

# Statistical Physics

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# Chapter 1

## Microscopic description of matter

### 1.1 Introduction

Statistical physics provides the *microscopic foundation* of thermodynamics. One of the goals of statistical physics is to calculate thermodynamic functions and fluctuations in the observable quantities from a knowledge of the microscopic properties of the system. It is therefore important to know something about the microscopic description of matter.

The results of many careful and quantitative experiments have led to the discovery of fundamental laws of nature, which seem to be universally valid. The number of basic physical laws is surprisingly small. The most prominent are Newton's law (later generalised by Einstein) for the dynamics of massive particles, Maxwell's equations for the dynamics of the electromagnetic field, and the Schrödinger equation for the dynamics of very small particles. We assume the reader is familiar with these fields; this chapter contains a brief recapitulation of classical and quantum mechanics.

### 1.2 Classical mechanics

#### 1.2.1 Equations of motion

When dealing with classical mechanics we assume that various positions in space are related to each other according to Euclidean geometry. So we know about straight lines, about parallel lines, perpendicular lines, etc.

According to Newton any particle that is sufficiently isolated from the rest of the world will move along a straight line with constant velocity. Only when the outside world interacts with the particle will it change its motion. For simplicity let us first restrict ourselves to changes of velocity, not accompanied by any change of direction of the motion. The position of the particle may then be described by one

coordinate, say  $x$ . The interaction with the outside world results in a change of the velocity  $\dot{x} = dx/dt$  according to

$$m \frac{d\dot{x}}{dt} = F. \quad (1.1)$$

$F$  is called the force exerted by the outside world on the particle. It is determined by the properties of the outside world, and may depend on  $x$ ,  $\dot{x}$ , and  $t$ . The mass  $m$  is a property of the particle on which the force is exerted. Eq. (1.1) is called Newton's equation of motion. Being a second order differential equation it requires an initial position  $x(0) = x_0$  and an initial velocity  $\dot{x}(0) = v_0$  as additional input in order to fully determine the position of the particle at all times. A simple example occurs when the particle is connected to the origin by means of a spring, such that the force is given by

$$F = -kx. \quad (1.2)$$

The equation of motion of this so-called harmonic oscillator reads

$$m \frac{d^2x}{dt^2} = -kx, \quad (1.3)$$

which has a solution

$$x(t) = a \sin\left(\sqrt{k/m}t\right) + b \cos\left(\sqrt{k/m}t\right). \quad (1.4)$$

This solution has two unknown coefficients, which are fixed by the initial conditions

$$\begin{aligned} x_0 &= b \\ v_0 &= a\sqrt{k/m}. \end{aligned}$$

Introducing the angular frequency  $\omega = \sqrt{k/m}$  we obtain

$$x(t) = \frac{v_0}{\omega} \sin(\omega t) + x_0 \cos(\omega t). \quad (1.5)$$

This fully determines  $x$  at all times  $t$ .

In the more general case not only the speed of a particle may be changed by its surroundings, but also the direction of its motion. In that case the particle moves in three dimensions and we must describe its position by means of a vector  $\mathbf{r} = (x, y, z)$  composed of the displacements from some origin in three mutually orthogonal directions.<sup>1</sup> The equations of motion then read

$$m \frac{d\mathbf{\dot{r}}}{dt} = \mathbf{F}, \quad (1.6)$$

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<sup>1</sup>Note that here and in the following vectors quantities are denoted in **boldface**, whereas their lengths appear in normal face.



where again a dot over a symbol denotes differentiation with respect to  $t$ , i.e.  $\dot{\mathbf{r}} = (dx/dt, dy/dt, dz/dt)$ .  $\mathbf{F}$  is the force acting on the particle, also composed of three numbers:  $\mathbf{F} = (F_x, F_y, F_z)$ . In case we study a system containing  $N$  particles, we have

$$m_i \frac{d\dot{\mathbf{r}}_i}{dt} = \mathbf{F}_i \quad (i = 1, \dots, N). \quad (1.7)$$

### 1.2.2 Example: classical treatment of two-atomic molecule

As an example we treat a system containing two particles, exerting forces on each other according to

$$\mathbf{F}_1 = -k(r - r_0) \frac{\mathbf{r}}{r} \quad (1.8)$$

$$\mathbf{F}_2 = k(r - r_0) \frac{\mathbf{r}}{r}, \quad (1.9)$$

with

$$\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2 \quad (1.10)$$

$$r = \sqrt{\mathbf{r} \cdot \mathbf{r}} \quad (1.11)$$

$$\mathbf{r} \cdot \mathbf{r} = r_x^2 + r_y^2 + r_z^2, \quad (1.12)$$

where  $r_x$ ,  $r_y$ , and  $r_z$  are the three components of  $\mathbf{r}$ . (In Problem 1-1 you are asked to make a drawing of this situation.) We assume that no further forces act on both particles. This system may be thought of as representing a two-atomic molecule. In order to analyse the motions of the two particles it is profitable to replace the unknown vectors  $\mathbf{r}_1$  and  $\mathbf{r}_2$  by two independent linear combinations:

$$\mathbf{R} = \frac{1}{m_1 + m_2} (m_1 \mathbf{r}_1 + m_2 \mathbf{r}_2) \quad (1.13)$$

$$\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2. \quad (1.14)$$

If we are able to calculate  $\mathbf{R}(t)$  and  $\mathbf{r}(t)$ , we automatically have  $\mathbf{r}_1(t)$  and  $\mathbf{r}_2(t)$  according to

$$\mathbf{r}_1(t) = \mathbf{R}(t) + \frac{m_2}{m_1 + m_2} \mathbf{r}(t) \quad (1.15)$$

$$\mathbf{r}_2(t) = \mathbf{R}(t) - \frac{m_1}{m_1 + m_2} \mathbf{r}(t). \quad (1.16)$$

Differentiating  $\mathbf{R}$  and  $\mathbf{r}$  twice with respect to time and using Eqs. (1.7) - (1.14) we obtain

$$M \frac{d\dot{\mathbf{R}}}{dt} = \mathbf{0} \quad (1.17)$$

$$\mu \frac{d\dot{\mathbf{r}}}{dt} = -k(r - r_0) \frac{\mathbf{r}}{r}, \quad (1.18)$$

where  $M = m_1 + m_2$  is the total mass and  $\mu = m_1 m_2 / (m_1 + m_2)$  is the so-called reduced mass. In Problem 1-2 you are asked to prove this.

