Appendix A

A.1 Physical Constants

In the following table the values of the fundamental physical constants are collected (Tables A.1).

Table A.1 Derived constants contain experimental uncertainties in brackets in units of the last digit

Constant	Symbol	Value
Avogadro constant	N_A	$6.02214129(27)10^{23}\ \mathrm{mol}^{-1}$
Speed of light in vacuum	c	$299{,}792{,}458\ \mathrm{m\,s}^{-1}$
Electric constant	ε_0	$8.854187817\ldots \times 10^{-12}\ \mathrm{A}^2\,\mathrm{s}^4\,\mathrm{kg}^{-1}\,\mathrm{m}^{-2}$
Elementary charge	e	$1.602176565(35) \times 10^{-19}\ \mathrm{A\,s}$
Planck constant	h	$6.62606957(29) \times 10^{-34}\ \mathrm{J\,s}$
Atomic mass unit	m_u	$1.660538921(73) \times 10^{-27}\ \mathrm{kg}$
Electron mass	m_e	$9.10938291(40) \times 10^{-31}\ \mathrm{kg}$
Boltzmann constant	k_B	$1.3806488(13) \times 10^{-23}\ \mathrm{J\,K}^{-1}$
Molar gas constant	R	$8.314462(75)\ \mathrm{J\,K}^{-1}\,\mathrm{mol}^{-1}$
Faraday constant	F	$96485.3365(21)\ \mathrm{A\,s\,mol}^{-1}$
Bohr radius	a_0	$0.52917721092(17) \times 10^{-10}\ \mathrm{m}$

Source: P.J. Mohr, B.N. Taylor, D.B. Newell, *CODATA recommended values of the fundamental physical constants: 2010*, Rev. Mod. Phys. **84** (2012), 1527

J. Vogt, *Exam Survival Guide: Physical Chemistry*,
DOI 10.1007/978-3-319-49810-2

Table A.2 Some common physical units and their relation to the respective SI unit

Name	Symbol	Relation to SI
Length, l		
Meter (SI unit)	m	
Centimeter	cm	10^{-2} m
Nanometer	nm	10^{-9} m
Bohr	a_0	5.29177×10^{-11} m
Ångström	Å	10^{-10} m
Energy, E		
Joule (SI unit)	J	
Erg (cgs unit)	erg	10^{-7} J
Hartree (au)	E_h	$\frac{\hbar^2}{m_e a_0^2} \approx 4.35975 \times 10^{-18}$ J
Rydberg	Ry	$\frac{E_h}{2} \approx 2.17987 \times 10^{-18}$ J
Electronvolt	eV	$e\,V \approx 1.60218 \times 10^{-19}$ J
Calorie, thermochemical	cal	4.184 J
Pressure, p		
Pascal (SI unit)	Pa	
Bar	bar	10^5 Pa
Torr	Torr	133.322 Pa

Source: IUPAC, I. Mills et al., *Quantities, units and symbols in physical chemistry*, Blackwell Science, 1993

A.2 Physical Units and Their Conversion

The correct use of physical quantities frequently involves a conversion between different units (Table A.2). The recommended system is the International system of units (SI) defining the meter, the kilogram, the second, and ampere as the physical units of length, mass, time, and electric current respectively. For reasons of practicality, atomic units (au) are common in quantum chemistry (see Sect. 9.1.4).

A.3 Compilation of Mathematical Formulas

A.3.1 Binomial Formulas

First binomial formula:

$$(a+b)^2 = a^2 + 2ab + b^2 \tag{A.1}$$

Second binomial formula:

$$(a-b)^2 = a^2 - 2ab + b^2 \tag{A.2}$$

Third binomial formula:

$$(a+b)(a-b) = a^2 - b^2 \tag{A.3}$$

A.3.2 Quadratic Equation

The roots of the quadratic equation $ax^2 + bx + c = 0$ are

$$x_{1,2} = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}; \qquad b^2 - 4ac > 0 \tag{A.4}$$

where $\Delta = b^2 - 4ac$ is called discriminant. If $\Delta = 0$, then the quadratic equation has only one root; if $\Delta > 0$, it has two real solutions, if $\Delta < 0$ the solutions are complex.

A.3.3 Logarithms

$$\ln(a) + \ln(b) = \ln(ab) \tag{A.5}$$

$$\ln(a) - \ln(b) = \ln\left(\frac{a}{b}\right) \tag{A.6}$$

$$\ln\left(a^x\right) = x \ln(a) \tag{A.7}$$

A.3.4 Complex Numbers

A complex number

$$z = u + iv \tag{A.8}$$

can be represented by a vector in a two-dimensional complex plane, spanned by the number line of the real part (horizontal axis), and the number line of the imaginary part (vertical axis), see Fig. A.1. The real part of z is $\mathrm{Re}(z) = u$, the imaginary part is $\mathrm{Im}(z) = v$. The **imaginary unit** is defined by

$$i^2 = -1. \tag{A.9}$$

The same number can be represented by:

$$z = |z| \mathrm{e}^{i\phi} \tag{A.10}$$

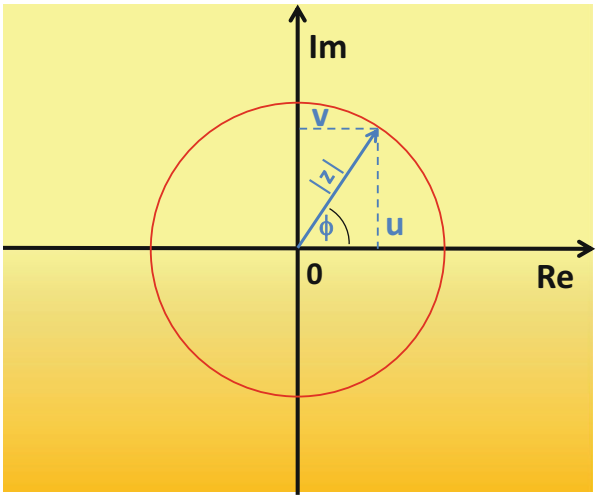


Fig. A.1 A complex number $z = u + iv$ in the two-dimensional complex plane

where $|z|$ is the absolute value of z and $e^{i\phi}$ is a phase factor depending on the angle ϕ defined in Fig. A.1. Particularly useful is **Euler's formula**

