Chapter 1
The Need for Quantum Mechanics

1.1 Electromagnetic spectra and evidence for discrete energy levels

Quantum mechanics was initially invented because classical mechanics, thermodynamics and electrodynamics provided no means to explain the properties of atoms, electrons, and electromagnetic radiation. Furthermore, it became clear after the introduction of Schrödinger's equation and the quantization of Maxwell's equations that we cannot explain *any* physical property of matter and radiation without the use of quantum theory. We will see a lot of evidence for this in the following chapters. However, in the present chapter we will briefly and selectively review the early experimental observations and discoveries which led to the development of quantum mechanics over a period of intense research between 1900 and 1928.

The first evidence that classical physics was incomplete appeared in unexpected properties of electromagnetic spectra. Thin gases of atoms or molecules emit line spectra which contradict the fact that a classical system of electric charges can oscillate at any frequency, and therefore can emit radiation of any frequency. This was a major scientific puzzle from the 1850s until the inception of the Schrödinger equation in 1926.

Contrary to a thin gas, a hot body does emit a continuous spectrum, but even those spectra were still puzzling because the shape of heat radiation spectra could not be explained by classical thermodynamics and electrodynamics. In fact, classical physics provided no means at all to predict any sensible shape for the spectrum of a heat source! But at last, hot bodies do emit a continuous spectrum and therefore, from a classical point of view, their spectra are not quite as strange and unexpected as line spectra. It is therefore not surprising that the first real clues for a solution to the puzzles of electromagnetic spectra emerged when Max Planck figured out a way to calculate the spectra of heat sources under the simple, but classically

R. Dick, *Advanced Quantum Mechanics*, Graduate Texts in Physics,
DOI 10.1007/978-3-319-25675-7_1

extremely counterintuitive assumption that the energy in heat radiation of frequency f is *quantized* in integer multiples of a minimal energy quantum hf,

$$E = nhf, \quad n \in \mathbb{N}. \tag{1.1}$$

The constant h that Planck had introduced to formulate this equation became known as Planck's constant and it could be measured from the shape of heat radiation spectra. A modern value is $h = 6.626 \times 10^{-34}\,\mathrm{J}\cdot\mathrm{s} = 4.136 \times 10^{-15}\,\mathrm{eV}\cdot\mathrm{s}$.

We will review the puzzle of heat radiation and Planck's solution in the next section, because Planck's calculation is instructive and important for the understanding of incandescent light sources and it illustrates in a simple way how quantization of energy levels yields results which are radically different from predictions of classical physics.

Albert Einstein then pointed out that equation (1.1) also explains the photoelectric effect. He also proposed that Planck's quantization condition is not a property of any particular mechanism for generation of electromagnetic waves, but an intrinsic property of electromagnetic waves. However, once equation (1.1) is accepted as an intrinsic property of electromagnetic waves, it is a small step to make the connection with line spectra of atoms and molecules and conclude that these line spectra imply existence of discrete energy levels in atoms and molecules. Somehow atoms and molecules seem to be able to emit radiation only by jumping from one discrete energy state into a lower discrete energy state. This line of reasoning, combined with classical dynamics between electrons and nuclei in atoms then naturally leads to the Bohr-Sommerfeld theory of atomic structure. This became known as *old quantum theory*.

Apparently, the property which underlies both the heat radiation puzzle and the puzzle of line spectra is discreteness of energy levels in atoms, molecules, and electromagnetic radiation. Therefore, *one major motivation for the development of quantum mechanics was to explain discrete energy levels in atoms, molecules, and electromagnetic radiation.*

It was Schrödinger's merit to find an explanation for the discreteness of energy levels in atoms and molecules through his wave equation[1] ($\hbar \equiv h/2\pi$)

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\psi(\boldsymbol{x},t) = -\frac{\hbar^2}{2m}\Delta\psi(\boldsymbol{x},t) + V(\boldsymbol{x})\psi(\boldsymbol{x},t). \tag{1.2}$$

A large part of this book will be dedicated to the discussion of Schrödinger's equation. An intuitive motivation for this equation will be given in Section 1.6.

Ironically, the fundamental energy quantization condition (1.1) for electromagnetic waves, which precedes the realization of discrete energy levels in atoms and molecules, cannot be derived by solving a wave equation, but emerges from the quantization of Maxwell's equations. This is at the heart of understanding photons

---

[1] E. Schrödinger, Annalen Phys. 386, 109 (1926).

and the quantum theory of electromagnetic waves. We will revisit this issue in Chapter 18. However, we can and will discuss already now the early quantum theory of the photon and what it means for the interpretation of spectra from incandescent sources.

1.2 Blackbody radiation and Planck's law

Historically, Planck's deciphering of the spectra of incandescent heat and light sources played a key role for the development of quantum mechanics, because it included the first proposal of energy quanta, and it implied that line spectra are a manifestation of energy quantization in atoms and molecules. Planck's radiation law is also extremely important in astrophysics and in the technology of heat and light sources.

Generically, the heat radiation from an incandescent source is contaminated with radiation reflected from the source. Pure heat radiation can therefore only be observed from a non-reflecting, i.e. perfectly black body. Hence the name blackbody radiation for pure heat radiation. Physicists in the late 19th century recognized that the best experimental realization of a black body is a hole in a cavity wall. If the cavity is kept at temperature T, the hole will emit perfect heat radiation without contamination from any reflected radiation.

Suppose we have a heat radiation source (or thermal emitter) at temperature T. The power per area radiated from a thermal emitter at temperature T is denoted as its *exitance* (or *emittance*) $e(T)$. In the blackbody experiments $e(T)\cdot A$ is the energy per time leaking through a hole of area A in a cavity wall.

To calculate $e(T)$ as a function of the temperature T, as a first step we need to find out how it is related to the density $u(T)$ of energy stored in the heat radiation. One half of the radiation will have a velocity component towards the hole, because all the radiation which moves under an angle $\vartheta \leq \pi/2$ relative to the axis going through the hole will have a velocity component $v(\vartheta) = c\cos\vartheta$ in the direction of the hole. To find out the average speed v of the radiation in the direction of the hole, we have to average $c\cos\vartheta$ over the solid angle $\Omega = 2\pi$ sr of the forward direction $0 \leq \varphi \leq 2\pi, 0 \leq \vartheta \leq \pi/2$:

$$v = \frac{c}{2\pi}\int_0^{2\pi} d\varphi \int_0^{\pi/2} d\vartheta\, \sin\vartheta\cos\vartheta = \frac{c}{2}.$$

The effective energy current density towards the hole is energy density moving in forward direction × average speed in forward direction:

$$\frac{u(T)}{2}\frac{c}{2} = u(T)\frac{c}{4},$$

and during the time t an amount of energy

$$E = u(T)\frac{c}{4}tA$$

will escape through the hole. Therefore the emitted power per area $E/(tA) = e(T)$ is

$$e(T) = u(T)\frac{c}{4}. \tag{1.3}$$

However, Planck's radiation law is concerned with the *spectral exitance* $e(f, T)$, which is defined in such a way that

$$e_{[f_1,f_2]}(T) = \int_{f_1}^{f_2} df\, e(f, T)$$

is the power per area emitted in radiation with frequencies $f_1 \leq f \leq f_2$. In particular, the total exitance is

$$e(T) = e_{[0,\infty]}(T) = \int_0^{\infty} df\, e(f, T).$$

Operationally, the spectral exitance is the power per area emitted with frequencies $f \leq f' \leq f + \Delta f$, and normalized by the width Δf of the frequency interval,

$$e(f, T) = \lim_{\Delta f \to 0} \frac{e_{[f,f+\Delta f]}(T)}{\Delta f} = \lim_{\Delta f \to 0} \frac{e_{[0,f+\Delta f]} - e_{[0,f]}(T)}{\Delta f} = \frac{\partial}{\partial f} e_{[0,f]}(T).$$

The spectral exitance $e(f, T)$ can also be denoted as the *emitted power per area and per unit of frequency* or as the *spectral exitance in the frequency scale*.

