Part I

Atom–light interaction

1

The classical physics pathway

1.1 Introduction

While it might appear that the nineteenth-century physics presented in this chapter has no place in a topic as quantum mechanically oriented as atomic physics, this is simply not the case. The purpose of this first chapter is to try to convince the readers that the material learned in their early years of studying physics is not disjoint from modern topics, but in fact can provide a foundation for their further understanding. Other examples will occur later.

The reader may be a bit surprised to see that the results of the classical description turn out to be so close to the quantum mechanical results. Where there are significant disagreements between classical and quantum descriptions, it is necessary to explain why these occur. The correspondence principle requires that in the limit of large quantum numbers the complete quantum mechanical description must agree with the classical one. It is always better to need fewer of these explanations and to be able to treat physics as a coherent whole instead of a collection of topics.

The consequences of classical physics are intuitively familiar, and this is often most helpful in gaining deeper understanding. In fact, the approach taken in very many of the chapters in this book is to start with a purely classical description of a topic, and then transport it directly into the Schrödinger equation. Radiation from an accelerated charge, as treated here in the harmonic case, provides an ideal setting for such pedagogy. Even though classical mechanics is used in place of quantum mechanics, for the case of harmonic motion, the results are quite compatible.

The early history of atomic physics contains many topics that are well worth reading about, especially the experimental facilities. For example, there were no electric motors, wire was not readily available, and making even a crude vacuum was an experimental tour de force. Very many textbooks have discussions of these topics, and so they will not be presented here. But the reader is warned that certain oft-repeated modern descriptions are simply wrong.

Perhaps the most important notion to be gained from this chapter is that the classical description of a harmonically bound electron provides quite accurate results about the interaction between atoms and light. Of course, the utility of this description is limited because the classical harmonic oscillator has no internal structure, is infinitely deep, and has a continuous energy spectrum. Atoms do not radiate or interact with waves that have too low a frequency, and they will ionize if exposed to too high a frequency. Still, this chapter will show that the classical description gives very good answers for damping rate of the excited state, the cross-section for light scattering, and the emitted spectrum of the light.

1.2 Damped harmonic oscillator

1.2.1 Introduction

The fact that atoms survive quite violent collisions surprisingly effectively suggests that disturbances to the electrons' motion are countered by restoring forces, and the lowest-order term in an expansion of such a force is linear. Thus $\vec{F} = -k(\vec{r} - \vec{r}_0)$, where $\vec{r}_0$ corresponds to a stable orbit about an infinitely massive nucleus. In this approximation, the equation of motion in one dimension is $\ddot{x} + \omega_0^2 x = 0$, where $\omega_0^2 = k/m$.

An electron in such an orbit radiates because it is an accelerating charge, and the radiation field is calculated in the appendix to this chapter. The energy flux (W/m^2) of the radiated field is given by the Poynting vector, $\vec{S} = \vec{\mathcal{E}} \times \vec{\mathcal{H}}$. Conservation of energy requires that the radiated energy be lost from the motion of the oscillator, and the result is equivalent to a damping force $\vec{F} = -(e^2\omega_0^2/6\pi\varepsilon_0 c^3)\vec{v} \equiv -\beta\vec{v}$ (also shown in App. 1.A).

The equation of motion for a damped harmonic oscillator is $\ddot{x} + \gamma\dot{x} + \omega_0^2 x = 0$ with solution

$$x = x_0 e^{-\gamma t/2}\cos(\omega_0' t + \phi), \quad \omega_0' = \sqrt{\omega_0^2 - \frac{\gamma^2}{4}}, \quad \gamma = \frac{e^2\omega_0^2}{6\pi\varepsilon_0 m c^3}, \tag{1.1}$$

where $\gamma \equiv \beta/m$ comes from the damping coefficient following Eq. (1.17) in App. 1.A. This solution is plotted in Fig. 1.1a.

For optical transitions (visible light) $\gamma \approx 5 \times 10^8$ rad/s. This value of γ corresponds to a lifetime $\tau \equiv 1/\gamma \approx 2$ ns and is typical of the value of atomic excited state lifetimes. It is most surprising that such a completely classical consideration results in an answer that matches laboratory measurements. Furthermore, for $\gamma \ll \omega_0$ the frequency shift from Eq. (1.1) is approximately $\gamma^2/8\omega_0 \sim 2$ rad/s, which is negligibly small compared with $\omega_0 \sim 10^{16}$ rad/s and even compared with $\gamma \sim 10^9$ rad/s, so it is not even apparent in Fig. 1.1b. In the following ω_0' will be replaced by ω_0.