$$e^{i\phi} = \cos\phi + i\sin\phi. \tag{A.11}$$

Moreover, an important operation is **complex conjugation**:

$$z^* = (u + iv)^* = (u - iv) = |z|e^{-i\phi}. \tag{A.12}$$

As a consequence, the absolute square of complex number z is:

$$|z|^2 = z^* z. \tag{A.13}$$

A.3.5 Derivatives

A.3.5.1 Basic Differentiation Rules

The sum rule

$$\frac{d}{dx}\left(af(x) + bg(x)\right) = a\frac{df(x)}{dx} + b\frac{dg(x)}{dx} \tag{A.14}$$

The product rule

$$\frac{d}{dx}\left(f(x)g(x)\right) = \frac{df(x)}{dx}g(x) + f(x)\frac{dg(x)}{dx} \tag{A.15}$$

The quotient rule

$$\frac{d}{dx}\frac{f(x)}{g(x)} = \frac{\frac{df(x)}{dx}g(x) - f(x)\frac{d\,g(x)}{dx}}{g^2(x)} \tag{A.16}$$

The chain rule

$$\frac{d}{dx}f\left(g\left(x\right)\right) = \frac{df(g)}{dg(x)}\frac{d\,g(x)}{dx} \tag{A.17}$$

A.3.5.2 Basic Derivatives

$$\frac{d}{dx}C = 0 \tag{A.18}$$

$$\frac{d}{dx}x = 1 \tag{A.19}$$

$$\frac{d}{dx}x^n = nx^{n-1} \tag{A.20}$$

$$\frac{d}{dx}e^x = e^x \tag{A.21}$$

$$\frac{d}{dx}a^x = a^x \ln\, a \tag{A.22}$$

$$\frac{d}{dx}\ln\, x = \frac{1}{x} \tag{A.23}$$

$$\frac{d}{dx}\log_a x = \frac{1}{x\ln\, a} \tag{A.24}$$

$$\frac{d}{dx}\sin\, x = \cos\, x \tag{A.25}$$

$$\frac{d}{dx}\cos\, x = -\sin\, x \tag{A.26}$$

A.3.5.3 Partial Derivatives and Total Derivatives

Consider a function $f(t, x, y)$ depending on several variables x, y, and t. As in the case of a function with one variable, the *partial* derivative with regard to x is defined by the difference quotient in the limit $h \to 0$:

$$\frac{\partial f(t,x,y)}{\partial x} = \lim_{h\to 0} \frac{f(t,x+h,y) - f(t,x,y)}{h}. \tag{A.27}$$

The rules for partial differentiation follow the above rules for the differentiation of a function with only one variable; the other variables are held constant. Example: consider $f(t, x, y) = 3x^2y - t$. The partial derivative with regard to x is:

$$\frac{\partial f}{\partial x} = 6xy. \tag{A.28}$$

Consider a case in which the variables $x(t)$ and $y(t)$ themselves depend on t. In this case, the *total* derivative of a function $f(t, x, y)$ with regard to time is:

$$\frac{df(x,y,t)}{dt} = \frac{\partial f}{\partial t} + \frac{\partial f}{\partial x}\frac{dx}{dt} + \frac{\partial f}{\partial y}\frac{dy}{dt}. \tag{A.29}$$

A.3.6 Basic Integration Rules

Multiplication by constant

$$\int af(x)\,dx = a\int f(x)\,dx \tag{A.30}$$

Sum rule

$$\int (f(x) + g(x))\,dx = \int f(x)\,dx + \int g(x)\,dx \tag{A.31}$$

Integration by parts

$$\int f(x)\frac{d\,g(x)}{dx}\,dx = f(x)g(x) - \int g(x)\frac{df(x)}{dx}\,dx \tag{A.32}$$

A.3.6.1 Multiple Integrals and Change of Variables

Consider a multiple integral of the form $\iint f(x, y)\,dx\,dy$. Frequently, a transformation of the variables x and y to a set of new variables u v is considered via

$$x = x(u, v) \qquad y = y(u, v).$$

Then, the double integral can be written

$$\iint f(x,y)\,dx\,dy = \iint f\left(x(u,v), y(u,v)\right) \frac{\partial\,(u,v)}{\partial(x,y)}\,du\,dv \tag{A.33}$$

with the **Jacobian**

$$\frac{\partial\,(u,v)}{\partial(x,y)} = \begin{vmatrix} \frac{\partial u}{\partial x} & \frac{\partial v}{\partial x} \\ \frac{\partial u}{\partial y} & \frac{\partial v}{\partial y} \end{vmatrix} \tag{A.34}$$

The method can be generalized to functions with more than two variables.

