

Chapter 2

Heisenberg's Year 1925

Abstract Starting from the known facts on spectral lines up to 1925, the crucial new ideas of Heisenberg are presented which led him to the introduction of his matrix quantum mechanics.

2.1 Spectral Lines

Nineteenth century research on spectral lines can be considered the starting point for quantum theory. These investigations are based on two measurable variables, namely the frequency and the brightness of the spectral lines. After all, the emitted light consists of very sharp frequencies. In the year 1850, Kirchhoff¹ and Bunsen² had discovered that chemical elements produce such characteristic lines in their spectra.

In the visible region of the *hydrogen spectrum*, four lines can be observed (the wavelengths get closer as they decrease). In 1885, the Swiss mathematician Balmer³ (a teacher at a lyceum) discovered that the wavelength λ of these lines can be calculated with the simple formula

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

where $A = 364.56 \times 10^{-9}$ m and $n = 3, 4, 5$, or 6 . This leads to the following wavelengths (in nanometers):

- 656.279 nm (red)
- 486.133 nm (blue-green)
- 434.047 nm (violet)
- 410.174 nm (violet)

¹Gustav Robert Kirchhoff, 1824–1887, German physicist.

²Robert Wilhelm Eberhard Bunsen, 1811–1899, German chemist.

³Johann Jakob Balmer, 1825–1898.

Table 2.1 Measured or calculated hydrogen spectral lines in the Balmer series

Transition $n \rightarrow m = 2$	$3 \rightarrow 2$	$4 \rightarrow 2$	$5 \rightarrow 2$	$6 \rightarrow 2$	$7 \rightarrow 2$	$8 \rightarrow 2$
Name	H_α	H_β	H_γ	H_δ	H_ϵ	H_ζ
Measured (nm)	656.2793	486.1327	434.0466	410.1738	397.0075	388.8052
Calculated	656.278	486.132	434.045	410.1735	397.0074	388.8057
Colour	Red	Blue-Green	Violet	Violet	Violet	Violet

For the wavelengths λ , we obtain the *Balmer formula*

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

where $R = 4/A$ is the so-called *Rydberg⁴ constant*.⁵ With explicit numbers, it reads

$$\frac{1}{\lambda} = 10973731 \left(\frac{1}{4} - \frac{1}{n^2} \right) [m^{-1}].$$

Table 2.1 is a table of the currently known spectral lines in the Balmer series, measured or calculated with the Balmer formula.

Five years later, in 1890, Rydberg generalized the Balmer equation into the Rydberg formula

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

with $m = 1, 2, \dots$ and $n = m + 1, m + 2, \dots$. For $m = 1$, one obtains the Lyman series. For $m = 2$, we get again Balmer's series, and $m = 3$ yields the Paschen series. For $m = 4$, the Brackett series is obtained, and $m = 5$ leads to the Pfund series. Each series is named after its discoverer; see Table 2.2 and Fig. 2.1.

For the spectra of other elements, different Rydberg constants are obtained. The Swiss physicist Ritz⁶ discovered in 1908 that one can derive new lines from the known spectral lines of an element without having to modify any constants. Here is why: from the above formulas it becomes obvious that the resulting frequencies ν depend on two integers, namely m and n , in other words,

$$\nu(m, n) = Rc \left(\frac{1}{m^2} - \frac{1}{n^2} \right). \quad (2.1)$$

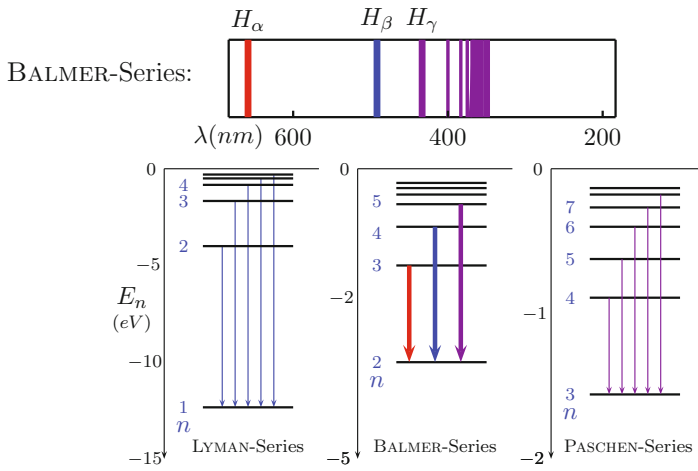
⁴Johannes Robert Rydberg, 1854–1919, Swedish physicist.