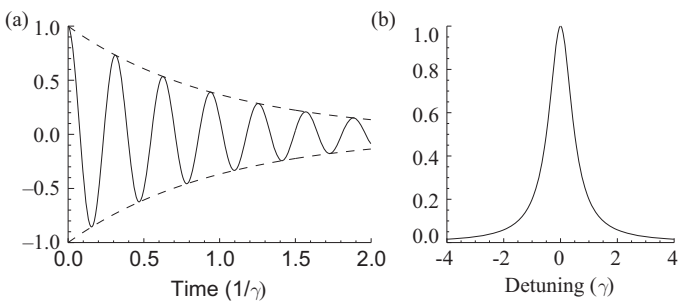

Figure 1.1 (a) Amplitude of a damped harmonic oscillator in the Lorentz model, where the motion is damped because of the acceleration of the electron. (b) Spectrum of the emitted radiation, where the width is inversely proportional to the lifetime.

The quantity $Q \equiv \omega_0/\gamma = 6\pi\varepsilon_0 mc^3/e^2\omega_0$ is the number of cycles during one damping time τ, which is called the quality factor. For optical transitions $Q \approx 2 \times 10^7$. The high Q domain extends all the way up to frequencies $3mc^2/2\hbar$ which includes the ultraviolet, X-ray, and gamma-ray regions, and ends where $E \sim 50\,\text{MeV}$.

1.2.2 Spectrum of emitted radiation

The spectrum of the emitted light can be found by calculating the Fourier transform of the emitted radiation. The emitted field for $t > 0$ is

$$\vec{\mathcal{E}}_{\text{rad}}(t) \equiv \vec{\mathcal{E}}^{(0)}_{\text{rad}}\, e^{-\gamma t/2} \cos(\omega_0 t + \phi) \tag{1.2}$$

where $\vec{\mathcal{E}}^{(0)}_{\text{rad}} \equiv e\omega_0^2 x_0/4\pi\varepsilon_0 c^2 r$ using Eq. (1.13) in Appendix 1.A and $\ddot{x} = -{\omega_0}^2 x$ for harmonic motion. The resulting Fourier transform is

$$\begin{aligned}
\vec{\mathcal{E}}_{\text{rad}}(\omega) &= \frac{\vec{\mathcal{E}}^{(0)}_{\text{rad}}}{2\pi} \int_0^\infty e^{-\gamma t/2} \cos(\omega_0 t + \phi) e^{-i\omega t} \mathrm{d}t \\
&= \frac{\vec{\mathcal{E}}^{(0)}_{\text{rad}}}{2\pi} \int_0^\infty e^{-\gamma t/2} \frac{1}{2} \left[e^{i(\omega_0 t + \phi)} + e^{-i(\omega_0 t + \phi)} \right] e^{-i\omega t} \mathrm{d}t \\
&= \frac{\vec{\mathcal{E}}^{(0)}_{\text{rad}}}{4\pi} \left[\frac{e^{i\phi}}{\gamma/2 + i(\omega - \omega_0)} + \frac{e^{-i\phi}}{\gamma/2 + i(\omega + \omega_0)} \right].
\end{aligned} \tag{1.3}$$

Since $\omega_0 \gg \gamma$, the second term in Eq. (1.3) can be dropped, and the energy spectrum in the vicinity of $\omega \sim \omega_0$ is described by the Lorentzian

$$\left| \vec{\mathcal{E}}_{\text{rad}}(\omega) \right|^2 = \frac{1}{16\pi^2} \left| \vec{\mathcal{E}}^{(0)}_{\text{rad}} \right|^2 \left[\frac{1}{\gamma^2/4 + (\omega - \omega_0)^2} \right], \tag{1.4}$$

which is plotted in Fig. 1.1b.

1.3 The damped driven oscillator

1.3.1 Radiated power

For a driven oscillating charge, the amplitude will be constant after the initial transients die out, so the radiation will be emitted at a constant rate. The frequency eventually settles to the driving frequency (not the natural frequency). Since the oscillator is constantly radiating energy, it can only be that the energy is taken from the driving field. Conservation of energy allows the calculation of the rate of re-radiation starting with the work done by the driving force $\int \vec{F} \cdot \vec{v}$ averaged over one cycle of the oscillation.

