

# The physics of water

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ABSTRACT. This is an introduction to water  $\text{H}_2\text{O}$ , and its various physical properties, focusing on thermodynamics, and with a look into basic chemistry too. We first discuss how water appears from hydrogen  ${}^1\text{H}$  and oxygen  ${}^8\text{O}$ , in theory and in practice, and with a look at ions and isotopes too. Then we embark on a lengthy thermodynamic discussion, and its various ramifications, notably around the triple point, which is something quite fascinating. Finally, we discuss some basic chemistry aspects, mostly in relation with the remarkable solvent properties of water, and the various soups that can appear.

## Preface

At the first glance, there is nothing spectacular about water. However, even armed with some basic physics only, we can see that water is a very particular substance. When freezing water dilates, which is something quite unusual. Also in relation with freezing, who has not admired various snowflakes, and wondered what is the mathematics behind. And then again in relation with freezing, and with boiling too, the required temperatures,  $0^{\circ}\text{C}$  and  $100^{\circ}\text{C}$ , are of key importance for calibrating our thermometers and other scientific devices, and this no matter what degrees you use, Celsius, Fahrenheit or Kelvin.

All this was physics, with the conclusion that, passed the molecules formed by single chemical elements, water is most likely the most interesting substance. But then comes chemistry, and biology too, with again the same conclusion, coming this time from the remarkable solvent properties of water, that this is the most important substance, there as well. As a example of what can be said here, make a soup of carbon  ${}_{6}\text{C}$ , nitrogen  ${}_{7}\text{N}$ , and a few other items, with hydrogen  ${}_{1}\text{H}$  and oxygen  ${}_{8}\text{O}$  not really needed, because already present in water  $\text{H}_2\text{O}$ , and let that soup boil for some time, under the influence of various cosmic rays, and other things that can happen, in our universe. In the end what you will get are some organic molecules, then cells, then dinosaurs, and finally certain bizarre creatures, bearing a clear resemblance with you, reader.

The present book is an introduction to water  $\text{H}_2\text{O}$ , and its various physical properties, mainly focusing on thermodynamics, and with a look into basic chemistry too. Normally this is a bit upside-down, because water means above everything chemistry. But this book is mostly written with physics motivations in mind, and as such, can stand as a useful complement, or introduction to, any standard chemistry text focusing on water.

The book is written quite informally, for scientists at large, not necessarily familiar with advanced physics or chemistry, and is organized in four parts, as follows:

Part I - We discuss here how water appears from hydrogen  ${}_{1}\text{H}$  and oxygen  ${}_{8}\text{O}$ , in theory and in practice, and with a look at ions and isotopes too.

Part II - This is a first thermodynamics discussion, dealing with hot water, around its boiling point. We talk here about many things, including steam engines.

Part III - This is a second thermodynamics discussion, this time about cold water, and its freezing point. Again, we talk here about many things, including snowflakes.

Part IV - This is an introduction to chemistry aspects, with focus on the remarkable solvent properties of water, and on the various soups that can appear.

In the hope that you will like this book. Again, we will focus here mostly on the physics of the water, and leave the truly interesting aspects, in relation with chemistry, only for the end of the book. But, the physics of water is something quite interesting too, worth discussing in detail, and it is mainly about this that we want to talk about.

This book is dedicated to everyone drinking tap water, and to my water company here in the French countryside, Sieva. With exceptions being of course some beer drinking friends, but please don't drink too much. Plus of course my cats, who don't seem to need any water or beer for functioning, but I guess they have their own tricks.

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Part I

The molecule

*Elle*  
*Rappelle-toi comme elle est belle*  
*Et touche-la, elle sent le sel*  
*C'est un don miraculeux*

## CHAPTER 1

### Hydrogen atom

#### 1a. Spectral lines

We recall that light is an electromagnetic wave, depending on frequency and wavelength. The classification of light, in a rough form, is as follows:

Frequency	Type	Wavelength
	—	
$10^{18} - 10^{20}$	$\gamma$ 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