The spectral energy density $u(f, T)$ is defined in the same way. If we measure the energy density $u_{[f,f+\Delta f]}(T)$ in radiation with frequency between f and $f + \Delta f$, then the energy per volume and per unit of frequency (i.e. the spectral energy density in the frequency scale) is

$$u(f, T) = \lim_{\Delta f \to 0} \frac{u_{[f,f+\Delta f]}(T)}{\Delta f} = \frac{\partial}{\partial f} u_{[0,f]}(T), \tag{1.4}$$

and the total energy density in radiation is

$$u(T) = \int_0^{\infty} df\, u(f, T).$$

The equation $e(T) = u(T)c/4$ also applies separately in each frequency interval $[f, f + \Delta f]$, and therefore must also hold for the corresponding spectral densities,

$$e(f, T) = u(f, T)\frac{c}{4}. \tag{1.5}$$

The following facts were known before Planck's work in 1900.

- The prediction from classical thermodynamics for the spectral exitance $e(f,T)$ (Rayleigh-Jeans law) was wrong, and actually non-sensible!
- The exitance $e(T)$ satisfies Stefan's law (Stefan, 1879; Boltzmann, 1884)

$$e(T) = \sigma T^4,$$

with the Stefan-Boltzmann constant

$$\sigma = 5.6704 \times 10^{-8}\, \frac{\mathrm{W}}{\mathrm{m}^2\mathrm{K}^4}.$$

- The spectral exitance $e(\lambda, T) = e(f,T)\Big|_{f=c/\lambda} \cdot c/\lambda^2$ per unit of wavelength (i.e. *the spectral exitance in the wavelength scale*) has a maximum at a wavelength

$$\lambda_{max} \cdot T = 2.898 \times 10^{-3}\,\mathrm{m}\cdot\mathrm{K} = 2898\,\mu\mathrm{m}\cdot\mathrm{K}.$$

This is Wien's displacement law (Wien, 1893).

The puzzle was to explain the observed curves $e(f,T)$ and to explain why classical thermodynamics had failed. We will explore these questions through a calculation of the spectral energy density $u(f,T)$. Equation (1.5) then also yields $e(f,T)$.

The key observation for the calculation of $u(f,T)$ is to realize that $u(f,T)$ can be split into two factors. If we want to know the radiation energy density $u_{[f,f+df]} = u(f,T)df$ in the small frequency interval $[f, f+df]$, then we can first ask ourselves how many different electromagnetic oscillation modes per volume, $\varrho(f)df$, exist in that frequency interval. Each oscillation mode will then contribute an energy $\langle E\rangle(f,T)$ to the radiation energy density, where $\langle E\rangle(f,T)$ is the expectation value of energy in an electromagnetic oscillation mode of frequency f at temperature T,

$$u(f,T)df = \varrho(f)df\langle E\rangle(f,T).$$

The spectral energy density $u(f,T)$ can therefore be calculated in two steps:

1. Calculate the number $\varrho(f)$ of oscillation modes per volume and per unit of frequency ("counting of oscillation modes").
2. Calculate the mean energy $\langle E\rangle(f,T)$ in an oscillation of frequency f at temperature T.

The results can then be combined to yield the spectral energy density $u(f,T) = \varrho(f)\langle E\rangle(f,T)$.

The number of electromagnetic oscillation modes per volume and per unit of frequency is an important quantity in quantum mechanics and will be calculated explicitly in Chapter 12, with the result

$$\varrho(f) = \frac{8\pi f^2}{c^3}. \tag{1.6}$$

The corresponding density of oscillation modes in the wavelength scale is

$$\varrho(\lambda) = \varrho(f)\Big|_{f=c/\lambda} \cdot \frac{c}{\lambda^2} = \frac{8\pi}{\lambda^4}.$$

Statistical physics predicts that the probability $P_T(E)$ to find an oscillation of energy E in a system at temperature T should be exponentially suppressed,

$$P_T(E) = \frac{1}{k_B T}\exp\left(-\frac{E}{k_B T}\right). \tag{1.7}$$

The possible values of E are not restricted in classical physics, but can vary continuously between $0 \leq E < \infty$. For example, for any classical oscillation with fixed frequency f, continually increasing the amplitude yields a continuous increase in energy. The mean energy of an oscillation at temperature T according to classical thermodynamics is therefore

$$\langle E\rangle\Big|_{classical} = \int_0^\infty dE\, E P_T(E) = \int_0^\infty dE\, \frac{E}{k_B T}\exp\left(-\frac{E}{k_B T}\right) = k_B T. \tag{1.8}$$

Therefore the spectral energy density in blackbody radiation and the corresponding spectral exitance according to classical thermodynamics should be

$$u(f,t) = \varrho(f)k_B T = \frac{8\pi f^2}{c^3}k_B T, \quad e(f,T) = u(f,T)\frac{c}{4} = \frac{2\pi f^2}{c^2}k_B T,$$

but this is obviously nonsensical: it would predict that every heat source should emit a diverging amount of energy at high frequencies/short wavelengths! This is the *ultraviolet catastrophe* of the Rayleigh-Jeans law.

Max Planck observed in 1900 that he could derive an equation which matches the spectra of heat sources perfectly if he assumes that the energy in electromagnetic waves of frequency f is quantized in multiples of the frequency,

$$E = nhf = n\frac{hc}{\lambda}, \quad n \in \mathbb{N}.$$

The exponential suppression of high energy oscillations then reads

$$P_T(E) = P_T(n) \propto \exp\left(-\frac{nhf}{k_B T}\right),$$

but due to the discreteness of the *energy quanta hf*, the normalized probabilities are now

$$\begin{aligned} P_T(E) = P_T(n) &= \left[1 - \exp\left(-\frac{hf}{k_B T}\right)\right]\exp\left(-\frac{nhf}{k_B T}\right) \\ &= \exp\left(-n\frac{hf}{k_B T}\right) - \exp\left(-(n+1)\frac{hf}{k_B T}\right), \end{aligned}$$

such that $\sum_{n=0}^{\infty} P_T(n) = 1$.

The resulting mean energy per oscillation mode is

$$\begin{aligned}\langle E\rangle &= \sum_{n=0}^{\infty} nhfP_T(n)\\ &= \sum_{n=0}^{\infty} nhf\exp\left(-n\frac{hf}{k_BT}\right) - \sum_{n=0}^{\infty} nhf\exp\left(-(n+1)\frac{hf}{k_BT}\right)\\ &= \sum_{n=0}^{\infty} nhf\exp\left(-n\frac{hf}{k_BT}\right) - \sum_{n=0}^{\infty}(n+1)hf\exp\left(-(n+1)\frac{hf}{k_BT}\right)\\ &\quad +hf\sum_{n=0}^{\infty}\exp\left(-(n+1)\frac{hf}{k_BT}\right)\end{aligned}$$

The first two sums cancel, and the last term yields the mean energy in an electromagnetic wave of frequency f at temperature T as

$$\langle E\rangle(f,T) = hf\frac{\exp\left(-\frac{hf}{k_BT}\right)}{1-\exp\left(-\frac{hf}{k_BT}\right)} = \frac{hf}{\exp\left(\frac{hf}{k_BT}\right)-1}. \tag{1.9}$$

Combination with $\varrho(f)$ from equation (1.6) yields Planck's formulas for the spectral energy density and spectral exitance in heat radiation,

$$u(f,T) = \frac{8\pi hf^3}{c^3}\frac{1}{\exp\left(\frac{hf}{k_BT}\right)-1}, \quad e(f,T) = \frac{2\pi hf^3}{c^2}\frac{1}{\exp\left(\frac{hf}{k_BT}\right)-1}. \tag{1.10}$$

These functions fitted the observed spectra perfectly! The spectrum $e(f,T)$ and the emitted power $e_{[0,f]}(T)$ with maximal frequency f are displayed for $T = 5780$ K in Figures 1.1 and 1.2.