For a driving field $\vec{\mathcal{E}} = \vec{\mathcal{E}}_0 \cos(\omega t)$ the resulting motion is $x = x_0 \cos(\omega t + \phi)$ with ω the driving frequency. The velocity $\dot{x}$ is calculated from the derivative of this motion, and for such a driving force

$$x_0 = \frac{e\,|\,\vec{\mathcal{E}}_0\,|\,/m}{\sqrt{(\omega_0^2 - \omega^2)^2 + \gamma^2\omega^2}} \quad \text{and} \quad \tan\phi = \frac{\gamma\omega}{\omega^2 - \omega_0^2}. \tag{1.5}$$

The average scattered power must equal the work done by the driving force, and can be found by integrating over one period $\Delta t = 2\pi/\omega$:

$$\begin{aligned} \overline{P}_{\text{rad}} &= \frac{1}{\Delta t}\int_t^{t+\Delta t} \vec{F}\cdot\vec{v}\,\mathrm{d}t \\ &= \frac{\omega e\,|\,\vec{\mathcal{E}}_0\,|\,x_0}{\Delta t}\int_t^{t+\Delta t} \sin(\omega t+\phi)\cos(\omega t)\,\mathrm{d}t \\ &= m\omega^2 x_0^2(\gamma/2) = \frac{e^2\mathcal{E}^2}{2m\gamma}, \end{aligned} \tag{1.6}$$

when Eq. (1.5) is evaluated at the resonance condition $\omega = \omega_0$.

1.3.2 Scattering of radiation

By conservation of energy, the rate of work done by the force exerted on the electron by the driving field must equal the radiated power. But knowing the fields allows calculation of the intensity, which is the power per unit area of the incoming light, not its total power. In order to relate scattered power to this incident intensity, there is need for an "effective area" or cross-section σ for the atom that characterizes its effective size for light scattering so that the scattered light power equals the incident light intensity times σ. Using Eq. (1.6) gives

$$\sigma = \frac{e^2\,|\,\vec{\mathcal{E}}_0\,|^2/2m\gamma}{\varepsilon_0 c\,|\,\vec{\mathcal{E}}_0\,|^2/2} = \frac{e^2}{\varepsilon_0 mc\gamma} = \frac{6\pi c^2}{\omega_0^2} = \frac{3\lambda^2}{2\pi}. \tag{1.7}$$

where the last steps come from using Eq. (1.1) for γ. Note that the incident light intensity has equal contributions from both the electric and magnetic fields, $\varepsilon_0 c\mathcal{E}^2/2 + c\mathcal{B}^2/2\mu_0$, and each of these is proportional to $\cos^2 \omega t$, whose time average is $^1/_2$. Thus the intensity is $\varepsilon_0 c\mathcal{E}_0^2/2$.

This is a most interesting and curious result. The resonant cross-section depends only on the wavelength of the incident light. It is completely independent of the type of atom and the properties of the electron. Not only that, it is huge. It is 10,000 times larger than the size of the atom itself.

1.4 The Bohr model

1.4.1 Introduction

In the nineteenth century Balmer had already noticed certain regularities in spectrum of electrical discharges of hydrogen gas. He was interested in number theory and its relation to natural phenomena, and studied the measured values of the wavelengths. He found that the wavelengths of the hydrogen spectrum satisfied

$$\nu_n = \frac{c}{\lambda_n} \propto \left(1 - \frac{4}{n^2}\right), \tag{1.8}$$

where $n \geq 3$ is an integer. In studies that were unrelated at the time, Planck had solved the long-standing problem of the spectrum of light from hot objects in 1900. He did this by assuming, with no physical basis whatsoever, that the light was emitted from oscillators in energy packets that had to be discrete, and the discretization was in terms of the light frequency ν. His now-famous formula is $E = h\nu$ where the constant $h = 6.626 \times 10^{-34}$ Js now bears his name.

