The physics of solids

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ABSTRACT. This is an introduction to the physics of solids. We first discuss general physics, thermodynamics, and condensed matter. Then we focus on the solids, and notably on their elasticity properties. We discuss then crystals and their mathematics. We end with an introduction to the metals, and their various properties.

Preface

Are the elementary particles, atoms and molecules intelligent? Certainly so, in the deep intergalactic space, where the presence of a single such tiny particle is tremendously good news, bringing some life there, as we know it. That is, with the said tiny particle doing the usual things that life does, namely moving around, absorbing or emitting radiation, standing her ground against other particles that might appear, but why not falling in love sometimes with one of these incoming particles, and so on. And, at times of rest, simply resting, and perhaps conversating with the vacuum, which is an intelligent creature too, this is, playing some sort of hide and seek games, for the fun.

Actually, there is no need to go in the deep space for observing such things, intelligent and playful particles. Indeed, quite often in the terrestrial life as we know it, breaking of equilibrium and of symmetry, in all sorts of situations involving classical mechanics, or electromagnetism, or even quantum mechanics, leading sometimes to huge scale consequences, can be produced by a single incoming particle, animated by good or bad intentions. With, as a notorious example here, duly observed by us humans, with fascination, and questioning about what true and strong intelligence really is, that single extra neutron producing a chain reaction inside an uranium or plutonium ball.

In short, physics, even at very small scales, is all about life, intelligence, interactions, and ultimately, love. But now, in view of this, and restricting the attention to the molecular scale, which is where a lot of interesting physics is known to happen, or at least to originate, here on Earth, what can we say about life and interactions there?

In answer, basic thermodynamics teaches us that, a bit like animals which can prefer to be solitary, or live in small groups, or in big groups, molecules can remain quite independent, by forming gases, but beware tough of the collisions happening there, or pleasantly live, reasonably close to each other, as liquids, or form strong civilizations, with countless rules and regulations, pollution, taxes and so on, in the form of solids.

It is about this latter form of matter, solids, which is a bit similar to our modern human world, that we will talk about, in this book. We will first discuss general physics, thermodynamics, and condensed matter. Then we will focus on the solids, and notably on

their elasticity properties. We will discuss then crystals and their mathematics. Finally, we will provide an introduction to the metals, and their various properties.

Many thanks to my cats, for precious help with the preparation of the present book, and notably for their teachings on phase transitions, in the carnivore world. Understanding the domestication of liquids will be a main theme of discussion, in this book.

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CHAPTER 1

Atoms

1a. Atomic theory

Quantum mechanics was born from the study of the hydrogen atom, which consists of a negative charge, the electron, spinning around a positive charge, a proton. Basic electrodynamics, you would say, that I can solve with the Maxwell equations, that I learned the hard way in school. Very good, so let us start indeed with these equations:

THEOREM 1.1. *Electrodynamics is governed by the formulae*

$$< \nabla, E >= \frac{\rho}{\varepsilon_0} \quad , \quad < \nabla, B >= 0$$

$$\nabla \times E = -\dot{B} \quad , \quad \nabla \times B = \mu_0 J + \mu_0 \varepsilon_0 \dot{E}$$

called Maxwell equations.

PROOF. This is something fundamental, appearing as a tricky mixture of physics facts and mathematical results, the idea being as follows:

(1) To start with, electrodynamics is the science of moving electrical charges. And this is something quite complicated, because unlike in classical mechanics, where the Newton law is good for both the static and the dynamic setting, the Coulomb law, which is actually very similar to the Newton law, does the job when the charges are static, but no longer describes well the situation when the charges are moving.

(2) The problem comes from the fact that moving charges produce magnetism, and with this being visible when putting together two electric wires, which will attract or repel, depending on orientation. Thus, in contrast with classical mechanics, where static or dynamic problems are described by a unique field, the gravitational one, in electrodynamics we have two fields, namely the electric field E, and the magnetic field B.

(3) Fortunately, there is a full set of equations relating the fields E and B, namely those above. To be more precise, the first formula is the Gauss law, ρ being the charge, and ε_0 being a constant, and with this Gauss law more or less replacing the Coulomb law from electrostatics. The second formula is something basic, and anonymous. The third formula is the Faraday law. As for the fourth formula, this is the Ampère law, as modified by Maxwell, with J being the volume current density, and μ_0 being a constant. $\square$

In relation now with the hydrogen atom, we have good and bad news. The bad news is that the Maxwell equations, as formulated above, are something rather statistical and macroscopic, and simply do not apply to the hydrogen atom. However, we have good news as well, the point here being that the same Maxwell equations can lead us, in a rather twisted way, via light, spectroscopy, and many more, to the hydrogen atom. So, let us explain this. We first have the following consequence of the Maxwell equations:

THEOREM 1.2. *In regions of space where there is no charge or current present the Maxwell equations for electrodynamics read*

$$< \nabla, E >=< \nabla, B >= 0$$

$$\nabla \times E = -\dot{B} \quad , \quad \nabla \times B = \dot{E}/c^2$$

and both the electric field E and magnetic field B are subject to the wave equation

$$\ddot{\varphi} = c^2 \Delta \varphi$$

where $\Delta = \sum_i d^2/dx_i^2$ is the Laplace operator, and c is the speed of light.

PROOF. Under the circumstances in the statement, namely no charge or current present, the Maxwell equations in Theorem 1.1 simply read:

$$< \nabla, E >=< \nabla, B >= 0$$

$$\nabla \times E = -\dot{B} \quad , \quad \nabla \times B = \dot{E}/c^2$$

Here we have used a key formula due to Biot-Savart, as follows:

$$\mu_0 \varepsilon_0 = \frac{1}{c^2}$$

Now by applying the curl operator to the last two equations, we obtain:

$$\nabla \times (\nabla \times E) = -\nabla \times \dot{B} = -(\nabla \times B)' = -\ddot{E}/c^2$$

$$\nabla \times (\nabla \times B) = \nabla \times \dot{E}/c^2 = (\nabla \times E)'/c^2 = -\ddot{B}/c^2$$

But the double curl operator is subject to the following formula:

$$\nabla \times (\nabla \times \varphi) = \nabla < \nabla, \varphi > -\Delta \varphi$$

Now by using the first two equations, we are led to the conclusion in the statement.   □

So, what is light? Light is the wave predicted by Theorem 1.2, traveling in vacuum at the maximum possible speed, c, and with an important extra property being that it depends on a real positive parameter, that can be called, upon taste, frequency, wavelength, or color. And in what regards the creation of light, the mechanism here is as follows:

FACT 1.3. *An accelerating or decelerating charge produces electromagnetic radiation, called light, whose frequency and wavelength can be explicitly computed.*

This phenomenon can be observed is a variety of situations, such as the usual light bulbs, where electrons get decelerated by the filament, acting as a resistor, or in usual fire, which is a chemical reaction, with the electrons moving around, as they do in any chemical reaction, or in more complicated machinery like nuclear plants, particle accelerators, and so on, leading there to all sorts of eerie glows, of various colors.

In practice now, the classification of light, in a rough form, is as follows:

Frequency	Type	Wavelength
	—	
$10^{18} - 10^{20}$	γ rays	$10^{-12} - 10^{-10}$
$10^{16} - 10^{18}$	X $-$ rays	$10^{-10} - 10^{-8}$
$10^{15} - 10^{16}$	UV	$10^{-8} - 10^{-7}$
	—	
$10^{14} - 10^{15}$	blue	$10^{-7} - 10^{-6}$
$10^{14} - 10^{15}$	yellow	$10^{-7} - 10^{-6}$
$10^{14} - 10^{15}$	red	$10^{-7} - 10^{-6}$
	—	
$10^{11} - 10^{14}$	IR	$10^{-6} - 10^{-3}$
$10^{9} - 10^{11}$	microwave	$10^{-3} - 10^{-1}$
$1 - 10^{9}$	radio	$10^{-1} - 10^{8}$

Observe the tiny space occupied by the visible light, all the colors there, and the many more missing, being squeezed under the $10^{14} - 10^{15}$ frequency banner. Here is a zoom on that part, with of course the remark that all this, colors, is something subjective:

Frequency THz $= 10^{12}$ Hz	Color	Wavelength nm $= 10^{-9}$ m
	—	
$670 - 790$	violet	$380 - 450$
$620 - 670$	blue	$450 - 485$
$600 - 620$	cyan	$485 - 500$
$530 - 600$	green	$500 - 565$
$510 - 530$	yellow	$565 - 590$
$480 - 510$	orange	$590 - 625$
$400 - 480$	red	$625 - 750$

Many things can be said about light and optics, and going now straight to the point, the idea is that, with this in hand, we can talk about spectroscopy:

FACT 1.4. *We can study events via spectroscopy, by capturing the light the event has produced, decomposing it with a prism, carefully recording its "spectral signature", consisting of the wavelenghts present, and their density, and then doing some reverse engineering, consisting in reconstructing the event out of its spectral signature.*

Going now towards atoms, there is a long story here, involving many discoveries, around 1890-1900, focusing on hydrogen H. We will present here things a bit retrospectively. First on our list is the following discovery, by Lyman in 1906:

FACT 1.5 (Lyman). *The hydrogen atom has spectral lines given by the formula*

$$\frac{1}{\lambda} = R\left(1 - \frac{1}{n^2}\right)$$

where $R \simeq 1.097 \times 10^7$ and $n \geq 2$, which are as follows,

n	Name	Wavelength	Color
2	α	121.567	UV
3	β	102.572	UV
4	γ	97.254	UV
$\vdots$	$\vdots$	$\vdots$	$\vdots$
∞	limit	91.175	UV

called Lyman series of the hydrogen atom.

Observe that all the Lyman series lies in UV, which is invisible to the naked eye. Due to this fact, this series, while theoretically being the most important, was discovered only second. The first discovery, which was the big one, and the breakthrough, was by Balmer, the founding father of all this, back in 1885, in the visible range, as follows:

FACT 1.6 (Balmer). *The hydrogen atom has spectral lines given by the formula*

$$\frac{1}{\lambda} = R\left(\frac{1}{4} - \frac{1}{n^2}\right)$$

where $R \simeq 1.097 \times 10^7$ and $n \geq 3$, which are as follows,

n	Name	Wavelength	Color
3	α	656.279	red
4	β	486.135	aqua
5	γ	434.047	blue
6	δ	410.173	violet
7	ε	397.007	UV
$\vdots$	$\vdots$	$\vdots$	$\vdots$
∞	limit	346.600	UV

called Balmer series of the hydrogen atom.

So, this was Balmer's original result, which started everything. As a third main result now, this time in IR, due to Paschen in 1908, we have:

FACT 1.7 (Paschen). *The hydrogen atom has spectral lines given by the formula*

$$\frac{1}{\lambda} = R\left(\frac{1}{9} - \frac{1}{n^2}\right)$$

where $R \simeq 1.097 \times 10^7$ and $n \geq 4$, which are as follows,

n	Name	Wavelength	Color
4	α	1875	IR
5	β	1282	IR
6	γ	1094	IR
$\vdots$	$\vdots$	$\vdots$	$\vdots$
∞	limit	820.4	IR

called Paschen series of the hydrogen atom.

Observe the striking similarity between the above three results. In fact, we have here the following fundamental, grand result, due to Rydberg in 1888, based on the Balmer series, and with later contributions by Ritz in 1908, using the Lyman series as well:

CONCLUSION 1.8 (Rydberg, Ritz). *The spectral lines of the hydrogen atom are given by the Rydberg formula, depending on integer parameters $n_1 < n_2$,*

$$\frac{1}{\lambda_{n_1 n_2}} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

with R being the Rydberg constant for hydrogen, which is as follows:

$$R \simeq 1.096\ 775\ 83 \times 10^7$$

These spectral lines combine according to the Ritz-Rydberg principle, as follows:

$$\frac{1}{\lambda_{n_1 n_2}} + \frac{1}{\lambda_{n_2 n_3}} = \frac{1}{\lambda_{n_1 n_3}}$$

Similar formulae hold for other atoms, with suitable fine-tunings of R.

Here the first part, the Rydberg formula, generalizes the results of Lyman, Balmer, Paschen, which appear at $n_1 = 1, 2, 3$, at least retrospectively. The Rydberg formula predicts further spectral lines, appearing at $n_1 = 4, 5, 6, \ldots$, and these were discovered later, by Brackett in 1922, Pfund in 1924, Humphreys in 1953, and others aftwerwards,

with all these extra lines being in far IR. The simplified complete table is as follows:

n_1	n_2	Series name	Wavelength $n_2 = \infty$	Color $n_2 = \infty$
		—	—	
1	$2 - \infty$	Lyman	91.13 nm	UV
2	$3 - \infty$	Balmer	364.51 nm	UV
3	$4 - \infty$	Paschen	820.14 nm	IR
		—	—	
4	$5 - \infty$	Brackett	1458.03 nm	far IR
5	$6 - \infty$	Pfund	2278.17 nm	far IR
6	$7 - \infty$	Humphreys	3280.56 nm	far IR
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$

Regarding the last assertion, concerning other elements, this is something conjectured and partly verified by Ritz, and fully verified and clarified later, via many experiments, the fine-tuning of R being basically $R \to RZ^2$, where Z is the atomic number.

From a theoretical physics viewpoint, the main result remains the middle assertion, called Ritz-Rydberg combination principle, which is something quite puzzling. But this combination principle reminds the formula $e_{n_1 n_2} e_{n_2 n_3} = e_{n_1 n_3}$ for the usual matrix units $e_{ij} : e_j \to e_i$. Thus, we are in familiar territory here, and we can start dreaming of:

THOUGHT 1.9. *Observables in quantum mechanics should be some sort of infinite matrices, generalizing the Lyman, Balmer, Paschen lines of the hydrogen atom, and multiplying between them as the matrices do, as to produce further observables.*

Now back to more concrete things, as a main problem that we would like to solve, we have the understanding the intimate structure of matter, at the atomic level. There is of course a long story here, regarding the intimate structure of matter, going back centuries and even millennia ago, and our presentation here will be quite simplified. As a starting point, since we need a starting point for all this, let us agree on:

CLAIM 1.10. *Ordinary matter is made of small particles called atoms, with each atom appearing as a mix of even smaller particles, namely protons $+$, neutrons 0 and electrons $-$, with the same number of protons $+$ and electrons $-$.*

As a first observation, this is something which does not look obvious at all, with probably lots of work, by many people, being involved, as to lead to this claim. And so it is. The story goes back to the discovery of charges and electricity, which were attributed to a small particle, the electron $-$. Now since matter is by default neutral, this naturally leads to the consideration to the proton $+$, having the same charge as the electron.

But, as a natural question, why should be these electrons $-$ and protons $+$ that small? And also, what about the neutron 0? These are not easy questions, and the fact that it

is so came from several clever experiments. Let us first recall that careful experiments with tiny particles are practically impossible. However, all sorts of brutal experiments, such as bombarding matter with other pieces of matter, accelerated to the extremes, or submitting it to huge electric and magnetic fields, do work. And it is such kind of experiments, due to Thomson, Rutherford and others, "peeling off" protons +, neutrons 0 and electrons − from matter, and observing them, that led to the conclusion that these small beasts +, 0, − exist indeed, in agreement with Claim 1.10.