Spectroscopy, a cheap and very useful technique, amounts in decomposing the light that an event has produced, by using a prism, recording the color components of that light, and trying to reconstruct that event, out of this data. This technique was key

to the beginnings of the atomic theory, 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 1.1 (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	$\alpha$	121.567	UV
3	$\beta$	102.572	UV
4	$\gamma$	97.254	UV
$\vdots$	$\vdots$	$\vdots$	$\vdots$
$\infty$	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 1.2 (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	$\alpha$	656.279	red
4	$\beta$	486.135	aqua
5	$\gamma$	434.047	blue
6	$\delta$	410.173	violet
7	$\varepsilon$	397.007	UV
$\vdots$	$\vdots$	$\vdots$	$\vdots$
$\infty$	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 1.3 (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	$\alpha$	1875	IR
5	$\beta$	1282	IR
6	$\gamma$	1094	IR
$\vdots$	$\vdots$	$\vdots$	$\vdots$
$\infty$	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 1.4 (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  $n_1 = 4, 5, 6, \dots$ , and these were discovered later, by Brackett in 1922, Pfund in 1924, Humphreys in 1953, and others afterwards,

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  $R \rightarrow RZ^2$ , 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  $e_{ij} : e_j \rightarrow e_i$ . Thus, we are in familiar territory here, and we can start dreaming of:

**THOUGHT 1.5.** *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.*

We will see in a moment that this thought can be made into a theorem.

### 1b. The Bohr model

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 1.6.** *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 1.6.

So, taking now Claim 1.6 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 1.6, but led to an improved version of it, as follows:

CLAIM 1.7. *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 1.8 (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  $1, 2, 3, \dots$ , 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  $n_1 \rightarrow n_2$  or  $n_2 \rightarrow n_1$ , 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 1.5.

### 1c. Matrix 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 1.9. *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 initial 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  $\gamma$ , 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 1.10. *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 1.11 (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 1.12. *In quantum mechanics the states of the system are vectors of a Hilbert space  $H$ , and the observables of the system are linear operators*

$$T : H \rightarrow H$$

*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:*

$$\langle T \rangle = \langle T\xi, \xi \rangle$$

*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  $\psi$  lives, and we have*

$$\langle T \rangle = \int_{\mathbb{R}^3} T(\psi) \cdot \bar{\psi} dx$$

*which is called “sandwiching” formula, with the operators*

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

*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.

### 1d. Energy formula

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

$$\begin{aligned} \frac{d}{dr} \left( r^2 \cdot \frac{d\rho}{dr} \right) - \frac{2mr^2}{\hbar^2} (V - E)\rho &= K\rho \\ \sin s \cdot \frac{d}{ds} \left( \sin s \cdot \frac{d\alpha}{ds} \right) + \frac{d^2\alpha}{dt^2} &= -K \sin^2 s \cdot \alpha \end{aligned}$$

*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 geometry or 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 in spherical coordinates as follows:

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

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:

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

In order to solve this equation, we will do two manipulations. First, by multiplying everything by  $2mr^2/(\hbar^2\rho\alpha)$ , this equation takes the following more convenient form:

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

Now observe that by moving the radial terms to the left, and the angular terms to the right, this latter equation can be written as follows:

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

Since this latter equation is now separated between radial and angular variables, both sides must be equal to a certain constant  $-K$ , as follows:

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

But this leads to the conclusion in the statement.  $\square$

Let us first study the angular equation. We first have the following result:

**PROPOSITION 1.14.** *The angular equation that we found before separates, for solutions of type  $\alpha = \sigma(s)\theta(t)$ , into two equations, as follows,*

$$\frac{1}{\theta} \cdot \frac{d^2\theta}{dt^2} = -m^2$$

$$\frac{\sin s}{\sigma} \cdot \frac{d}{ds} \left( \sin s \cdot \frac{d\sigma}{ds} \right) + K \sin^2 s = m^2$$

with  $m$  being a constant, called azimuthal equation, and polar equation.