We now understand why it is convenient to replace  $\mathbf{r}_1$  and  $\mathbf{r}_2$  by  $\mathbf{R}$  and  $\mathbf{r}$ . The vector  $\mathbf{R}$ , pointing at the centre of mass of the two particles, according to Eq. (1.17) is not influenced by any force and performs a rectilinear motion given by

$$\mathbf{R}(t) = \mathbf{R}_0 + \mathbf{V}_0 t, \quad (1.19)$$

where  $\mathbf{R}_0$  and  $\mathbf{V}_0$  are the initial position and initial velocity of the center of mass.

Several methods exist to arrive at a solution of the equation of motion of the connecting vector  $\mathbf{r}$ , Eq. (1.18). We present one of them. First, notice that during a small time interval  $\Delta t$  the connecting vector changes from  $\mathbf{r}(t)$  to  $\mathbf{r}(t) + \dot{\mathbf{r}}(t)\Delta t$ . Similarly the corresponding velocity changes from  $\dot{\mathbf{r}}(t)$  to  $\dot{\mathbf{r}}(t) + \ddot{\mathbf{r}}(t)\Delta t$ . According to Eq. (1.18) the latter vector is in the plane spanned by  $\mathbf{r}(t)$  and  $\dot{\mathbf{r}}(t)$ . So both  $\mathbf{r}(t + \Delta t)$  and  $\dot{\mathbf{r}}(t + \Delta t)$  are in the plane spanned by  $\mathbf{r}(t)$  and  $\dot{\mathbf{r}}(t)$ . Repeating the argument we conclude that  $\mathbf{r}(t)$  and  $\dot{\mathbf{r}}(t)$  are in the plane spanned by  $\mathbf{r}_0$  and  $\mathbf{v}_0$  at all times  $t$ . This means that  $\mathbf{r}(t) \times \dot{\mathbf{r}}(t)$  has a constant direction at all times. Let us check if it changes its length, i.e. if it changes at all, with time (Problem 1-3):

$$\frac{d}{dt} (\mathbf{r} \times \dot{\mathbf{r}}) = \dot{\mathbf{r}} \times \dot{\mathbf{r}} + \mathbf{r} \times \ddot{\mathbf{r}} = 0. \quad (1.20)$$

We conclude that  $\mathbf{r} \times \dot{\mathbf{r}}$  is a constant vector

$$\mathbf{r} \times \dot{\mathbf{r}} = \frac{\mathbf{l}}{\mu}. \quad (1.21)$$

The constant  $1/\mu$  is introduced only to comply with general conventions (where  $\mathbf{l}$  in Eq. (1.21) is referred to as the *angular momentum*). Since both  $\mathbf{r}$  and  $\dot{\mathbf{r}}$  are in the plane perpendicular to  $\mathbf{l}$  we may write

$$\dot{\mathbf{r}} = \alpha \mathbf{r} + \beta \mathbf{r} \times \mathbf{l}. \quad (1.22)$$

Since  $\mathbf{r} \times \mathbf{l}$  is perpendicular to  $\mathbf{r}$  it will not change the length of  $\mathbf{r}$ . So the time derivative  $\dot{r}$  must be determined by  $\alpha$ . Indeed,

$$\alpha = \frac{1}{r^2} \dot{\mathbf{r}} \cdot \mathbf{r} = \frac{1}{2r^2} \frac{d}{dt} \mathbf{r} \cdot \mathbf{r} = \frac{1}{2r^2} \frac{d}{dt} r^2 = \frac{\dot{r}}{r}. \quad (1.23)$$

Moreover, introducing  $\dot{\mathbf{r}}$  from Eq. (1.22) into Eq. (1.23) we obtain

$$\beta \mathbf{r} \times (\mathbf{r} \times \mathbf{l}) = \frac{\mathbf{l}}{\mu}. \quad (1.24)$$

We evaluate the triple product at the left hand side using the general equation (Problem 1-4)

$$\mathbf{a} \times (\mathbf{b} \times \mathbf{c}) = (\mathbf{a} \cdot \mathbf{c}) \mathbf{b} - (\mathbf{a} \cdot \mathbf{b}) \mathbf{c}, \quad (1.25)$$

obtaining

$$-\beta r^2 \mathbf{l} = \frac{\mathbf{l}}{\mu}. \quad (1.26)$$

Introducing  $\alpha$  and  $\beta$  just found into Eq. (1.22) we get

$$\dot{\mathbf{r}} = \frac{\dot{r}}{r} \mathbf{r} - \frac{1}{\mu r^2} \mathbf{r} \times \mathbf{l}. \quad (1.27)$$

We now solve Eq. (1.18). In our new notation this reads

$$\left\{ \frac{\ddot{r}}{r} - \left( \frac{\dot{r}}{r} \right)^2 \right\} \mathbf{r} + \frac{\dot{r}}{r} \dot{\mathbf{r}} + \frac{2\dot{r}}{\mu r^3} \mathbf{r} \times \mathbf{l} - \frac{1}{\mu r^2} \dot{\mathbf{r}} \times \mathbf{l} = -\frac{\omega^2}{r} (r - r_0) \mathbf{r}, \quad (1.28)$$

where  $\omega = \sqrt{k/\mu}$ . Introducing  $\dot{\mathbf{r}}$  from Eq. (1.27) and using  $(\mathbf{r} \times \mathbf{l}) \times \mathbf{l} = -\mathbf{l} \times (\mathbf{r} \times \mathbf{l}) = -l^2 \mathbf{r}$  we obtain

$$\left\{ \frac{\ddot{r}}{r} - \frac{l^2}{\mu^2 r^4} \right\} \mathbf{r} = -\frac{\omega^2}{r} (r - r_0) \mathbf{r}, \quad (1.29)$$

holding true at all times  $t$ . So finally we end up with a second order differential equation for  $r$ :

$$\ddot{r} = -\omega^2 (r - r_0) + \frac{l^2}{\mu^2 r^3}. \quad (1.30)$$

Note that this may be converted to an energy conservation equation (Problem 1-5).