So, taking now Claim 1.10 for granted, how are then the atoms organized, as mixtures of protons +, neutrons 0 and electrons −? The answer here lies again in the above-mentioned "brutal" experiments of Thomson, Rutherford and others, which not only proved Claim 1.10, but led to an improved version of it, as follows:

CLAIM 1.11. *The atoms are formed by a core of protons + and neutrons 0, surrounded by a cloud of electrons −, gravitating around the core.*

This is a considerable advance, because we are now into familiar territory, namely some kind of mechanics. And with this in mind, all the pieces of our puzzle start fitting together, and we are led to the following grand conclusion:

CLAIM 1.12 (Bohr and others). *The atoms are formed by a core of protons and neutrons, surrounded by a cloud of electrons, basically obeying to a modified version of electromagnetism. And with a fine mechanism involved, as follows:*

(1) *The electrons are free to move only on certain specified elliptic orbits, labelled $1, 2, 3, \ldots$, situated at certain specific heights.*
(2) *The electrons can jump or fall between orbits $n_1 < n_2$, absorbing or emitting light and heat, that is, electromagnetic waves, as accelerating charges.*
(3) *The energy of such a wave, coming from $n_1 \to n_2$ or $n_2 \to n_1$, is given, via the Planck viewpoint, by the Rydberg formula, applied with $n_1 < n_2$.*
(4) *The simplest such jumps are those observed by Lyman, Balmer, Paschen. And multiple jumps explain the Ritz-Rydberg formula.*

And isn't this beautiful. Moreover, following now Heisenberg, the next claim is that the underlying mathematics in all the above can lead to a beautiful axiomatization of quantum mechanics, as a "matrix mechanics", along the lines of Thought 1.9.

1b. Quantum mechanics

Before explaining what Heisenberg was saying, based on Lyman, Balmer, Paschen, namely developing some sort of "matrix mechanics", let us hear as well the point of view of Schrödinger, which came a few years later. His idea was to forget about exact things, and try to investigate the hydrogen atom statistically. Let us start with:

QUESTION 1.13. *In the context of the hydrogen atom, assuming that the proton is fixed, what is the probability density $\varphi_t(x)$ of the position of the electron e, at time t,*

$$P_t(e \in V) = \int_V \varphi_t(x)dx$$

as function of an intial probability density $\varphi_0(x)$? Moreover, can the corresponding equation be solved, and will this prove the Bohr claims for hydrogen, statistically?

In order to get familiar with this question, let us first look at examples coming from classical mechanics. In the context of a particle whose position at time t is given by $x_0 + \gamma(t)$, the evolution of the probability density will be given by:

$$\varphi_t(x) = \varphi_0(x) + \gamma(t)$$

However, such examples are somewhat trivial, of course not in relation with the computation of γ, usually a difficult question, but in relation with our questions, and do not apply to the electron. The point indeed is that, in what regards the electron, we have:

FACT 1.14. *In respect with various simple interference experiments:*
  (1) *The electron is definitely not a particle in the usual sense.*
  (2) *But in most situations it behaves exactly like a wave.*
  (3) *But in other situations it behaves like a particle.*

Getting back now to the Schrödinger question, all this suggests to use, as for the waves, an amplitude function $\psi_t(x) \in \mathbb{C}$, related to the density $\varphi_t(x) > 0$ by the formula $\varphi_t(x) = |\psi_t(x)|^2$. Not that a big deal, you would say, because the two are related by simple formulae as follows, with $\theta_t(x)$ being an arbitrary phase function:

$$\varphi_t(x) = |\psi_t(x)|^2 \quad , \quad \psi_t(x) = e^{i\theta_t(x)}\sqrt{\varphi_t(x)}$$

However, such manipulations can be crucial, raising for instance the possibility that the amplitude function satisfies some simple equation, while the density itself, maybe not. And this is what happens indeed. Schrödinger was led in this way to:

CLAIM 1.15 (Schrödinger). *In the context of the hydrogen atom, the amplitude function of the electron $\psi = \psi_t(x)$ is subject to the Schrödinger equation*

$$ih\dot{\psi} = -\frac{h^2}{2m}\Delta\psi + V\psi$$

m being the mass, $h = h_0/2\pi$ the reduced Planck constant, and V the Coulomb potential of the proton. The same holds for movements of the electron under any potential V.

Observe the similarity with the wave equation $\ddot{\varphi} = v^2\Delta\varphi$, and with the heat equation $\dot{\varphi} = \alpha\Delta\varphi$ too. Many things can be said here. Following now Heisenberg and Schrödinger, and then especially Dirac, who did the axiomatization work, we have:

DEFINITION 1.16. *In quantum mechanics the states of the system are vectors of a Hilbert space H, and the observables of the system are linear operators*

$$T : H \to H$$

which can be densely defined, and are taken self-adjoint, $T = T^*$. The average value of such an observable T, evaluated on a state $\xi \in H$, is given by:

$$< T >=< T\xi, \xi >$$

In the context of the Schrödinger mechanics of the hydrogen atom, the Hilbert space is the space $H = L^2(\mathbb{R}^3)$ where the wave function ψ lives, and we have

$$< T >= \int_{\mathbb{R}^3} T(\psi) \cdot \bar{\psi} \, dx$$

which is called "sandwiching" formula, with the operators

$$x \quad , \quad -\frac{ih}{m}\nabla \quad , \quad -ih\nabla \quad , \quad -\frac{h^2\Delta}{2m} \quad , \quad -\frac{h^2\Delta}{2m} + V$$

representing the position, speed, momentum, kinetic energy, and total energy.

In other words, we are doing here two things. First, we are declaring by axiom that various "sandwiching" formulae found before by Heisenberg, involving the operators at the end, that we will not get into in detail here, hold true. And second, we are raising the possibility for other quantum mechanical systems, more complicated, to be described as well by the mathematics of the operators on a certain Hilbert space H, as above.

Now, let us go back to the Schrödinger equation from Claim 1.15. We have:

PROPOSITION 1.17. *We have the following formula,*

$$\dot{\varphi} = \frac{ih}{2m} \left(\Delta\psi \cdot \bar{\psi} - \Delta\bar{\psi} \cdot \psi \right)$$

for the time derivative of the probability density function $\varphi = |\psi|^2$.

PROOF. According to the Leibnitz product rule, we have the following formula:

$$\dot{\varphi} = \frac{d}{dt}|\psi|^2 = \frac{d}{dt}(\psi\bar{\psi}) = \dot{\psi}\bar{\psi} + \psi\dot{\bar{\psi}}$$

On the other hand, the Schrödinger equation and its conjugate read:

$$\dot{\psi} = \frac{ih}{2m}\left(\Delta\psi - \frac{2m}{h^2}V\psi\right) \quad , \quad \dot{\bar{\psi}} = -\frac{ih}{2m}\left(\Delta\bar{\psi} - \frac{2m}{h^2}V\bar{\psi}\right)$$

By plugging this data, we obtain the following formula:

$$\dot{\varphi} = \frac{ih}{2m}\left[\left(\Delta\psi - \frac{2m}{h^2}V\psi\right)\bar{\psi} - \left(\Delta\bar{\psi} - \frac{2m}{h^2}V\bar{\psi}\right)\psi\right]$$

But this gives, after simplifying, the formula in the statement. $\square$

As an important application of Proposition 1.17, we have:

THEOREM 1.18. *The Schrödinger equation conserves probability amplitudes,*

$$\int_{\mathbb{R}^3} |\psi_0|^2 = 1 \implies \int_{\mathbb{R}^3} |\psi_t|^2 = 1$$

in agreement with the basic probabilistic requirement, $P = 1$ overall.

PROOF. According to the formula in Proposition 1.17, we have:

$$
\begin{aligned}
\frac{d}{dt} \int_{\mathbb{R}^3} |\psi|^2 \, dx &= \int_{\mathbb{R}^3} \frac{d}{dt} |\psi|^2 \, dx \\
&= \int_{\mathbb{R}^3} \dot{\varphi} \, dx \\
&= \frac{ih}{2m} \int_{\mathbb{R}^3} \left(\Delta\psi \cdot \bar{\psi} - \Delta\bar{\psi} \cdot \psi \right) dx
\end{aligned}
$$

Now by remembering the definition of the Laplace operator, we have:

$$
\begin{aligned}
\frac{d}{dt} \int_{\mathbb{R}^3} |\psi|^2 \, dx &= \frac{ih}{2m} \int_{\mathbb{R}^3} \sum_i \left(\frac{d^2\psi}{dx_i^2} \cdot \bar{\psi} - \frac{d^2\bar{\psi}}{dx_i^2} \cdot \psi \right) dx \\
&= \frac{ih}{2m} \sum_i \int_{\mathbb{R}^3} \frac{d}{dx_i} \left(\frac{d\psi}{dx_i} \cdot \bar{\psi} - \frac{d\bar{\psi}}{dx_i} \cdot \psi \right) dx \\
&= \frac{ih}{2m} \sum_i \int_{\mathbb{R}^2} \left[\frac{d\psi}{dx} \cdot \bar{\psi} - \frac{d\bar{\psi}}{dx} \cdot \psi \right]_{-\infty}^{\infty} \frac{dx}{dx_i} \\
&= 0
\end{aligned}
$$

Thus, we are led to the conclusion in the statement.   □

Moving now towards hydrogen, we have here the following result:

THEOREM 1.19. *In the case of time-independent potentials V, including the Coulomb potential of the proton, the solutions of the Schrödinger equation*

$$ih\dot{\psi} = -\frac{h^2}{2m} \Delta\psi + V\psi$$

which are of the following special form, with the time and space variables separated,

$$\psi_t(x) = w_t \phi(x)$$

are given by the following formulae, with E being a certain constant,

$$w = e^{-iEt/h} w_0 \quad , \quad E\phi = -\frac{h^2}{2m} \Delta\phi + V\phi$$

with the equation for ϕ being called time-independent Schrödinger equation.

PROOF. By dividing by ψ, the Schrödinger equation becomes:

$$ih \cdot \frac{\dot{w}}{w} = -\frac{h^2}{2m} \cdot \frac{\Delta\phi}{\phi} + V$$

Now since the left-hand side depends only on time, and the right-hand side depends only on space, both quantities must equal a constant E, and this gives the result. $\square$

Moving ahead with theory, we can further build on Theorem 1.19, with a number of key observations on the time-independent Schrödinger equation, as follows:

THEOREM 1.20. *In the case of time-independent potentials V, the Schrödinger equation and its time-independent version have the following properties:*

(1) *For solutions of type $\psi = w_t\phi(x)$, the density $\varphi = |\psi|$ is time-independent, and more generally, all quantities of type $< T >$ are time-independent.*
(2) *The time-independent Schrödinger equation can be written as $\widehat{H}\phi = E\phi$, with $H = T + V$ being the total energy, of Hamiltonian.*
(3) *For solutions of type $\psi = w_t\phi(x)$ we have $< H^k >= E^k$ for any k. In particular we have $< H >= E$, and the variance is $< H^2 > - < H >^2 = 0$.*

PROOF. All the formulae are clear indeed from the fact that, when using the sandwiching formula for computing averages, the phases will cancel:

$$< T >= \int_{\mathbb{R}^3} \bar{\psi} \cdot T \cdot \psi \, dx = \int_{\mathbb{R}^3} \bar{\phi} \cdot T \cdot \phi \, dx$$

Thus, we are led to the various conclusions in the statement. $\square$

We have as well the following key result, mathematical this time:

THEOREM 1.21. *The solutions of the Schrödinger equation with time-independent potential V appear as linear combinations of separated solutions*

$$\psi = \sum_n c_n e^{-iE_n t/h} \phi_h$$

with the absolute values of the coefficients being given by

$$< H >= \sum_n |c_n|^2 E_n$$

$|c_n|$ *being the probability for a measurement to return the energy value E_n.*

PROOF. This is something standard, which follows from Fourier analysis, which allows the decomposition of ψ as in the statement, and that we will not really need, in what follows next. As before, for a physical discussion here, we refer to Griffiths [44]. $\square$

1c. Hydrogen atom

In order to solve now the hydrogen atom, by using the Schrödinger equation, the idea will be that of reformulating this equation in spherical coordinates. We have:

THEOREM 1.22. *The time-independent Schrödinger equation in spherical coordinates separates, for solutions of type $\phi = \rho(r)\alpha(s,t)$, into two equations, as follows,*

$$\frac{d}{dr}\left(r^2 \cdot \frac{d\rho}{dr}\right) - \frac{2mr^2}{h^2}(V - E)\rho = K\rho$$

$$\sin s \cdot \frac{d}{ds}\left(\sin s \cdot \frac{d\alpha}{ds}\right) + \frac{d^2\alpha}{dt^2} = -K\sin^2 s \cdot \alpha$$

with K being a constant, called radial equation, and angular equation.

PROOF. We use the following well-known formula for the Laplace operator in spherical coordinates, whose proof can be found in any advanced calculus book:

$$\Delta = \frac{1}{r^2} \cdot \frac{d}{dr}\left(r^2 \cdot \frac{d}{dr}\right) + \frac{1}{r^2 \sin s} \cdot \frac{d}{ds}\left(\sin s \cdot \frac{d}{ds}\right) + \frac{1}{r^2 \sin^2 s} \cdot \frac{d^2}{dt^2}$$

By using this formula, the time-independent Schrödinger equation reformulates as:

$$(V - E)\phi = \frac{h^2}{2m}\left[\frac{1}{r^2} \cdot \frac{d}{dr}\left(r^2 \cdot \frac{d\phi}{dr}\right) + \frac{1}{r^2 \sin s} \cdot \frac{d}{ds}\left(\sin s \cdot \frac{d\phi}{ds}\right) + \frac{1}{r^2 \sin^2 s} \cdot \frac{d^2\phi}{dt^2}\right]$$

Let us look now for separable solutions for this latter equation, consisting of a radial part and an angular part, as in the statement, namely:

$$\phi(r, s, t) = \rho(r)\alpha(s, t)$$

By plugging this function into our equation, we obtain:

$$(V - E)\rho\alpha = \frac{h^2}{2m}\left[\frac{\alpha}{r^2} \cdot \frac{d}{dr}\left(r^2 \cdot \frac{d\rho}{dr}\right) + \frac{\rho}{r^2 \sin s} \cdot \frac{d}{ds}\left(\sin s \cdot \frac{d\alpha}{ds}\right) + \frac{\rho}{r^2 \sin^2 s} \cdot \frac{d^2\alpha}{dt^2}\right]$$

By multiplying everything by $2mr^2/(h^2\rho\alpha)$, and then moving the radial terms to the left, and the angular terms to the right, this latter equation can be written as follows:

$$\frac{2mr^2}{h^2}(V - E) - \frac{1}{\rho} \cdot \frac{d}{dr}\left(r^2 \cdot \frac{d\rho}{dr}\right) = \frac{1}{\alpha \sin^2 s}\left[\sin s \cdot \frac{d}{ds}\left(\sin s \cdot \frac{d\alpha}{ds}\right) + \frac{d^2\alpha}{dt^2}\right]$$

Since this latter equation is now separated between radial and angular variables, both sides must be equal to a certain constant $-K$, and this gives the result. $\square$

Let us first study the angular equation. The result here is as follows:

THEOREM 1.23. *The separated solutions $\alpha = \sigma(s)\theta(t)$ of the angular equation,*

$$\sin s \cdot \frac{d}{ds}\left(\sin s \cdot \frac{d\alpha}{ds}\right) + \frac{d^2\alpha}{dt^2} = -K\sin^2 s \cdot \alpha$$

are given by the following formulae, where $l \in \mathbb{N}$ is such that $K = l(l+1)$,

$$\sigma(s) = P_l^m(\cos s) \quad , \quad \theta(t) = e^{imt}$$

and where $m \in \mathbb{Z}$ is a constant, and with P_l^m being the Legendre function,

$$P_l^m(x) = (-1)^m(1-x^2)^{m/2}\left(\frac{d}{dx}\right)^m P_l(x)$$

where P_l are the Legendre polynomials, given by the following formula:

$$P_l(x) = \frac{1}{2^l l!}\left(\frac{d}{dx}\right)^l (x^2-1)^l$$

These solutions $\alpha = \sigma(s)\theta(t)$ are called spherical harmonics.

