high temperatures tends to 0, given that for a system with a finite number of energy levels the internal energy tends to a constant that corresponds to the equipopulation of the levels.

Let us now consider the problem of the other degrees of freedom of the diatomic molecule: in the first place let us consider the degree of freedom relative to the rotation around the line that joins the nuclei. Also for this rotational degree of freedom we shall have energy levels of the type:

$$E_n = \frac{\hbar^2}{2I'} n^2$$

in which, in comparison with (2.35), only the moment of inertia is changed.

A diatomic molecule has the structure reported in Fig. 2.13: the nuclei are heavy, but small ($10^{-12} \div 10^{-13} \text{ cm}$), so the main contribution to I' is given by the electrons that are light, but rotate at a distance of about 10^{-8} cm from the nuclei. So, for example, in H_2 , since the ratio between the masses of nuclei and electrons is about 2000, it follows that $I' \simeq I/2000$.

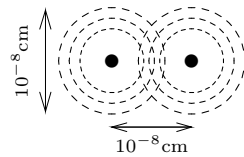


Fig. 2.13

As a consequence, in this case, the ΔE and the characteristic temperature are about 2000 times higher than in the previous case: $\Delta E \simeq 10 \text{ eV} \Rightarrow T_c \simeq 10^5 \text{ K}$. Therefore this degree of freedom does not contribute to C_V inasmuch as permanently frozen, even at temperatures of some thousand degrees.

Finally, to conclude, let us consider the vibrational degree of freedom of the diatomic molecule. As of now, it will be clear that, in order to understand whether this degree of freedom contributes to C_V or not at a given temperature, one must compare the $k_B T$ we are interested in with the ΔE that, dealing with a harmonic oscillator, equals $\hbar \omega$. Clearly $\hbar \omega$ depends on the ‘hardness’, i.e. on the elastic constant of the ‘spring’ that binds the two atoms.

Let us therefore try to get an idea of how much is ω for a molecule. We know the potential $V(r)$ that binds the atoms is of the type reported in Fig. 1.3. In the approximation of small oscillations around the equilibrium point, we are interested in approximating $V(r)$ around the point $r = d$ as (Fig. 2.14):

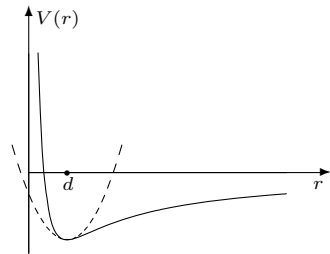


Fig. 2.14

$$V^{\text{harm}}(r) = \frac{1}{2} k (r - d)^2 - V_0. \quad (2.37)$$

Let us try to estimate k by exploiting the following information:

- i) an energy of the order of some electronvolt is needed to dissociate a molecule, so $V_0 \simeq 1 \text{ eV}$;
- ii) the distance between the atoms is of the order of the ångström; so also the distance among the points where $V^{\text{harm}}(r) \simeq 0$ will be of the same order of magnitude.

These data are sufficient to determine k in (2.37) and, apart from numerical factors, it turns out that (M is the mass of the nuclei; better: the reduced mass):

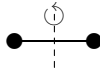
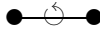
$$k = \frac{V_0}{d^2} \quad \Rightarrow \quad \omega = \sqrt{\frac{k}{M}} = \sqrt{\frac{V_0}{M d^2}} \simeq 10^{14} \text{ s}^{-1}. \quad (2.38)$$

The result is reasonable, the fact that a molecule radiates in the infrared being known. In conclusion: $\Delta E = \hbar \omega \simeq 10^{-1} \text{ eV}$.

It appears that at room temperature ($k_B T = 1/40 \text{ eV}$) this degree of freedom practically is frozen, but at temperatures even not so higher ($T \simeq 10^3 \text{ K}$) it may give an appreciable contribution to the C_V . We report, as an example, the characteristic temperatures $T_c^{\text{vib}} \equiv \hbar \omega / k_B$ relative to the vibrational degrees freedom for some molecules:

$$\text{H}_2 : 6100 \text{ K}, \quad \text{N}_2 : 3340 \text{ K}, \quad \text{O}_2 : 2230 \text{ K}.$$

Let us summarize in a table the results we have found, reporting for the several degrees of freedom of a diatomic molecule the typical values of ΔE and the relative characteristic temperatures T_c .