A.3.7 Integral Table

Improper integrals (C is a constant):

$$\int x^n\,dx = \frac{1}{n+1}x^{n+1} + C; \qquad n \neq -1 \tag{A.35}$$

$$\int \frac{dx}{x} = \ln x + C \tag{A.36}$$

$$\int \frac{dx}{ax+b} = \frac{1}{a}\ln(ax+b) + C \tag{A.37}$$

$$\int \frac{dx}{(ax+b)(fx+g)} = \frac{1}{bf-ag}\ln\frac{fx+g}{ax+b} \tag{A.38}$$

$$\int \sin(ax)\,dx = -\frac{1}{a}\cos(ax) \tag{A.39}$$

$$\int \cos(ax)\,dx = \frac{1}{a}\sin(ax) \tag{A.40}$$

$$\int \sin(ax)\cos(ax)\,dx = \frac{1}{2a}\sin^2(ax) \tag{A.41}$$

$$\int e^{ax}\,dx = \frac{e^{ax}}{a} \tag{A.42}$$

$$\int xe^{ax}\,dx = \frac{e^{ax}}{a^2}(ax-1) \tag{A.43}$$

$$\int x^2e^{ax}\,dx = e^{ax}\left(\frac{x^2}{a} - \frac{2x}{a^2} + \frac{2}{a^3}\right) \tag{A.44}$$

Some definite integrals:

$$\int_0^\infty x^n e^{-ax} = \frac{n!}{a^{n+1}} \tag{A.45}$$

$$\int_0^\infty e^{-a^2x^2}\,dx = \frac{\sqrt{\pi}}{2a}, \qquad a > 0 \tag{A.46}$$

$$\int_0^\infty x^2 e^{-a^2x^2}\,dx = \frac{\sqrt{\pi}}{4a^3}, \qquad a > 0 \tag{A.47}$$

$$\int_0^\infty x^n e^{-ax^2}\,dx = \frac{k!}{2a^{k+1}}, \quad a > 0, \text{ for every odd positive integer } n = 2k+1 \tag{A.48}$$

$$\int_0^\infty x^n e^{-ax^2}\,dx = \frac{1\cdot 3\cdot \ldots \cdot (2k-1)}{2^{k+1}}\sqrt{\frac{\pi}{a^{2k+1}}},$$

$$a > 0, \text{ for every even positive integer } n = 2k \tag{A.49}$$

$$\int_0^u e^{-x^2}\,dx = \frac{\sqrt{\pi}}{2}\,\mathrm{erf}(u), \qquad \text{see Eq. (A.60)} \tag{A.50}$$

$$\int_{-\infty}^{+\infty} \frac{\sin^2(ax)}{x^2}\,dx = \pi|a| \tag{A.51}$$

Dirac's delta function:

$$\int_{-\infty}^{+\infty} \delta(x)\,dx = 1 \quad \text{where } \delta(x) = \begin{cases} +\infty, & x = 0 \\ 0, & x \neq 0 \end{cases} \tag{A.52}$$

For an arbitrary function $f(x)$, the following equation holds:

$$\int_{-\infty}^{+\infty} f(x)\delta(x)\,dx = f(0) \tag{A.53}$$

A.3.8 Power Series Expansions

Taylor series for a function $f(x)$ around its value at x_0:

$$f(x) = \sum_n^\infty \frac{f^{(n)}(x_0)}{n!}(x - x_0)^n \tag{A.54}$$

Further power series expansions:

$$\mathrm{e}^x = \sum_{n=0}^\infty \frac{x^n}{n!} = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots \tag{A.55}$$

$$\ln(1+x) = \sum_{n=1}^{\infty} (-1)^{n+1} \frac{x^n}{n} = x - \frac{x^2}{2} + \frac{x^3}{3} + \cdots \tag{A.56}$$

$$\frac{1}{1-x} = \sum_{n=0}^{\infty} x^n = 1 + x + x^2 + x^3 + \cdots \tag{A.57}$$

$$\frac{x}{\mathrm{e}^x - 1} = 1 - \frac{x}{2} + B_1 \frac{x^2}{2!} - B_2 \frac{x^4}{4!} + \cdots \tag{A.58}$$

where B_n are the Bernoulli numbers; $B_1 = \frac{1}{6}$, $B_2 = \frac{1}{30}$.

$$(1 \pm x)^{\frac{1}{2}} = 1 \pm \frac{1}{2}x - \frac{1 \cdot 1}{2 \cdot 4}x^2 \pm \frac{1 \cdot 1 \cdot 3}{2 \cdot 4 \cdot 6}x^3 - \frac{1 \cdot 1 \cdot 3 \cdot 5}{2 \cdot 4 \cdot 6 \cdot 8}x^4 \ldots \tag{A.59}$$

$$\mathrm{erf}(x) = \frac{2}{\sqrt{\pi}} \sum_{n=0}^{\infty} \frac{(-1)^n x^{2n+1}}{n!(2n+1)} = \frac{2}{\sqrt{\pi}} \left(x - \frac{x^3}{3} + \frac{x^5}{10} - \frac{x^7}{42} + \cdots \right) \tag{A.60}$$

A.3.9 Factorials and the Stirling Formula

The factorial $n!$ is defined as the product

$$n! = n(n-1)(n-2)\ldots(2)(1) \tag{A.61}$$

Stirling's approximation for $n!$ is:

$$\ln\, n! = n \ln\, n - n. \tag{A.62}$$

A more accurate Stirling formula is:

$$\ln\, n! = \left(n + \frac{1}{2} \right) \ln\, n - n + \ln\, \sqrt{2\pi} \tag{A.63}$$

A.3.10 Normal Distribution

The normal distribution is a continuous distribution used in probability theory and statistics:

$$F(x) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left[-\frac{1}{2} \left(\frac{x-\mu}{\sigma} \right)^2 \right] \tag{A.64}$$

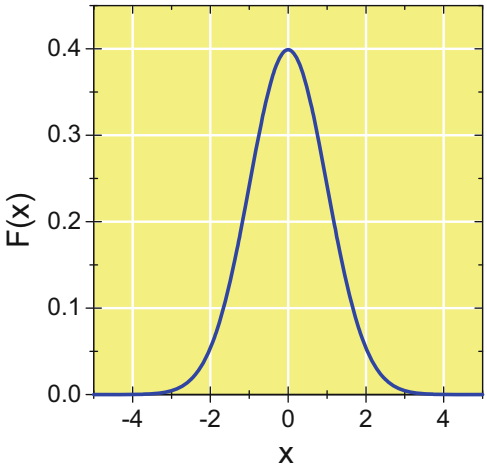


Fig. A.2 Plot of a normal distribution around an average value $\mu = 0$ and a standard deviation $\sigma = 1$