PROOF. This follows indeed from all the above, and with the comment that everything is taken up to linear combinations. We will normalize the wave function later. $\square$

In order to finish our study, it remains to solve the radial equation, for the Coulomb potential V of the proton. As a first manipulation on the radial equation, we have:

PROPOSITION 1.24. *The radial equation, written with $K = l(l+1)$,*

$$(r^2\rho')' - \frac{2mr^2}{h^2}(V-E)\rho = l(l+1)\rho$$

takes with $\rho = u/r$ the following form, called modified radial equation,

$$Eu = -\frac{h^2}{2m}\cdot u'' + \left(V + \frac{h^2 l(l+1)}{2mr^2}\right)u$$

which is a time-independent 1D Schrödinger equation.

PROOF. With $\rho = u/r$ as in the statement, we have:

$$\rho = \frac{u}{r} \quad , \quad \rho' = \frac{u'r - u}{r^2} \quad , \quad (r^2\rho')' = u''r$$

By plugging this data into the radial equation, this becomes:

$$u''r - \frac{2mr}{h^2}(V-E)u = \frac{l(l+1)}{r}\cdot u$$

By multiplying everything by $h^2/(2mr)$, this latter equation becomes:

$$\frac{h^2}{2m}\cdot u'' - (V-E)u = \frac{h^2 l(l+1)}{2mr^2}\cdot u$$

But this gives the formula in the statement. As for the interpretation, as time-independent 1D Schrödinger equation, this is clear as well, and with the comment here that the term added to the potential V is some sort of centrifugal term.   □

It remains to solve the above equation, for the Coulomb potential of the proton. And we have here the following result, which proves the original claims by Bohr:

THEOREM 1.25 (Schrödinger). *In the case of the hydrogen atom, where V is the Coulomb potential of the proton, the modified radial equation, which reads*

$$Eu = -\frac{h^2}{2m} \cdot u'' + \left(-\frac{Ke^2}{r} + \frac{h^2 l(l+1)}{2mr^2}\right) u$$

leads to the Bohr formula for allowed energies,

$$E_n = -\frac{m}{2}\left(\frac{Ke^2}{h}\right)^2 \cdot \frac{1}{n^2}$$

with $n \in \mathbb{N}$, the binding energy being

$$E_1 \simeq -2.177 \times 10^{-18}$$

with means $E_1 \simeq -13.591$ eV.

PROOF. This is again something non-trivial, the idea being as follows:

(1) By dividing our modified radial equation by E, this becomes:

$$-\frac{h^2}{2mE} \cdot u'' = \left(1 + \frac{Ke^2}{Er} - \frac{h^2 l(l+1)}{2mEr^2}\right) u$$

In terms of $\alpha = \sqrt{-2mE}/h$, this equation takes the following form:

$$\frac{u''}{\alpha^2} = \left(1 + \frac{Ke^2}{Er} + \frac{l(l+1)}{(\alpha r)^2}\right) u$$

In terms of the new variable $p = \alpha r$, this latter equation reads:

$$u'' = \left(1 + \frac{\alpha Ke^2}{Ep} + \frac{l(l+1)}{p^2}\right) u$$

Now let us introduce a new constant S for our problem, as follows:

$$S = -\frac{\alpha Ke^2}{E}$$

In terms of this new constant, our equation reads:

$$u'' = \left(1 - \frac{S}{p} + \frac{l(l+1)}{p^2}\right) u$$

(2) The idea will be that of looking for a solution written as a power series, but before that, we must "peel off" the asymptotic behavior. Which is something that can be done,

of course, heuristically. With $p \to \infty$ we are led to $u'' = u$, and ignoring the solution $u = e^p$ which blows up, our approximate asymptotic solution is:

$$u \sim e^{-p}$$

Similarly, with $p \to 0$ we are led to $u'' = l(l+1)u/p^2$, and ignoring the solution $u = p^{-l}$ which blows up, our approximate asymptotic solution is:

$$u \sim p^{l+1}$$

(3) The above heuristic considerations suggest writing our function u as follows:

$$u = p^{l+1}e^{-p}v$$

So, let us do this. In terms of v, we have the following formula:

$$u' = p^l e^{-p} \left[(l+1-p)v + pv' \right]$$

Differentiating a second time gives the following formula:

$$u'' = p^l e^{-p} \left[\left(\frac{l(l+1)}{p} - 2l - 2 + p \right) v + 2(l+1-p)v' + pv'' \right]$$

Thus the radial equation, as modified in (1) above, reads:

$$pv'' + 2(l+1-p)v' + (S - 2(l+1))v = 0$$

(4) We will be looking for a solution v appearing as a power series:

$$v = \sum_{j=0}^{\infty} c_j p^j$$

But our equation leads to the following recurrence formula for the coefficients:

$$c_{j+1} = \frac{2(j+l+1) - S}{(j+1)(j+2l+2)} \cdot c_j$$

(5) We are in principle done, but we still must check that, with this choice for the coefficients c_j, our solution v, or rather our solution u, does not blow up. And the whole point is here. Indeed, at $j >> 0$ our recurrence formula reads, approximately:

$$c_{j+1} \simeq \frac{2c_j}{j}$$

But, surprisingly, this leads to $v \simeq c_0 e^{2p}$, and so to $u \simeq c_0 p^{l+1} e^p$, which blows up.

(6) As a conclusion, the only possibility for u not to blow up is that where the series defining v terminates at some point. Thus, we must have for a certain index j:

$$2(j+l+1) = S$$

In other words, we must have, for a certain integer $n > l$:

$$S = 2n$$

(7) We are almost there. Recall from (1) above that S was defined as follows:

$$S = -\frac{\alpha K e^2}{E} \quad : \quad \alpha = \frac{\sqrt{-2mE}}{h}$$

Thus, we have the following formula for the square of S:

$$S^2 = \frac{\alpha^2 K^2 e^4}{E^2} = -\frac{2mE}{h^2} \cdot \frac{K^2 e^4}{E^2} = -\frac{2mK^2 e^4}{h^2 E}$$

Now by using the formula $S = 2n$ from (6), the energy E must be of the form:

$$E = -\frac{2mK^2 e^4}{h^2 S^2} = -\frac{mK^2 e^4}{2h^2 n^2}$$

Calling this energy E_n, depending on $n \in \mathbb{N}$, we have, as claimed:

$$E_n = -\frac{m}{2} \left(\frac{Ke^2}{h} \right)^2 \cdot \frac{1}{n^2}$$

(8) Thus, we proved the Bohr formula. Regarding numerics, the data is as follows:

$$K = 8.988 \times 10^9 \quad , \quad e = 1.602 \times 10^{-19}$$

$$h = 1.055 \times 10^{-34} \quad , \quad m = 9.109 \times 10^{-31}$$

But this gives the formula of E_1 in the statement. $\qquad\square$

As a first remark, all this agrees with the Rydberg formula, due to:

THEOREM 1.26. *The Rydberg constant for hydrogen is given by*

$$R = -\frac{E_1}{h_0 c}$$

where E_1 is the Bohr binding energy, and the Rydberg formula itself, namely

$$\frac{1}{\lambda_{n_1 n_2}} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

simply reads, via the energy formula in Theorem 1.25,

$$\frac{1}{\lambda_{n_1 n_2}} = \frac{E_{n_2} - E_{n_1}}{h_0 c}$$

which is in agreement with the Planck formula $E = h_0 c / \lambda$.

PROOF. Here the first assertion is something numeric, coming from the fact that the formula in the statement gives, when evaluated, the Rydberg constant:

$$R = \frac{-E_1}{h_0 c} = \frac{2.177 \times 10^{-18}}{6.626 \times 10^{-34} \times 2.998 \times 10^8} = 1.096 \times 10^7$$

Regarding now the second assertion, by dividing $R = -E_1/(h_0 c)$ by any number of type n^2 we obtain, according to the energy convention in Theorem 1.25:

$$\frac{R}{n^2} = -\frac{E_n}{h_0 c}$$

But these are exactly the numbers which are subject to substraction in the Rydberg formula, and so we are led to the conclusion in the statement. □

In order to investigate heavier atoms, we need to know more about hydrogen. So, let us go back to our study of the Schrödinger equation for it. Our conclusions so far are:

THEOREM 1.27. *The wave functions of the hydrogen atom are the following functions, labelled by three quantum numbers, n, l, m,*

$$\phi_{nlm}(r, s, t) = \rho_{nl}(r)\alpha_l^m(s, t)$$

where $\rho_{nl}(r) = p^{l+1}e^{-p}v(p)/r$ with $p = \alpha r$ as before, with the coefficients of v subject to

$$c_{j+1} = \frac{2(j + l + 1 - n)}{(j + 1)(j + 2l + 2)} \cdot c_j$$

and $\alpha_l^m(s, t)$ being the spherical harmonics found before.

PROOF. This follows indeed by putting together all the results obtained so far, and with the remark that everything is up to the normalization of the wave function. □

In what regards the main wave function, that of the ground state, we have:

THEOREM 1.28. *With the hydrogen atom in its ground state, the wave function is*

$$\phi_{100}(r, s, t) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}$$

where $a = 1/\alpha$ is the inverse of the parameter appearing in our computations above,

$$\alpha = \frac{\sqrt{-2mE}}{h}$$

called Bohr radius of the hydrogen atom. This Bohr radius is given by

$$a = \frac{h^2}{mKe^2}$$

which numerically means $a \simeq 5.291 \times 10^{-11}$.

PROOF. According to our formulae above, the parameter α there is given by:

$$\alpha = \frac{\sqrt{-2mE}}{h} = \frac{1}{h} \cdot m \cdot \frac{Ke^2}{h} = \frac{mKe^2}{h^2}$$

Thus, the inverse $\alpha = 1/a$ is indeed given by the formula in the statement. Regarding now the wave function, we know from the above that this consists of:

$$\rho_{10}(r) = \frac{2e^{-r/a}}{\sqrt{a^3}} \quad , \quad \alpha_0^0(s,t) = \frac{1}{2\sqrt{\pi}}$$

By making the product, we obtain the formula of ϕ_{100} in the statement. Finally, in what regards the numerics, these are as follows:

$$a = \frac{1.055^2 \times 10^{-68}}{9.109 \times 10^{-31} \times 8.988 \times 10^9 \times 1.602^2 \times 10^{-38}} = 5.297 \times 10^{-11}$$

Thus, we are led to the conclusions in the statement. $\square$

In order to improve our results, we will need the following standard fact:

PROPOSITION 1.29. *The polynomials $v(p)$ are given by the formula*

$$v(p) = L_{n-l-1}^{2l+1}(p)$$

where the polynomials on the right, called associated Laguerre polynomials, are given by

$$L_q^p(x) = (-1)^p \left(\frac{d}{dx}\right)^p L_{p+q}(x)$$

with L_{p+q} being the Laguerre polynomials, given by the following formula,

$$L_q(x) = \frac{e^x}{q!} \left(\frac{d}{dx}\right)^q (e^{-x} x^q)$$

called Rodrigues formula for the Laguerre polynomials.

PROOF. The story here is very similar to that of the Legendre polynomials. Consider the Hilbert space $H = L^2[0,\infty)$, with the following scalar product on it:

$$< f, g > = \int_0^\infty f(x)g(x)e^{-x} \, dx$$

The orthogonal basis obtained by applying Gram-Schmidt to the Weierstrass basis $\{x^q\}$ is then formed by the Laguerre polynomials $\{L_q\}$, and this gives the results. $\square$

With the above result in hand, we can now improve our main results, as follows:

THEOREM 1.30. *The wave functions of the hydrogen atom are given by*

$$\phi_{nlm}(r,s,t) = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-l-1)!}{2n(n+l)!}} e^{-r/na} \left(\frac{2r}{na}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na}\right) \alpha_l^m(s,t)$$

with $\alpha_l^m(s,t)$ being the spherical harmonics found before.

PROOF. This follows indeed by putting together what we have, and then doing some remaining work, concerning the normalization of the wave function. $\square$

1d. Fine structure

What is next? All sorts of corrections to the solution that we found, due to various phenomena that we neglected in our computations, or rather in our modeling of the problem, which can be both of electric and relativistic nature.

So, let us explain now the standard corrections to the Schrödinger solution to the hydrogen atom. We will focus on energy only, so let us start by recalling:

THEOREM 1.31 (Schrödinger). *The energy of the ϕ_{nlm} state of the hydrogen atom is independent on the quantum numbers l, m, given by the Bohr formula*

$$E_n = -\frac{\alpha^2}{n^2} \cdot \frac{mc^2}{2}$$

where α is a dimensionless constant, called fine structure constant, given by

$$\alpha = \frac{Ke^2}{hc}$$

which in practice means $\alpha \simeq 1/137$.

PROOF. This is the Bohr energy formula that we know, proved by Schrödinger, and reformulated in terms of Sommerfeld's fine structure constant:

(1) We know from Theorem 1.25 that we have the following formula, which can be written as in the statement, by using the fine structure constant α:

$$E_n = -\frac{m}{2} \left(\frac{Ke^2}{h} \right)^2 \cdot \frac{1}{n^2}$$

(2) Observe now that our modified Bohr formula can be further reformulated as follows, with T_c being the kinetic energy of the electron traveling at speed c:

$$E_n = -\frac{\alpha^2}{n^2} \cdot T_c$$

Thus α^2, and so α too, is dimensionless, as being a quotient of energies.