PROOF. Let us first recall that, according to our conventions for spherical coordinates,  $r \in [0, \infty)$  is the radius,  $s \in [0, \pi]$  is the polar angle, and  $t \in [0, 2\pi]$  is the azimuthal angle. By plugging now  $\alpha = \sigma(s)\theta(t)$  into the angular equation, we obtain:

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

By dividing everything by  $\sigma\theta$ , this equation can be written as follows:

$$-\frac{1}{\theta} \cdot \frac{d^2\theta}{dt^2} = \frac{\sin s}{\sigma} \cdot \frac{d}{ds} \left( \sin s \cdot \frac{d\sigma}{ds} \right) + K \sin^2 s$$

Since the variables are separated, we must have, for a certain constant  $m$ :

$$\begin{aligned} \frac{1}{\theta} \cdot \frac{d^2\theta}{dt^2} &= -m^2 \\ \frac{\sin s}{\sigma} \cdot \frac{d}{ds} \left( \sin s \cdot \frac{d\sigma}{ds} \right) + K \sin^2 s &= m^2 \end{aligned}$$

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

Regarding the azimuthal equation, things here are quickly settled, as follows:

PROPOSITION 1.15. *The solutions of the azimuthal equation, namely*

$$\frac{1}{\theta} \cdot \frac{d^2\theta}{dt^2} = -m^2$$

*are the functions as follows, with  $a, b \in \mathbb{C}$  being parameters,*

$$\theta(t) = ae^{imt} + be^{-imt}$$

*and with only the case  $m \in \mathbb{Z}$  being acceptable, on physical grounds.*

PROOF. The first assertion is clear, because we have a second order equation, and two obvious solutions for it,  $e^{\pm imt}$ , and then their linear combinations, and that's all. Regarding the last assertion, the point here is that by using  $\theta(t) = \theta(t + 2\pi)$ , which is a natural physical assumption on the wave function, we are led to  $m \in \mathbb{Z}$ , as stated.  $\square$

We are now about to solve the angular equation, with only the polar equation remaining to be studied. However, this is quite difficult, so be patient. We first have:

PROPOSITION 1.16. *The polar equation that we found before, namely*

$$\frac{\sin s}{\sigma} \cdot \frac{d}{ds} \left( \sin s \cdot \frac{d\sigma}{ds} \right) + K \sin^2 s = m^2$$

*with  $m \in \mathbb{Z}$ , translates via  $\sigma(s) = f(\cos s)$  into the following equation,*

$$(1 - x^2)f''(x) - 2xf'(x) = \left( \frac{m^2}{1 - x^2} - K \right) f(x)$$

*where  $x = \cos s$ , called Legendre equation.*

PROOF. Let us first do a number of manipulations on our equation, before making the change of variables. By multiplying by  $\sigma$ , our equation becomes:

$$\sin s \cdot \frac{d}{ds} \left( \sin s \cdot \frac{d\sigma}{ds} \right) = (m^2 - K \sin^2 s) \sigma$$

By differentiating at left, this equation becomes:

$$\sin s (\cos s \cdot \sigma' + \sin s \cdot \sigma'') = (m^2 - K \sin^2 s) \sigma$$

Finally, by dividing everything by  $\sin^2 s$ , our equation becomes:

$$\sigma'' + \frac{\cos s}{\sin s} \cdot \sigma' = \left( \frac{m^2}{\sin^2 s} - K \right) \sigma$$

Now let us set  $\sigma(s) = f(\cos s)$ . With this change of variables, we have:

$$\sigma = f(\cos s)$$

$$\sigma' = -\sin s \cdot f'(\cos s)$$

$$\sigma'' = -\cos s \cdot f'(\cos s) + \sin^2 s \cdot f''(\cos s)$$

By plugging this data, our radial equation becomes:

$$\sin^2 s \cdot f''(\cos s) - 2 \cos s \cdot f'(\cos s) = \left( \frac{m^2}{\sin^2 s} - K \right) f(\cos s)$$

Now with  $x = \cos s$ , we obtain the Legendre equation, as stated. □

Here comes now the difficult point. We have the following non-trivial result:

**THEOREM 1.17.** *The solutions of the Legendre equation, namely*

$$(1 - x^2)f''(x) - 2xf'(x) = \left( \frac{m^2}{1 - x^2} - K \right) f(x)$$

*can be explicitly computed, via complicated math, and only the case*

$$K = l(l + 1) \quad : \quad l \in \mathbb{N}$$

*is acceptable, on physical grounds.*

PROOF. The first part is something quite complicated, involving the hypergeometric functions  ${}_2F_1$ , that you don't want to hear about, believe me. As for the second part, analysis and physics, this is something not trivial either. See Griffiths [40]. □