μ is the average of the random variable x, σ^2 its variance, and σ its standard deviation (Fig. A.2). The half width or *full width at half maximum FWHM* is

$$\text{FWHM} = 2\sigma\sqrt{2\ln 2}. \tag{A.65}$$

A.3.11 Spherical Coordinates

For problems with spherical symmetry, the use of spherical coordinates $r = \sqrt{x^2+y^2+z^2}$ (radial coordinate, interval $[0,\infty]$), $\theta = \arccos\left(\frac{z}{\sqrt{x^2+y^2+z^2}}\right)$ (inclination, interval $[0,\pi]$), and $\phi = \arctan\left(\frac{y}{x}\right)$ (azimuth, interval $[0,2\pi]$) are often used instead of Cartesian coordinates x, y, and z:

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} r\,\sin\theta\,\cos\phi \\ r\,\sin\theta\,\sin\phi \\ r\cos\theta \end{pmatrix} \tag{A.66}$$

The volume element in spherical coordinates is:

$$dV = r^2\sin\theta\,dr\,d\theta\,d\phi. \tag{A.67}$$

In spherical coordinates, the Laplace operator has the following form:

$$\Delta = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin\theta}\frac{\partial^2}{\partial\phi^2} \tag{A.68}$$

A.3.12 Cylindrical Coordinates

For problems with cylindrical symmetry, the use of cylindrical coordinates $r = \sqrt{x^2 + y^2}$ (radial distance, interval $[0, \infty]$), z (height, interval $[-\infty, \infty]$), and ϕ (azimuth, interval $[0, 2\pi]$) is appropriate:

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} r\cos\phi \\ r\sin\phi \\ z \end{pmatrix}. \tag{A.69}$$

The volume element is:

$$dV = r\,dr\,d\phi\,dz. \tag{A.70}$$

In cylindrical coordinates, the Laplace operator has the following form:

$$\Delta = \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2}{\partial\phi^2} + \frac{\partial^2}{\partial z^2} \tag{A.71}$$

A.3.13 Harmonic Oscillator Wave Functions

Explicit expressions for the harmonic oscillator wave functions are ($\alpha = \frac{m\omega}{\hbar}$, $y = \sqrt{\alpha}x$)

$$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} \mathrm{e}^{-\frac{y^2}{2}} \tag{A.72}$$

$$\psi_1(x) = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} \sqrt{2}y\,\mathrm{e}^{-\frac{y^2}{2}} \tag{A.73}$$

$$\psi_2(x) = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} \frac{1}{\sqrt{2}}\left(2y^2 - 1\right) \mathrm{e}^{-\frac{y^2}{2}} \tag{A.74}$$

$$\psi_3(x) = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} \frac{1}{\sqrt{3}}\left(2y^3 - 3y\right) \mathrm{e}^{-\frac{y^2}{2}} \tag{A.75}$$

The formula for general n is:

$$\psi_n(x) = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} \frac{1}{\sqrt{2^n n!}} H_n(y)\,\mathrm{e}^{-\frac{y^2}{2}} \tag{A.76}$$

where $H_n(y)$ is a Hermite polynomial. To obtain wave functions with higher n, the recurrence relation

$$H_{n+1}(y) = 2yH_n(y) - 2nH_{n-1}(y) \tag{A.77}$$

can be used starting from $H_0(y) = 1$ and $H_1(y) = 2y$.

A.3.14 Spherical Harmonics

Explicit expressions for spherical harmonics $Y_{lm}(\theta, \phi)$ for $l = 0, 1, 2, \ldots$ and $m = -l, -l+1, \ldots, -1, 0, +1, \ldots, l-1, l$:

$$Y_{00} = \frac{1}{\sqrt{4\pi}} \tag{A.78}$$

$$Y_{10} = \sqrt{\frac{3}{4\pi}} \cos\theta \tag{A.79}$$

$$Y_{1\pm1} = \mp\sqrt{\frac{3}{8\pi}} \sin\theta \, e^{\pm i\phi} \tag{A.80}$$

$$Y_{20} = \sqrt{\frac{5}{16\pi}} \left(3\cos^2\theta - 1\right) \tag{A.81}$$

$$Y_{2\pm1} = \mp\sqrt{\frac{15}{8\pi}} \sin\theta \, \cos\theta \, e^{\pm i\phi} \tag{A.82}$$

$$Y_{2\pm2} = \sqrt{\frac{15}{32\pi}} \sin^2\theta \, e^{\pm 2i\phi} \tag{A.83}$$

For general l, m:

$$Y_{lm}(\theta, \phi) = \sqrt{\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!}} P_{lm}(\cos\theta) \mathrm{e}^{im\phi} \tag{A.84}$$

with the associated Legendre polynomial

$$P_{lm}(x) = \frac{(-1)^m}{2^l l!} (1-x^2)^{\frac{m}{2}} \frac{d^{l+m}}{dx^{l+m}} (x^2-1)^l \tag{A.85}$$