At that time, the prevailing theory of atomic structure was Thomson's "plum pudding" model: tiny negative particles embedded in a uniform sea of positive charge that had the atomic size. Thomson's idea was replaced after Rutherford's experiments in 1908 that could only be explained by the "solar system" model still currently in use. However, the "solar system" model conflicted directly with Maxwell's electromagnetic theory that underlies Sec. 1.2. It requires that the orbiting electrons would necessarily emit radiation, because of their acceleration, until the atom collapsed.

Finally, in 1913 Bohr proposed his model. He supposed the "solar system" model but with two additional postulates that were outside the realm of classical physics. One was that the electrons in certain special discrete orbits do not emit classical radiation, and the other was that when they make a transition between discrete orbits whose energy differs by ΔE, they emit radiation according to Planck's formula $\Delta E = h\nu$. A more detailed description is in Sec. 1.4.2. He found that found the measured wavelengths agreed with his calculations to very high precision. In

many texts it is asserted that Bohr quantized the orbital angular momentum, but this is simply not true [2, 3].

1.4.2 Energy levels

In his 1913 paper [2] (see also Ref. [3]) Bohr addressed the problem posed by the Rutherford model with two postulates. First, in spite of the tenets of classical mechanics and electrodynamics, there were only discrete allowed orbits of the Kepler motion of electrons in the Coulomb field of a massive nucleus, and these were stable against radiation. Second, transitions between these allowed orbits conserved energy by emitting or absorbing radiation whose frequency is given by the Planck condition $E = h\nu$. This was a radical choice because classical electrodynamics requires that the radiation be at the harmonic frequencies of the orbital motion, but classical electrodynamics had to be discarded for the quantum theory anyway because of the postulate of orbital stability.

Newtonian mechanics for a circular orbit in the Coulomb field requires

$$F = \frac{mv^2}{r} = \frac{e^2}{4\pi\varepsilon_0 r^2}. \tag{1.9}$$

The total energy of such an orbit is given by the sum of kinetic and potential energy terms, and Eq. (1.9) leads to

$$E = T + V = \frac{mv^2}{2} - \frac{e^2}{4\pi\varepsilon_0 r} = \frac{1}{4\pi\varepsilon_0}\left[\frac{e^2}{2r} - \frac{e^2}{r}\right] = -\frac{e^2}{8\pi\varepsilon_0 r}. \tag{1.10}$$

The ratio of kinetic to potential energy is $1/2$, which is an example of the virial theorem. The total energy is negative because these are the bound states of the atoms.

Bohr adapted Balmer's formula for the measured frequencies in the spectrum of atomic hydrogen and the Ritz combination principle to find that the energies of these discrete orbits were given by $E_n = -R_\infty/n^2$ where n is an integer and

$$R_\infty \equiv \frac{e^2}{8\pi\varepsilon_0 a_0} \tag{1.11}$$

from Eq. (1.10). The length a_0 is characteristic of atomic dimensions. He combined this formula for E_n with Eq. (1.10) to find that the size of these fixed orbits was $r_n = n^2e^2/8\pi\varepsilon_0 R_\infty \equiv n^2 a_0$.

He then reasoned that orbits with very high values of n should correspond to classical motion (the embryo of his later correspondence principle) so that the frequency of the emitted radiation should be the same as the orbital frequency ω_{rot}. Equation (1.9) gives $\omega_{\text{rot}} = v/r = \sqrt{e^2/(4\pi\varepsilon_0 m r^3)}$ and the energy separation between adjacent high n states is $\Delta E = -(2R_\infty/n^3)\Delta n$ with $\Delta n = 1$. Then setting

$\hbar\omega_{\rm rot} = 2R_\infty/n^3$ and using $r_n = n^2 a_0$ gives $a_0 = 4\pi\varepsilon_0\hbar^2/me^2 = 0.529 \times 10^{-10}$ m, so the total energy is

$$E = -\frac{\hbar^2}{2ma_0^2 n^2} \equiv -\frac{R_\infty}{n^2}. \tag{1.12}$$

The Rydberg constant $R_\infty \approx 13.6$ eV sets the scale for all energies of atomic phenomena. These results are simpler to reach by quantizing orbital angular momentum as $mvr = n\hbar$ but, in spite of statements in many textbooks, this was *not* the path Bohr followed.