In order to construct the solutions, we will need:

**THEOREM 1.18.** *The orthonormal basis of  $L^2[-1, 1]$  obtained by starting with the Weierstrass basis  $\{x^l\}$ , and doing Gram-Schmidt, is the family of polynomials  $\{P_l\}$ , with each  $P_l$  being of degree  $l$ , and with positive leading coefficient, subject to:*

$$\int_{-1}^1 P_k(x)P_l(x) dx = \delta_{kl}$$

*These polynomials, called Legendre polynomials, satisfy the equation*

$$(1 - x^2)P_l''(x) - 2xP_l'(x) + l(l + 1)P_l(x) = 0$$

*which is the Legendre equation at  $m = 0$ , and with  $K = l(l + 1)$ . Moreover,*

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

*which is called the Rodrigues formula for Legendre polynomials.*

**PROOF.** The first assertion is clear, because the Gram-Schmidt procedure applied to the Weierstrass basis  $\{x^l\}$  can only lead to a certain family of polynomials  $\{P_l\}$ . Now thinking at what Gram-Schmidt does, this is something by recurrence, and this leads to the Legendre equation. As for the Rodrigues formula, this is something standard too.  $\square$

Going ahead now, we can solve in fact the Legendre equation at any  $m$ , as follows:

**PROPOSITION 1.19.** *The general Legendre equation, with parameters  $m \in \mathbb{N}$  and  $K = l(l + 1)$  with  $l \in \mathbb{N}$ , namely*

$$(1 - x^2)f''(x) - 2xf'(x) = \left( \frac{m^2}{1 - x^2} - l(l + 1) \right) f(x)$$

*is solved by the following functions, called Legendre functions,*

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

*where  $P_l$  are as before the Legendre polynomials. Also, we have*

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

*called Rodrigues formula for Legendre functions.*

**PROOF.** The first assertion is something elementary, coming by differentiating  $m$  times the Legendre equation, which leads to the general Legendre equation. As for the second assertion, this follows from the Rodrigues formula for Legendre polynomials.  $\square$

By putting together all the above results, we are led to the following conclusion:

THEOREM 1.20. *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. Let us begin with some generalities, valid for any time-independent potential  $V$ . As a first manipulation on the radial equation, we have:

PROPOSITION 1.21. *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.  $\square$

Getting back now to the Coulomb potential of the proton, we have here:

FACT 1.22. *The Coulomb potential of the hydrogen atom proton, acting on the electron by attraction, is given according to the Coulomb law by*

$$V = -\frac{Kep}{r}$$

where  $p$  is the charge of the proton, and  $K$  is the Coulomb constant. In practice however we have  $p \simeq e$  up to order  $10^{-7}$ , and so our formula can be written as

$$V \simeq -\frac{Ke^2}{r}$$

and we will use this latter formula, and with  $=$  sign, for simplifying.

Getting back now to math, it remains to solve the modified radial equation, for the above potential  $V$ . And we have here the following result, which does not exactly solve this radial equation, but provides us instead with something far better, namely the proof of the original claim by Bohr, which was at the origin of everything:

THEOREM 1.23 (Schrödinger). *In the case of the hydrogen atom, where  $V$  is the Coulomb potential of the proton, the modified radial equation, which reads*

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

leads to the Bohr formula for allowed energies,

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

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, and we will be following Griffiths [40], with some details missing. The idea is as follows:

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

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

In terms of  $\alpha = \sqrt{-2mE}/\hbar$ , 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  $p \rightarrow \infty$  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  $p \rightarrow 0$  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:

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

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  $j \gg 0$  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:

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

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

$$\begin{aligned} K &= 8.988 \times 10^9 \quad , \quad e = 1.602 \times 10^{-19} \\ h &= 1.055 \times 10^{-34} \quad , \quad m = 9.109 \times 10^{-31} \end{aligned}$$

But this gives the formula of  $E_1$  in the statement. □

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

THEOREM 1.24. *The Rydberg constant for hydrogen is given by*

$$R = -\frac{E_1}{h_0c}$$

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

$$\frac{1}{\lambda_{n_1n_2}} = R \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

simply reads, via the energy formula in Theorem 1.23,

$$\frac{1}{\lambda_{n_1n_2}} = \frac{E_{n_2} - E_{n_1}}{h_0c}$$

which is in agreement with the Planck formula  $E = h_0c/\lambda$ .