A.3.15 Radial Wave Functions of the Hydrogen Problem

Explicit radial wave functions $R_{nl}(r)$ for the $n = 1, 2, 3$, $l = 0, \ldots, n-1$ (Bohr radius $a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}$):

$$R_{10}(r) = 2a_0^{-\frac{3}{2}} \mathrm{e}^{-\frac{r}{a_0}} \tag{A.86}$$

$$R_{20}(r) = \frac{1}{\sqrt{2}} a_0^{-\frac{3}{2}} \left(1 - \frac{r}{2a_0}\right) \mathrm{e}^{-\frac{r}{2a_0}} \tag{A.87}$$

$$R_{21}(r) = \frac{1}{\sqrt{24}} a_0^{-\frac{3}{2}} \frac{r}{a_0} \mathrm{e}^{-\frac{r}{2a_0}} \tag{A.88}$$

$$R_{30}(r) = \frac{2}{\sqrt{27}} a_0^{-\frac{3}{2}} \left(1 - \frac{2r}{3a_0} + \frac{2r^2}{27a_0^2}\right) \mathrm{e}^{-\frac{r}{3a_0}} \tag{A.89}$$

$$R_{31}(r) = \frac{8}{27\sqrt{6}} a_0^{-\frac{3}{2}} \left(1 - \frac{r}{6a_0}\right) \frac{r}{a_0} \mathrm{e}^{-\frac{r}{3a_0}} \tag{A.90}$$

$$R_{32}(r) = \frac{4}{81\sqrt{30}} a_0^{-\frac{3}{2}} \frac{r^2}{a_0^2} \mathrm{e}^{-\frac{r}{3a_0}} \tag{A.91}$$

For general n, l, the radial wave function is:

$$R_{nl}(r) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n\left[(n+l)!\right]^3}} \mathrm{e}^{-\frac{r}{na_0}} \left(\frac{2r}{na_0}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right) \tag{A.92}$$

where $L_j^k(\rho)$ is an associated Laguerre polynomial. The functions are normalized according to $\int_0^\infty R_{nl}(r) R_{nl}(r) r^2 \, dr = 1$.

A.3.16 Matrices

A (n,m) matrix $\mathbf{A}$ is an arrangement of numbers in n rows and m columns:

$$\mathbf{A} = \begin{pmatrix} a_{11} & a_{12} & \cdots & a_{1m} \\ a_{21} & a_{22} & \cdots & a_{2m} \\ \vdots & \vdots & \ddots & \vdots \\ a_{n1} & a_{n2} & \cdots & a_{nm} \end{pmatrix} \tag{A.93}$$

The **trace** of a (n,n) square matrix $\mathbf{A}$ is the sum over its diagonal elements:

$$\mathrm{Tr}\,\mathbf{A} = \sum_{i}^{n} a_{ii} \tag{A.94}$$

The sum of two (n,m) matrices $\mathbf{A}$ and $\mathbf{B}$ is a (n,m) matrix $\mathbf{C}$. Its matrix elements are obtained by simple summation:

$$c_{ij} = a_{ij} + b_{ij}; \qquad i = 1,\ldots,n;\;\; j = 1,\ldots,m \tag{A.95}$$

Multiplication of a matrix $\mathbf{A}$ with a scalar number c is calculated by multiplying each matrix element with this number. The matrix elements of the result $\mathbf{B}$ are thus:

$$b_{ij} = c\,a_{ij}. \tag{A.96}$$

The multiplication of a (n,p) matrix $\mathbf{A}$ with a (p,m) matrix $\mathbf{B}$ yields a (n,m) matrix $\mathbf{C}$. Its matrix elements are obtained by summation over products of matrix elements:

$$c_{ij} = \sum_{k}^{p} a_{ik}\,b_{kj} \tag{A.97}$$

The inverse $\mathbf{A}^{-1}$ of a (n,n) square matrix $\mathbf{A}$ is defined by

$$\mathbf{A}^{-1}\,\mathbf{A} = \mathbf{I}_n \tag{A.98}$$

where is $\mathbf{I}_n$ is a (n,n) unit matrix.

A.3.17 Cramer's Rule for the Solution of a System of Linear Equations

Although there are numerically more efficient methods of solving a system of linear equations available, Cramer's rule is often used in *paper and pencil* problems. If $\mathbf{A}$ is a square $n \times n$ coefficient matrix and $\mathbf{y}$ is a column vector with n elements, then the system of equations $\mathbf{Ax} = \mathbf{y}$ with the solution vector $\mathbf{x}$ containing the n solutions can be solved by forming the determinant of the coefficient matrix,

$$\det\mathbf{A} = \begin{vmatrix} a_{11} & a_{12} & \cdots & a_{1n} \\ a_{21} & a_{22} & \cdots & a_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ a_{n1} & a_{n2} & \cdots & a_{nn} \end{vmatrix}, \tag{A.99}$$

in addition to the n determinants

$$\det \mathbf{A}_i = \begin{vmatrix} a_{11} & a_{12} & \cdots & y_1 & \cdots & a_{1n} \\ a_{21} & a_{22} & \cdots & y_2 & \cdots & a_{2n} \\ \vdots & \vdots & \cdots & \vdots & \cdots & \vdots \\ a_{j1} & a_{j2} & \cdots & y_j & \cdots & a_{jn} \\ \vdots & \vdots & \cdots & \vdots & \cdots & \vdots \\ a_{n1} & a_{n2} & \cdots & y_n & \cdots & a_{nn} \end{vmatrix}; \qquad i = 1, \ldots, n \tag{A.100}$$

in which the i-th column is replaced by the elements of the vector $\mathbf{y}$. Then, the solution vector $\mathbf{x}$ is given by the n elements

$$x_i = \frac{\det \mathbf{A}_i}{\det \mathbf{A}}; \qquad i = 1, \ldots, n. \tag{A.101}$$