⁵Today, R is an accurately known fundamental constant with $R_\infty = 10973731.568539(55) m^{-1}$. The index ∞ indicates that an infinitely large nucleus mass is assumed.

⁶Walter Ritz, 1878–1909, Swiss theoretical physicist.

Table 2.2 Hydrogen spectral lines series

Name	n_1	n_2	Formula	Spectrum range/Colour
LYMAN-Series	1	2, 3, 4, ...	$\tilde{\nu} = R \left(1 - \frac{1}{n_2^2} \right)$	Vacuum-UV (121 nm \rightarrow 91 nm)
BALMER-Series	2	3, 4, 5, ...	$\tilde{\nu} = R \left(\frac{1}{2^2} - \frac{1}{n_2^2} \right)$	red, blue-green, 4 \times violet, then transition to near-UV \rightarrow 365 nm
PASCHEN-Series	3	4, 5, 6, ...	$\tilde{\nu} = R \left(\frac{1}{3^2} - \frac{1}{n_2^2} \right)$	IR-A (1875 nm \rightarrow 820 nm)
BRACKETT-Series	4	5, 6, 7, ...	$\tilde{\nu} = R \left(\frac{1}{4^2} - \frac{1}{n_2^2} \right)$	IR-B (4050 nm \rightarrow 1460 nm)
PFUND-Series	5	6, 7, 8, ...	$\tilde{\nu} = R \left(\frac{1}{5^2} - \frac{1}{n_2^2} \right)$	IR-B (7457 nm \rightarrow 2280 nm)

**Fig. 2.1** The visible part of the hydrogen spectrum of the Balmer series (above). Energy levels and transitions (below)

Adding two different frequencies $\nu(m_1, n_1)$ and $\nu(m_2, n_2)$ of a spectrum, one obtains

$$\nu(m_1, n_1) + \nu(m_2, n_2) = Rc \left(\frac{1}{m_1^2} - \frac{1}{n_1^2} + \frac{1}{m_2^2} - \frac{1}{n_2^2} \right). \quad (2.2)$$

For $n_1 = m_2$ we obtain the new frequency according to the *Ritz combination principle*:

$$\underline{\underline{\nu(m_1, n_2) = \nu(m_1, n_1) + \nu(n_1, n_2)}} = R \cdot c \left(\frac{1}{m_1^2} - \frac{1}{n_2^2} \right). \quad (2.3)$$

And then the time of Niels Bohr came! It can be safely assumed that he was inspired by the Rydberg formula

$$\nu(m, n) = R \cdot c \left(\frac{1}{m^2} - \frac{1}{n^2} \right).$$

We can write this formula without brackets:

$$\nu(m, n) = R \cdot c \frac{1}{m^2} - R \cdot c \frac{1}{n^2}. \quad (2.4)$$

On the other hand, we have

$$E = h \cdot \nu,$$

and therefore

$$\nu = \frac{E}{h}.$$

It seems very plausible to rewrite for (2.4)

$$\nu(m, n) = \frac{E_m}{h} - \frac{E_n}{h}. \quad (2.5)$$

From this follows

$$E_k = \frac{h \cdot R \cdot c}{k^2}.$$

Note that the dimensions in the formula are consistent: the action quantum h has dimension $J s$, $R \cdot c$ has dimension s^{-1} and k is a dimensionless integer, so E_k has indeed the dimension J .

We need to emphasize once again that in quantum theory the mechanical behavior of an atom is characterized by two basic parameters, namely the energy E_n of the stationary state n and the probability per unit time $A(n, m)$ for the spontaneous transition from state n to the state m . In a spectroscopic study, we measure the radiation as emitted by the atom, that is, the line spectrum. Quantum theory then puts the mechanical properties (namely E_n and $A(n, m)$) into relation to the spectral characteristics (namely the frequency and intensity of the emitted light). Hereby, the transition energy $E_n - E_m$ determines the frequency of the light, and the transition probability $A(n, m)$ determines its intensity.