(3) Let us doublecheck however this latter fact, the check being instructive. With respect to the SI system that we use, the units for K, e, h, c are:

$$U_K = \frac{m^3 \cdot kg}{s^2 \cdot C^2} \quad , \quad U_e = C \quad , \quad U_h = \frac{m^2 \cdot kg}{s} \quad , \quad U_c = \frac{m}{s}$$

Thus the units for the fine structure constant α are, as claimed:

$$U_\alpha = U_C \cdot U_e^2 \cdot U_h^{-1} \cdot U_c^{-1} = \frac{m^3 \cdot kg}{s^2 \cdot C^2} \cdot C^2 \cdot \frac{s}{m^2 \cdot kg} \cdot \frac{s}{m} = 1$$

(4) In what regards now the numerics, these are as follows:

$$\alpha = \frac{Ke^2/h}{c} \simeq \frac{2.186 \times 10^6}{2.998 \times 10^8} = 7.291 \times 10^{-3} \simeq \frac{1}{137}$$

Here we used a standard estimate for Ke^2/h, from the proof of Theorem 1.25. $\square$

The fine structure constant α is a remarkable quantity, as obvious from the above, and more on it in a moment. Among its other magic features, it manages well 2π factors. Indeed, by using $K = 1/(4\pi\varepsilon_0)$ and $h = h_0/2\pi$, we can write this constant as:

$$\alpha = \frac{e^2}{2\varepsilon_0 h_0 c}$$

Finally, let us record the complete official data for α and its inverse α^{-1}:

$$\alpha = 0.007\ 297\ 352\ 5693(11)$$

$$\alpha^{-1} = 137.035\ 999\ 084(21)$$

As a final comment here, all this lengthy discussion about α might sound a bit like mania, or mysticism. But wait for it. Sometimes soon α will be part of your life.

Moving ahead now with corrections to Theorem 1.31, we will be quite brief, and for further details, we refer as usual to our favorite books, Feynman [**33**], Griffiths [**44**] and Weinberg [**92**]. We first have the following result, which is something non-trivial:

THEOREM 1.32. *There is a relativistic correction to be made to the Bohr energy E_n of the state ϕ_{nlm}, depending on the quantum number l, given by*

$$\mathcal{E}_{nl} = \frac{\alpha^2 E_n}{n^2}\left(\frac{n}{l+1/2} - \frac{3}{4}\right)$$

coming by replacing the kinetic energy by the relativistic kinetic energy.

PROOF. According to Einstein, the relativistic kinetic energy is given by:

$$T = \frac{p^2}{2m} - \frac{p^4}{8m^3 c^2} + \dots$$

The Schrödinger equation, based on $T = p^2/2m$, must be therefore corrected with a $\mathcal{T} = -p^4/(8m^3 c^2)$ term, and this leads to the above correction term $\mathcal{E}_{nl}$. $\square$

Equally non-trivial is the following correction, independent from the above one:

THEOREM 1.33. *There is a spin-related correction to be made to the Bohr energy E_n of the state ϕ_{nlm}, depending on the number $j = l \pm 1/2$, given by*

$$\mathcal{E}_{nj} = -\frac{\alpha^2 E_n}{n^2} \cdot \frac{n(j-l)}{(l+1/2)(j+1/2)}$$

coming from the torque of the proton on the magnetic moment of the electron.

PROOF. As we will explain in chapter 2 below, the electron has a spin $\pm 1/2$, which is naturally associated to the quantum number l, leading to the parameter $j = l \pm 1/2$. But, knowing now that the electron has a spin, the proton which moves around it certainly acts on its magnetic moment, and this leads to the above correction term $\mathcal{E}_{nj}$. $\qquad\square$

So, these are the first two corrections to be made, and again, we refer to Feynman [**33**], Griffiths [**44**], Weinberg [**92**] for details. Obviously we don't quite know what we're doing here, but let us add now the above corrections to E_n, and see what we get. We obtain in this way one of the most famous formulae in quantum mechanics, namely:

THEOREM 1.34. *The energy levels of the hydrogen atom, taking into account the fine structure coming from the relativistic and spin-related correction, are given by*

$$E_{nj} = E_n \left[1 + \frac{\alpha^2}{n^2} \left(\frac{n}{j + 1/2} - \frac{3}{4} \right) \right]$$

with $j = l \pm 1/2$ being as above, and with α being the fine structure constant.

PROOF. We have the following computation, based on the above formulae:

$$\begin{aligned}
\mathcal{E}_{nl} + \mathcal{E}_{nj} &= \frac{\alpha^2 E_n}{n^2} \left(\frac{n}{l + 1/2} - \frac{3}{4} - \frac{n(j - l)}{(l + 1/2)(j + 1/2)} \right) \\
&= \frac{\alpha^2 E_n}{n^2} \left(\frac{n}{l + 1/2} \left(1 - \frac{j - l}{j + 1/2} \right) - \frac{3}{4} \right) \\
&= \frac{\alpha^2 E_n}{n^2} \left(\frac{n}{j + 1/2} - \frac{3}{4} \right)
\end{aligned}$$

Thus the corrected formula of the energy is as follows:

$$\begin{aligned}
E_{nj} &= E_n + \mathcal{E}_{nl} + \mathcal{E}_{nj} \\
&= E_n + \frac{\alpha^2 E_n}{n^2} \left(\frac{n}{j + 1/2} - \frac{3}{4} \right)
\end{aligned}$$

We are therefore led to the conclusion in the statement. $\qquad\square$

Summarizing, quantum mechanics is more complicated than what originally appears from Schrödinger's solution of the hydrogen atom. Which was something quite complicated too, we must admit that. And the story is not over here, because on top of the above fine structure correction, which is of order α^2, we have afterwards the Lamb shift, which is an order α^3 correction, then the hyperfine splitting, and more.

Quite remarkably, Feynman and others managed to find a global way of viewing all the phenomena that can appear, corresponding to an infinite series in α. To be more precise, their theory, called quantum electrodynamics (QED), is an advanced version of quantum mechanics, still used nowadays for any delicate computation.

1e. Exercises

Exercises:

EXERCISE 1.35.

EXERCISE 1.36.

EXERCISE 1.37.

EXERCISE 1.38.

EXERCISE 1.39.

EXERCISE 1.40.

Bonus exercise.

CHAPTER 2

Molecules

2a. Periodic table

Let us investigate now the case of arbitrary atoms. We will need some general theory for the many-particle systems in quantum mechanics. Let us start with:

DEFINITION 2.1. *The wave function of a system of electrons $e_1, \ldots, e_Z$, given by*

$$P_t\big(e_1 \in V_1, \ldots, e_Z \in V_Z\big) = \int_{V_1 \times \ldots \times V_Z} |\psi_t(x_1, \ldots, x_Z)|^2 dx$$

is governed by the Schrödinger equation $ih\dot{\psi} = \widehat{H}\psi$, with Hamiltonian as follows,

$$\widehat{H} = -\frac{h}{2m} \sum_i \Delta_i + Ke^2 \sum_{i<j} \frac{1}{||x_i - x_j||} + V(x_1, \ldots, x_Z)$$

with the middle sum standing for the Coulomb repulsions between them.

As before with the one-particle Schrödinger equation, there is a long story with all this, and for cutting short with the discussion here, this is what experiments lead to.

In general, and in fact at any $Z > 1$, and so even at $Z = 2$, the above Schrödinger equation is pretty much impossible to solve, due to the Coulomb repulsion term, which makes the mathematics extremely complicated. In fact, as an illustrating analogy here, managing that Coulomb repulsion term is more or less the same thing as solving the N-body problem in classical mechanics, for bodies with equal mass.

We will be interested here in the case of atoms, where V is the Coulomb attraction potential coming from a Ze charge. Here the problem to be solved is as follows:

PROBLEM 2.2. *Consider an atom of atomic number Z, meaning a fixed Ze charge, surrounded by electrons $e_1, \ldots, e_Z$. The problem is to solve the Schrödinger equation*

$$ih\dot{\psi} = \widehat{H}\psi$$

with Hamiltonian as follows,

$$\widehat{H} = \sum_i \left(-\frac{h}{2m} \Delta_i - \frac{KZe^2}{||x_i||} \right) + Ke^2 \sum_{i<j} \frac{1}{||x_i - x_j||}$$

or at least to understand how $e_1, \ldots, e_Z$ manage to live together, in a stable way.

A first idea would be of course that of ignoring the right term, Coulomb repulsion. In the simplest case, that of the helium atom, the situation is as follows:

FACT 2.3. *For the helium atom, $Z = 2$, ignoring the Coulomb repulsion between electrons leads, via separation of variables, to product wave functions*

$$\phi(x_1, x_2) = \phi'_{n_1 l_1 m_1}(x_1)\phi'_{n_2 l_2 m_2}(x_2)$$

with the prime signs standing for the doubling $e \to 2e$ of the central charge, with energies:

$$E_{n_1 n_2} = 4(E_{n_1} + E_{n_2})$$

This model predicts a ground state energy for helium given by

$$E_0 = 8 \times (-13.6) = -109 \text{ eV}$$

which is considerably smaller than the observed $E_0 = -79$ eV.

As a partial conclusion to what we have so far, things not going on every well, and in order to advance, we will probably need to invest a lot of time in learning how to solve complicated Schrödinger equations, and why not buying a super-computer too.

Moving ahead, let us focus on a more modest question, that at the end of Problem 2.2, namely understanding how the electrons $e_1, \ldots, e_Z$ manage to live together. Here our method of ignoring the Coulomb repulsion between electrons is not that bad, and for helium for instance, we are led in this way to some interesting conclusions. For instance the excited states of helium must appear as products as follows:

$$\phi_{100}(x_1)\phi_{nlm}(x_2) \quad , \quad \phi_{nlm}(x_1)\phi_{100}(x_2)$$

And this is actually quite close to reality, if we add the particle spin to our discussion. So, speaking now spin, this is indeed something that we ignored so far in the above. And spin is in fact a key component to our problem, because we have:

FACT 2.4 (Pauli exclusion principle). *Two electrons cannot occupy the same quantum numbers n, l, m, with same spin $s = \pm 1/2$.*

So, this is the famous Pauli exclusion principle, giving the golden key to the understanding of $Z \geq 2$ atoms. There are of course many things that can be said about it. A sample quantum mechanics book will probably tell you first something about bosons and fermions, coming with exactly 0 evidence, then some more things about electrons, of type "they are the same, but not really, and everything is entangled, but is it really entangled", and finally formulate the Pauli exclusion principle, as a theorem.

We will not get into this here, and take the Pauli exclusion principle as it is, a physics fact. However, talking philosophy, personally I always think at it as coming from the "human nature of electrons". To be more precise, when I'm at my office typing the present book, I feel like occupying some precise quantum numbers, with precise spin.

And if 30 colleagues, all typing physics books too, manage to come by surprise to my office, and squeeze there like sardines, I will surely find a way of getting rid of them, and disposing of their bodies. So now that a poor human like me can do this, why shouldn't a mighty electron be able to do the same. This is the Pauli exclusion principle.

We have now all the ingredients for discussing the known atoms, or chemical elements, $Z = 1, \ldots, 118$. These can be arranged in a table, called periodic table, as follows:

	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 1																		He 2
2	Li 3	Be 4												B 5	C 6	N 7	O 8	F 9	Ne 10
3	Na 11	Mg 12												Al 13	Si 14	P 15	S 16	Cl 17	Ar 18
4	K 19	Ca 20		Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
5	Rb 37	Sr 38		Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
6	Cs 55	Ba 56	l	Lu 71	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86
7	Fr 87	Ra 88	a	Lr 103	Rf 104	Db 105	Sg 106	Bh 107	Hs 108	Mt 109	Ds 110	Rg 111	Cn 112	Nh 113	Fl 114	Mc 115	Lv 116	Ts 117	Og 118

			l :	La 57	Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70			
			a :	Ac 89	Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102			

Here the horizontal parameter $1, \ldots, 18$ is called the group, and the vertical parameter $1, \ldots, 7$ is called the period. The two bottom rows consist of lanthanum $_{57}$La and its followers, called lanthanides, and of actinium $_{89}$Ac and its followers, called actinides.

Thus, the periodic table, when correctly drawn, but no one does that because of obvious typographical reasons, is in fact a 7×32 table. Note here that, according to our 7×18 convention, which is the standard one, lanthanides and actinides don't have a group number $1, \ldots, 18$. Their group is by definition "lanthanides" and "actinides".

We will comment in a moment on all this, but before anything:

ADVICE 2.5. *Learn their names.*

This is a serious advice, the periodic table being the main theorem of mathematics, physics, chemistry, biology and engineering combined. So if there's one theorem to be learned, full statement, that is the one. In case you're out of memory, just erase from your brain everything that you learned so far from this book of mine, and learn instead that 118 elements. Please do it for me, this being my final wish, from the death bed.

Actually, in order to get started here, here are the names up to krypton $_{36}$Kr, which are absolutely needed for everything, and must be all learned, to start with:

DEFINITION 2.6. *The elements up to krypton $_{36}$Kr are as follows:*

(1) *Hydrogen $_1$H, helium $_2$He.*
(2) *Lithium $_3$Li, beryllium $_4$Be, boron $_5$B, carbon $_6$C, nitrogen $_7$N, oxygen $_8$O, fluorine $_9$F, neon $_{10}$Ne.*
(3) *Sodium $_{11}$Na, magnesium $_{12}$Mg, aluminium $_{13}$Al, silicon $_{14}$Si, phosphorus $_{15}$P, sulfur $_{16}$S, chlorine $_{17}$Cl, argon $_{18}$Ar.*
(4) *Potassium $_{19}$K, calcium $_{20}$Ca, scandium $_{21}$Sc, titanium $_{22}$Ti, vanadium $_{23}$V, chromium $_{24}$Cr, manganese $_{25}$Mn, iron $_{26}$Fe, cobalt $_{27}$Co.*
(5) *Nickel $_{28}$Ni, copper $_{29}$Cu, zinc $_{30}$Zn, gallium $_{31}$Ga, germanium $_{32}$Ge, arsenic $_{33}$As, selenium $_{34}$Se, bromine $_{35}$Br, krypton $_{36}$Kr.*

Observe that all names fit with the abbreviations, expect for sodium $_{11}$Na, coming from the Latin natrium, potassium $_{19}$K, coming from the Latin kalium, iron $_{26}$Fe coming from the Latin ferrum, and also copper $_{29}$Cu, coming from the Latin cuprum.

In what regards the elements heavier than krypton $_{36}$Kr, it is heartbreaking to sort them out, but as a useful complement to the above list, we have:

FACT 2.7. *Remarkable elements heavier than krypton $_{36}$Kr include:*

(1) *Noble gases: xenon $_{54}$Xe, radon $_{86}$Rn.*
(2) *Noble metals: silver $_{47}$Ag, iridium $_{77}$Ir, platinum $_{78}$Pt, gold $_{47}$Au.*
(3) *Heavy metals: mercury $_{80}$Hg, lead $_{82}$Pb.*
(4) *Radioactive: polonium $_{84}$Po, radium $_{88}$Ra, uranium $_{92}$U, plutonium $_{94}$Pu.*
(5) *Miscellaneous: rubidium $_{37}$Rb, strontium $_{38}$Sr, molybdenum $_{42}$Mo, technetium $_{43}$Tc, cadmium $_{48}$Cd, tin $_{50}$Sn, iodine $_{53}$I, caesium $_{55}$Cs, tungsten $_{74}$Tu, bismuth $_{83}$Bi, francium $_{87}$Fr, americium $_{95}$Am.*

Here the abbreviations not fitting with English names come from the Latin or sometimes Greek argentum $_{47}$Ag, aurum $_{47}$Au, hydrargyrum $_{80}$Hg, plumbum $_{82}$Pb and stannum $_{50}$Sn. The noble gases in (1) normally include oganesson $_{118}$Og as well. The noble metals in (2) are something subjective. There are of course plenty of other heavy metals (3), or radioactive elements (4). As for the list in (5), this is something subjective, basically a mixture of well-known metals used in engineering, and some well-known bad guys in the context of nuclear fallout. Technetium $_{43}$Tc is a bizarre element, human-made.