Suppose  $\omega$  is large. In this case  $r$  is not very different from  $r_0$  at all times  $t$ . We therefore write  $r = r_0 + y$ . Then:

$$\ddot{y} = -\omega^2 y + \frac{l^2}{\mu^2 r_0^3} - \frac{3l^2}{\mu^2 r_0^4} y, \quad (1.31)$$

where we have used  $1/r^3 \approx 1/r_0^3 - 3y/r_0^4$ . All this is equivalent to

$$r = r_0 + \frac{l^2 r_0}{\mu^2 \omega^2 r_0^4 + 3l^2} + z \quad (1.32)$$

$$\ddot{z} = -\omega_{eff}^2 z \quad (1.33)$$

$$\omega_{eff} = \sqrt{\omega^2 + \frac{3l^2}{\mu^2 r_0^4}}. \quad (1.34)$$

Let us first discuss this result for the case when  $l = 0$ . The connecting vector  $\mathbf{r}$  does not change direction and only changes its length,  $\dot{\mathbf{r}} = \dot{r} \mathbf{r}/r$  according to Eq. (1.27). Its length still oscillates with frequency  $\omega = \sqrt{k/\mu}$  around an average value  $r_0$ . Now if  $l \neq 0$ , the connecting vector rotates in a plane perpendicular to  $\mathbf{l}$  while its length vibrates around an equilibrium value  $r_0 + l^2 r_0 / (\mu^2 \omega^2 r_0^4 + 3l^2)$ , shifted to some larger value with respect to  $r_0$ , with frequency  $\omega_{eff}$ , also shifted to some larger value with respect to the rotation-free value  $\omega$ .

### 1.2.3 Energy and energy changes

Let us again have a look at Newton's equation for one particle, Eq. (1.6). In many cases the force  $\mathbf{F}$  is a conservative force, i.e., a force that is (minus) the gradient of a potential energy  $\mathbf{F}(\mathbf{r}) = -\nabla\Phi(\mathbf{r})$ , where  $\nabla = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)$ . Then, with  $\mathbf{v} = \dot{\mathbf{r}}$ ,

$$\begin{aligned}m\frac{d\mathbf{v}}{dt} &= -\nabla\Phi \\m\frac{d\mathbf{v}}{dt} \cdot \mathbf{v} &= -\nabla\Phi \cdot \mathbf{v} \\ \frac{d}{dt} \left( \frac{1}{2}mv^2 \right) &= -\frac{d\Phi}{dt} \\ \Rightarrow \frac{d}{dt}\mathcal{H} &= 0\end{aligned}\tag{1.35}$$

$$\mathcal{H} = \frac{1}{2}mv^2 + \Phi.\tag{1.36}$$

Eq. (1.35) shows that the total energy, expressed as the Hamiltonian  $\mathcal{H}$ , is a conserved quantity:

$$\mathcal{H}(t) = \mathcal{H}(0) = E.\tag{1.37}$$

This does not mean that the potential energy and the kinetic energy are conserved quantities! There is a constant exchange of energy between the kinetic energy  $K = \frac{1}{2}mv^2$  and the potential energy  $\Phi$  such that their sum is constant and equal to the total energy  $E$ . In Problem 1-6 you are asked to explicitly check the conservation of energy for the case of the harmonic oscillator.

When  $N$  particles are present and the forces on these particles are conservative, this result is easily generalized. Using the notation  $\nabla_i = \left(\frac{\partial}{\partial x_i}, \frac{\partial}{\partial y_i}, \frac{\partial}{\partial z_i}\right)$  we may write the force on particle  $i$  as  $\mathbf{F}_i = -\nabla_i\Phi$ . Hence:

$$\begin{aligned}m_i\frac{d\mathbf{v}_i}{dt} &= -\nabla_i\Phi \\ \sum_{i=1}^N m_i\frac{d\mathbf{v}_i}{dt} \cdot \mathbf{v}_i &= -\sum_{i=1}^N \nabla_i\Phi \cdot \mathbf{v}_i \\ \frac{d}{dt} \left( \sum_i \frac{1}{2}m_i v_i^2 \right) &= -\frac{d}{dt}\Phi \\ \Rightarrow \frac{d}{dt}\mathcal{H} &= 0\end{aligned}\tag{1.38}$$

$$\mathcal{H} = \sum_{i=1}^N \frac{1}{2}m_i v_i^2 + \Phi.\tag{1.39}$$

Again, the total energy is a conserved quantity:  $\mathcal{H}(t) = \mathcal{H}(0) = E$ .

The total energy of a system of particles is not always conserved. It can be changed by performing *work* on the system. This may be accomplished by applying an external force to the  $N$ -particle system. The equations of motion then read

$$m_i \frac{d\mathbf{v}_i}{dt} = -\nabla_i \Phi + \mathbf{F}_i^{ext}, \quad (1.40)$$

where  $\mathbf{F}_i^{ext}$  is the external force on particle  $i$ . As a consequence the Hamiltonian will change in time:

$$\frac{d}{dt} \mathcal{H} = \sum_{i=1}^N \mathbf{F}_i^{ext} \cdot \mathbf{v}_i = \sum_{i=1}^N \mathbf{F}_i^{ext} \cdot \frac{d\mathbf{r}_i}{dt}. \quad (1.41)$$

On the left hand side we find the change of energy per second, on the right the work done per second by the external forces. So the total increase in energy of the  $N$ -particle system is equal to the total amount of work done on the system:

$$\Delta E = w = \sum_{i=1}^N \int \mathbf{F}_i^{ext} \cdot d\mathbf{r}_i. \quad (1.42)$$