The emission of radiation by an atom is the result of electrons jumping between two discrete electron orbits. The transition probability determines the occurrence of a quantum jump. The radiation emitted during the transition $n \rightarrow m$ then has the frequency $\nu(n, m)$. Therefore, a mechanical energy loss $E_m - E_n$ occurs during

the transition $n \rightarrow m$. Because⁷ the photon energy is $h \nu(n, m) = \hbar \omega(n, m)$, energy conservation requires $E_m = E_n + \hbar \omega(n, m)$; that is,

$$E_m - E_n = \hbar \omega(n, m). \quad (2.6)$$

Note that a single photon only generates a flash of light on a spectral line. The complete spectral line is produced only if many atoms emit many photons. The number of photons with frequency $\nu(n, m)$ that arrives at a given area of the spectrometer per unit time determines the intensity of the line. In other words, the line intensity is a function of the number of jumping electrons, that is, the transition rate $A(n, m)$.

Let us consider a set of atoms, each in the state n . Then the light intensity $P(n, m)$ of the transition $n \rightarrow m$ defined by the amount of energy emitted per unit time Δt and per atom is

$$P(n, m) \stackrel{\text{def}}{=} \frac{1}{N_n} \frac{\Delta E(n, m)}{\Delta t}, \quad (2.7)$$

where N_n is the number of atoms in the state n , and $\Delta E(n, m)$ is the energy consumption of all atoms accomplishing the transition $n \rightarrow m$ in the time interval Δt . Again, the conservation of energy requires

$$\Delta E(n, m) = \Delta N(n, m) \hbar \omega(n, m),$$

where $\Delta N(n, m)$ is the number of atoms jumping from n to m in the time interval Δt . For large N_n , the portion of jumping atoms equals the probability for an atom to jump, namely

$$\Delta N(n, m)/N_n = A(n, m) \Delta t.$$

$A(n, m)$ is therefore the probability per unit time. From (2.7) we get

$$P(n, m) = \frac{\Delta N(n, m) \hbar \omega(n, m)}{N_n \Delta t} = A(n, m) \hbar \omega(n, m). \quad (2.8)$$

This result implies that intense lines are very probable transitions, and weak lines are improbable transitions.

2.2 Introduction of Matrices

Werner Heisenberg started off from the principle that concepts which do not correspond to *physically observable facts* should not be used in a theoretical description. Heisenberg therefore banished the idea of electron orbits with fixed radii and orbital

⁷ $\hbar \stackrel{\text{def}}{=} \frac{h}{2\pi}$.

periods, because these quantities cannot be observed. Instead, he postulated that the theory was to be constructed with the help of abstract quadratic schemes. Rather than describing the motion by a time-dependent coordinate $x(t)$, he suggested determining a scheme of transition amplitudes x_{mn} . Heisenberg's theory is entirely based on measurable quantities, namely the frequencies and strengths of the spectral lines of atoms.

From Rydberg's formula it follows that each frequency $\nu(n, m)$ of the observed spectrum can be written as the difference of two energy terms E_n and E_m :

$$h\nu(n, m) = E_n - E_m. \quad (2.9)$$

This immediately leads to the Ritz combination principle

$$\nu(n, k) + \nu(k, m) = \frac{1}{h} ((E_n - E_k) + (E_k - E_m)) = \frac{1}{h} (E_n - E_m) = \nu(n, m), \quad (2.10)$$

where the ν s are the observable frequencies of the spectrum. From (2.9), we also find that

$$\nu(n, m) = \frac{1}{h} (E_n - E_m) = -\frac{1}{h} (E_m - E_n) = -\nu(m, n), \quad (2.11)$$

and that

$$\nu(n, n) = \frac{1}{h} (E_n - E_n) = 0. \quad (2.12)$$

For an objective observer, the frequencies and intensities of the spectral lines are the only available data of what is happening inside an atom. Because the occurring frequencies depend on *two* terms, it makes perfect sense to arrange the frequencies in a table. The first row contains all frequencies that are generated from E_0 , that is,

$$\nu(0, 0), \nu(0, 1), \nu(0, 2), \dots$$

The second row contains frequencies that can be generated starting from E_1 , namely

$$\nu(1, 0), \nu(1, 1), \nu(1, 2), \dots$$

The columns always contain all frequencies (in rising order) that can be generated upon reaching a certain level. Eventually, the table can be written in the form of a matrix Ω as

$$\Omega = 2\pi \begin{pmatrix} \nu(0, 0) & \nu(0, 1) & \nu(0, 2) & \cdots \\ \nu(1, 0) & \nu(1, 1) & \nu(1, 2) & \cdots \\ \nu(2, 0) & \nu(2, 1) & \nu(2, 2) & \cdots \\ \vdots & \vdots & \vdots & \vdots \end{pmatrix}. \quad (2.13)$$