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

$$R = \frac{-E_1}{h_0c} = \frac{2.177 \times 10^{-18}}{6.626 \times 10^{-34} \times 2.998 \times 10^8} = 1.096 \times 10^7$$

Regarding now the second assertion, by dividing  $R = -E_1/(h_0c)$  by any number of type  $n^2$  we obtain, according to the energy convention in Theorem 1.23:

$$\frac{R}{n^2} = -\frac{E_n}{h_0c}$$

But these are exactly the numbers which are subject to subtraction in the Rydberg formula, and so we are led to the conclusion in the statement.  $\square$

### 1e. Exercises

Exercises:

EXERCISE 1.25.

EXERCISE 1.26.

EXERCISE 1.27.

EXERCISE 1.28.

EXERCISE 1.29.

EXERCISE 1.30.

Bonus exercise.

## CHAPTER 2

### Oxygen atom

#### 2a. Heavier atoms

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 2.1.** *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  $\rho_{nl}(r) = p^{l+1}e^{-pv}(p)/r$  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.  $\square$

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

**THEOREM 2.2.** *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 the mean distance between the electron and the proton, in the ground state, and is given by the formula

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

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

PROOF. There are several things going on here, as follows:

(1) According to the various formulae from chapter 1, taken at  $n = 1$ , the parameter  $\alpha$  appearing in the computations 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.

(2) Regarding the wave function, we know from chapter 1 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  $\phi_{100}$  in the statement.

(3) But this formula of  $\phi_{100}$  shows in particular that the Bohr radius  $a$  is indeed the mean distance between the electron and the proton, in the ground state.

(4) 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.  $\square$

Getting back now to the general setting from chapter 1, the point is that the polynomials  $v(p)$  appearing there are well-known objects in mathematics, as follows:

PROPOSITION 2.3. *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:

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

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:

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

(1) The orthogonal basis obtained by applying Gram-Schmidt to the Weierstrass basis  $\{x^q\}$  is then the basis formed by the Laguerre polynomials  $\{L_q\}$ .

(2) We have the explicit formula for  $L_q$  in the statement, which is analogous to the Rodrigues formula for the Legendre polynomials.

(3) The first assertion follows from the fact that the coefficients of the associated Laguerre polynomials satisfy the equation for the coefficients of  $v(p)$ .

(4) Alternatively, the first assertion follows as well by using an equation for the Laguerre polynomials, which is very similar to the Legendre equation.  $\square$

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

**THEOREM 2.4.** *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, namely the results from chapter 1 and Proposition 2.3, and then doing some remaining work, concerning the normalization of the wave function, which leads to the normalization factor above.  $\square$

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 2.5.** *The wave function of a system of electrons  $e_1, \dots, e_Z$ , given by*

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

is governed by the Schrödinger equation  $i\hbar\dot{\psi} = \hat{H}\psi$ , with Hamiltonian as follows,

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

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 Schrödinger equation in Definition 2.5 is pretty much impossible to solve, due to the Coulomb repulsion term, which makes the math 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 are 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 2.6. Consider an atom of atomic number  $Z$ , meaning a fixed  $Ze$  charge, surrounded by electrons  $e_1, \dots, e_Z$ . The problem is to solve the Schrödinger equation

$$i\hbar\dot{\psi} = \hat{H}\psi$$

with Hamiltonian as follows,

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

or at least to understand how  $e_1, \dots, e_Z$  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 2.7. 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  $e \rightarrow 2e$  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  $E_0 = -79 \text{ eV}$ .

Moving ahead, let us focus on a more modest question, that at the end of Problem 2.6, namely understanding how the electrons  $e_1, \dots, e_Z$  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 not very far from reality, and is actually quite close to reality, if we add the spin to our discussion. For some explanations here, we refer to Griffiths [40].

## 2b. Electron spin

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 2.8 (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.