## 1.3 Quantum mechanics

### 1.3.1 The uncertainty principle

The behaviour of small particles like electrons cannot be described by the laws of classical mechanics. Instead, a quantum mechanical treatment is necessary. Note that in quantum mechanics we usually use momenta instead of velocities, in which case the Hamiltonian is expressed as:

$$\mathcal{H} = \frac{p^2}{2m} + \Phi \quad (1.43)$$

$$\mathbf{p} = m\mathbf{v}. \quad (1.44)$$

For a quantum mechanical particle it is impossible to measure both its position and its momentum with infinite precision *simultaneously*. Rather, there is an uncertainty given by Heisenberg's uncertainty principle:

$$\Delta x \Delta p \geq \frac{1}{2} \hbar, \quad (1.45)$$

where  $\Delta x$  is the uncertainty in position and  $\Delta p$  the uncertainty in momentum. Here  $\hbar = h/(2\pi)$ , where  $h = 6.626 \times 10^{-34}$  J·s is Planck's constant. This relation

implies that the more precise we specify the position, the more uncertain will be the momentum of a particle, and vice versa. Note that Eq. (1.45) holds for each cartesian component. In this section we will focus on a particle in one dimension.

Since we cannot specify the position and momentum precisely, at a certain time  $t$  we can only give a probability distribution  $P_X$  for encountering the particle at position  $x$  and a probability distribution  $P_P$  for encountering the particle with a momentum  $p$ . In quantum mechanics it is shown that these probability distributions are given by<sup>2</sup>

$$P_X(x, t) = \Psi(x, t)\Psi^*(x, t) = |\Psi(x, t)|^2 \quad (1.46)$$

$$P_P(p, t) = F(p, t)F^*(p, t) = |F(p, t)|^2, \quad (1.47)$$

where  $\Psi(x, t)$  and  $F(p, t)$  are complex and normalised “wave” functions, interrelated by Fourier transforms:

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi}} \int dp e^{ipx/\hbar} F(p, t) \quad (1.48)$$

$$F(p, t) = \frac{1}{\sqrt{2\pi}} \int dx e^{-ipx/\hbar} \Psi(x, t). \quad (1.49)$$

From the distribution functions we can calculate all kinds of averages. For example, the average position is given by

$$\langle x \rangle (t) = \int dx \Psi^*(x, t)x\Psi(x, t) \quad (1.50)$$

and the average momentum is given by

$$\begin{aligned} \langle p \rangle (t) &= \int dp F(p, t)pF^*(p, t) \\ &= \int dp F(p, t)p\frac{1}{\sqrt{2\pi}} \int dx e^{ipx/\hbar}\Psi^*(x, t) \\ &= \int dp F(p, t)\frac{1}{\sqrt{2\pi}} \int dx \Psi^*(x, t)\frac{\hbar}{i}\frac{\partial}{\partial x}e^{ipx/\hbar} \\ &= \int dx \Psi^*(x, t)\frac{\hbar}{i}\frac{\partial}{\partial x}\frac{1}{\sqrt{2\pi}} \int dp F(p, t)e^{ipx/\hbar} \\ &= \int dx \Psi^*(x, t)\frac{\hbar}{i}\frac{\partial}{\partial x}\Psi(x, t). \end{aligned} \quad (1.51)$$

So, if one works in the ‘position representation’  $\Psi(x, t)$ , the position is associated with the operator  $x$  (multiplication by  $x$ ) and the momentum is associated with the operator  $\frac{\hbar}{i}\frac{\partial}{\partial x}$ .

---

<sup>2</sup> $\Psi^*$  is the complex conjugate of  $\Psi$ , meaning that the imaginary part is negated.  $\Psi\Psi^*$  is therefore a real number.

### 1.3.2 Operators and eigenfunctions

In general, all observables are associated with certain operators. An operator transforms one function into another function,  $\mathcal{O}f = g$ . For example, with  $\mathcal{O} = d/dx$ , then  $f = \sin(kx)$  leads to  $g = k \cos(kx)$ . The next table contains the most important classical observables and their associated quantum mechanical operators, now in 3 dimensions.

Classical	Quantum
$\mathbf{r}$	$\mathbf{r}$
$\mathbf{p}$	$\frac{\hbar}{i} \nabla$
$\mathcal{H}$	$-\frac{\hbar^2}{2m} \nabla^2 + \Phi$

In quantum mechanics, the outcome of a single measurement is an eigenvalue of the operator associated with the observable, and the wave function is said to collapse into an eigenfunction (eigenstate) of this operator.

It is important to realise that all information about the system is contained in the wave function  $\Psi(\mathbf{r}, t)$ . When no explicit measurement is made, only the probability for the value of an observable can be derived from the wave function. For example, as we have seen, the probability to find a quantum particle at position  $\mathbf{r}$  at time  $t$  is given by  $|\Psi(\mathbf{r}, t)|^2 = \Psi^*(\mathbf{r}, t)\Psi(\mathbf{r}, t)$ . The average outcome (say of many identical experiments) can then be expressed as an expectation value of the associated operator:

$$\langle \mathbf{r} \rangle (t) = \int d^3r \Psi^*(\mathbf{r}, t) \mathbf{r} \Psi(\mathbf{r}, t) \quad (1.52)$$

$$\langle \mathbf{p} \rangle (t) = \int d^3r \Psi^*(\mathbf{r}, t) \frac{\hbar}{i} \nabla \Psi(\mathbf{r}, t) \quad (1.53)$$

$$\langle \mathcal{H} \rangle (t) = \int d^3r \Psi^*(\mathbf{r}, t) \left\{ -\frac{\hbar^2}{2m} \nabla^2 + \Phi(\mathbf{r}) \right\} \Psi(\mathbf{r}, t). \quad (1.54)$$