But let us not forget about quantum mechanics, and what we wanted to do, namely discuss electron structure. As a first observation, we have:

FACT 2.8. *Any $Z = 1, \ldots, 118$ corresponds to a unique element, having Z protons in the core, and Z electrons around it. This element might come with isotopes, depending on the number of neutrons in the core, can be in ground state or excited states, can get ionized, and so on, but all there versions are "family", and the element is unique.*

This fact is something which might look very natural, with no need for explanation for it, but after some thinking, is this really that natural. And the answer here is that no, if you don't know quantum mechanics, and yes, if you know some, as we do:

(1) For the purposes of our question, we can assume that we are in the context of Problem 2.2, and with the Coulomb repulsions between electrons ignored.

(2) But then, we are a bit in the same situation as in Fact 2.3, and the analysis there, based on hydrogen theory modified via $e \to Ze$, carries over.

(3) And so, the Z electrons will arrange on various energy levels, subject to Pauli exclusion, as to occupy a state of lowest possible energy, so the solution is unique.

In fact, we can now understand the electron structure of the various elements, and also how the periodic table is exactly made, the conclusions here being as follows:

FACT 2.9. *For the element having atomic number Z, the electrons will occupy succesively the various positions with quantum numbers $n, l, m \in \mathbb{N}$ and spin $s = \pm 1/2$, such as the total binding energy to be minimal. In practice, the period $1, \ldots, 7$ corresponds to the highest n occupied, and the group $1, \ldots, 18$ comes from l, m, s.*

This is of course something very basic, and there is a detailed analysis to be done afterwards, for $Z = 1, \ldots, 118$. For the elements up to krypton ${}_{36}$Kr, the list of electron configurations can be found for instance in Feynman [**33**] or Griffiths [**44**].

2b. Isotopes, ionization

Time now for more advanced mathematics, for the many-electron atoms, and by talking about isotopes and ionization too, and this even for the hydrogen atom. All this knowledge will be very useful, among others for going towards molecules, afterwards.

In other words, this means that we will be interested in what happens to a system of Z electrons $e_1, \ldots, e_Z$, surrounding a central positive charge $Z'e$. For a usual atom, which is globally electrically neutral, we have $Z = Z'$, but for isotopes and ions we can have $Z < Z'$ or $Z > Z'$. Thus, we will assume that the numbers Z, Z' are unrelated.

In practice, this corresponds to the following version of Problem 2.2:

PROBLEM 2.10. *Consider a system of atomic number Z', meaning a fixed $Z'e$ charge, surrounded by electrons $e_1, \ldots, e_Z$. The problem is to solve the Schrödinger equation*

$$ih\dot{\psi} = \widehat{H}\psi$$

with Hamiltonian as follows,

$$\widehat{H} = \sum_i \left(-\frac{h}{2m}\Delta_i - \frac{KZ'e^2}{||x_i||} \right) + Ke^2 \sum_{i<j} \frac{1}{||x_i - x_j||}$$

or at least to understand how $e_1, \ldots, e_Z$ manage to live together, in a stable way.

As explained in the discussion following Problem 2.2, a first idea is to simply ignore the Coulomb repulsion term on the right. Indeed, this simplifies a lot the mathematics, and by separation of variables we are led to a product of wave functions, with the numerics being worked out, in the simplest case of the helium atom, in Fact 2.3.

So, let us see how this works in general, in the framework of Problem 2.10. As before with helium, in view of the fact that the interactions between the electrons are ignored, this amounts in decomposing the Hamiltonian into Z components, as follows:

$$\widehat{H} = \widehat{H}_1 + \ldots + \widehat{H}_Z$$

By separation of variables, we are led to products of wave functions as follows, called Hartree products, with the prime signs standing for the modification of the central charge, $e \to Z'e$, from the case of hydrogen, to the case of the system under investigation:

$$\phi(x_1, \ldots, x_Z) = \phi'(x_1) \ldots \phi'(x_Z)$$

Here we have opted, for simplifying notations, to not include the quantum numbers, as in Fact 2.3, at least in the present, preliminary stage of our study.

With this done, we are quite far from something reliable, because as explained in Fact 2.3, such an approximation gives quite average results, with respect to the observed values, even in the simplest case of helium. So, the following question appears:

QUESTION 2.11. *How to further improve the Hartree products, without however getting into Problem 2.10 as stated, which is something of extreme difficulty?*

In order to solve this question, let us get back to helium, $Z = Z' = 2$. If we denote for simplifying by $1, 2$ the first two lowest energy orbits, we have two possible Hartree functions for the simplest excited state of our helium atom, namely:

$$\phi_{12}(x_1, x_2) = \phi'_1(x_1)\phi'_2(x_2) \quad , \quad \phi_{21}(x_1, x_2) = \phi'_2(x_1)\phi'_1(x_2)$$

A natural idea, in order to have some symmetry going on, for our solution, is that of considering a suitable linear combination of these solutions. But since the overall electron

density function $|\phi|^2$ must be invariant under electron exchange, we are led, up to a normalization of the wave function, to linear combinations as follows:

$$\phi = \pm\phi_{12} \pm \phi_{21}$$

Moreover, by taking now into account spin, the Pauli exclusion principle tells us that the correct symmetry property of ϕ is actually antisymmetry. Thus, up to a global $\pm$ sign, and again up to a normalization of the wave function, the solution must be:

$$\begin{aligned}
\phi &= \phi_{12} - \phi_{21} \\
&= \phi_1'(x_1)\phi_2'(x_2) - \phi_2'(x_1)\phi_1'(x_2) \\
&= \begin{vmatrix} \phi_1'(x_1) & \phi_2'(x_1) \\ \phi_1'(x_2) & \phi_2'(x_2) \end{vmatrix}
\end{aligned}$$

Getting now to the normalization factor, a simple computation shows that this factor is $1/\sqrt{2}$. Thus, as a conclusion, our symmetrization method leads to:

$$\phi = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1'(x_1) & \phi_2'(x_1) \\ \phi_1'(x_2) & \phi_2'(x_2) \end{vmatrix}$$

More generally now, the above method applies in the same way to a system of Z electrons, and we are led to the following preliminary answer to Question 2.11:

ANSWER 2.12. *The correct linear combinations of Hartree products, having the correct antisymmetrization property for the electrons, are the quantities*

$$\phi = \frac{1}{\sqrt{Z!}} \begin{vmatrix} \phi_1'(x_1) & \ldots & \phi_Z'(x_1) \\ \vdots & & \vdots \\ \phi_1'(x_Z) & \ldots & \phi_Z'(x_Z) \end{vmatrix}$$

with the subscripts standing for the hydrogen-like energy levels, and the primes standing for the central charge modification $e \to Z'e$, called Slater determinants.

To be more precise here, the fact that we must indeed consider a determinant is standard, by reasoning as above, and with this actually corresponding to a well-known theorem in mathematics, stating that the determinant is the unique antisymmetric multilinear form $\det : \mathbb{R}^N \to \mathbb{R}$, normalized as to produce 1 for the standard basis of $\mathbb{R}^N$. As for the computation of the normalization factor, this is again standard, as above.

Moving ahead now, the electron spin was certainly taken into account when formulating the above answer, due to the Pauli exclusion principle which was used. However, when fully taking spin into account, we are led to the following refinement of the above formula, valid this time for a system of $Z = 2N$ electrons, with the subscripts ignoring

spin, and with the bars, and lack of bars, standing for spin up and down:

$$\phi = \frac{1}{\sqrt{Z!}} \begin{vmatrix} \phi'_1(x_1) & \bar{\phi}'_1(x_1) & \dots & \dots & \phi'_N(x_1) & \bar{\phi}'_N(x_1) \\ \phi'_1(x_2) & \bar{\phi}'_1(x_2) & \dots & \dots & \phi'_N(x_2) & \bar{\phi}'_N(x_2) \\ \vdots & \vdots & & & \vdots & \vdots \\ \vdots & \vdots & & & \vdots & \vdots \\ \phi'_1(x_{Z-1}) & \bar{\phi}'_1(x_{Z-1}) & \dots & \dots & \phi'_N(x_{Z-1}) & \bar{\phi}'_N(x_{Z-1}) \\ \phi'_1(x_Z) & \bar{\phi}'_1(x_Z) & \dots & \dots & \phi'_N(x_Z) & \bar{\phi}'_N(x_Z) \end{vmatrix}$$

However, we will not get into full details here, because an even better approximation method, called Hartree-Fock approximation, beating the above, is still to come.

As an example, however, for all this, let us discuss the case of the beryllium atom $_4$Be. Here the Slater determinant, taking into account spin, as above, is as follows:

$$\phi = \frac{1}{\sqrt{24}} \begin{vmatrix} \phi'_1(x_1) & \bar{\phi}'_1(x_1) & \phi'_2(x_1) & \bar{\phi}'_2(x_1) \\ \phi'_1(x_2) & \bar{\phi}'_1(x_2) & \phi'_2(x_2) & \bar{\phi}'_2(x_2) \\ \phi'_1(x_3) & \bar{\phi}'_1(x_3) & \phi'_2(x_3) & \bar{\phi}'_2(x_3) \\ \phi'_1(x_4) & \bar{\phi}'_1(x_4) & \phi'_2(x_4) & \bar{\phi}'_2(x_4) \end{vmatrix}$$

Getting now to the excited states of the same beryllium $_4$Be, we need to add here a third orbital, that we will label 3. And then, following a discussion about spin, which must be subject to certain rules, we are led to the conclusion that the correct linear combination of Hartree products is a difference of two Slater determinants, as follows:

$$\phi = \frac{1}{\sqrt{24}} \begin{vmatrix} \phi'_1(x_1) & \bar{\phi}'_1(x_1) & \phi'_2(x_1) & \bar{\phi}'_3(x_1) \\ \phi'_1(x_2) & \bar{\phi}'_1(x_2) & \phi'_2(x_2) & \bar{\phi}'_3(x_2) \\ \phi'_1(x_3) & \bar{\phi}'_1(x_3) & \phi'_2(x_3) & \bar{\phi}'_3(x_3) \\ \phi'_1(x_4) & \bar{\phi}'_1(x_4) & \phi'_2(x_4) & \bar{\phi}'_3(x_4) \end{vmatrix}$$

$$- \frac{1}{\sqrt{24}} \begin{vmatrix} \phi'_1(x_1) & \bar{\phi}'_1(x_1) & \bar{\phi}'_2(x_1) & \phi'_3(x_1) \\ \phi'_1(x_2) & \bar{\phi}'_1(x_2) & \bar{\phi}'_2(x_2) & \phi'_3(x_2) \\ \phi'_1(x_3) & \bar{\phi}'_1(x_3) & \bar{\phi}'_2(x_3) & \phi'_3(x_3) \\ \phi'_1(x_4) & \bar{\phi}'_1(x_4) & \bar{\phi}'_2(x_4) & \phi'_3(x_4) \end{vmatrix}$$

As already mentioned, we will not get into full details here, because an even better approximation method, called Hartree-Fock approximation, is still to come.

Central field approximation.

Adding spin, Hartree-Fock approximation.

Many things can be said here, with this being a quite powerful method.

2c. Bonding, molecules

With what we know from the above about atoms, and in particular with the knowledge of the Hartree-Fock method, we can now talk about molecules.

Indeed, the idea here is that a molecule can be investigated a bit like a multi-electron atom, by replacing the central charge with a system of positive charges.

In practice, by further building on the Hartree-Fock method for the atoms, we are led in this way to the Born-Oppenheimer method for the molecules.

Many things can be said here, notably with a number of more advanced models for the simplest molecule of them all, which is the hydrogen molecule.

2d. Into chemistry

With what we know about molecules, we can now start doing some chemistry. There is an enormous quantity of things that can be said here, the simplest of which being:

THEOREM 2.13. *The group* 18 *elements, namely*

(1) *Helium* $_2$He,
(2) *Neon* $_{10}$Ne,
(3) *Argon* $_{18}$Ar,
(4) *Krypton* $_{36}$Kr,
(5) *Xenon* $_{54}$Xe,
(6) *Radon* $_{86}$Rn,

called noble gases, are allergic to chemistry.

PROOF. This follows from the electron structure, because the group 18 elements are precisely those with all possible electron positions fully occupied, up to a certain $n \in \mathbb{N}$, which makes them very unfriendly to any chemistry proposition from the outside. By the way, oganesson $_{118}$Og is normally part of this group too, but since this element has only been created and observed for a tiny fraction of a second, who really knows, and by the standard scientific etiquette, in the lack of experiments, no comment about it.   □

More about noble gases.

The particular case of helium $_2$He, which is a remarkable element.

Discussion about radon $_{86}$Rn too, going beyond basic physics and chemistry.

2e. Exercises

Exercises:

EXERCISE 2.14.

EXERCISE 2.15.

EXERCISE 2.16.

EXERCISE 2.17.

EXERCISE 2.18.

EXERCISE 2.19.

Bonus exercise.

CHAPTER 3

Thermodynamics

3a. Ideal gases

In order to get started with states of matter, we must first talk about gases. Things however are quite tricky here, and leaving aside excessive rigor, which does not fit well with thermodynamics, let us start with the following basic fact, which was the beginning of everything, going back to work of Boyle, Charles, Avogardo, Gay-Lussac, Clapeyron and others from the 17th, 18th and 19th centuries, and with final touches from Maxwell, Boltzmann, Gibbs and others, in the late 19th and early 20th centuries:

FACT 3.1. *The ideal gases satisfy the equation $PV = kT$, where:*
(1) *V is the volume of the gas, independently of the shape of the container used.*
(2) *P is the pressure of the gas, measured with a manometer.*
(3) *T is the temperature of the has, measured with a thermometer.*
(4) *k is a constant, depending on the gas.*
That is, $PV = kT$ basically tells us that "pressure and temperature are the same thing".

At the first glance, for instance if you are a mathematician not used to this, this looks more like a joke. Why not defining then $P = T$ or vice-versa, you would say, and what is the point with that long list of distinguished gentlemen having worked hard on this.

Error. The point indeed comes from the following:

EXPLANATION 3.2. *In the equation of state $PV = kT$, as formulated above, the pressure P and the temperature T appear more precisely as follows,*
(1) *The manometer read comes from the gas molecules pushing a piston, so P is a statistical quantity, coming from the statistics of the molecular speeds,*
(2) *The thermometer read is something even more complicated, and T is as well a statistical quantity, coming from the statistics of the molecular speeds,*
so $PV = kT$ is something non-trivial, telling us that the mathematical machinery producing P, T, via manometer and thermometer, out of the molecular speeds, is the same.

Hope you got my point, and getting back now to historical details, Boyle, Charles, Avogardo, Gay-Lussac, Clapeyron, joined by Clausius, Carnot, Joule, Lord Kelvin and others, first observed $PV = kT$, and then reached to a good understanding of what this means, via an axiomatization of P and T. Later Maxwell started to look into the

molecular speeds and their statistics, then Boltzmann came with a tough mathematical computation, proving $PV = kT$, and then, even later, Gibbs and others further built on all this, by formalizing modern thermodynamics, in the form that is still used today.