translations		$\Delta E \simeq 0,$	$T_c \simeq 0$
rotations		$\Delta E: 10^{-4} \div 10^{-2} \text{ eV},$	$T_c: 1 \div 100 \text{ K}$
vibrations		$\Delta E \simeq 10^{-1} \text{ eV},$	$T_c \simeq 10^3 \text{ K}$
(electrons		$\Delta E \simeq 1 \text{ eV},$	$T_c \simeq 10^4 \text{ K})$
(rotations		$\Delta E \simeq 10 \text{ eV},$	$T_c \simeq 10^5 \text{ K})$

Here is how the hypothesis of energy levels solves the problem of the ambiguity in the counting of the degrees of freedom: let us attribute to the system all the degrees of freedom we wish (electrons in the atoms, nucleons in the nuclei, quarks in the nucleons ...), but in the end, in order to decide whether they do contribute to the C_V , we must check how much is the distance between the energy levels associated with such degrees of freedom; for the electrons we shall find a ΔE of the order of some eV, for nucleons of some MeV, ... and in all such cases we discover that these degrees of freedom can be ignored at any reasonable temperature.

2.8 Wave-like Behaviour of Particles: the Bragg and Davisson–Germer Experiments

In the previous sections of this chapter we have introduced a certain number of hypotheses:

1. the existence of photons;
2. the Bohr hypothesis of quantization;
3. the Bohr hypothesis that relates the frequency radiated in a transition with the energy jumps.

These hypotheses have then been used with a remarkable success to explain several experimental facts. At this point it is natural to ask what survives of classical physics: are the above hypotheses a sort of ‘amendments’ to the laws of classical physics that, however, keeps its structure substantially untouched or, rather, the success of the above hypotheses hints at the necessity of profoundly modifying the concepts of classical physics? At the end of the present section there will be no doubt about which the answer should be.

In 1923, about ten years after Bohr had proposed his theory, L. de Broglie put forward the following problem. The electromagnetic radiation, to which always and correctly a wave-like nature had been attributed, also behaves in a totally different way, i.e. in a corpuscular way (photons). The relationship between the two aspects, wave-like $\rightarrow$ corpuscular, is provided by Planck’s constant h . But h also enters, through Bohr–Sommerfeld quantization condition, problems where particles are dealt with. Furthermore, in the quantization condition integer numbers n do intervene: any physicist knows by experience that the presence of integer numbers often indicates one is dealing with undulatory phenomena (for example: interference fringes, standing waves on a

string, ...). In conclusion: could it not be that, through h , one should make the contrary step, namely look for a wave-like behaviour in what has always been considered corpuscular (particles)?

Let us consider, for example, a particle going a certain orbit (an electron in a circular orbit in hydrogen, or a particle in a segment): then the Bohr–Sommerfeld condition $\oint p \, dq = n h$ entails:

$$p L = n h \quad (L = \text{length of the orbit}) \quad (2.39)$$

If we rewrite (2.39) in the form

$$L = n \frac{h}{p} \quad (2.40)$$

and recall that for a photon $h/p = \lambda$, then (2.40) suggests the following interpretation

de Broglie hypothesis: a wave is associated with each particle. The relationship between the wavelength λ and the momentum p is given, as for photons, by $\lambda = h/p$. The allowed orbits are those that contain an integer number of wavelengths.

Bohr quantization condition is therefore looked upon in a totally new light.

But so far we are in the field of hypotheses. Is de Broglie's hypothesis only a new terminology or there is something more in it? What kind of wave is one talking about? We know two types of waves: elastic waves and electromagnetic waves. Certainly one is not dealing with elastic waves and, presumably, not even with electromagnetic waves, inasmuch as the de Broglie hypothesis does not necessarily refer to charged particles. It is likely that we shall have to deal with a third type of waves. In this case intuition is of little help: it is convenient to ask oneself which are the general features of waves. Waves are entities that can be summed with each other or, in loose terms, waves are things that *interfere*. So, if these de Broglie waves really exist, they must be revealed by means of interference phenomena.

Before thinking of an experiment that emphasizes the wave-like aspect of particles, it is convenient to realize the size of the wavelengths one has to deal with. Let us consider free particles: from the relations $\lambda = h/p$ and $p = \sqrt{2mE}$ one obtains the **de Broglie wavelength**:

$$\lambda = \frac{h}{\sqrt{2mE}}. \quad (2.41)$$

If, as customary, we express λ in Å and E in eV, for an *electron* one has

$$\lambda[\text{Å}] = \frac{12.4}{\sqrt{E[\text{eV}]}} \quad (\text{for electrons}) \quad (2.42)$$

i.e. for an electron of energy 1 eV, $\lambda = 12.4 \text{ Å}$.