A.3.18 Analytic Solution for a First-Order Inhomogeneous Differential Equation

A first-order inhomogeneous differential equation

$$\frac{d\,y(x)}{dx} + f(x)\,y = g(x) \tag{A.102}$$

has the analytic solution

$$y(x) = \frac{1}{M(x)} \left(\int g(x) M(x)\, dx + C \right). \tag{A.103}$$

C is an integration constant defined by the boundary conditions, and M is the *integrating factor*:

$$M(x) = e^{\int f(x)\, dx}. \tag{A.104}$$

A.3.19 Newton's Method of Solving a Nonlinear System of Equations

Consider a general system of equations

$$\mathbf{f}(\mathbf{x}) = \begin{bmatrix} f_1(x_1, \ldots, x_n) \\ f_2(x_1, \ldots, x_n) \\ \vdots \\ f_n(x_1, \ldots, x_n) \end{bmatrix} = 0 \tag{A.105}$$

for which the solution vector $\mathbf{x} = \boldsymbol{\xi} = (\xi_1 \ldots \xi_n)^T$ is to be determined. If the solution exists and if $\mathbf{x}^0$ is a first guess that is reasonably close to the solution $\boldsymbol{\xi}$, an iterative method can be set up such that the updated approximations $\mathbf{x}^{i+1}$ converge toward $\boldsymbol{\xi}$. Starting from the first guess ($i = 0$), the next improved vector is:

$$\mathbf{x}^{i+1} = \mathbf{x}^i - \mathbf{J}^{-1}\mathbf{f}(\mathbf{x}^\mathbf{i}) \tag{A.106}$$

where

$$\mathbf{J} = \begin{pmatrix} \frac{\partial f_1}{\partial x_1} & \cdots & \frac{\partial f_1}{\partial x_n} \\ \vdots & & \vdots \\ \frac{\partial f_n}{\partial x_1} & \cdots & \frac{\partial f_n}{\partial x_n} \end{pmatrix} \tag{A.107}$$

is the derivative matrix (**Jacobian** matrix) whose determinant must be nonzero. For simple problems (e.g., $n = 2$) the formation of the inverse $\mathbf{J}^{-1}$ is straightforward. For larger systems, however, the numerically expensive formation of the inverse can be avoided. If $\mathbf{v}^i = \mathbf{x}^{\mathbf{i+1}} - \mathbf{x}^i$ is the difference vector between successive iterations, Eq. (A.107) is equivalent to the linear system of equations

$$\mathbf{J}\mathbf{v}^i = \mathbf{f}(\mathbf{x}^\mathbf{i}). \tag{A.108}$$

A.3.20 Bernoulli Differential Equation

A differential equation of the form

$$\frac{dy}{dx} = f(x)\,y + g(x)\,y^n \qquad n \neq 0, 1 \tag{A.109}$$

is called a Bernoulli equation. A Bernoulli equation can be transformed into a linear differential equation, if we introduce:

$$\tilde{y} = y^{1-n}. \tag{A.110}$$

Then, we obtain:

$$\frac{d\tilde{y}}{dx} = (1-n)f(x)\tilde{y} + (1-n)g(x), \tag{A.111}$$

which can be treated as described in Sect. A.3.18.

A.3.21 Numerical Integration Schemes for the Initial Value Problem $\dot{y}(t) = f(t, y)$

Consider the initial value problem

$$\frac{d\,y(t)}{dt} = f\,(t, y\,(t)) \tag{A.112}$$

with the initial condition $y(t_0 = 0) = y_0$. Numerical approximations on a grid of equidistant points t_n ($n = 1, 2, 3, \ldots$) with the step interval $h = t_{n+1} - t_n$ are available with different error orders[1]:

- The Euler method (error $O(h^2)$):

$$y_{n+1} = y_n + hf(t_n, y_n) \tag{A.113}$$

- Second-order Runge-Kutta method (error $O(h^3)$)

$$k_1 = hf(t_n, y_n) \tag{A.114}$$

$$k_2 = hf(t_n + \frac{h}{2}, y_n + \frac{k_1}{2}) \tag{A.115}$$

$$y_{n+1} = y_n + k_2 \tag{A.116}$$

- Fourth-order Runge-Kutta method (error $O(h^5)$)

$$k_1 = hf(t_n, y_n) \tag{A.117}$$

$$k_2 = hf\left(t_n + \frac{h}{2}, y_n + \frac{k_1}{2}\right) \tag{A.118}$$

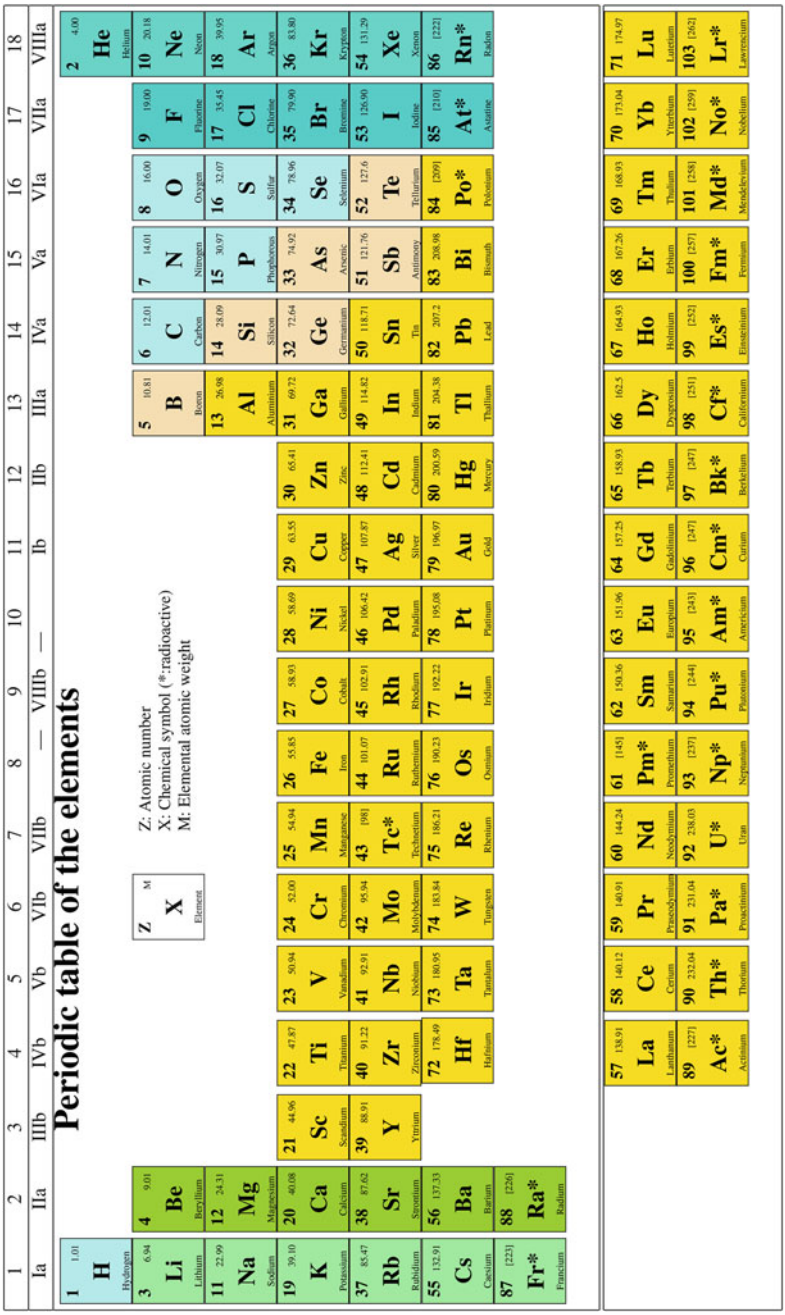
$$k_3 = hf\left(t_n + \frac{h}{2}, y_n + \frac{k_2}{2}\right) \tag{A.119}$$