## 2c. Periodic table

We have now all the ingredients for discussing the known atoms, or chemical elements,  $Z = 1, \dots, 118$ . 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	$\frac{\text{H}}{1}$																	$\frac{\text{He}}{2}$	
2	$\frac{\text{Li}}{3}$	$\frac{\text{Be}}{4}$											$\frac{\text{B}}{5}$	$\frac{\text{C}}{6}$	$\frac{\text{N}}{7}$	$\frac{\text{O}}{8}$	$\frac{\text{F}}{9}$	$\frac{\text{Ne}}{10}$	
3	$\frac{\text{Na}}{11}$	$\frac{\text{Mg}}{12}$											$\frac{\text{Al}}{13}$	$\frac{\text{Si}}{14}$	$\frac{\text{P}}{15}$	$\frac{\text{S}}{16}$	$\frac{\text{Cl}}{17}$	$\frac{\text{Ar}}{18}$	
4	$\frac{\text{K}}{19}$	$\frac{\text{Ca}}{20}$	$\frac{\text{Sc}}{21}$	$\frac{\text{Ti}}{22}$	$\frac{\text{V}}{23}$	$\frac{\text{Cr}}{24}$	$\frac{\text{Mn}}{25}$	$\frac{\text{Fe}}{26}$	$\frac{\text{Co}}{27}$	$\frac{\text{Ni}}{28}$	$\frac{\text{Cu}}{29}$	$\frac{\text{Zn}}{30}$	$\frac{\text{Ga}}{31}$	$\frac{\text{Ge}}{32}$	$\frac{\text{As}}{33}$	$\frac{\text{Se}}{34}$	$\frac{\text{Br}}{35}$	$\frac{\text{Kr}}{36}$	
5	$\frac{\text{Rb}}{37}$	$\frac{\text{Sr}}{38}$	$\frac{\text{Y}}{39}$	$\frac{\text{Zr}}{40}$	$\frac{\text{Nb}}{41}$	$\frac{\text{Mo}}{42}$	$\frac{\text{Tc}}{43}$	$\frac{\text{Ru}}{44}$	$\frac{\text{Rh}}{45}$	$\frac{\text{Pd}}{46}$	$\frac{\text{Ag}}{47}$	$\frac{\text{Cd}}{48}$	$\frac{\text{In}}{49}$	$\frac{\text{Sn}}{50}$	$\frac{\text{Sb}}{51}$	$\frac{\text{Te}}{52}$	$\frac{\text{I}}{53}$	$\frac{\text{Xe}}{54}$	
6	$\frac{\text{Cs}}{55}$	$\frac{\text{Ba}}{56}$	<i>l</i>	$\frac{\text{Lu}}{71}$	$\frac{\text{Hf}}{72}$	$\frac{\text{Ta}}{73}$	$\frac{\text{W}}{74}$	$\frac{\text{Re}}{75}$	$\frac{\text{Os}}{76}$	$\frac{\text{Ir}}{77}$	$\frac{\text{Pt}}{78}$	$\frac{\text{Au}}{79}$	$\frac{\text{Hg}}{80}$	$\frac{\text{Tl}}{81}$	$\frac{\text{Pb}}{82}$	$\frac{\text{Bi}}{83}$	$\frac{\text{Po}}{84}$	$\frac{\text{At}}{85}$	$\frac{\text{Rn}}{86}$
7	$\frac{\text{Fr}}{87}$	$\frac{\text{Ra}}{88}$	<i>a</i>	$\frac{\text{Lr}}{103}$	$\frac{\text{Rf}}{104}$	$\frac{\text{Db}}{105}$	$\frac{\text{Sg}}{106}$	$\frac{\text{Bh}}{107}$	$\frac{\text{Hs}}{108}$	$\frac{\text{Mt}}{109}$	$\frac{\text{Ds}}{110}$	$\frac{\text{Rg}}{111}$	$\frac{\text{Cn}}{112}$	$\frac{\text{Nh}}{113}$	$\frac{\text{Fl}}{114}$	$\frac{\text{Mc}}{115}$	$\frac{\text{Lv}}{116}$	$\frac{\text{Ts}}{117}$	$\frac{\text{Og}}{118}$
			<i>l</i> :	$\frac{\text{La}}{57}$	$\frac{\text{Ce}}{58}$	$\frac{\text{Pr}}{59}$	$\frac{\text{Nd}}{60}$	$\frac{\text{Pm}}{61}$	$\frac{\text{Sm}}{62}$	$\frac{\text{Eu}}{63}$	$\frac{\text{Gd}}{64}$	$\frac{\text{Tb}}{65}$	$\frac{\text{Dy}}{66}$	$\frac{\text{Ho}}{67}$	$\frac{\text{Er}}{68}$	$\frac{\text{Tm}}{69}$	$\frac{\text{Yb}}{70}$		
			<i>a</i> :	$\frac{\text{Ac}}{89}$	$\frac{\text{Th}}{90}$	$\frac{\text{Pa}}{91}$	$\frac{\text{U}}{92}$	$\frac{\text{Np}}{93}$	$\frac{\text{Pu}}{94}$	$\frac{\text{Am}}{95}$	$\frac{\text{Cm}}{96}$	$\frac{\text{Bk}}{97}$	$\frac{\text{Cf}}{98}$	$\frac{\text{Es}}{99}$	$\frac{\text{Fm}}{100}$	$\frac{\text{Md}}{101}$	$\frac{\text{No}}{102}$		