Note that, while for photons λ is proportional to $1/E$, for massive (non-relativistic) particles λ is proportional to $1/\sqrt{E}$. In addition, the higher the mass, the lower – for a given energy – the wavelength λ . In conclusion, for electrons with energy of the order of 100 eV, λ is of the order of the ångström, i.e. of the same order of magnitude of the X-ray wavelengths.

A way to show that X-rays are electromagnetic waves consists in analyzing the reflection of X-rays by a crystal (**Bragg reflection**). Let us consider a crystal; the regularity of the arrangement of the atoms (or ions) determines many families of lattice planes: in Fig. 2.15 one of these families is represented, for example that parallel to a face of the crystal. The distance d between the lattice planes (of a family) is called **lattice spacing**: d normally is of the order of a few ångström.

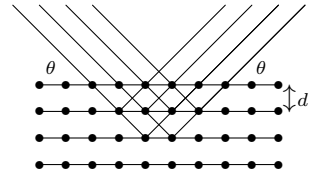


Fig. 2.15

If we let some monochromatic X-rays impinge on the crystal, at an angle θ with respect to the crystal face, and observe the specularly reflected (i.e. emerging at the same angle θ) radiation, one notes that the radiation is reflected only for certain particular values of θ : $\theta_1, \theta_2, \dots$. More precisely, very sharp maxima in the intensity of the reflected radiation are observed in correspondence of the angles $\theta_1, \theta_2, \dots$, alternating with minima in which the intensity is practically vanishing.

The explanation of this fact is the following: X-rays are reflected by the various lattice planes (Fig. 2.15): the waves reflected by two adjacent planes (Fig. 2.16) go optical paths whose difference is $2d \sin \theta$ (the darker segments in Fig. 2.16). When $2d \sin \theta$ is an integer multiple of the wave-

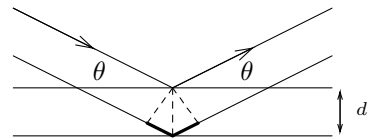


Fig. 2.16

length λ , all the reflected waves are in phase with one another and there occurs a constructive interference, i.e. a maximum in the reflected intensity. If, on the contrary, $2d \sin \theta$ is an odd integer multiple of $\lambda/2$, the waves reflected by two adjacent lattice planes are in opposition of phase and there occurs destructive interference, i.e. no reflected radiation is observed. In the intermediate cases there occurs destructive interference among the waves reflected by several lattice planes, which results in an almost vanishing intensity. In conclusion the maxima in the intensity of the reflected radiation occur for those angles θ that satisfy the **Bragg condition**:

$$2d \sin \theta = n \lambda . \quad (2.43)$$

The number of maxima observed when θ is let to vary from 0 to $\pi/2$ is the maximum integer contained in $2d/\lambda$: this explains why, in order to easily observe the phenomenon with X-rays ($\lambda \simeq 1 \text{ \AA}$), it is necessary that d be of the same order of magnitude of λ , i.e. why crystals are used in this type

of experiments. It is also clear that the knowledge of the angles θ satisfying (2.43) allows for the determination of λ , given d ; or viceversa of d , given λ .

The same experiment was made by C. Davisson and L. Germer in 1927 replacing X-rays with a sharp beam of (as much as possible) monoenergetic *electrons*.

It was observed that in this case also the electrons were specularly reflected only for some values of θ in agreement with (2.43): this proves that also electrons possess a wave-like behaviour. Furthermore, the Davisson–Germer experiment allows one to determine λ from (2.43) and to verify the relationship (2.41) between λ and E .

We add that, along with the development of experimental techniques, Davisson–Germer experiment has been repeated also with different particles: protons, neutrons, He atoms, ions; and in all these cases the Bragg condition has been confirmed for matter particles.

So the de Broglie idea of associating a wave with each particle was not simply a smart theoretical speculation, but a well precise physical reality corresponded to it.

Davisson experiment first, and Davisson–Germer experiments later had an accidental origin: as a consequence of the explosion of a bottle of liquid air in the laboratory where Davisson was making experiments that used electron beams, a vacuum tube with an electrode of poly-crystalline nickel went broken; owing to the thermal treatment the electrode underwent in order to be fixed, nickel crystallized in coarse grains and this led to results that, for what regarded the angular distribution of the electrons reflected by the electrode, were completely different from the previous ones.



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