1.3 Blackbody spectra and photon fluxes

Their technical relevance for the quantitative analysis of incandescent light sources makes it worthwhile to take a closer look at blackbody spectra. Blackbody spectra are also helpful to elucidate the notion of spectra more closely, and to explain that a maximum in a spectrum strongly depends on the choice of independent variable (e.g. wavelength or frequency) and dependent variable (e.g. energy flux or photon flux). In particular, it is sometimes claimed that our sun has maximal radiation output at a wavelength $\lambda_{\max} \simeq 500$ nm. This statement is actually very misleading if the notion of "radiation output" is not clearly defined, and if no explanation

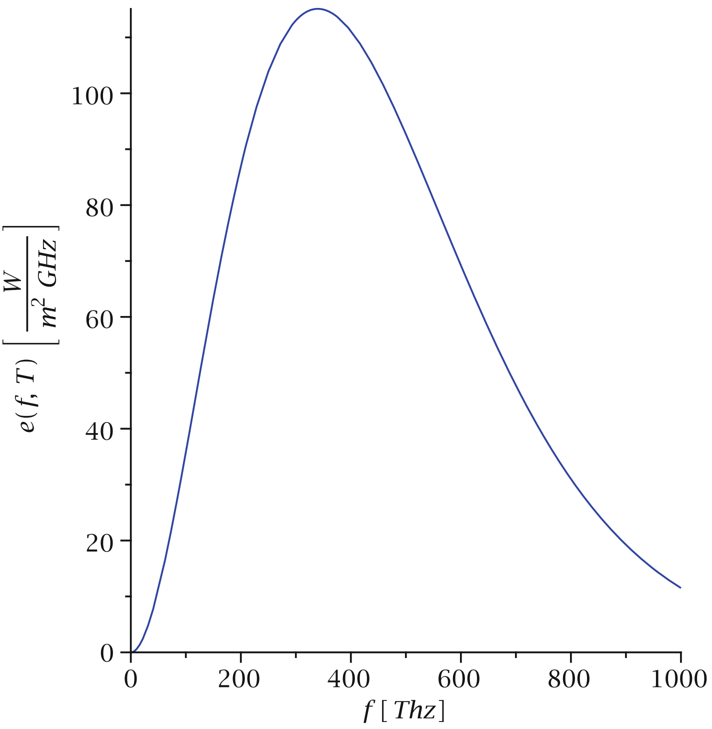

Fig. 1.1 The spectral emittance $e(f, T)$ for a heat source of temperature $T = 5780$ K

is included that different perfectly suitable notions of radiation output yield very different wavelengths or frequencies of maximal emission. We will see below that the statement above only applies to *maximal power output per unit of wavelength*, i.e. if we use a monochromator which slices the *wavelength* axis into intervals of equal length $d\lambda = c|df|/f^2$, then we find maximal power output in an interval around $\lambda_{max} \simeq 500$ nm. However, we will also see that if we use a monochromator which slices the *frequency* axis into intervals of equal length $df = c|d\lambda|/\lambda^2$, then we find maximal power output in an interval around $f_{max} \simeq 340$ THz, corresponding to a wavelength $c/f_{\max} \simeq 880$ nm. If we ask for maximal photon counts instead of maximal power output, we find yet other values for peaks in the spectra.

Since Planck's radiation law (1.10) yielded perfect matches to observed black-body spectra, it must also imply Stefan's law and Wien's law. Stefan's law is readily derived in the following way. The emitted power per area is

$$e(T) = \int_0^\infty df\, e(f, T) = \int_0^\infty d\lambda\, e(\lambda, T) = 2\pi \frac{k_B^4 T^4}{h^3 c^2} \int_0^\infty dx\, \frac{x^3}{\exp(x) - 1}.$$

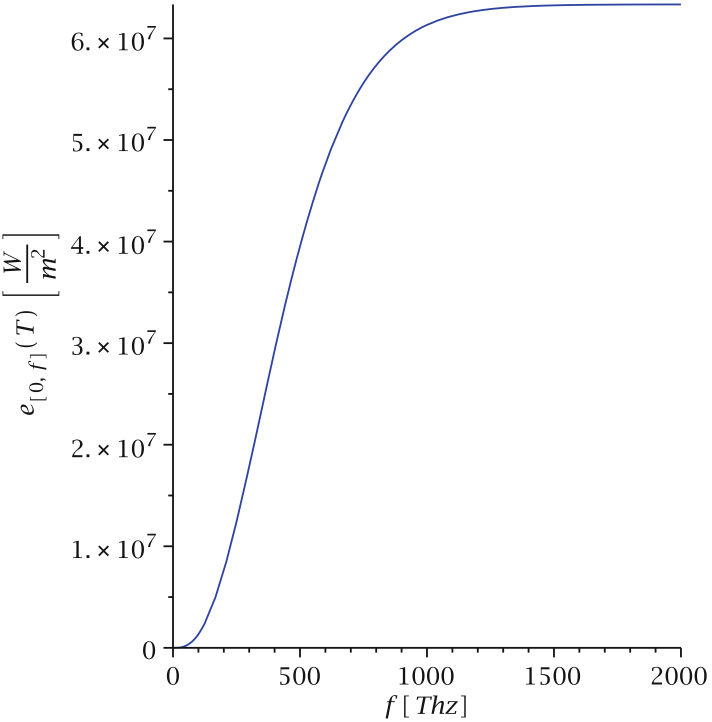

Fig. 1.2 The emittance $e_{[0,f]}(T) = \int_0^f df'\, e(f', T)$ (i.e. emitted power per area in radiation with maximal frequency f) for a heat source of temperature $T = 5780$ K. The asymptote for $f \to \infty$ is $e_{[0,\infty]}(T) \equiv e(T) = \sigma T^4 = 6.33 \times 10^7\,\mathrm{W/m^2}$ for the temperature $T = 5780$ K

Evaluation of the integral

$$\begin{aligned}\int_0^\infty dx\,\frac{x^3}{\exp(x)-1} &= \int_0^\infty dx\,x^3\sum_{n=0}^\infty \exp[-(n+1)x]\\ &= -\sum_{n=1}^\infty \frac{d^3}{dn^3}\int_0^\infty dx\,\exp(-nx) = -\sum_{n=1}^\infty \frac{d^3}{dn^3}\frac{1}{n}\\ &= \sum_{n=1}^\infty \frac{6}{n^4} = 6\zeta(4) = \frac{\pi^4}{15}\end{aligned}$$

implies

$$e(T) = \frac{2\pi^5 k_B^4}{15h^3c^2}T^4,$$

i.e. Planck's law implied a prediction for the Stefan-Boltzmann constant in terms of the Planck constant h, which could be determined previously from a fit to the spectra,

$$\sigma = \frac{2\pi^5 k_B^4}{15h^3c^2}.$$

An energy flux $e(T) = 6.33 \times 10^7\,\mathrm{W/m^2}$ from the Sun yields a remnant energy flux at Earth's orbit of magnitude $e(T) \times (R_\odot/r_\oplus)^2 = 1.37\,\mathrm{kW/m^2}$. Here $R_\odot = 6.955 \times 10^8$ m is the radius of the Sun and $r_\oplus = 1.496 \times 10^{11}$ m is the radius of Earth's orbit.