But probably too much talking, let us get to work. As a first result now, dealing with pressure only, and for the gases without collisions between molecules, we have:

THEOREM 3.3. *The pressure P, volume V and total kinetic energy K of a gas, having point molecules, with no collisions between them, satisfy*

$$PV = \frac{2K}{d}$$

where $d = 1, 2, 3$ is the dimensionality of the gas, $d = 3$ for usual 3D gases.

PROOF. We can do this in several steps, as follows:

(1) Let us first assume that the gas is enclosed in a cubic volume, $V = L^3$. We want to compute the pressure P on the right wall. Since there are no collisions, we can assume by linearity that our gas has 1 molecule, having mass m and travelling at speed v. We must compute the pressure P exterted by this molecule on the right wall:

$$
\begin{array}{ccccc}
= & = & = & & \\
|| & & & || & \\
|| & & \nearrow v & || & \rightarrow P \\
|| & \bullet m & & || & \\
= & = & = & &
\end{array}
$$
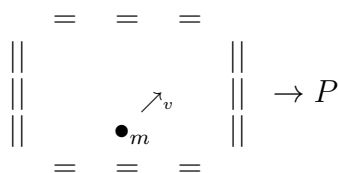
(2) We first look at a 1D gas. Our molecule hits the right wall at every $\Delta t = 2L/v$ interval, with its change of momentum being $\Delta p = 2mv$. We obtain, as desired:

$$P = \frac{F}{L^2} = \frac{\Delta p}{L^2 \Delta t} = \frac{2mv}{L^2 \cdot 2L/v} = \frac{mv^2}{L^3} = \frac{2K}{V}$$

(3) In the case of a d-dimensional gas, exactly the same computation takes place, but this time with v being replaced by its horizontal component v_1. Thus, we have:

$$P = \frac{mv_1^2}{V}$$

But, we have the following formula, with the equality on the right being understood in a statistical sense, our molecule being assumed to follow a random direction:

$$||v||^2 = v_1^2 + \ldots + v_d^2 = dv_1^2$$

Thus, the pressure in this case is given by the following formula, as desired:

$$P = \frac{m||v||^2}{dV} = \frac{2K}{dV}$$

(4) It remains to extend our result to arbitrary volume shapes. For this purpose, let us first redo the above computations for a parallelepiped, $V = L_1 L_2 L_3$. Here the above 1D gas computation carries on, and gives the same result, as follows:

$$P = \frac{F}{L_2 L_3} = \frac{\Delta p}{L_2 L_3 \Delta t} = \frac{2mv}{L_2 L_3 \cdot 2L_1/v} = \frac{mv^2}{L_1 L_2 L_3} = \frac{2K}{V}$$

Thus the d-dimensional computation carries on too, and gives the result.

(5) In order now to reach to arbitrary shapes, the idea will be that of stacking thin parallelepipeds, best approximating the shape that we have in mind, as follows:
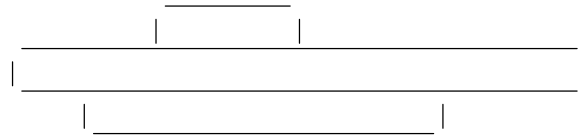
(6) But for this purpose it is better to drop our assumption that the gas has 1 molecule, and use N molecules instead. With $\rho = N/V$ being the molecular density, and K_0 being the kinetic energy of a single molecule, our computation in (4) for the parallelepiped, with now N molecules instead of 1, reformulates as follows:

$$P = \frac{2K}{dV} = \frac{2NK_0}{dV} = \frac{2\rho V K_0}{dV} = \frac{2\rho K_0}{d}$$

(7) But this latter formula shows that the pressure has nothing to do with the precise volume V, but just with the molecular density $\rho = N/V$. Thus, we can stack indeed parallelepipeds, with of course the assumption that ρ is constant over these parallelepipeds, and we obtain that the above formula holds for an arbitrary volume shape V:

$$P = \frac{2\rho K_0}{d}$$

Now by getting back to the volume V, we obtain the following formula:

$$P = \frac{2\rho K_0}{d} = \frac{2NK_0}{dV} = \frac{2K}{dV}$$

Thus, we are led to the conclusion in the statement. $\square$

Observe that, when carefully looking at the above proof, and more specifically at step (3), we can see that pressure P is not something instantaneous, but rather something statistical. Which is of course in tune with our experience, from the real life.

In short, pressure reading is not instantaneous, and we have the following result:

THEOREM 3.4. *In the context of a gas consisting of point molecules, with no collisions between them, the correct time for reading the correct pressure is*

$$ t_f = \frac{2\sqrt{d}\, V^{1/3}}{||v||} \quad : \quad P_f = \frac{2K}{dV} $$

with $||v||$ being the average molecular speed, with the precise pressure reading being

$$
\begin{array}{l}
P \\
\uparrow \\
P_f \\
\uparrow \\
0 \quad\longrightarrow t_f \quad\longrightarrow t
\end{array}
$$
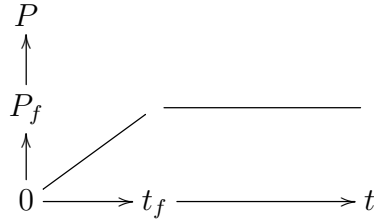
and with this being taken in an approximate, statistical sense.

PROOF. We can do this in two steps, as follows:

(1) Let us first look at a 1D gas. We can assume that we are in a cubic container, $V = L^3$, and we know that each molecule i hits the right wall, where P is measured, at $\Delta t_i = 2L/|v_i|$ intervals. But with this picture in hand, it is quite clear that, on average, the pressure reading process will be linear, starting from $P = 0$, up to time $t_f = 2L/|v|$, with $|v|$ being the average molecular speed, where the correct pressure $P_f = 2K/V$ will be read, and constant at P_f afterwards. Now since $L = V^{1/3}$, this gives, as desired:

$$ t_f = \frac{2V^{1/3}}{|v|} \quad : \quad P_f = \frac{2K}{V} $$

(2) In the general case now, that of a d-dimensional gas, with $d = 1, 2, 3$, the same argument carries on, with the only change being that each molecular speed $v_i \in \mathbb{R}^d$ is now replaced by its horizontal component $v_{i1} \in \mathbb{R}$, which by statistical reasons has squared magnitude as follows, as explained in the proof of Theorem 3.3:

$$ v_{i1}^2 = ||v_i||^2/d $$

Thus, with respect to (1), the correct final pressure must be adjusted by a d factor, and becomes $P_f = 2K/dV$, as in Theorem 3.3. As for the correct reading time, this must be adjusted by a $\sqrt{d}$ factor, and becomes $t_f = 2\sqrt{d}\, V^{1/3}/||v||$, as claimed. $\square$

All this is quite interesting, and we will be back to it later.

At a more advanced level now, dealing with the internal mechanism of the $PV = kT$ formula, we have the following key result, due to Maxwell and Boltzmann:

THEOREM 3.5 (Maxwell, Boltzmann). *The molecular speeds $v \in \mathbb{R}^3$ of a gas in thermal equilibrium are subject to the Maxwell-Boltzmann distribution formula*

$$P(v) = \left(\frac{m}{2\pi bT}\right)^{3/2} \exp\left(-\frac{m||v||^2}{2bT}\right)$$

with m being the mass of the molecules, and b being the Boltzmann constant.

PROOF. As before with other things, this is something in between fact and theorem. Maxwell came upon it as a fact, or perhaps as a sort of pseudo-theorem, and a bit later Boltzmann came with a proof. In what follows we will present the original argument of Maxwell, then briefly discuss Boltzmann's proof. Here is Maxwell's argument:

(1) We are looking for the precise probability distribution P of the molecular speeds $v = (v_1, v_2, v_3)$ which makes the mechanics of gases work. Intuition tells us that P has no corellations between the x, y, z directions of space, and so we must have:

$$P(v) = f(v_1)g(v_2)h(v_3)$$

Moreover, by rotational symmetry the functions f, g, h must coincide, and so:

$$P(v) = f(v_1)f(v_2)f(v_3)$$

(2) Further thinking, again invoking rotational symmetry, leads to the conclusion that $P(v)$ must depend only on the magnitude $||v||$ of the velocity $v \in \mathbb{R}^3$, and not on the direction. Thus, we must have as well a formula of the following type:

$$P(v) = \varphi(||v||^2)$$

(3) Now by comparing the requirements in (1) and (2), we are led via some math to the conclusion that φ must be an exponential, which amounts in saying that:

$$P(v) = \lambda \exp\left(-C||v||^2\right)$$

(4) Obviously we must have $C > 0$, for things to be bounded, and then by integrating we can obtain λ as function of C, and our formula becomes:

$$P(v) = \left(\frac{C}{\pi}\right)^{3/2} \exp\left(-C||v||^2\right)$$

(5) It remains to find the value of $C > 0$. But for this purpose, observe that, now that we have our distribution, be that still depending on $C > 0$, we can compute everything that we want to, just by integrating. In particular, we find that on average:

$$v_1^2 = v_2^2 = v_3^2 = \frac{1}{2C}$$

Thus the average magnitude of the molecular speed is given by:

$$||v|| = \frac{3}{2C}$$

It follows that the average kinetic energy of the molecules is:

$$K_0 = \frac{m||v||^2}{2} = \frac{3m}{4C}$$

(6) On the other hand, recall from our discussions above that one of the many equivalent formulations of $PV = kT$, using $PV = 2K/3$, was as follows:

$$\frac{2K_0}{3} = bT$$

Thus we obtain $m/(2C) = bT$, and so $C = m/(2bT)$, as desired.

(7) Observe that the above proof has in fact little physical content, with the whole thing being basically obtained by using $PV = 2K/3$, which is a mathematical theorem, then $PV = kT$, which is a crucial physics fact, and finally by invoking several times a number of clever symmetry arguments, and doing some calculus.

(8) However, Boltzmann came later with a more rigorous argument, fully establishing the above formula, via detailed computations in relation with the internal collisions.   □

We will be back to the Maxwell-Boltzmann formula later, with some further details.

3b. Work, energy

Going now towards more advanced thermodynamics, and states of matter, our scope will be quite broad, because we would like to talk about all sorts of matter, solid, liquid or gaseous, with a look into the extremes $T \to 0$ and $T >> 0$ too, where other forms of matter appear, and finally with our matter being as 3D as possible, with this meaning occupying a precise body $B \subset \mathbb{R}^3$, instead of just a volume $V = vol(B) \in \mathbb{R}$.

In order to discuss this, we first need to talk about work, motivated by:

QUESTIONS 3.6. *What is the work done by a gas pushing a piston? What about the work done by a gas evolving on a path γ, in the state space $f(P, V, T) = 0$?*

In order to answer this question, we will need some mathematics. Let us start with something quite elementary, namely the contour integrals over curves. We have here:

THEOREM 3.7. *Given a path $\gamma \subset \mathbb{R}^3$, we can talk about integrals of type*

$$I = \int_\gamma f(x)dx_1 + g(x)dx_2 + h(x)dx_3$$

with $f, g, h : \mathbb{R}^3 \to \mathbb{R}$, which are independent on the chosen parametrization of the path.

PROOF. This is something quite straightforward, the idea being as follows:

(1) Regarding the statement itself, assume indeed that we have a path in $\mathbb{R}^3$, which can be best thought of as corresponding to a function as follows:

$$\gamma : [a, b] \to \mathbb{R}^3$$

Observe that this function γ is not exactly the path itself, for instance because the following functions produce the same path, parametrized differently:

$$\delta : [0, b - a] \to \mathbb{R}^3 \quad , \quad \delta(t) = \gamma(t + a)$$
$$\varepsilon : [0, 1] \to \mathbb{R}^3 \quad , \quad \varepsilon(t) = \delta((b - a)t)$$
$$\varphi : [0, 1] \to \mathbb{R}^3 \quad , \quad \varphi(t) = \varepsilon(t^2)$$
$$\psi : [0, 1] \to \mathbb{R}^3 \quad , \quad \psi(t) = \varepsilon(1 - t)$$
$$\vdots$$

Our claim, however, is that we can talk about integrals as follows, with $f, g, h : \mathbb{R}^3 \to \mathbb{R}$, which are independent on the chosen parametrization of our path:

$$I = \int_\gamma f(x)dx_1 + g(x)dx_2 + h(x)dx_3$$

(2) In order to prove this, let us choose a parametrization $\gamma : [a, b] \to \mathbb{R}^3$ as above. This parametrization has as components three functions $\gamma_1, \gamma_2, \gamma_3$, given by:

$$\gamma = (\gamma_1, \gamma_2, \gamma_3) : [a, b] \to \mathbb{R}^3$$

In order to construct the integral I, it is quite clear, by suitably cutting our path into pieces, that we can restrict the attention to the case where all three components $\gamma_1, \gamma_2, \gamma_3 : [a, b] \to \mathbb{R}$ are increasing, or decreasing. Thus, we can assume that these three components are as follows, increasing or decreasing, and bijective on their images:

$$\gamma_i : [a, b] \to [a_i, b_i]$$

(3) Moreover, by using the obvious symmetry between the coordinates x_1, x_2, x_3, in order to construct I, we just need to construct integrals of the following type:

$$I_1 = \int_\gamma f(x)dx_1$$

(4) So, let us construct this latter integral I_1, under the assumptions in (2). The simplest case is when the first path, $\gamma_1 : [a, b] \to [a_1, b_1]$, is the identity:

$$\gamma_1 : [a, b] \to [a, b] \quad , \quad \gamma_1(x) = x$$

In other words, the simplest case is when our path is of the following form, with $\gamma_2, \gamma_3 : [a, b] \to \mathbb{R}$ being certain functions, that should be increasing or decreasing, as per our conventions (2) above, but in what follows we will not need this assumption:

$$\gamma(x_1) = (x_1, \gamma_2(x_1), \gamma_3(x_1))$$

But now, with this convention made, we can define our contour integral, or rather its first component, as explained above, as a usual one-variable integral, as follows:

$$I_1 = \int_a^b f(x_1, \gamma_2(x_1), \gamma_3(x_1))dx_1$$

(5) With this understood, let us examine now the general case, where the first path, $\gamma_1 : [a, b] \to [a_1, b_1]$, is arbitrary, increasing or decreasing, and bijective on its image. In this case we can reparametrize our curve, as to have it as in (4) above, as follows:

$$\tilde{\gamma} = (id, \gamma_2\gamma_1^{-1}, \gamma_3\gamma_1^{-1}) : [a_1, b_1] \to \mathbb{R}^3$$

Now since we want our integral $I_1 = \int_\gamma f(x)dx_1$ to be independent of the parametrization, we are led to the following formula for it, coming from the formula in (4):

$$\begin{aligned} I_1 &= \int_{\tilde{\gamma}} f(x)dx_1 \\ &= \int_{a_1}^{b_1} f(x_1, \gamma_2\gamma_1^{-1}(x_1), \gamma_3\gamma_1^{-1}(x_1))dx_1 \\ &= \int_a^b f(\gamma_1(y_1), \gamma_2(y_1), \gamma_3(y_1))\gamma_1'(y_1)dy_1 \end{aligned}$$

Here we have used at the end the change of variable formula, with $x_1 = \gamma_1(y_1)$.