$$k_4 = hf(t_n + h, y_n + k_3) \tag{A.120}$$

$$y_{n+1} = y_n + \frac{k_1}{6} + \frac{k_2}{3} + \frac{k_3}{3} + \frac{k_4}{6} \tag{A.121}$$

[1] Source: W.H. Press, S. Teukolsky, W.T. Vetterling, B.P. Flannery *Numerical recipes in C: the art of scientific computing*, Cambridge University Press, Cambridge, 1988

A.4 Periodic Table of Elements



A.5 List of Symbols

Latin symbols:

A	(1) Helmholtz free energy (1 J); (2) Absorbance; (3) Area ($1\,m^2$); (4) Pre-exponential factor in reaction kinetics (unit depends on reaction order)
A_{nm}	Einstein coefficient of spontaneous emission ($1\,Hz{=}1\,s^{-1}$)
a	(1) First van der Waals parameter ($1\,kg\,m^5\,mol^{-2}\,s^{-2}$); (2) Activity of a substance
a_0	Bohr radius (see Sect. A.1)
B	(1) Rotational constant ($1\,Hz{=}1\,s^{-1}$); (2) Second virial coefficient ($1\,m^3\,mol^{-1}$); (3) Bernoulli number
B_{nm}	Einstein coefficient of induced emission or induced absorption ($1\,J^{-1}\,m^3\,s^{-2}$)
b	Second van der Waals parameter ($1\,m^3\,mol^{-1}$)
C	(1) Heat capacity ($1\,J\,K^{-1}$); (2) Third virial coefficient ($1\,m^6\,mol^{-2}$)
C_p	Constant pressure heat capacity ($1\,J\,K^{-1}$)
C_V	Constant volume heat capacity ($1\,J\,K^{-1}$)
$\hat{C}_n$	Rotation operation related to an n-fold rotation axis
c	(1) Concentration ($1\,mol\,m^{-3}$); (2) Speed of light (physical constant, see Sect. A.1)
c_p	Constant pressure heat capacity ($1\,J\,K^{-1}\,mol^{-1}$)
c_v	Constant volume molar heat capacity ($1\,J\,K^{-1}\,mol^{-1}$)
D	Diffusion constant ($1\,m^2\,s^{-1}$)
D_e	Well depth of Morse potential (1 J)
$\bar{D}_e$	Centrifugal distortion constant ($1\,Hz = 1\,s^{-1}$)
D^J_{MK}	Wigner rotation function, generalized spherical harmonic
E	Energy (1 J)
$\hat{E}$	Identity operation
E_a	Energy of activation ($1\,J\,mol^{-1}$)
F	Force ($1\,N = 1\,kg\,m\,s^{-2}$)
G	Gibbs free energy (1 J)
g_i	(1) Molar Gibbs free energy ($1\,J\,mol^{-1}$); (2) Degree of degeneracy of the ith energy level
H	(1) Enthalpy (1 J); (2) Hamiltonian, i.e., total kinetic and potential energy of a system (1 J)
$\bar{H}$	Energy functional (1 J)
h	(1) Planck constant (physical constant, see Sect. A.1); (2) Molar enthalpy ($1\,J\,K^{-1}\,mol^{-1}$)
$\hbar = \frac{h}{2\pi}$	Planck constant divided by 2π
I	(1) Impingement rate ($1\,m^{-2}\,s^{-1}$); (2) Moment of inertia ($1\,kg\,m^2$); (3) Nuclear spin
i	Imaginary unit