For the derivation of Wien's law, we set

$$x = \frac{hc}{\lambda k_B T} = \frac{hf}{k_B T}.$$

Then we have with $e(\lambda, T) = e(f, T)|_{f=c/\lambda} c/\lambda^2$,

$$\begin{aligned} \frac{\partial}{\partial\lambda} e(\lambda, T) &= \frac{2\pi hc^2}{\lambda^5} \frac{1}{\exp\left(\frac{hc}{\lambda k_B T}\right) - 1} \left(\frac{hc}{\lambda^2 k_B T} \frac{\exp\left(\frac{hc}{\lambda k_B T}\right)}{\exp\left(\frac{hc}{\lambda k_B T}\right) - 1} - \frac{5}{\lambda} \right) \\ &= \frac{2\pi hc^2}{\lambda^6} \frac{1}{\exp(x) - 1} \left(x \frac{\exp(x)}{\exp(x) - 1} - 5 \right), \end{aligned}$$

which implies that $\partial e(\lambda, T)/\partial\lambda = 0$ is satisfied if and only if

$$\exp(x) = \frac{5}{5 - x}.$$

This condition yields $x \simeq 4.965$. The wavelength of maximal spectral emittance $e(\lambda, T)$ therefore satisfies

$$\lambda_{\max} \cdot T \simeq \frac{hc}{4.965 k_B} = 2898\,\mu\mathrm{m} \cdot \mathrm{K}.$$

For a heat source of temperature $T = 5780$ K, like the surface of our sun, this yields

$$\lambda_{\max} = 501\,\mathrm{nm}, \quad \frac{c}{\lambda_{\max}} = 598\,\mathrm{THz},$$

see Figure 1.3.

One can also derive an analogue of Wien's law for the frequency $f_{\max}$ of maximal spectral emittance $e(f, T)$. We have

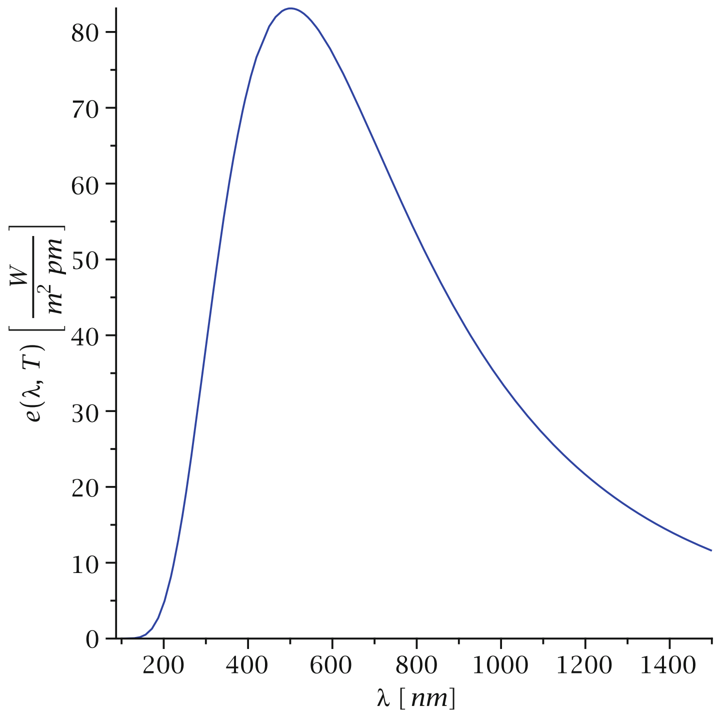

Fig. 1.3 The spectral emittance $e(\lambda, T)$ for a heat source of temperature $T = 5780$ K

$$\frac{\partial}{\partial f}e(f,T) = \frac{2\pi hf^2}{c^2}\frac{1}{\exp\left(\frac{hf}{k_BT}\right)-1}\left(3-\frac{hf}{k_BT}\frac{\exp\left(\frac{hc}{\lambda k_BT}\right)}{\exp\left(\frac{hc}{\lambda k_BT}\right)-1}\right)$$
$$= \frac{2\pi hf^2}{c^2}\frac{1}{\exp(x)-1}\left(3-x\frac{\exp(x)}{\exp(x)-1}\right),$$

which implies that $\partial e(f,T)/\partial f = 0$ is satisfied if and only if

$$\exp(x) = \frac{3}{3-x},$$

with solution $x \simeq 2.821$. The frequency of maximal spectral emittance $e(f,T)$ therefore satisfies

$$\frac{f_{\max}}{T} \simeq 2.821\frac{k_B}{h} = 58.79\,\frac{\text{GHz}}{\text{K}}.$$

This yields for a heat source of temperature $T = 5780$ K, as in Figure 1.1,

$$f_{\max} = 340\,\mathrm{THz}, \quad \frac{c}{f_{\max}} = 882\,\mathrm{nm}.$$

The photon fluxes in the wavelength scale and in the frequency scale, $j(\lambda, T)$ and $j(f, T)$, are defined below. The spectral emittance per unit of frequency, $e(f, T)$, is directly related to the photon flux per fractional wavelength or frequency interval $d\ln f = df/f = -d\ln\lambda = -d\lambda/\lambda$. We have with the notations used in (1.4) for spectral densities and integrated fluxes the relations

$$\begin{aligned} e(f,T) &= hfj(f,T) = hf\frac{\partial}{\partial f}j_{[0,f]}(T) = h\frac{\partial}{\partial\ln(f/f_0)}j_{[0,f]}(T) \\ &= hj(\ln(f/f_0),T) = h\lambda j(\lambda,T) = hj(\ln(\lambda/\lambda_0),T). \end{aligned}$$

Optimization of the energy flux of a light source for given frequency bandwidth df is therefore equivalent to optimization of photon flux for fixed fractional bandwidth $df/f = |d\lambda/\lambda|$.

The number of photons per area, per second, and per unit of wavelength emitted from a heat source of temperature T is

$$j(\lambda,T) = \frac{\lambda}{hc}e(\lambda,T) = \frac{2\pi c}{\lambda^4}\frac{1}{\exp\left(\frac{hc}{\lambda k_B T}\right) - 1}.$$

This satisfies

$$\frac{\partial}{\partial\lambda}j(\lambda,T) = \frac{j(\lambda,T)}{\lambda}\left(x\frac{\exp(x)}{\exp(x)-1} - 4\right) = 0$$

if

$$\exp(x) = \frac{4}{4-x}.$$

This has the solution $x \simeq 3.921$. The wavelength of maximal spectral photon flux $j(\lambda, T)$ therefore satisfies

$$\lambda_{\max}\cdot T \simeq \frac{hc}{3.921k_B} = 3670\,\mu\mathrm{m}\cdot\mathrm{K}.$$

This yields for a heat source of temperature $T = 5780$ K

$$\lambda_{\max} = 635\,\mathrm{nm}, \quad \frac{c}{\lambda_{\max}} = 472\,\mathrm{THz},$$

see Figure 1.4.