(6) Thus, job done, we have our definition for the contour integrals, with the formula being as follows, obtained by using (5) for all three coordinates x_1, x_2, x_3:

$$\begin{aligned} I &= \int_a^b f(\gamma_1(y_1), \gamma_2(y_1), \gamma_3(y_1))\gamma_1'(y_1)dy_1 \\ &\quad + \int_a^b g(\gamma_1(y_2), \gamma_2(y_2), \gamma_3(y_2))\gamma_2'(y_2)dy_2 \\ &\quad + \int_a^b h(\gamma_1(y_3), \gamma_2(y_3), \gamma_3(y_3))\gamma_3'(y_3)dy_3 \end{aligned}$$

And with this, we are led to the conclusion in the statement. $\square$

Let us record as well the following more compact form of Theorem 3.7 and its proof, containing what is needed to know, in practice, for computing contour integrals:

THEOREM 3.8. *The contour integrals over a curve* $\gamma : [a, b] \to \mathbb{R}^3$ *are given by*

$$\int_\gamma < F(x), dx >= \int_a^b < F(\gamma(y)), \gamma'(y)dy >$$

valid for any $F : \mathbb{R}^3 \to \mathbb{R}^3$, *where on the right* $\gamma'(y)dy = (\gamma_i'(y_i)dy_i)_i$.

PROOF. This is a fancy reformulation of what we did in Theorem 3.7 and its proof. Indeed, with the notation $F = (F_1, F_2, F_3) = (f, g, h)$, the integral computed there is:

$$\int_\gamma < F(x), dx >= \int_\gamma F_1(x)dx_1 + F_2(x)dx_2 + F_3(x)dx_3$$

As for the value of this integral, according to the proof of Theorem 3.7, this is:

$$\begin{aligned}\int_\gamma < F(x), dx > \ = \ & \int_a^b F_1(\gamma_1(y_1), \gamma_2(y_1), \gamma_3(y_1))\gamma_1'(y_1)dy_1 \\ & + \int_a^b F_2(\gamma_1(y_2), \gamma_2(y_2), \gamma_3(y_2))\gamma_2'(y_2)dy_2 \\ & + \int_a^b F_3(\gamma_1(y_3), \gamma_2(y_3), \gamma_3(y_3))\gamma_3'(y_3)dy_3\end{aligned}$$

Now observe that we can write this in a more compact way, as follows:

$$\begin{aligned}\int_\gamma < F(x), dx > \ = \ & \int_a^b F_1(\gamma(y_1))\gamma'(y_1)dy_1 \\ & + \int_a^b F_2(\gamma(y_2))\gamma'(y_2)dy_2 \\ & + \int_a^b F_3(\gamma(y_3))\gamma'(y_3)dy_3\end{aligned}$$

And we can do even better. Indeed, we have only one integral here, $\int_a^b$, and in order to best express the integrand, consider the formal vector in the statement, namely:

$$\gamma'(y)dy = \begin{pmatrix} \gamma_1'(y_1)dy_1 \\ \gamma_2'(y_2)dy_2 \\ \gamma_3'(y_3)dy_3 \end{pmatrix}$$

Our integrand appears then as the scalar product of $F(\gamma(y))$ with this latter vector $\gamma'(y)dy$, so our formula above for the contour integral takes the following form:

$$\int_\gamma < F(x), dx >= \int_a^b < F(\gamma(y)), \gamma'(y)dy >$$

Thus, we are led to the conclusion in the statement. $\square$

More concretely now, let us temporarily forget about the paths γ, and have a look at the quantities which are to be integrated, namely:

$$\alpha = F_1(x)dx_1 + F_2(x)dx_2 + F_3(x)dx_3$$

Obviously, these are something rather mathematical, and many things can be said here. However, we can have some physical intuition on them. Assume indeed that we

are given a function as follows, that you can think for instance as corresponding to an external force, with $F(x) \in \mathbb{R}^3$ being the force vector applied at a given point $x \in \mathbb{R}^3$:

$$F : \mathbb{R}^3 \to \mathbb{R}^3$$

By writing $F = (F_1, F_2, F_3)$, we can then consider the following quantity, and when $F : \mathbb{R}^3 \to \mathbb{R}^3$ varies, we obtain exactly the abstract quantities α considered above:

$$< F(x), dx >= F_1(x)dx_1 + F_2(x)dx_2 + F_3(x)dx_3$$

Thus, all in all, what we have done in the above with our construction of contour integrals, was to define quantities as follows, with γ being a path in $\mathbb{R}^3$, and with $F : \mathbb{R}^3 \to \mathbb{R}^3$ being a certain function, that we can think of, if we want, as being a force:

$$I = \int_\gamma < F(x), dx >$$

Which brings us into physics. Indeed, by assuming now that $F : \mathbb{R}^3 \to \mathbb{R}^3$ does correspond to a force, we can formulate the following definition:

DEFINITION 3.9. *The work done by a force $F = F(x)$ for moving a particle from point $p \in \mathbb{R}^3$ to point $q \in \mathbb{R}^3$ via a given path $\gamma : p \to q$ is the following quantity:*

$$W(\gamma) = \int_\gamma < F(x), dx >$$

We say that F is conservative if this work quantity $W(\gamma)$ does not depend on the chosen path $\gamma : p \to q$, and in this case we denote this quantity by $W(p, q)$.

Now back to gases, we want to compute the work W done by a gas, pushing a piston. This work is quite easy to compute, and we are led to the following statement:

PROPOSITION 3.10. *The mechanical work done by a gas pushing a piston is*

$$W = \int_a^b PdV$$

where $[a, b]$ is the interval where the piston has travelled.

PROOF. In order to compute mechanical work W done by the gas, observe that, infinitesimally, if we denote by dl the distance traveled by the piston in time dt, we have the following formula, with S being the area of the piston:

$$dW = Fdl = PSdl = Pd(Sl) = PdV$$

Here we have used the standard interpretation of the pressure P, as explained before. Now assuming that the piston has traveled from a to b, we obtain:

$$W = \int_a^b dW = \int_a^b PdV$$

Thus, we are led to the formula in the statement.   □

Obviously what we have above is a general formula, which will hold in more general situations, not necessarily involving a container with a piston. So, let us formulate:

THEOREM 3.11. *The mechanical work done by a gas evolving on a path γ, in the state space $f(P, V, T) = 0$, is given by:*

$$W_\gamma = \int_\gamma P dV$$

When representing the transformation γ as a one-variable function $P = \varphi(V)$, with T being determined at each moment by $f(P, V, T) = 0$, this formula reads

$$W_\gamma = \int_{V_0}^{V_1} \varphi(V) dV$$

with V_0 being the initial volume, and V_1 being the final volume.

PROOF. This is quite clear from the previous discussion, involving the cylinder with a piston, the argument there carrying on to the general case without problems, and giving the first formula. As for the second formula, this follows from it, with again the case of the cylinder with a piston being a good illustration, φ being there linear. $\square$

In order to discuss now examples, let us introduce as well the following notions:

DEFINITION 3.12. *A transformation of a gas is called:*

(1) *Isobaric, if P is constant.*
(2) *Isochoric, if V is constant.*
(3) *Isothermal, if T is constant.*

Here all terminology comes from Greek, with isos meaning equal, baros meaning weight, chora meaning space, and therme meaning heat. In what regards the isochoric transformations, some authors, including Fermi [**30**], use the convention that this means $W = 0$, which is not the same as V being constant. Finally, there is as well a 4th class of transformations, the adiabatic ones, coming from the Greek adiabatos, meaning impassable. These latter transformations are the scary ones, and more on them later.

As an illustration for Theorem 3.11, for an ideal gas, we have the following result:

THEOREM 3.13. *For an ideal gas, $PV = kT$, isothermally expanding, we have*

$$W = T \log \frac{V_1}{V_0}$$

where V_0 is the initial volume, and V_1 is the final volume.

PROOF. This follows indeed from Theorem 3.11, in either formulation:

(1) With the first formula the work is readily computed, as follows:

$$
\begin{aligned}
W &= \int_{\gamma} P dV \\
&= kT \int_{\gamma} \frac{dV}{V} \\
&= T \log \frac{V_1}{V_0}
\end{aligned}
$$

(2) With the second formulation, since we have $PV = kT$ by the equation of state, and T constant by assumption, the transformation is given by $\varphi(V) = kT/V$, and so:

$$
\begin{aligned}
W &= \int_{V_0}^{V_1} \frac{kT}{V} dV \\
&= kT \int_{V_0}^{V_1} \frac{dV}{V} \\
&= T \log \frac{V_1}{V_0}
\end{aligned}
$$

Thus, we are led to the conclusions in the statement. $\qquad\square$

Finally, the first law of thermodynamics invites us to introduce, as a complement to the various elementary notions from Definition 3.12:

DEFINITION 3.14. *A transformation is called adiabatic if:*

$$
Q = 0
$$

Equivalently, we must have the energy conservation law $\Delta E = -W$.

Obviously, this is something a bit complicated. As basic examples here we have the transformations of the thermally insulated systems obeying to $Q = C\Delta T$, with $C > 0$. As an important result about adiabatics, regarding the ideal gases, we have:

THEOREM 3.15. *The adiabatic transformations of an ideal gas, $PV = kT$, satisfy*

$$
TV^{K-1} = \text{constant}
$$

where K is a modified version of k, appearing as follows:

$$
K = \frac{C_P}{C_V} = 1 + \frac{k}{C_V}
$$

Together with $PV = kT$, the above equation produces certain curves, called adiabatics.

PROOF. We use here the Joule formula $C_V dT + P dV = dE$. Since for an adiabatic transformation we have $dE = 0$, the Joule formula becomes:

$$
C_V dT + P dV = 0
$$

Now by using $PV = kT$, we succesively obtain:

$$
\begin{aligned}
PV = kT \quad \Longrightarrow \quad & C_V dT + \frac{kT}{V}\, dV = 0 \\
\Longrightarrow \quad & \frac{dT}{T} + \frac{k}{C_V} \cdot \frac{dV}{V} = 0 \\
\Longrightarrow \quad & \log T + \frac{k}{C_V}\, \log V = \text{constant} \\
\Longrightarrow \quad & TV^{k/C_V} = \text{constant}
\end{aligned}
$$

Thus, we are led to the conclusion in the statement. $\square$

3c. Van der Waals gases

All the above theory concerns the ideal gases, but in practice, things are more complicated than this. The key result here, due to Van der Waals, is as follows:

THEOREM 3.16. *Beyond the ideal gas setting, stating that we should have $PV = kT$, the gases are subject to the Van der Waals equation*

$$
\left(P + \frac{\alpha}{V^2} \right) (V - \beta) = kT
$$

depending on two parameters $\alpha, \beta > 0$.

PROOF. This is something quite tricky, with the correction parameters $\alpha, \beta > 0$ appearing from a detailed study of the gas, from a kinetic viewpoint. It it possible of course to specify the parameters $\alpha, \beta > 0$, via various lists and tables, and even make some speculations on the precise meaning of these two parameters, using basic chemistry. $\square$

The above result is of key importance, and takes us into rethinking everything that what we know about the ideal gases, which must be replaced with Van der Waals gases, at the advanced level. Among the main consequences of this replacement, the isobars, isochores, isothermals and adiabatics of the ideal gases, given by simple formulae, must be replaced by isobars, isochores, isothermals and adiabatics for the Van der Waals gases, which are no longer something trivial, with some interesting math being now involved.

Among others, the study of the Van der Waals gases makes appear some interesting points on the isothermals, called triple and critical points of the gas.

3d. States of matter

The results that we obtained so far about gases, via simple mathematics, make the connection with the general theory of matter, which can be summarized as follows:

FACT 3.17. *Ordinary matter appears in 3 forms, namely solid, liquid and gaseous, roughly appearing according to the following generic diagram*
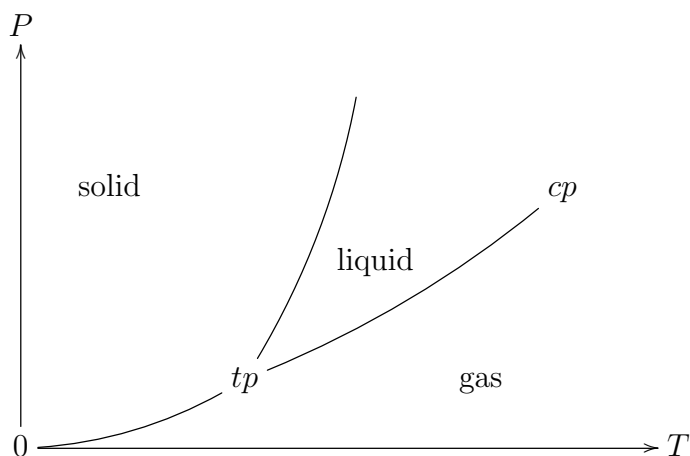
with tp, cp standing for the triple and critical points. Also, at low or high temperatures we have interesting phenonema like Bose-Einstein condensation, and plasma.

All this is extremely interesting, and as already mentioned above, part of it simply comes by looking at the Van der Waals gases, with elementary mathematical tools.

3e. Exercises

Exercises:

EXERCISE 3.18.

EXERCISE 3.19.

EXERCISE 3.20.

EXERCISE 3.21.

EXERCISE 3.22.

EXERCISE 3.23.

Bonus exercise.

CHAPTER 4

Condensed matter

4a. Static liquids

In order to get introduced to the main properties of condensed matter, of mechanical nature, let us first have a look at the liquids. Generally speaking, the mechanics of liquids is a quite complex science, which can be best organized by taking into account the two main properties that a liquid can have or not, which are as follows:

(1) Compressibility.

(2) Viscosity.

Regarding compressibility, this is certainly a property of the gases, but not of most of the liquids, at least when idealized. We will often assume that our fluid is incompressible, which in practice means more or less that we are dealing with liquids, of rather "regular" type. However, this will be not the general rule, for instance because materials like sand, or snow, that we are also interested in, in view of their obvious strong link with classical mechanics, and with our modelling abilities so far, are incompressible too.

Regarding viscosity, this is something far more tricky. Intuitively, this comes from the mutual "friction" of the constituent molecules, when the fluid is moving, and with this being something quite difficult to model and understand, via precise mathematical equations. Without getting into details, for the moment, let us mention that, from this point of view, the fluids, or rather liquids, fall into 3 main classes, namely:

– Inviscid. This is intuitively the case of regular water, and other familiar liquids. However, this remains an idealization, with the true inviscid fluids, in the real life, being basically only the superfluids, met at very low temperatures.

– Newtonian. This is intuitively the case for most of the familiar visquous fluids, from the real life, whose viscosity is proportional to the applied stress, and with this proportionality being known as Newton's law on viscosity.

– Non-Newtonian. These are visquous fluids which do not obey to Newton's law on viscosity, and there are plenty of them, all very interesting, such as paint, toothpaste, ketchup and many more, not to forget basic things like snow or sand.

As a conclusion to all this, we can see that, even when looking at the simplest 2 possible things that can be said about a fluid, namely compressibility and viscosity, we end up with a whole menagerie of fluids, with each of them corresponding to its own branch of fluid mechanics. In what concerns us, let us first fix the following goal:

GOAL 4.1. *We will be first interested in the basic modeling of the incompressible fluids, which can be either inviscid, or non-Newtonian.*

Here our incompressibility assumption comes from our discussion above regarding compressibility, and is certainly somehing quite natural, and with this being the simplest situation anyway, mathematically speaking, that we would like to study first. As for our second assumption, "either inviscid or non-Newtonian", this might sound a bit exotic, but the point here is that we want to avoid, at least in the beginning, the Newtonian, visquous case, whose basic mathematics is notoriously quite complicated.