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

Here are the elements up to krypton  ${}_{36}\text{Kr}$ , absolutely needed for everything:

DEFINITION 2.9. *The elements up to krypton  ${}_{36}\text{Kr}$  are as follows:*

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

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

FACT 2.10. *Remarkable elements heavier than krypton  ${}_{36}\text{Kr}$  include:*

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

Here the noble gases in (1) normally include oganesson  ${}_{118}\text{Og}$  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  ${}_{43}\text{Tc}$  is a bizarre element, human-made.

In relation with quantum mechanics, we have here:

FACT 2.11. *For the element having atomic number  $Z$ , the electrons will occupy successively 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  $1, \dots, 7$  corresponds to the highest  $n$  occupied, and the group  $1, \dots, 18$  comes from  $l, m, s$ .*

This is of course something very basic, and there is a detailed analysis to be done afterwards, for  $Z = 1, \dots, 118$ . For the elements up to krypton  ${}_{36}\text{Kr}$ , the list of electron configurations can be found for instance in Feynman [30] or Griffiths [40].

## 2d. Oxygen atom

Oxygen atom.

### 2e. Exercises

Exercises:

EXERCISE 2.12.

EXERCISE 2.13.

EXERCISE 2.14.

EXERCISE 2.15.

EXERCISE 2.16.

EXERCISE 2.17.

Bonus exercise.



## CHAPTER 3

### Water molecule

**3a.**

**3b.**

**3c.**

**3d.**

#### **3e. Exercises**

Exercises:

EXERCISE 3.1.

EXERCISE 3.2.

EXERCISE 3.3.

EXERCISE 3.4.

EXERCISE 3.5.

EXERCISE 3.6.

Bonus exercise.



## CHAPTER 4

### Ions, isotopes

4a.

4b.

4c.

4d.

#### 4e. Exercises

Exercises:

EXERCISE 4.1.

EXERCISE 4.2.

EXERCISE 4.3.

EXERCISE 4.4.

EXERCISE 4.5.

EXERCISE 4.6.

Bonus exercise.



Part II

Hot water

*I am sailing, I am sailing  
Home again, cross the sea  
I am sailing stormy waters  
To be near you, to be free*

CHAPTER 5

**Thermodynamics**

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

### Critical point

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

### Gas and beyond

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

### Steam engines

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

Cold water

*Freezing, can't move at all  
Screaming, can't hear my call  
I am dying to live, cry out  
I'm trapped under ice*



## CHAPTER 9

### Liquid state

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

### Ice and snow

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

### Triple point

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

### Towards zero

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**

**Into chemistry**

*Water, water everywhere  
And all the boards did shrink  
Water, water everywhere  
Nor any drop to drink*

CHAPTER 13

**Basic chemistry**

**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

**Solvent properties**

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

**Water suspensions**

**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

### **Life soups**

**16a.**

**16b.**

**16c.**

**16d.**

**16e. Exercises**

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



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