All operators associated with a measurable quantity are Hermitian,

$$\mathcal{O} = \mathcal{O}^\dagger, \quad (1.55)$$

with  $\mathcal{O}^\dagger$  the Hermitian conjugate defined by

$$\int d^3r \Psi_1^*(\mathbf{r}) \mathcal{O}^\dagger \Psi_2(\mathbf{r}) = \int d^3r \{ \mathcal{O} \Psi_1(\mathbf{r}) \}^* \Psi_2(\mathbf{r}), \quad (1.56)$$

and have complete sets of orthogonal eigenfunctions with real eigenvalues. Instead of the general symbol  $\mathcal{O}$  we will use the Hamiltonian  $\mathcal{H}$  as an example. The eigen-

functions of  $\mathcal{H}$  are functions  $\psi_n$  for which

$$\mathcal{H}(\mathbf{r})\psi_n(\mathbf{r}) = E(n)\psi_n(\mathbf{r}) \quad (1.57)$$

$$\langle \psi_n | \psi_m \rangle \equiv \int d^3r \psi_n^*(\mathbf{r})\psi_m(\mathbf{r}) = \delta_{nm} \quad (1.58)$$

$$\sum_n \psi_n(\mathbf{r})\psi_n^*(\mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}'). \quad (1.59)$$

Eq. (1.58) states that different eigenfunctions are orthogonal and that each eigenfunction is normalised.<sup>3</sup> Eq. (1.59) is called the completeness relation.

$\delta(\mathbf{r}) = \delta(x)\delta(y)\delta(z)$  is the Dirac-delta function in 3 dimensions. The one-dimensional function  $\delta(x)$  has the following property

$$f(x) = \int dy f(y)\delta(x - y), \quad (1.60)$$

where  $f$  is a smooth function. If we now introduce the completeness relation, we find

$$\begin{aligned} f(x) &= \sum_n \int dy f(y)\psi_n(x)\psi_n^*(y) \\ &= \sum_n \psi_n(x) \int dy f(y)\psi_n^*(y) \\ &= \sum_n \psi_n(x)c_n. \end{aligned} \quad (1.61)$$

The result is that  $f(x)$  has been written as a linear combination of eigenfunctions  $\psi_n(x)$ . In a sense we may say that the eigenfunctions  $\psi_n(x)$  form a complete set, hence the name completeness relation for Eq. (1.59).

### 1.3.3 Time evolution of the wave function

The equation of motion of the wave function is given by the Schrödinger equation,

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) = \mathcal{H}(\mathbf{r})\Psi(\mathbf{r}, t). \quad (1.62)$$

Using the Schrödinger equation, it can be shown (Problem 1-7) that the time derivative of the expectation value of a certain observable  $A$  is given by the commutator of  $A$  and the Hamiltonian operator,

$$\frac{d\langle A \rangle}{dt} = \frac{1}{i\hbar} [A, \mathcal{H}] \equiv \frac{1}{i\hbar} \int d^3r \Psi^*(\mathbf{r}, t)(A\mathcal{H} - \mathcal{H}A)\Psi(\mathbf{r}, t), \quad (1.63)$$

---

<sup>3</sup>Of course it is not necessary that the eigenfunctions are normalised, but we choose them to be normalised to simplify our expressions.



where the last equation defines the commutator. One special case is when  $A = \mathcal{H}$ . It is clear that the commutator of the Hamiltonian with itself is zero. This implies that the expectation value of the Hamiltonian is conserved, similar to what was found in classical mechanics,

$$\frac{d\langle \mathcal{H} \rangle}{dt} = \frac{1}{i\hbar} [\mathcal{H}, \mathcal{H}] = 0. \quad (1.64)$$

As another application of Eq. (1.63) we calculate the time derivative of the expectation value of the momentum:

$$\begin{aligned} \frac{d\langle \mathbf{p} \rangle}{dt} &= \frac{1}{i\hbar} \left[ \frac{\hbar}{i} \nabla, \mathcal{H} \right] = - \left[ \nabla, -\frac{\hbar^2}{2m} \nabla^2 + \Phi(\mathbf{r}) \right] = - [\nabla, \Phi(\mathbf{r})] \\ &= - \int d^3r \Psi^*(\mathbf{r}, t) \{ \nabla \Phi(\mathbf{r}) \Psi(\mathbf{r}, t) - \Phi(\mathbf{r}) \nabla \Psi(\mathbf{r}, t) \} \\ &= - \int d^3r \Psi^*(\mathbf{r}, t) \{ \nabla \Phi(\mathbf{r}) \} \Psi(\mathbf{r}, t) = - \langle \nabla \Phi(\mathbf{r}) \rangle. \end{aligned} \quad (1.65)$$

So the expectation values obey Newton's equation for a classical particle, see the first of Eq. (1.35).

We will now solve Eq. (1.62) in general terms. The space and time dependence of the wave function  $\Psi(\mathbf{r}, t)$  can be written as a linear combination of spatial eigenfunctions  $\psi_n(\mathbf{r})$  with time-varying coefficients  $a_n(t)$ :

$$\begin{aligned} \Psi(\mathbf{r}, t) &= \int d^3r' \Psi(\mathbf{r}', t) \delta(\mathbf{r} - \mathbf{r}') \\ &= \sum_n \psi_n(\mathbf{r}) \left\{ \int d^3r' \psi_n^*(\mathbf{r}') \Psi(\mathbf{r}', t) \right\} \\ &\equiv \sum_n \psi_n(\mathbf{r}) a_n(t) \end{aligned} \quad (1.66)$$

The time dependence of the coefficients  $a_n$  is given by (Problem 1-8)

$$a_n(t) = a_n(0) \exp(-iE(n)t/\hbar). \quad (1.67)$$

The expectation value of the Hamiltonian can be expressed in terms of these coefficients:

$$\langle \mathcal{H} \rangle (t) = \sum_n |a_n|^2 E(n). \quad (1.68)$$

Because  $|a_n(t)|^2 = |a_n(0)|^2$ , we again conclude that the expectation value for the total energy is conserved. However, because the coefficients  $a_n(t)$  oscillate in time, the wave function and its amplitude are changing continuously. Only if the wave function is a single eigenfunction of the Hamiltonian, the amplitude will remain constant.