For a harmonically bound electron, the position $x(n, t)$, where the stationary state is labeled by n , can be written as a Fourier series

$$x(n, t) = \sum_{\alpha=-\infty}^{\infty} a_{\alpha} e^{i\omega(n)t}. \quad (2.14)$$

Heisenberg observed that the α th component of the classical motion corresponds to the quantum mechanical transition from the state n to the state $n - \alpha$. So Heisenberg replaced the classical component

$$a_{\alpha} e^{i\omega(n)t}$$

by

$$a(n, n - \alpha) e^{i\omega(n, n - \alpha)t}.$$

In order to account for the transition from one stationary state n to another $(n - \alpha)$, he replaced (2.14) by

$$x \rightarrow a(n, n - \alpha) e^{i\omega(n, n - \alpha)t},$$

or

$$x_{nm} = a(n, m) e^{i\omega(n, m)t}, \quad (2.15)$$

and summed over transition components as in (2.14). Heisenberg represented the position by a set of transition components, x_{mn} , and he replaced $x_{\alpha}(n)$ by x_{mn} and $\alpha\omega(n)$ by $\omega(n, m)$.

Additionally Heisenberg modified the old Bohr–Sommerfeld quantization rule (1.18)

$$J = \int p \, dq = \int m \dot{x}^2 \, dt = h n,$$

integrated over a full period of the motion. If one expressed this equation in terms of the Fourier series (2.14) for $x(n, t)$ one would obtain

$$h n = 2\pi m \sum_{\alpha=-\infty}^{\infty} |a_{\alpha}(n)|^2 \alpha^2 \omega_n. \quad (2.16)$$

The presence of the integer n in (2.16) seemed for Heisenberg to be an arbitrary condition, and he concluded that this equation must be replaced by a new condition and that the new condition must be about the transition between states. By differentiation (2.16) with respect to n Heisenberg found

$$h = 2\pi m \sum_{\alpha=-\infty}^{\infty} \alpha \frac{d}{dn} (\alpha \omega_n |a_{\alpha}|^2).$$

Heisenberg replaced the derivative by a difference:

$$h = 4\pi m \sum_{\alpha=0}^{\infty} \{|a(n, n + \alpha)|^2 \omega(n, n + \alpha) - |a(n, n - \alpha)|^2 \omega(n, n - \alpha)\}. \quad (2.17)$$

This is Heisenberg's quantum condition; it relates the amplitudes of different lines within an atomic spectrum.

How is the quantity $(x(t))^2$ to be represented in quantum mechanics, which appears, for example, by modeling an anharmonic oscillator? The answer in classical theory is obviously:

$$b_{\beta}(n)e^{i\omega(n)\beta t} = \sum_{\alpha=-\infty}^{\infty} a_{\alpha}a_{\beta-\alpha}e^{i\omega(n)(\alpha+\beta-\alpha)t}, \quad (2.18)$$

so that

$$(x(t))^2 = \sum_{\beta=-\infty}^{\infty} b_{\beta}(n)e^{i\omega(n)\beta t}. \quad (2.19)$$

To Heisenberg it seemed that in quantum mechanics the simplest and most natural assumption would be to replace (2.18) by:

$$b(n, n - \beta)e^{i\omega(n, n - \beta)t} = \sum_{\alpha=-\infty}^{\infty} a(n, n - \alpha)a(n - \alpha, n - \beta)e^{i\omega(n, n - \beta)t}. \quad (2.20)$$

Max Born studied Heisenberg's manuscript and discovered that Heisenberg's symbolic multiplication was nothing but matrix multiplication.

By collecting all possible transitions in a matrix (similar to the frequencies ν in Ω), we obtain a matrix of the form⁸

$$X = (a(n, m) e^{i2\pi\nu(n, m)t}).$$

Due to $\nu(n, m) = -\nu(m, n)$ and $a(m, n) = a^*(n, m)$, we get $x(n, m) = x^*(m, n)$; that is, the matrix X is an Hermitian⁹ matrix. When transposing an Hermitian matrix X , each component becomes its complex conjugate value. If we introduce a matrix multiplication as XX^{\dagger} , the elements of the product matrix are

$$a(n, m)a(m, n) = a(n, m)a^*(n, m) = |a(n, m)|^2. \quad (2.21)$$

⁸The matrix components $x(n, m) = a(n, m) e^{2\pi i \nu(n, m)t}$ are not to be confused with the classical coefficients $a_{\alpha} e^{i\alpha\omega t}$ of a Fourier series (see Appendix C), where we sum up from $\alpha = -\infty$ to $\alpha = +\infty$ in order to obtain the periodic function $x(t)$.