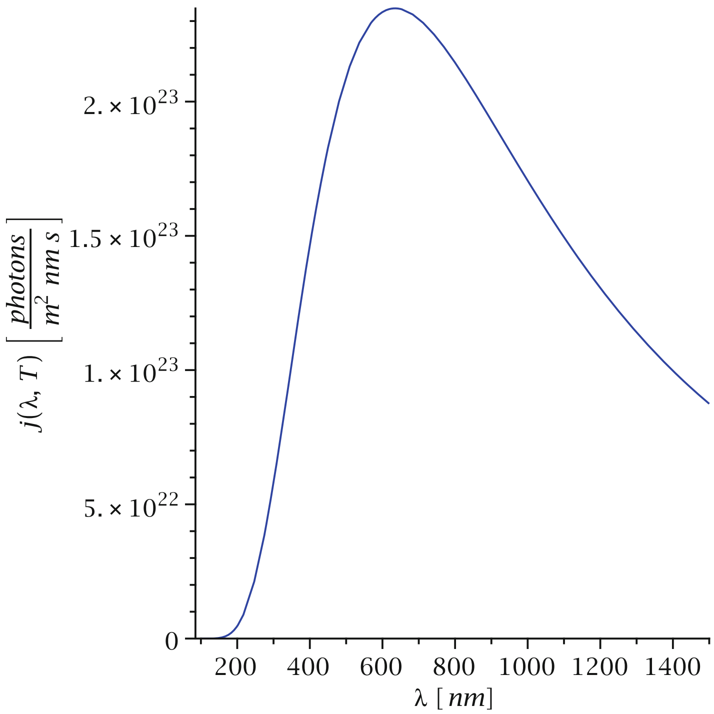

Fig. 1.4 The spectral photon flux $j(\lambda, T)$ for a heat source of temperature $T = 5780$ K

The photon flux in the wavelength scale, $j(\lambda, T)$, is also related to the energy fluxes per fractional wavelength or frequency interval $d\ln\lambda = d\lambda/\lambda = -d\ln f = -df/f$,

$$j(\lambda, T) = \frac{\lambda}{hc}e(\lambda, T) = \frac{1}{hc}e(\ln(\lambda/\lambda_0), T) = \frac{f}{hc}e(f, T) = \frac{1}{hc}e(\ln(f/f_0), T).$$

Therefore optimization of photon flux for fixed wavelength bandwidth $d\lambda$ is equivalent to optimization of energy flux for fixed fractional bandwidth $d\lambda/\lambda = |df/f|$.

Finally, the number of photons per area, per second, and per unit of frequency emitted from a heat source of temperature T is

$$j(f, T) = \frac{e(f, T)}{hf} = \frac{2\pi f^2}{c^2}\frac{1}{\exp\left(\frac{hf}{k_BT}\right) - 1}.$$

This satisfies

$$\frac{\partial}{\partial f}j(f, T) = \frac{j(f, T)}{f}\left(2 - x\frac{\exp(x)}{\exp(x) - 1}\right) = 0$$

if

$$\exp(x) = \frac{2}{2-x}.$$

This condition is solved by $x \simeq 1.594$. Therefore the frequency of maximal spectral photon flux $j(f,T)$ in the frequency scale satisfies

$$\frac{f_{\text{max}}}{T} \simeq 1.594\frac{k_B}{h} = 33.21\,\frac{\text{GHz}}{\text{K}}.$$

This yields for a heat source of temperature $T = 5780$ K

$$f_{\text{max}} = 192\,\text{THz}, \quad \frac{c}{f_{\text{max}}} = 1.56\,\mu\text{m},$$

see Figure 1.5.

The flux of emitted photons is

$$j(T) = \int_0^\infty df\, j(f,T) = 2\pi\frac{k_B^3 T^3}{h^3 c^2}\int_0^\infty dx\,\frac{x^2}{\exp(x)-1}.$$

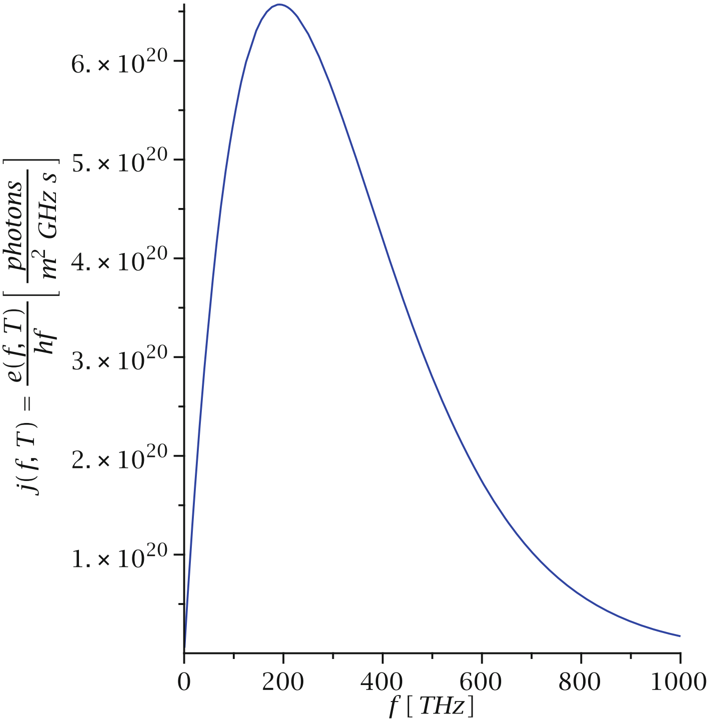

Fig. 1.5 The spectral photon flux $j(f,T)$ for a heat source of temperature $T = 5780$ K

Evaluation of the integral

$$\begin{aligned}\int_0^\infty dx\,\frac{x^2}{\exp(x)-1} &= \int_0^\infty dx\,x^2\sum_{n=0}^{\infty}\exp[-(n+1)x]\\ &= \sum_{n=1}^{\infty}\frac{d^2}{dn^2}\int_0^\infty dx\,\exp(-nx) = \sum_{n=1}^{\infty}\frac{d^2}{dn^2}\frac{1}{n}\\ &= \sum_{n=1}^{\infty}\frac{2}{n^3} = 2\zeta(3)\end{aligned}$$

yields

$$j(T) = \frac{4\pi\zeta(3)k_B^3}{h^3c^2}T^3 = 1.5205\times 10^{15}\frac{T^3}{\mathrm{m}^2\cdot\mathrm{s}\cdot\mathrm{K}^3}.$$

A surface temperature $T = 5780$ K for our sun yields a photon flux at the solar surface $2.94\times 10^{26}\,\mathrm{m}^{-2}\,\mathrm{s}^{-1}$ and a resulting photon flux at Earth's orbit of $6.35\times 10^{21}\,\mathrm{m}^{-2}\,\mathrm{s}^{-1}$. The average photon energy $e(T)/j(T) = 1.35\,\mathrm{eV}$ is in the infrared.

1.4 The photoelectric effect

The notion of energy quanta in radiation was so revolutionary in 1900 that Planck himself speculated that this must somehow be related to the emission mechanism of radiation from the material of the source. In 1905 Albert Einstein pointed out that hitherto unexplained properties of the photoelectric effect can also be explained through energy quanta hf in ultraviolet light, and proposed that this energy quantization is likely an intrinsic property of electromagnetic waves irrespective of how they are generated. In short, the photoelectric effect observations by J.J. Thomson and Lenard revealed the following key properties:

- An ultraviolet light source of frequency f will generate photoelectrons of maximal kinetic energy $hf - hf_0$ if $f > f_0$, where $hf_0 = \phi$ is the minimal energy to liberate photoelectrons from the photocathode.
- Increasing the intensity of the incident ultraviolet light without changing its frequency will increase the photocurrent, but not change the maximal kinetic energy of the photoelectrons. Increasing the intensity must therefore liberate more photoelectrons from the photocathode, but does not impart more energy on single electrons.

Einstein realized that this behavior can be explained if the incident ultraviolet light of frequency f comes in energy parcels of magnitude hf, and if the electrons in the metal can (predominantly) only absorb a single of these energy parcels.