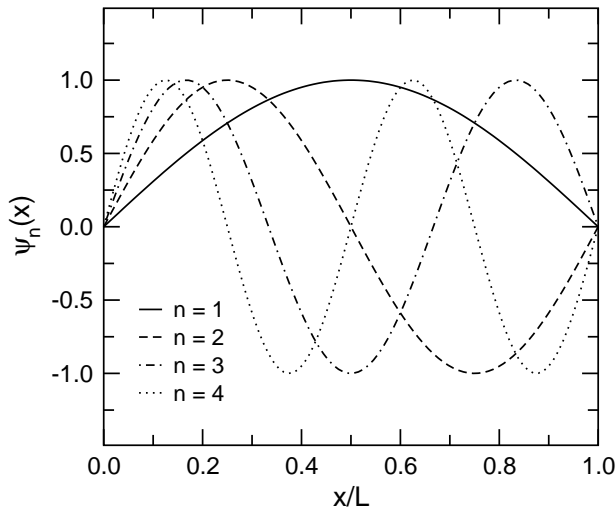


Figure 1.1: First four eigenfunctions of a one-dimensional particle in a box. Note that the boundary conditions  $\psi_n(0) = \psi_n(L) = 0$  are satisfied, and that the number of nodes increases with  $n$ .

### 1.3.4 The quantum mechanical particle in a box

An example will make things more clear. We will treat a quantum mechanical particle of mass  $m$  in a box in one dimension of length  $L$ . This means that the particle is constrained on a line between 0 and  $L$ . Everywhere in the box the potential energy is zero, but outside it is infinite. This means that the particle cannot be encountered outside the box. The eigenfunctions of the Hamiltonian then should obey

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi_n(x) = \epsilon(n) \psi_n(x), \quad (1.69)$$

with boundary conditions

$$\psi_n(0) = \psi_n(L) = 0. \quad (1.70)$$

The general solution to the differential equation (1.69) is

$$\psi(x) = A \cos(kx) + B \sin(kx), \quad (1.71)$$

with  $A$ ,  $B$  and  $k$  constants to be determined by the boundary conditions and the fact that we want the eigenfunctions to be normalised. The boundary condition  $\psi(0) = 0$  immediately implies  $A = 0$ . The boundary condition  $\psi(L) = 0$  can then be satisfied if  $k = n\pi/L$ , with  $n$  an integer number. We can label each eigenfunction with the integer  $n$ , which we now call a quantum number. Note that negative  $n$  give the same eigenfunctions as positive  $n$ . Note also that  $n = 0$  results in no eigenfunction ( $\psi = 0$  everywhere), so we may restrict our quantum numbers  $n$  to the positive integers. Finally, the eigenfunctions are normalised if

$$\int_0^L \psi_n^*(x) \psi_n(x) dx = \int_0^L B^2 \sin^2 \left( \frac{n\pi x}{L} \right) dx = B^2 \frac{L}{2} = 1, \quad (1.72)$$

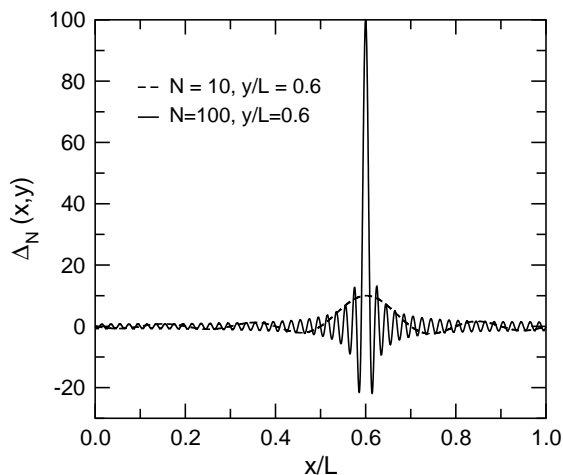


Figure 1.2: Illustration of the completeness relation. Interference of the particle-in-a-box eigenfunctions leads to a sharply peaked function  $\Delta_N(x, y) = \sum_{n=1}^N \psi_n(x)\psi_n^*(y)$ , in this case plotted for  $y = 0.6L$  and  $N = 10$  and  $100$ , respectively.

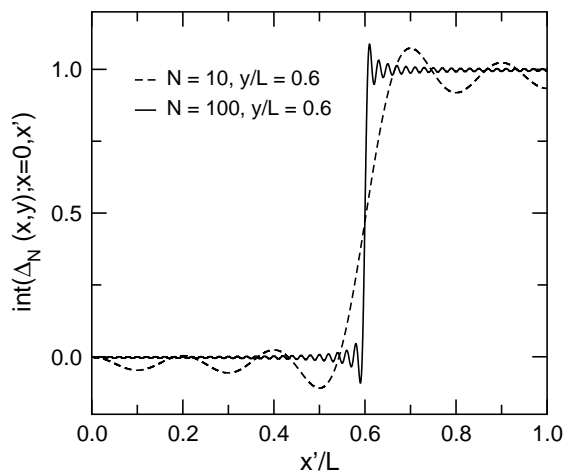


Figure 1.3: Integral of the functions in Fig. 1.2 from  $x = 0$  to  $x = x'$ . Note how the integral more and more resembles a step function as  $N$  grows larger.

i.e.  $B = \sqrt{2/L}$ . In conclusion we are left with the following possible eigenfunctions and eigenvalues:

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \quad (1.73)$$

$$\epsilon(n) = \frac{h^2}{8mL^2} n^2. \quad (1.74)$$

The first four eigenfunctions are depicted in Fig. 1.1. Note that the energy of the quantum mechanical particle in a box can only attain certain values: the energy is *quantized*. We will use the expression for the energy of a particle in a box many times in the coming chapters. Note also that the number of nodes of the wave function increases with increasing  $n$ . It is a general observation in quantum mechanics that the number of nodes of a wave function increases with increasing energy.

In Problem 1-9 we will consider the case of a particle enclosed in a three-dimensional cubic box.