⁹Charles Hermite, 1822–1901, French mathematician.

Born and Jordan postulated in [5] that (2.21) is the *likelihood* for the transitions $n \rightleftharpoons m$ from the atomic state n into the state m , and vice versa.

The description is based on the idea of state transitions, therefore the diagonal elements of the matrix X must vanish; that is,

$$\nu(n, n) = 0$$

for all n . After all, no transition takes place from n to n . Altogether we get the form

$$X = \begin{pmatrix} 0 & a(0, 1) e^{2\pi i \nu(0,1)t} & a(0, 2) e^{2\pi i \nu(0,2)t} & \dots \\ a(1, 0) e^{2\pi i \nu(1,0)t} & 0 & a(1, 2) e^{2\pi i \nu(1,2)t} & \dots \\ a(2, 0) e^{2\pi i \nu(2,0)t} & a(2, 1) e^{2\pi i \nu(2,1)t} & 0 & \dots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}. \quad (2.22)$$

Note that it is not summed over any coefficients as in a Fourier series. Rather, all the transition components that are collected in the matrix X reproduce all the possibilities for transitions of the system from the perspective of quantum theory. The aim of quantum theory is to create a mathematical model such that:

1. It allows the calculation of measurable frequency spectra of atoms (namely frequency and intensity of the spectral lines).
2. The classical theory is contained in the limit $h \rightarrow 0$, where h is Planck's quantum of action.

For the time derivatives of the elements $x(n, m)$ of the matrix X one gets

$$\dot{x}(n, m) = 2\pi i \nu(n, m) a(n, m) e^{2\pi i \nu(n, m)t}. \quad (2.23)$$

We introduce the diagonal matrix E with the matrix elements

$$E(n, m) \stackrel{\text{def}}{=} \delta_{n,m} E_n, \quad (2.24)$$

that is,

$$E = \begin{pmatrix} E_0 & 0 & 0 & \dots \\ 0 & E_1 & 0 & \dots \\ 0 & 0 & E_2 & \ddots \\ 0 & 0 & 0 & \ddots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}.$$

With (2.9), we then get for (2.23)

$$\dot{x}(n, m) = 2\pi i \nu(n, m) x(n, m) = \frac{2\pi i}{h} (E_n - E_m) x(n, m). \quad (2.25)$$

Because E is diagonal, we have for matrix elements

$$E_n x(n, m) = (EX)(n, m)$$

and

$$E_m x(n, m) = (XE)(n, m).$$

Therefore we get

$$\dot{x}(n, m) = \frac{2\pi i}{h} ((EX)(n, m) - (XE)(n, m)),$$

and because this applies to every element of the matrix

$$\boxed{\dot{X} = \frac{2\pi i}{h} (EX - XE)}. \quad (2.26)$$

This is the simplest form of the so-called *quantum mechanical equation of motion*, or *Heisenberg's equation of motion*. Here for the first time a *commutator* enters in the form

$$[EX] \stackrel{\text{def}}{=} (EX - XE).$$

In the theory of quantum mechanics such commutators play an important role, as we show later. For a single matrix element, (2.26) means (2.25). Dividing by $2\pi i x(n, m)$ again yields the frequency condition $h\nu(n, m) = E_n - E_m$.

2.3 Problems

- 2.1 Hermitian Matrices:** Under which conditions is the product of two Hermitian matrices again an Hermitian matrix?
- 2.2 Eigenvectors:** Show that eigenvectors belonging to different eigenvalues are linearly independent.
- 2.3 Eigenvalues of an Hermitian Matrix:** Show that the eigenvalues of an Hermitian matrix are real.
- 2.4 Eigenvalues of a Unitary Matrix:** What general property do the eigenvalues of a unitary matrix have?
- 2.5 Eigenvectors:** In an N -dimensional space, N linear independent vectors \mathbf{a}_j are given. Construct a set of N normalized orthogonal vectors \mathbf{e}_j .

2.6 Normalized Eigenvectors: The two linear independent vectors $\begin{pmatrix} 1 \\ 1 \end{pmatrix}$ and $\begin{pmatrix} -1 \\ 1 \end{pmatrix}$ are given. Which transformation matrix \mathbf{T} transforms these two vectors into $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$? Which vectors would be obtained by using the method of Problem 2.5?

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