1.5 Wave-particle duality

When X-rays of wavelength λ_0 are scattered off atoms, one observes scattered X-rays of the same wavelength λ_0 in all directions. However, in the years 1921–1923 Arthur H. Compton observed that under every scattering angle ϑ against the direction of incidence, there is also a component of scattered X-rays with a longer wavelength

$$\lambda = \lambda_0 + \lambda_C(1 - \cos\vartheta)\,.$$

The constant $\lambda_C = 2.426$ pm has the same value for every atom. Compton (and also Debye) recognized that this longer wavelength component in the scattered radiation can be explained as a consequence of particle like collisions of Planck's and Einstein's energy parcels hf with weakly bound electrons *if the energy parcels also carry momentum* h/λ. Energy conservation during the collision of the electromagnetics energy parcels (meanwhile called photons) with weakly bound electrons ($\boldsymbol{p}'_e$ is the momentum of the recoiling electron),

$$m_e c + \frac{h}{\lambda_0} = \sqrt{p_e'^2 + m_e^2 c^2} + \frac{h}{\lambda},$$

yields

$$p_e'^2 = \frac{h^2}{\lambda_0^2} + \frac{h^2}{\lambda^2} - 2\frac{h^2}{\lambda\lambda_0} + 2m_e hc\left(\frac{1}{\lambda_0} - \frac{1}{\lambda}\right),$$

while momentum conservation implies

$$p_e'^2 = \frac{h^2}{\lambda_0^2} + \frac{h^2}{\lambda^2} - 2\frac{h^2}{\lambda\lambda_0}\cos\vartheta.$$

This yields for the wavelength of the scattered photon

$$\lambda = \lambda_0 + \frac{h}{m_e c}(1 - \cos\vartheta)\,, \tag{1.11}$$

with excellent numerical agreement between $h/m_e c$ and the measured value of λ_C.

From the experimental findings on blackbody radiation, the photoelectric effect, and Compton scattering, and the ideas of Planck, Einstein, and Compton, an electromagnetic wave of frequency $f = c/\lambda$ appears like a current of particles with energy hf and momentum h/λ. However, electromagnetic waves also show wavelike properties like diffraction and interference. The findings of Planck, Einstein, and Compton combined with the wavelike properties of electromagnetic waves (observed for the first time by Heinrich Hertz) constitute the first observation of *wave-particle duality*. Depending on the experimental setup, a physical system can sometimes behave like a wave and sometimes behave like a particle.

However, the puzzle did not end there. Louis de Broglie recognized in 1923 that the orbits of the old Bohr model could be explained through closed circular electron waves if the electrons are assigned a wavelength $\lambda = h/p$, like photons. Soon thereafter, wavelike behavior of electrons was observed by Clinton Davisson and Lester Germer in 1927, when they observed interference of non-relativistic electrons scattered off the surface of Nickel crystals. At the same time, George Thomson was sending high energy electron beams (with kinetic energies between 20 keV and 60 keV) through thin metal foils and observed interference of the transmitted electrons, thus also confirming the wave nature of electrons. We can therefore also conclude that *another major motivation for the development of quantum mechanics was to explain wave-particle duality*.

1.6 Why Schrödinger's equation?

The foundations of quantum mechanics were developed between 1900 and 1950 by some of the greatest minds of the 20th century, from Max Planck and Albert Einstein to Richard Feynman and Freeman Dyson. The inner circle of geniuses who brought the nascent theory to maturity were Heisenberg, Born, Jordan, Schrödinger, Pauli, Dirac, and Wigner. Among all the outstanding contributions of these scientists, Schrödinger's invention of his wave equation (1.2) was likely the most important *single step* in the development of quantum mechanics. Understanding this step, albeit in a simplified pedagogical way, is important for learning and understanding quantum mechanics.

Ultimately, basic equations in physics have to prove themselves in comparison with experiments, and the Schrödinger equation was extremely successful in that regard. However, this does not explain how to come up with such an equation. Basic equations in physics cannot be derived from any rigorous theoretical or mathematical framework. There is no algorithm which could have told Newton to come up with Newton's equation, or would have told Schrödinger how to come up with his equation (or could tell us how to come up with a fundamental theory of quantum gravity). Basic equations in physics have to be invented in an act of creative ingenuity, which certainly requires a lot of brainstorming and diligent review of pertinent experimental facts and solutions of related problems (where known).

It is much easier to accept an equation and start to explore its consequences if the equation makes intuitive sense – if we can start our discussion of Schrödinger's equation with the premise "yes, the hypothesis that Schrödinger's equation solves the problems of energy quantization and wave-particle duality seems intuitively promising and is worth pursuing".

Therefore I will point out how Schrödinger *could* have invented the Schrödinger equation (although his actual thought process was much more involved and was motivated by the connection of the quantization rules of old quantum mechanics with the Hamilton-Jacobi equation of classical mechanics [39]).

The problem is to come up with an equation for the motion of particles, which explains both quantization of energy levels and wave-particle duality.

As a starting point, we recall that the motion of a non-relativistic particle under the influence of a conservative force $\boldsymbol{F}(\boldsymbol{x}) = -\nabla V(\boldsymbol{x})$ is classically described by Newton's equation

$$m\frac{d^2\boldsymbol{x}(t)}{dt^2} = -\nabla V(\boldsymbol{x}(t)),$$

and this equation also implies energy conservation,

$$E = \frac{\boldsymbol{p}^2}{2m} + V(\boldsymbol{x}). \tag{1.12}$$

However, this cannot be the whole story, because Davisson and Germer, and G.P. Thomson had shown that at least electrons sometimes also behave like waves with wavelength $\lambda = h/p$, as predicted by de Broglie. Furthermore, Compton has demonstrated that photons of energy $E = hf$ satisfy the relation $\lambda = h/p$ between wavelength and momentum. This motivates the hypothesis that a non-relativistic particle might also satisfy the relation $E = hf$. A monochromatic plane wave of frequency f, wavelength λ, and direction of motion $\hat{\boldsymbol{k}}$ can be described by a wave function

$$\psi(\boldsymbol{x},t) = A\exp\left[2\pi\mathrm{i}\left(\frac{\hat{\boldsymbol{k}}\cdot\boldsymbol{x}}{\lambda} - ft\right)\right].$$

Substitution of the relations

$$\lambda = \frac{h}{p}, \quad E = hf = \frac{\boldsymbol{p}^2}{2m}$$

yields with $\hbar \equiv h/2\pi$

$$\psi(\boldsymbol{x},t) = A\exp\left[\mathrm{i}\left(\frac{\boldsymbol{p}\cdot\boldsymbol{x}}{\hbar} - \frac{\boldsymbol{p}^2}{2m\hbar}t\right)\right].$$

Under the supposition of wave-particle duality, we have to assume that this wave function must somehow be related to the wave properties of free particles as observed in the electron diffraction experiments. However, this wave function satisfies a differential equation

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\psi(\boldsymbol{x},t) = E\psi(\boldsymbol{x},t) = \frac{\boldsymbol{p}^2}{2m}\psi(\boldsymbol{x},t) = -\frac{\hbar^2}{2m}\Delta\psi(\boldsymbol{x},t), \tag{1.13}$$

because under the assumption of wave-particle duality we had to replace f with E/h in the exponent, and we used $E = \boldsymbol{p}^2/2m$ for a free particle.

This does not yet tell us how to calculate the wave function which would describe motion of particles in a potential $V(\boldsymbol{x})$. However, comparison of the differential equation (1.13) with the classical energy equation (1.12) can give us the idea to try

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\psi(\boldsymbol{x},t) = -\frac{\hbar^2}{2m}\Delta\psi(\boldsymbol{x},t) + V(\boldsymbol{x})\psi(\boldsymbol{x},t) \tag{1.14}$$

as a starting point for the calculation of wave functions for particles moving in a potential $V(\boldsymbol{x})$. Schrödinger actually found this equation after he had found the time-independent Schrödinger equation (3.3) below, and he had demonstrated that these equations yield the correct spectrum for hydrogen atoms, where

$$V(\boldsymbol{x}) = -\frac{e^2}{4\pi\epsilon_0|\boldsymbol{x}|}.$$

Schrödinger's solution of the hydrogen atom will be discussed in Chapter 7.