As an illustration of the completeness relation Eq. (1.59), in Fig. 1.2 we show the following sum of products of the eigenfunctions:

$$\Delta_N(x, y) = \sum_{n=1}^N \psi_n(x)\psi_n^*(y). \quad (1.75)$$

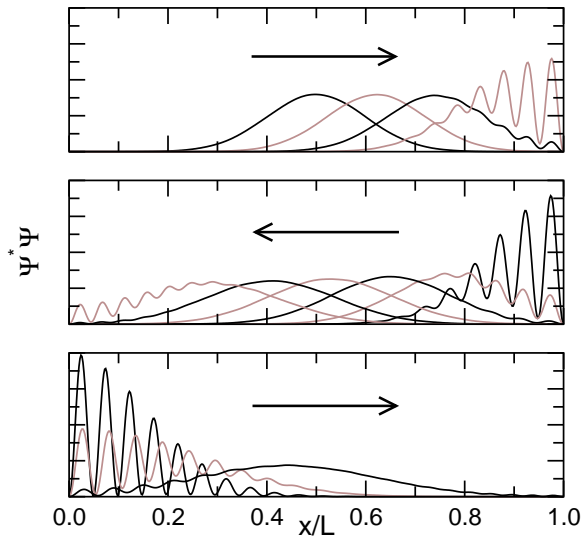


Figure 1.4: Time evolution of the probability  $\Psi^*(x,t)\Psi(x,y)$  to encounter the particle at  $x$  at time  $t$  for the case of a particle in a box. We start out with a wave packet that more or less sharply defines the position of the particle and give it a positive momentum. Upon collision with the wall the wave character becomes more prominent. With time the spatial uncertainty of the wave packet becomes larger and larger.

In this case we choose a particular value for  $y$ , namely  $y = 0.6L$ , and plot  $\Delta_N$  as a function of  $x$  for two values of the upper limit of summation  $N$ . It is clear that the more eigenfunctions we include, the more narrow and peaked the resulting function. In the limit of  $N \rightarrow \infty$  the Dirac-delta function remains. The integral over the Dirac-delta function is a step function. Fig. 1.3 shows the integral of  $\Delta_N$  over  $x$  from  $x = 0$  to  $x = x'$ . Indeed, for larger  $N$ , the calculated integral more and more resembles a step function with the step occurring at  $x' = y = 0.6L$ .

Finally, in Fig. 1.4 we show the time evolution of the probability  $\Psi^*(x,t)\Psi(x,y)$  to encounter a particle at  $x$  at time  $t$  for the case of a particle in a box. We start out with a wave packet that more or less sharply defines the position of the particle and give it a positive momentum. Upon collision with the wall the wave character becomes more prominent. With time the spatial uncertainty of the wave packet becomes larger and larger. This general behaviour is called decoherence of a wave packet. The rate of decoherence depends on the choice of the initial wave packet and on the mass of the particle.

### 1.3.5 The quantum mechanical harmonic oscillator

As another example we will treat the quantum mechanical harmonic oscillator in one dimension. Suppose a mass  $m$  is connected to the origin by a spring with spring constant  $k = m\omega^2$ . Our task is to find the eigenfunctions and eigenvalues of the Hamiltonian

$$\mathcal{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2} m\omega^2 x^2. \quad (1.76)$$

Although this example may seem somewhat artificial, many problems in quantum mechanics may be reduced to the problem of a set of harmonic oscillators.

We are looking for a function  $\psi(x)$  such that

$$\left\{ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2} m \omega^2 x^2 \right\} \psi(x) = \epsilon \psi(x). \quad (1.77)$$

Note that differentiation of  $e^{-ax^2}$  leads to  $-2axe^{-ax^2}$ . Differentiating again gives  $-2ae^{-ax^2} + 4a^2x^2e^{-ax^2}$ , so this may work. We therefore try

$$\psi_0(x) = C_0 e^{-ax^2}. \quad (1.78)$$

Inserting this in Eq. (1.77) we find

$$\left\{ \frac{\hbar^2 a}{m} - \left( \frac{2\hbar^2 a^2}{m} - \frac{1}{2} m \omega^2 \right) x^2 \right\} \psi_0(x) = \epsilon(0) \psi_0(x). \quad (1.79)$$

We can eliminate the factor before  $x^2$  by carefully choosing  $a$  equal to

$$a = \frac{m\omega}{2\hbar}. \quad (1.80)$$

The eigenvalue  $\epsilon(0)$  then is

$$\epsilon(0) = \frac{1}{2} \hbar \omega. \quad (1.81)$$

So we have derived, in a very simple way, a possible eigenfunction of the harmonic oscillator. The constant  $C_0$  is determined by the fact that  $\psi_0$  must be properly normalized (see Appendix A at the end of this book):

$$\int \psi_0^*(x) \psi_0(x) dx = 1. \quad (1.82)$$

Incidentally, Eq. (1.81) is also the lowest possible eigenvalue. In Problem 1-10 you are asked to study trial functions of the form

$$\psi_n(x) = P_n(x) e^{-ax^2}, \quad (1.83)$$

with  $P_n(x)$  some polynomial of degree  $n$ . The resulting eigenvalues of a harmonic oscillator are found to be

$$\epsilon(n) = \left( n + \frac{1}{2} \right) \hbar \omega. \quad (1.84)$$

This result will be used regularly in the coming chapters.

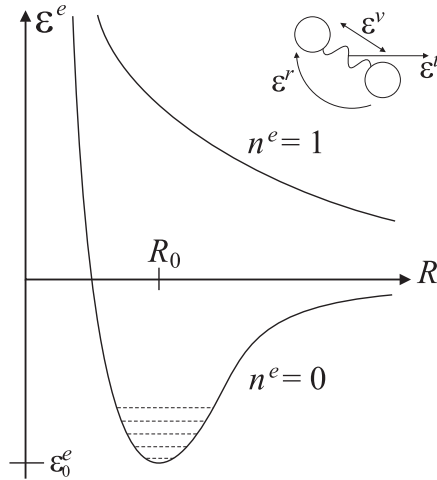


Figure 1.5: Sketch of the effective (electronically averaged) potential energy of a two-atomic molecule as a function of the distance between the nuclei. For each electronic state  $n^e$  there is a different curve; only the first two are depicted here. The ground state energy has a minimum  $\epsilon^e(0)$  at a distance  $R_0$ . Vibrations around this minimum are approximated by a (quantum mechanical) harmonic oscillator, with energy levels indicated by the dashed lines.