4b. Phase transitions

In order to get started with our study, let us go back to the general theory of the states of matter, that we discussed in some detail, with due explanations, in chapter 3. We know from there that the basics of the theory can be summarized as follows:

FACT 4.2. *Ordinary matter appears in* 3 *forms, namely solid, liquid and gaseous, roughly appearing according to the following generic diagram*
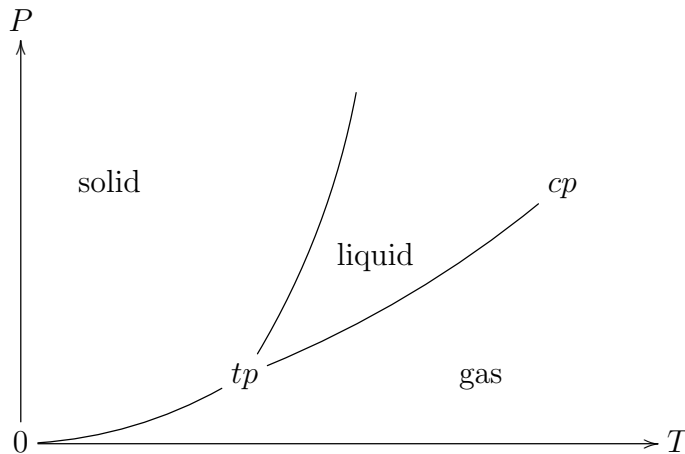
with tp, cp *standing for the triple and critical points. Also, at low or high temperatures we have interesting phenonema like Bose-Einstein condensation, and plasma.*

As explained in chapter 3, quite remarkably, part of this picture simply comes by looking at the Van der Waals gases, with elementary mathematical tools.

Finally, no discussion here would be complete without a word on the heat equation. The result here, which is quite similar to the one for the waves, is as follows:

THEOREM 4.3. *Heat diffusion in $\mathbb{R}^N$ is described by the heat equation*

$$\dot{\varphi} = \alpha \Delta \varphi$$

where $\alpha > 0$ is the thermal diffusivity of the medium, and Δ is the Laplace operator.

PROOF. The study here is quite similar to the study of waves, as follows:

(1) To start with, as an intuitive explanation for the equation, since the second derivative φ'' in one dimension, or the quantity $\Delta \varphi$ in general, computes the average value of a function φ around a point, minus the value of φ at that point, the heat equation as formulated above tells us that the rate of change $\dot{\varphi}$ of the temperature of the material at any given point must be proportional, with proportionality factor $\alpha > 0$, to the average difference of temperature between that given point and the surrounding material.

(2) In practice, we can recover this equation a bit as we did for the wave equation before. At $N = 1$ our model looks as follows, with distance $l > 0$ between neighbors:

$$\underline{\quad\quad} \circ_{x-l} \xrightarrow{\ \ l\ \ } \circ_x \xrightarrow{\ \ l\ \ } \circ_{x+l} \underline{\quad\quad}$$

(3) In order to model heat diffusion, we have to implement the intuitive mechanism explained above. In practice, this leads to a condition as follows, expressing the change of the temperature φ, over a small period of time $\delta > 0$:

$$\varphi(x, t + \delta) = \varphi(x, t) + \frac{\alpha \delta}{l^2} \sum_{x \sim y} [\varphi(y, t) - \varphi(x, t)]$$

To be more precise, we have made several assumptions here, as follows:

– General heat diffusion assumption: the change of temperature at any given point x is proportional to the average over neighbors, $y \sim x$, of the differences $\varphi(y, t) - \varphi(x, t)$ between the temperatures at x, and at these neighbors y.

– Infinitesimal time and length conditions: in our model, the change of temperature at a given point x is proportional to small period of time involved, $\delta > 0$, and is inverse proportional to the square of the distance between neighbors, l^2.

(4) Regarding these latter assumptions, the one regarding the proportionality with the time elapsed $\delta > 0$ is something quite natural, physically speaking, and mathematically speaking too, because we can rewrite our equation as follows, making it clear that we have here an equation regarding the rate of change of temperature at x:

$$\frac{\varphi(x, t + \delta) - \varphi(x, t)}{\delta} = \frac{\alpha}{l^2} \sum_{x \sim y} [\varphi(y, t) - \varphi(x, t)]$$

As for the second assumption that we made above, namely inverse proportionality with l^2, this can be justified on physical grounds too, but again, perhaps the best is to do the math, which will show right away where this proportionality comes from.

(5) So, let us do the math. In the context of our 1D model the neighbors of x are the points $x \pm l$, and so the equation that we wrote above takes the following form:

$$\frac{\varphi(x, t+\delta) - \varphi(x, t)}{\delta} = \frac{\alpha}{l^2} \Big[(\varphi(x+l, t) - \varphi(x, t)) + (\varphi(x-l, t) - \varphi(x, t)) \Big]$$

Now observe that we can write this equation as follows:

$$\frac{\varphi(x, t+\delta) - \varphi(x, t)}{\delta} = \alpha \cdot \frac{\varphi(x+l, t) - 2\varphi(x, t) + \varphi(x-l, t)}{l^2}$$

(6) As it was the case with the wave equation before, we recognize on the right the usual approximation of the second derivative, coming from calculus. Thus, when taking the continuous limit of our model, $l \to 0$, we obtain the following equation:

$$\frac{\varphi(x, t+\delta) - \varphi(x, t)}{\delta} = \alpha \cdot \varphi''(x, t)$$

Now with $t \to 0$, we are led in this way to the heat equation, namely:

$$\dot{\varphi}(x, t) = \alpha \cdot \varphi''(x, t)$$

(7) With this done, let us discuss now 2 dimensions. Here, as before for the waves, we can use a lattice model as follows, with all lengths being $l > 0$, for simplifying:
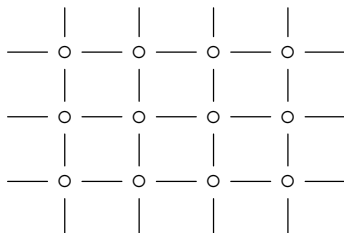
(8) We have to implement now the physical heat diffusion mechanism, namely "the rate of change of the temperature of the material at any given point must be proportional, with proportionality factor $\alpha > 0$, to the average difference of temperature between that given point and the surrounding material". In practice, this leads to a condition as follows, expressing the change of the temperature φ, over a small period of time $\delta > 0$:

$$\varphi(x, y, t+\delta) = \varphi(x, y, t) + \frac{\alpha\delta}{l^2} \sum_{(x,y) \sim (u,v)} [\varphi(u, v, t) - \varphi(x, y, t)]$$

In fact, we can rewrite our equation as follows, making it clear that we have here an equation regarding the rate of change of temperature at x:

$$\frac{\varphi(x, y, t+\delta) - \varphi(x, y, t)}{\delta} = \frac{\alpha}{l^2} \sum_{(x,y) \sim (u,v)} [\varphi(u, v, t) - \varphi(x, y, t)]$$

(9) So, let us do the math. In the context of our 2D model the neighbors of x are the points $(x \pm l, y \pm l)$, so the equation above takes the following form:

$$\frac{\varphi(x, y, t + \delta) - \varphi(x, y, t)}{\delta}$$
$$= \frac{\alpha}{l^2} \Big[(\varphi(x + l, y, t) - \varphi(x, y, t)) + (\varphi(x - l, y, t) - \varphi(x, y, t)) \Big]$$
$$+ \frac{\alpha}{l^2} \Big[(\varphi(x, y + l, t) - \varphi(x, y, t)) + (\varphi(x, y - l, t) - \varphi(x, y, t)) \Big]$$

Now observe that we can write this equation as follows:

$$\frac{\varphi(x, y, t + \delta) - \varphi(x, y, t)}{\delta} = \alpha \cdot \frac{\varphi(x + l, y, t) - 2\varphi(x, y, t) + \varphi(x - l, y, t)}{l^2}$$
$$+ \alpha \cdot \frac{\varphi(x, y + l, t) - 2\varphi(x, y, t) + \varphi(x, y - l, t)}{l^2}$$

(10) We recognize on the right the usual approximation of the second derivative. Thus, when taking the continuous limit, $l \to 0$, we obtain the following equation:

$$\frac{\varphi(x, y, t + \delta) - \varphi(x, y, t)}{\delta} = \alpha \left(\frac{d^2 \varphi}{dx^2} + \frac{d^2 \varphi}{dy^2} \right) (x, y, t)$$

Now with $t \to 0$, we are led in this way to the heat equation, namely:

$$\dot{\varphi}(x, y, t) = \alpha \cdot \Delta \varphi(x, y, t)$$

Finally, in arbitrary N dimensions the same argument carries over, namely a straight-forward lattice model, and gives the heat equation, as formulated in the statement. $\square$

4c. Into dynamics

Let us discuss now the dynamics of liquids. As a first observation, which is of key importance in advanced fluid dynamics, we have:

OBSERVATION 4.4. *An incompressible fluid is right away something mathematical, whose dynamics is described by a diffeomorphism, evolving in time $t > 0$.*

Obviously, this is something very basic, coming from the very nature of the incompressibility property. To be more precise, assuming for instance that we have colored our fluid initially, say into tiny little cubes of red, yellow, green and so on, after some time $t > 0$ we will obviously still have a mixture of red, yellow, green and so on, appearing in equal parts, and the function $f : \mathbb{R}^3 \to \mathbb{R}^3$ mapping red to red, yellow to yellow, green to green, and so on, is what we call in mathematics a diffeomorphism.

In practice now, in order to reach from this to a PDE, let us assume that we are in the simplest case, where our fluid is inviscid, and also adiabatic, or with zero thermal

conductivity. The dynamics of the diffeomorphisms $f : \mathbb{R}^3 \to \mathbb{R}^3$ will be then, intuitively speaking, basically governed by the mechanics of the red, yellow, green and so on components, and we are led in this way to the Euler equations, which are as follows:

$$\dot{u} + <u, \nabla> u = -\nabla w \quad , \quad <\nabla, u> = 0$$

Here u is the vector velocity field, and w is the thermodynamic work, with the quantity on the right from the first equation being as follows, p being the pressure:

$$\nabla w = \frac{\nabla p}{\rho}$$

With this replacement made, the Euler equations become:

$$\dot{u} + <u, \nabla> u = -\frac{\nabla p}{\rho} \quad , \quad <\nabla, u> = 0$$

Here the first equation, which is the important one, is called the Euler momentum equation. This equation can be further complicated by adding an acceleration term $+g$ on the right, accounting for exterior forces, gravitational, or magnetic or of some other kind. As for the second equation, this is the incompressibility constraint.

In the visquous case the Euler momentum equation gets replaced by the Navier-Stokes equation, which is as follows, with v being the kinematic viscosity:

$$\dot{u} + <u, \nabla> u = -\frac{\nabla p}{\rho} + v\Delta u$$

Summarizing, in relation with our modeling questions for the incompressible fluids, we will be mostly interested in the Euler equation, and its versions.

4d. Critical dynamics

Critical dynamics.

4e. Exercises

Exercises:

EXERCISE 4.5.

EXERCISE 4.6.

EXERCISE 4.7.

EXERCISE 4.8.

EXERCISE 4.9.

EXERCISE 4.10.

Bonus exercise.

Part II

Solids, elasticity

This beat is, this beat is
This beat is Technotronic
This beat is Technotronic
And Eric's got lyrics for ya

CHAPTER 5

5a.

5b.

5c.

5d.

5e. Exercises

Exercises:

EXERCISE 5.1.

EXERCISE 5.2.

EXERCISE 5.3.

EXERCISE 5.4.

EXERCISE 5.5.

EXERCISE 5.6.

Bonus exercise.

CHAPTER 6

6a.

6b.

6c.

6d.

6e. Exercises

Exercises:

EXERCISE 6.1.

EXERCISE 6.2.

EXERCISE 6.3.

EXERCISE 6.4.

EXERCISE 6.5.

EXERCISE 6.6.

Bonus exercise.

CHAPTER 7

7a.

7b.

7c.

7d.

7e. Exercises

Exercises:

EXERCISE 7.1.

EXERCISE 7.2.

EXERCISE 7.3.

EXERCISE 7.4.

EXERCISE 7.5.

EXERCISE 7.6.

Bonus exercise.

CHAPTER 8

8a.

8b.

8c.

8d.

8e. Exercises

Exercises:

EXERCISE 8.1.

EXERCISE 8.2.

EXERCISE 8.3.

EXERCISE 8.4.

EXERCISE 8.5.

EXERCISE 8.6.

Bonus exercise.

Part III

Crystals, math

You know that I want you
And you know that I need you
I want it bad
Your bad romance

CHAPTER 9

9a.

9b.

9c.

9d.

9e. Exercises

Exercises:

EXERCISE 9.1.

EXERCISE 9.2.

EXERCISE 9.3.

EXERCISE 9.4.

EXERCISE 9.5.

EXERCISE 9.6.

Bonus exercise.

CHAPTER 10

10a.

10b.

10c.

10d.

10e. Exercises

Exercises:

EXERCISE 10.1.

EXERCISE 10.2.

EXERCISE 10.3.

EXERCISE 10.4.

EXERCISE 10.5.

EXERCISE 10.6.

Bonus exercise.

CHAPTER 11

11a.

11b.

11c.

11d.

11e. Exercises

Exercises:

EXERCISE 11.1.

EXERCISE 11.2.

EXERCISE 11.3.

EXERCISE 11.4.

EXERCISE 11.5.

EXERCISE 11.6.

Bonus exercise.

CHAPTER 12

12a.

12b.

12c.

12d.

12e. Exercises

Exercises:

EXERCISE 12.1.

EXERCISE 12.2.

EXERCISE 12.3.

EXERCISE 12.4.

EXERCISE 12.5.

EXERCISE 12.6.

Bonus exercise.

Part IV

World of metals

Die
By my hand
I creep across the land
Killing first born man

CHAPTER 13

13a.

13b.

13c.

13d.

13e. Exercises

Exercises:

EXERCISE 13.1.

EXERCISE 13.2.

EXERCISE 13.3.

EXERCISE 13.4.

EXERCISE 13.5.

EXERCISE 13.6.

Bonus exercise.

CHAPTER 14

14a.

14b.

14c.

14d.

14e. Exercises

Exercises:

EXERCISE 14.1.

EXERCISE 14.2.

EXERCISE 14.3.

EXERCISE 14.4.

EXERCISE 14.5.

EXERCISE 14.6.

Bonus exercise.

CHAPTER 15

15a.

15b.

15c.

15d.

15e. Exercises

Exercises:

EXERCISE 15.1.

EXERCISE 15.2.

EXERCISE 15.3.

EXERCISE 15.4.

EXERCISE 15.5.

EXERCISE 15.6.

Bonus exercise.

CHAPTER 16

16a.

16b.

16c.

16d.

16e. Exercises

Congratulations for having read this book, and no exercises for this final chapter.

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