1.7 Interpretation of Schrödinger's wave function

The Schrödinger equation was a spectacular success right from the start, but it was not immediately clear what the physical meaning of the complex wave function $\psi(\boldsymbol{x},t)$ is. A natural first guess would be to assume that $|\psi(\boldsymbol{x},t)|^2$ corresponds to a physical density of the particle described by the wave function $\psi(\boldsymbol{x},t)$. In this interpretation, an electron in a quantum state $\psi(\boldsymbol{x},t)$ would have a spatial mass density $m\,|\psi(\boldsymbol{x},t)|^2$ and a charge density $-e\,|\psi(\boldsymbol{x},t)|^2$. This interpretation would imply that waves would have prevailed over particles in wave-particle duality.

However, quantum leaps are difficult to reconcile with a physical density interpretation for $|\psi(\boldsymbol{x},t)|^2$, and Schrödinger, Bohr, Born and Heisenberg developed a statistical interpretation of the wave function which is still the leading paradigm for quantum mechanics. Already in June 1926, the view began to emerge that the wave function $\psi(\boldsymbol{x},t)$ should be interpreted as a *probability density amplitude*[2] in

---

[2] E. Schrödinger, Annalen Phys. 386, 109 (1926), paragraph on pp. 134–135, sentences 2–4: "$\psi\overline{\psi}$ is a kind of *weight function* in the configuration space of the system. The *wave mechanical* configuration of the system is a *superposition* of many, strictly speaking of *all*, kinematically possible point mechanical configurations. Thereby each point mechanical configuration contributes with a certain *weight* to the true wave mechanical configuration, where the weight is just given by $\psi\overline{\psi}$." Of course, a weakness of this early hint at the probability interpretation is the vague reference to a "true wave mechanical configuration". A clearer formulation of this point was offered by Born essentially simultaneously, see the following reference. While there was (and always has been) agreement on the importance of a probabilistic interpretation, the question of the concept which underlies those probabilities was a contentious point between Schrödinger, who at that time may have preferred to advance a de Broglie type pilot wave interpretation, and Bohr and Born and their particle-wave complementarity interpretation. In the end the complementarity picture prevailed:

the sense that

$$P_V(t) = \int_V d^3\boldsymbol{x}\ |\psi(\boldsymbol{x},t)|^2 \tag{1.15}$$

is the probability to find a particle (or rather, an excitation of the vacuum with minimal energy mc^2 and certain other quantum numbers) in the volume V at time t. This equation implies that $|\psi(\boldsymbol{x},t)|^2$ is the *probability density* to find the particle in the location $\boldsymbol{x}$ at time t. The expectation value for the location of the particle at time t is then

$$\langle\boldsymbol{x}\rangle(t) = \int d^3\boldsymbol{x}\,\boldsymbol{x}\,|\psi(\boldsymbol{x},t)|^2\,, \tag{1.16}$$

where integrals without explicit limits are taken over the full range of the integration variable, i.e. here over all of $\mathbb{R}^3$. Many individual particle measurements will yield the location $\boldsymbol{x}$ with a frequency proportionally to $|\psi(\boldsymbol{x},t)|^2$, and averaging over the observations will yield the expectation value (1.16) with a variance e.g. for the x coordinate

$$\begin{aligned}\Delta x^2(t) &= \langle(x-\langle x\rangle)^2\rangle(t) = \langle x^2\rangle(t) - \langle x\rangle^2(t)\\ &= \int d^3\boldsymbol{x}\,x^2\,|\psi(\boldsymbol{x},t)|^2 - \left(\int d^3\boldsymbol{x}\,x\,|\psi(\boldsymbol{x},t)|^2\right)^2.\end{aligned}$$

This interpretation of the relation between the wave function and particle properties was essentially proposed by Max Born in an early paper on quantum mechanical scattering[3].

The Schrödinger equation (1.2) implies a local conservation law for probability

$$\frac{\partial}{\partial t}\,|\psi(\boldsymbol{x},t)|^2 + \nabla\cdot\boldsymbol{j}(\boldsymbol{x},t) = 0 \tag{1.17}$$

with the probability current density

$$\boldsymbol{j}(\boldsymbol{x},t) = \frac{\hbar}{2\mathrm{i}m}\Big(\psi^+(\boldsymbol{x},t)\cdot\nabla\psi(\boldsymbol{x},t) - \nabla\psi^+(\boldsymbol{x},t)\cdot\psi(\boldsymbol{x},t)\Big). \tag{1.18}$$

There are fundamental degrees of freedom with certain quantum numbers. These degrees of freedom are quantal excitations of the vacuum, and mathematically they are described by quantum fields. Depending on the way they are probed, they exhibit wavelike or corpuscular properties. Whether or not to denote these degrees of freedom as particles is a matter of convenience and tradition.

[3] M. Born, Z. Phys. 38, 803 (1926).

The conservation law (1.17) is important for consistency of the probability interpretation of Schrödinger theory. We assume that the integral

$$P(t) = \int d^3\boldsymbol{x}\ |\psi(\boldsymbol{x},t)|^2$$

over $\mathbb{R}^3$ converges. *A priori* this should yield a time-dependent function $P(t)$. However, equation (1.17) implies

$$\frac{d}{dt}P(t) = 0, \tag{1.19}$$

whence $P(t) \equiv P$ is a positive constant. This allows for rescaling $\psi(\boldsymbol{x},t) \to \psi(\boldsymbol{x},t)/\sqrt{P}$ such that the new wave function still satisfies equation (1.2) and yields a normalized integral

$$\int d^3\boldsymbol{x}\ |\psi(\boldsymbol{x},t)|^2 = 1. \tag{1.20}$$

This means that the probability to find the particle anywhere at time t is 1, as it should be. The equations (1.15) and (1.16) make sense only in conjunction with the normalization condition (1.20)

We can also substitute the Schrödinger equation or the local conservation law (1.17) into

$$\langle \boldsymbol{p}\rangle(t) = m\frac{d}{dt}\langle \boldsymbol{x}\rangle(t) = m\int d^3\boldsymbol{x}\,\boldsymbol{x}\frac{\partial}{\partial t}\,|\psi(\boldsymbol{x},t)|^2 \tag{1.21}$$

to find

$$\langle \boldsymbol{p}\rangle(t) = \int d^3\boldsymbol{x}\,\psi^+(\boldsymbol{x},t)\frac{\hbar}{\mathrm{i}}\nabla\psi(\boldsymbol{x},t). \tag{1.22}$$

Equations (1.16) and (1.22) tell us how to extract particle like properties from the wave function $\psi(\boldsymbol{x},t)$. At first sight, equation (1.22) does not seem to make a lot of intuitive sense. Why should the momentum of a particle be related to the gradient of its wave function? However, recall the Compton-de Broglie relation $p = h/\lambda$. Wave packets which are composed of shorter wavelength components oscillate more rapidly as a function of $\boldsymbol{x}$, and therefore have a larger average gradient. Equation (1.22) is therefore in agreement with a basic relation of wave-particle duality.