1.5 de Broglie waves

In 1923 de Broglie [4] suggested matter waves and claimed that they must undergo constructive interference in atomic orbits in order to have the stationary states of the Bohr model. The length of the orbit must be an integral number of de Broglie wavelengths as shown in Fig. 1.2, and since their wavelength is $\lambda = h/p$, the constructive interference condition is $2\pi r = n\lambda$. This condition is the same as quantizing the angular momentum of the orbit yielding $mvr = n\hbar$ and many authors claim that this is the derivation used by Bohr. It is not. In fact, it is not even sensible because the orbital angular momentum quantum number ℓ is quite different from the principal quantum number n.

Sometime later Debye asked the question "What is the wave equation for a de Broglie matter wave?" There are wave equations for acoustic, water, and electromagnetic waves, so there should be one for matter waves. Later, Schrödinger proposed the one that bears his name, and it became the basis of modern quantum mechanics because of its success. The first major accomplishment was the

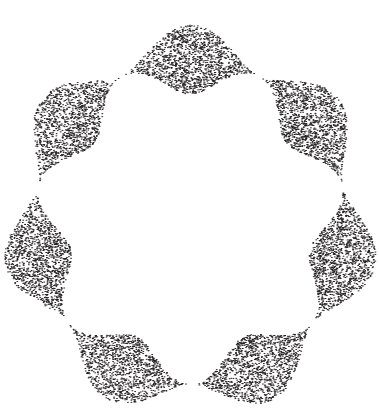

Figure 1.2 Artist sketch of the standing de Broglie waves in a circular orbit of an H-atom with seven nodes.

calculation of Bohr's formula for the energy levels of the hydrogen atom starting from its time-independent form.

Appendices

1.A Damping force on an accelerating charge

An electron bound to a nucleus in a Kepler-like orbit can be represented by linear harmonic oscillators. Since it is an accelerating charge it should radiate an electric field as illustrated in Fig. 1.3 (see Ref. [5], section 14.2). The electric and magnetic fields at position $\vec{r}$ ($\hat{r}$ is a unit vector in the $\vec{r}$ direction) are given by

$$\vec{\mathcal{E}} = \frac{e}{4\pi\varepsilon_0 c^2}\left[\frac{\hat{r}\times(\hat{r}\times\ddot{\vec{x}})}{r}\right]_{t-r/c}, \quad \vec{\mathcal{H}} = \sqrt{\frac{\varepsilon_0}{\mu_0}}(\hat{r}\times\vec{\mathcal{E}}). \tag{1.13}$$

Note that $\vec{\mathcal{E}} \perp \hat{r}$ and also that $\vec{\mathcal{E}} \not\perp \ddot{\vec{x}}$.

The energy of the radiated field given by the Poynting vector $\vec{\mathcal{S}} = \vec{\mathcal{E}}\times\vec{\mathcal{H}}$ must be lost from the oscillating charge, and this loss implies a "radiative" force that does work on the charge. To calculate this force, start with the rate of energy loss, which is the same as the rate of radiated energy. Begin by calculating $\vec{\mathcal{S}}$ from the fields:

$$\begin{aligned}\vec{\mathcal{S}} &= \sqrt{\frac{\varepsilon_0}{\mu_0}}\left|\vec{\mathcal{E}}\right|^2\hat{r} = \frac{e^2}{16\pi^2\varepsilon_0^2 c^4}\frac{|\hat{r}\times\ddot{\vec{x}}|^2}{r^2}\sqrt{\frac{\varepsilon_0}{\mu_0}}\,\hat{r}\\ &= \frac{e^2}{4\pi\varepsilon_0}\frac{1}{4\pi r^2}\frac{(\ddot{x}\sin\theta)^2}{c^3}\,\hat{r},\end{aligned} \tag{1.14}$$

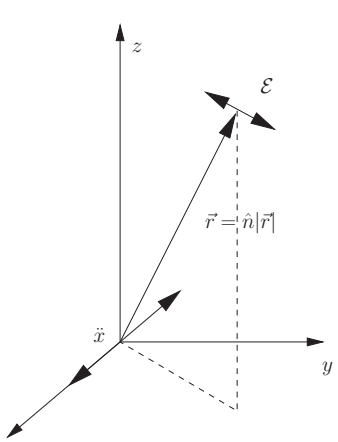

Figure 1.3 The electric field $\vec{\mathcal{E}}$ at location $\vec{r}$ from a charge accelerating along the x-axis at the origin with acceleration $\ddot{x}$.