J	Rotational quantum number
$\mathbf{J}$	Angular momentum vector ($1\,\mathrm{kg\,m^2\,s^{-1}}$)
K	Equilibrium constant of a chemical reaction
K_a	Dissociation constant
Kn	Knudsen number
k	(1) Rate constant of a chemical reaction (unit depends on reaction order); (2) Force constant ($1\,\mathrm{N\,m^{-1}}$)
k_B	Boltzmann constant (physical constant, see Sect. A.1)
L	Optical path length (1 m)
$\hat{L}$	Operator of the orbital angular momentum
l	Quantum number of the orbital angular momentum in the hydrogen problem
M	(1) Molar mass ($1\,\mathrm{kg\,mol^{-1}}$); (2) Magnetic or orientational quantum number
m	(1) Mass (1 kg); (2) Magnetic quantum number in the hydrogen problem
m_u	Atomic mass unit (physical constant, see Sect. A.1)
m_e	Electron mass (physical constant, see Sect. A.1)
N	Number of particles
$\mathscr{N}$	Number density of particles ($1\,\mathrm{m^{-3}}$)
$\mathcal{N}$	Number of identical copies in a statistical ensemble
n	(1) Amount of substance (1 mol); (2) Vibrational quantum number; (3) Principal quantum number in the hydrogen problem
N_A	Avogadro constant (physical constant, see Sect. A.1)
P	Power ($1\,\mathrm{W} = 1\,\mathrm{J\,s^{-1}}$)
$\hat{P}$	Parity operator
P_{lm}	Associated Legendre polynomial
p	(1) Pressure ($1\,\mathrm{Pa}{=}1\,\mathrm{kg\,m^{-1}\,s^{-2}}$); (2) Momentum ($1\,\mathrm{kg\,m\,s^{-1}}$); (3) Probability
$p^{\ominus}$	Standard pressure (100,000 Pa)
Q	(1) Heat (1 J); (2) Partition function of a system
q	Partition function
R	(1) Molar gas constant (physical constant, see Sect. A.1); (2) Radial wave function in the hydrogen problem
r	(1) Reaction rate ($1\,\mathrm{mol\,m^{-3}\,s^{-1}}$); (2) Radial coordinate (1 m)
S	Entropy ($1\,\mathrm{J\,K^{-1}}$)
s	(1) Distance (1 m); (2) Molar entropy ($1\,\mathrm{J\,K^{-1}\,mol^{-1}}$)
T	(1) Temperature (1 K); (2) Transmittance
$\hat{T}$	Exchange operator
t	Time (1 s)
$t_{\frac{1}{2}}$	Half life (1 s)
U	Internal energy (1 J)
u	(1) Molar internal energy ($1\,\mathrm{J\,mol^{-1}}$); (2) Spectral energy density of the electromagnetic radiation field ($1\,\mathrm{J\,s\,m^{-3}}$)

V	(1) Volume (1 m^3); (2) Potential energy (1 J)
v	(1) Velocity (1 $m\,s^{-1}$); (2) Molar volume (1 $m^3\,mol^{-1}$)
W	(1) Work (1 J); (2) Statistical weight
x	(1) Mole fraction; (2) Cartesian coordinate, position (1 m)
x_e	Anharmonicity constant of diatomic molecule
x_{ij}	Anharmonicity constant of the *i*th and the *j*th vibrational mode of a polyatomic molecule (1 Hz=1 s^{-1})
Y_{lm}, Y_{JM}	Spherical harmonic function
y	Cartesian coordinate (1 m)
Z	Atomic number of an element
z	(1) Cartesian coordinate (1 m); (2) Collision frequency (1 Hz=1 s^{-1})

Greek symbols:

α	Isobaric thermal expansion coefficient (1 K^{-1})
α_e	Vibration-rotation coupling constant (1 Hz = 1 s^{-1})
β	Parameter $(k_B T)^{-1}$ in statistical thermodynamics
Γ	Representation in group theory
γ	(1) Heat capacity ratio; (2) Surface energy density or surface tension (1 $J\,m^{-2}$); (3) Activity coefficient
Δ	(1) Delta operator, partial derivative with regard to the extent of the reaction; (2) Laplace operator; (3) Difference between energy levels
δ_{nm}	Kronecker delta, $\delta_{nm} = 1$ if $n = m$ and zero otherwise
δ_l	Quantum defect
ϵ_0	Electric constant (physical constant, see Sect. A.1)
θ	Inclination or polar angle (1 rad)
κ	(1) Isothermal compressibility (1 Pa^{-1} = 1 $kg^{-1}\,m\,s^2$); (2) Asymmetry parameter in molecular rotation spectroscopy
Λ	Thermal wavelength (1 m)
λ	(1) Mean free path (1 m); (2) Wave length (1 m)
μ	(1) Chemical potential (J mol^{-1}); (2) Effective mass (1 kg)
ν	(1) Stoichiometric number of substance; (2) Frequency (1 Hz=1 s^{-1})
$\tilde{\nu}$	Wave number (1 m^{-1})
ξ	Extent of reaction (1 mol)
ξ^{eq}	Equilibrium extent of reaction (1 mol)
Π	Internal pressure (1 Pa = 1 $kg\,m^{-1}\,s^{-2}$)
ρ	Mass density (1 $kg\,m^{-3}$)
σ	(1) Stefan-Boltzmann constant (see Eq. (9.8) at page 215); (2) Attenuation cross section in spectroscopy (1 m^2); (3) Variance of a distribution function
σ_x, σ_y, σ_z	Pauli spin matrices
$\hat{\sigma}_h$	Mirror operation related to a horizontal mirror plane
$\hat{\sigma}_v$	Mirror operation related to a vertical mirror plane

τ	(1) Optical depth; (2) Lifetime (1 s)
Φ	Photon density (1 m^{-3})
ϕ	Azimuthal angle (1 rad)
χ_i	Character of representation i
ψ	Quantum mechanical wave function
ω	Angular frequency (1 rad s^{-1})

A.6 List of Acronyms

AFM	Atomic force microscopy
COM	Center of mass
ESCA	Electron spectroscopy for chemical analysis
IR	Infrared spectral range
LASER	Light amplification by stimulated emission of radiation
LCAO	Linear combination of atomic orbitals
LEED	Low-energy electron diffraction
MIR	Mid infrared spectral range
Nd:YAG	Neodymium-doped yttrium aluminum garnet (Nd:$Y_3Al_5O_{12}$)
NIR	Near infrared spectral range
PET	Positron emission tomography
PSE	Periodic system of elements
RRHO	Rigid rotor harmonic oscillator approximation in molecular spectroscopy
STM	Scanning tunneling microscopy
SI	International system of units (Système international d'unités)
TCA	Trichloroacetic acid
TOF	Time of flight
UHV	Ultrahigh vacuum
UV	Ultraviolet spectral range
UPS	Ultraviolet photoelectron spectroscopy
XPS	X-ray photoelectron spectroscopy

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