A related argument in favor of equation (1.22) arises from substitution of the Fourier transforms[4]

---

[4] Fourier transformation is reviewed in Section 2.1.

$$\psi(\boldsymbol{x},t) = \frac{1}{\sqrt{2\pi}^3}\int d^3\boldsymbol{k}\,\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x})\psi(\boldsymbol{k},t),$$

$$\psi^+(\boldsymbol{x},t) = \frac{1}{\sqrt{2\pi}^3}\int d^3\boldsymbol{k}\,\exp(-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x})\psi^+(\boldsymbol{k},t)$$

in equations (1.20) and (1.22). This yields

$$\int d^3\boldsymbol{k}\,|\psi(\boldsymbol{k},t)|^2 = 1$$

and

$$\langle\boldsymbol{p}\rangle(t) = \int d^3\boldsymbol{k}\,\hbar\boldsymbol{k}\,|\psi(\boldsymbol{k},t)|^2,$$

in perfect agreement with the Compton-de Broglie relation $\boldsymbol{p} = \hbar\boldsymbol{k}$. Apparently $|\psi(\boldsymbol{k},t)|^2$ is a probability density in $\boldsymbol{k}$ space in the sense that

$$P_{\tilde{V}}(t) = \int_{\tilde{V}} d^3\boldsymbol{k}\,|\psi(\boldsymbol{k},t)|^2$$

is the probability to find the particle with a wave vector $\boldsymbol{k}$ contained in a volume $\tilde{V}$ in $\boldsymbol{k}$ space.

We can also identify an expression for the energy of a particle which is described by a wave function $\psi(\boldsymbol{x},t)$. The Schrödinger equation (1.2) implies the conservation law

$$\frac{d}{dt}\int d^3\boldsymbol{x}\,\psi^+(\boldsymbol{x},t)\left(-\frac{\hbar^2}{2m}\Delta + V(\boldsymbol{x})\right)\psi(\boldsymbol{x},t) = 0. \tag{1.23}$$

Here it plays a role that we assumed time-independent potential[5]. In classical mechanics, the conservation law which appears for motion in a time-independent potential is energy conservation. Therefore, we expect that the expectation value for energy is given by

$$\langle E\rangle = \int d^3\boldsymbol{x}\,\psi^+(\boldsymbol{x},t)\left(-\frac{\hbar^2}{2m}\Delta + V(\boldsymbol{x})\right)\psi(\boldsymbol{x},t). \tag{1.24}$$

We will also rederive this at a more advanced level in Chapter 17. From the classical relation (1.12) between energy and momentum of a particle, we should also have

$$\langle E\rangle = \frac{\langle\boldsymbol{p}^2\rangle}{2m} + \langle V(\boldsymbol{x})\rangle. \tag{1.25}$$

---

[5] Examples of the Schrödinger equation with time-dependent potentials will be discussed in Chapter 13 and following chapters.

Comparison of equations (1.22) and (1.24) yields

$$\langle \boldsymbol{p}^2\rangle(t) = \int d^3\boldsymbol{x}\,\psi^+(\boldsymbol{x},t)(-\mathrm{i}\hbar\nabla)^2\psi(\boldsymbol{x},t),$$

such that calculation of expectation values of powers of momentum apparently amounts to corresponding powers of the differential operator $-\mathrm{i}\hbar\nabla$ acting on the wave function $\psi(\boldsymbol{x},t)$.

Maybe one of the most direct observational confirmations of the statistical interpretation of the wave function was the observation of single particle interference by Tonomura, Endo, Matsuda and Kawasaski[6] in 1988. Electrons are passing through a double slit with a time difference that makes it extremely unlikely that two electrons interfere during their passages through the slit. Behind the slit the electrons are observed with a scintillation screen or a camera. Each individual electron is observed to generate only a single dot on the screen. This is the behavior expected from a pointlike particle which is not spread over a physical density distribution. The first few electrons seem to generate a random pattern of dots. However, when more and more electrons hit the screen, their dots generate a collective pattern which exactly corresponds to a distribution $|\psi(\boldsymbol{x},t)|^2$ for double slit interference. This implies that $|\psi(x,y,z_0,t)|^2$ is indeed the probability density for an electron to hit the point $\{x,y\}$ on the screen which is located at z_0, but it is not the physical density of a spatially extended electron[7].

A recent three-slit experiment also confirmed the statistical interpretation of the wave function by proving that the interference patterns from many sequential single particle paths agree with the probability density interpretation of $|\psi(\boldsymbol{x},t)|^2$ for single slit diffraction, double-slit interference, and triple-slit interference[8].

1.8 Problems

1.1. Plot the emittance $e_{[0,\lambda]}(T)$ of our sun.

1.2. Suppose that the resolution of a particular monochromator scales with $1/f$, i.e. if the monochromator is set to a particular frequency f the product $fdf = df^2/2$ of frequency and bandwidth is constant. Furthermore, assume that the monochromator is coupled to a device which produces a signal proportional to the energy of the incident radiation. In the limit $df \to 0$, is the signal curve from this apparatus proportional to $e(f,T)$, $e(\lambda,T)$, $j(f,T)$ or $j(\lambda,T)$?

---

[6] A. Tonomura, J. Endo, T. Matsuda, T. Kawasaski, Amer. J. Phys. 57, 117 (1989).

[7] It has been argued that Bohmian mechanics can also explain the Tonomura experiment through a pilot wave interpretation of the wave function. However, Bohmian mechanics has other problems. We will briefly return to Bohmian mechanics in Problem 7.17.

[8] U. Sinha, C. Couteau, T. Jennewein, R. Laflamme, G. Weihs, Science 329, 418 (2010).

1.3. Suppose that the resolution of a particular monochromator scales with f, i.e. if the monochromator is set to a particular frequency f the fractional bandwidth df/f is constant. The monochromator is coupled to a device which produces a signal proportional to the energy of the incident radiation. The device is used for observation of a Planck spectrum. For which relation between frequency and temperature does this device yield maximal signal?

1.4. Derive the probability conservation law (1.17) from the Schrödinger equation. Hint: Multiply the Schrödinger equation with $\psi^+(\boldsymbol{x},t)$ and use also the complex conjugate equation.

1.5. We will often deal with quantum mechanics in d spatial dimensions. There are many motivations to go beyond the standard case $d = 3$. E.g. $d = 0$ is the number of spatial dimensions for an idealized quantum dot, $d = 1$ is often used for pedagogical purposes and also for idealized quantum wires or nanowires, and $d = 2$ is used for physics on surfaces and interfaces.

We consider a normalized wave function $\psi(\boldsymbol{x},t)$ in d dimensions. What are the SI units of the wave function? What are the SI units of the d-dimensional current density $\boldsymbol{j}$ for the wave function $\psi(\boldsymbol{x},t)$?

1.6. Derive equation (1.22) from (1.21).

1.7. Show that the Schrödinger equation (1.14) implies the conservation laws

$$\frac{d}{dt}\int d^3\boldsymbol{x}\,\psi^+(\boldsymbol{x},t)\left(-\frac{\hbar^2}{2m}\Delta + V(\boldsymbol{x})\right)^n\psi(\boldsymbol{x},t) = 0, \quad n \in \mathbb{N}_0. \tag{1.26}$$

Two particular cases of this equation appeared in Section 1.7. Which are those cases and what are the related conserved quantities?

Why is there usually not much interest in the infinitely many higher order conservation laws (1.26) for $n > 1$? Hint: Think about the classical interpretation of these conservation laws.

Why do the higher order conservation laws nevertheless matter in quantum mechanics? Hint: Equation (1.26) is generically different from the "similar" conservation law $d(\langle E\rangle^n)/dt = 0$. Is there an interesting implication of the two conservation laws for $n = 2$?

1.8. Equation (1.21) implies that the equation $\boldsymbol{p}(t) = md\boldsymbol{x}(t)/dt$ from non-relativistic classical mechanics is realized as an equation between expectation values in non-relativistic quantum mechanics. Show that Newton's law holds in the following sense in non-relativistic quantum mechanics (Ehrenfest's theorem),

$$\frac{d}{dt}\langle\boldsymbol{p}\rangle(t) = -\langle\nabla V(\boldsymbol{x})\rangle(t). \tag{1.27}$$