where θ is the angle between $\hat{r}$ and $\ddot{\vec{x}}$, and $|\hat{r}\times(\hat{r}\times\ddot{\vec{x}})|$ simplifies to $|\hat{r}\times\ddot{\vec{x}}|$ because $\hat{r}\perp(\hat{r}\times\ddot{\vec{x}})$. The total radiated power at a given instant of the oscillator is then the integral of $\vec{\mathcal{S}}$ over a closed surface. For a sphere, the area element $\mathrm{d}A = (r\mathrm{d}\theta)(r\sin\theta\mathrm{d}\phi) = r^2\sin\theta\mathrm{d}\theta\mathrm{d}\phi$ so the total radiated power at any instant is

$$\oiint \vec{\mathcal{S}}\cdot\mathrm{d}\vec{A} = \frac{e^2\ddot{x}^2}{16\pi^2\varepsilon_0 c^3}\int_0^{2\pi}\mathrm{d}\phi\int_0^{\pi}\mathrm{d}\theta\sin^3\theta = \frac{e^2\ddot{x}^2}{6\pi\varepsilon_0 c^3}, \tag{1.15}$$

where the integral over ϕ yields 2π and the integral over θ becomes $4/3$. Since $\ddot{x}$ is time-dependent, it is necessary to average Eq. (1.15) over one cycle. Then

$$\left\langle \ddot{x}^2\right\rangle = \frac{1}{\Delta t}\int_t^{t+\Delta t}\ddot{x}^2\mathrm{d}t' = \frac{1}{\Delta t}\,\ddot{x}\dot{x}\Big|_t^{t+\Delta t} - \frac{1}{\Delta t}\int_t^{t+\Delta t}\dddot{x}\dot{x}\mathrm{d}t', \tag{1.16}$$

where $\Delta t = 2\pi/\omega_0$. Because $\ddot{x}\dot{x}$ is periodic, the average $\langle\ddot{x}\dot{x}\rangle = 0$. The energy lost by the oscillator is the total radiated power and is given by

$$P = \left\langle \oiint \vec{\mathcal{S}}\cdot d\vec{A}\right\rangle = -\frac{e^2}{6\pi\varepsilon_0 c^3}\frac{1}{\Delta t}\int_t^{t+\Delta t}\dddot{x}\dot{x}\mathrm{d}t' = -\frac{1}{\Delta t}\int_t^{t+\Delta t}\vec{F}\cdot\vec{v}\,\mathrm{d}t' \tag{1.17}$$

where the $(-)$ sign arises because it is an energy loss. Using $\dot{\vec{x}} = \vec{v}$, and identifying the terms in Eq. (1.17), leads to $\vec{F} = -(e^2\omega_0^2/6\pi\varepsilon_0 c^3)\vec{v}$ since $\dddot{x} = -\omega_0^2\dot{x}$ for harmonic motion. Notice that $\vec{F}\propto -\vec{v}$, as is the usual case for a damping force. Such a dependence is found in very many common physical systems, for example air resistance at low Reynold's number.

1.B Hanle effect

Suppose a harmonically bound electron is oscillating along the y-axis, for example excited by the electric field of linearly polarized light incident along the x-axis and polarized in the y-direction as shown in Fig. 1.4. The doughnut-shaped radiation pattern expected from Eq. (1.13) is shown at the origin. It clearly shows that there is no power radiated in the y-direction because that is the direction of the acceleration, and also that the light radiated in any direction in the $x-z$ plane is linearly polarized parallel to the y-axis.

Now suppose a magnetic field $\vec{\mathcal{B}} = \hat{z}\mathcal{B}$ is applied in the z-direction. Since there is a velocity v_y there is a force F_x causing the motion to deviate from the y-axis. In fact, the Lorentz force $e(\vec{v}\times\vec{\mathcal{B}})$ combined with the harmonic force produces a complicated motion in the $x-y$ plane and the result is radiation emitted in all directions. A characteristic frequency of this motion is $\omega_\mathrm{L} = v/r = e|\vec{\mathcal{B}}|/m$. However, the oscillator decays at a rate given by Eq. (1.1) and so the instantaneous y-directed power P_y is calculated from its electric field using $|\vec{\mathcal{E}}|^2 = e^{-\gamma t}\sin^2\omega_\mathrm{L}t$ and its average value is given by