### 1.3.6 Quantum mechanical treatment of two-atomic molecule

As a final example we treat a two-atomic molecule. The energy of a two-atomic molecule consists of several parts. First, there is the electrical energy that describes the motion of the electrons around the nuclei. This energy  $\epsilon^e$  depends on the distance  $R$  between the two nuclei and a quantum number  $n^e$  describing the electric state. We are going to concentrate on a molecule in the electric ground state  $n^e = 0$ , but in the general case it may be excited to a higher state. A sketch is given in Fig. 1.5. Note that we have used the *Born-Oppenheimer* approximation, where it is imagined that the electrons move much faster than the nuclei, so that the nuclear kinetic energy may be neglected when determining the electronic wave function. In the ground state the electronic energy has a minimum  $\epsilon_0^e$  at  $R = R_0$ ; this is the equilibrium distance between the nuclei in the ground state. In the neighbourhood of this minimum, the energy may be approximated by a harmonic potential  $\epsilon^e(0) + \frac{1}{2}\mu\omega^2(R - R_0)^2$ , where  $\mu$  is the (reduced) mass of the molecule, and  $\omega$  a characteristic frequency. In a way, the nuclei behave as if they are connected by a spring with spring constant  $k = \mu\omega^2$ . This causes the two nuclei to vibrate relative to each other, giving a contribution  $\epsilon^v$  to the total energy of the molecule. Finally, the molecule as a whole may rotate, contributing an energy  $\epsilon^r$ , and translate, contributing an energy  $\epsilon^t$ . Note that we assume that vibrational and rotational motions of the molecule are uncoupled. This is often a good approximation because the vibrations are usually much faster than the rotations.

So the energy of a two-atomic molecule consists of electronic, vibrational, rotational, and translational contributions, each associated with certain quantum numbers. The total energy may therefore be written as:

$$\epsilon(n^e, n^v, n^r, n^t) = \epsilon^e(n^e) + \epsilon^v(n^v) + \epsilon^r(n^r) + \epsilon^t(n^t), \quad (1.85)$$

where  $n^e$ ,  $n^v$ ,  $n^r$  and  $n^t$  are not necessarily single quantum numbers. Rather, they

each represent a set of quantum numbers, a set as large as is needed to fully specify the exact energy eigenfunction. We will call such a fully specified eigenfunction a *state*, not only in the case of a two-atomic molecule, but quite generally. As it turns out, energy states are often *degenerate*, meaning that more than one eigenfunction is associated with the same energy (eigenvalue)  $\epsilon$ . It is therefore useful to distinguish between states and *energy levels*. We denote the number of ways in which an energy level may be realised by the symbol  $\omega$  and call it the *degeneracy* of that energy level. In Problem 1-11 we will study the degeneracy of the energy levels for a particle in a three-dimensional box and a three-dimensional harmonic oscillator.

Back to our specific example of a two-atomic molecule. Usually there is just one electronic ground state (with  $n^e = 0$ ). This is written as  $\omega_0^e = 1$ . Notable exceptions are  $O_2$ , for which  $\omega_0^e = 3$ , and  $NO$ , for which  $\omega_0^e = 2$ . The vibrations of the two nuclei are approximately harmonic, so these are specified by just one quantum number  $n^v (= 0, 1, 2, \dots)$ , with energy

$$\epsilon^v(n^v) = (n^v + \frac{1}{2})\hbar\omega. \quad (1.86)$$

As already mentioned, the vibrations are usually much faster than the rotations. To a good approximation, the molecule therefore rotates as a rigid body, with the nuclei fixed at the equilibrium distance  $R_0$ . The moment of inertia for rotations around an axis through the centre of the molecule, perpendicular to the axis connecting the two nuclei, is therefore

$$I = \frac{m_1 m_2}{m_1 + m_2} R_0^2 = \mu R_0^2, \quad (1.87)$$

where  $\mu$  is the reduced mass of the molecule. In quantum mechanics it is shown that for such a system the rotational energy is given by

$$\epsilon^r(J, M) = \frac{\hbar^2}{2I} J(J+1). \quad (1.88)$$

Here  $J$  is the (main) rotation-quantum number, which can attain the values  $0, 1, 2, \dots$ . At any given value of  $J$  different states are possible, each labeled by another quantum number  $M$ , which can have the values  $-J, -J+1, \dots, 0, \dots, J-1, J$ . The degeneracy of the energy level associated with rotation-quantum number  $J$  is therefore  $\omega_J = 2J+1$ .

The translational energy for a free molecule in a box, finally, is given by the 3-dimensional equivalent of Eq. (1.74),

$$\epsilon^t(n_x, n_y, n_z) = \frac{\hbar^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2), \quad (1.89)$$

where  $m = m_1 + m_2$  is the total mass of the molecule. We will use this description of the energy of a two-atomic molecule in section 6.3 when we treat the statistical mechanics of an ideal gas of such molecules.

## Problems

**1-1. Two-atomic molecule (1).** In subsection 1.2.1 we treat the equation of motion of a two-atomic molecule. Make a drawing containing  $\mathbf{r}_1$ ,  $\mathbf{r}_2$ ,  $\mathbf{r}$ ,  $\mathbf{F}_1$ , and  $\mathbf{F}_2$ .

**1-2. Two-atomic molecule (2).** Prove Eqs. (1.17) and (1.18).

**1-3. Conservation of angular momentum.** Prove Eq. (1.20).

**1-4. The triple product.** Using

$$\mathbf{a} \times \mathbf{b} = (a_y b_z - a_z b_y, a_z b_x - a_x b_z, a_x b_y - a_y b_x),$$

check that

$$\mathbf{a} \times (\mathbf{b} \times \mathbf{c}) = (\mathbf{a} \cdot \mathbf{c}) \mathbf{b} - (\mathbf{a} \cdot \mathbf{b}) \mathbf{c}.$$

**1-5. Conservation of energy.** Multiply Eq. (1.30) by  $\dot{r}$  and prove

$$\frac{1}{2} \mu \dot{r}^2 + \frac{l^2}{2\mu r^2} + \frac{1}{2} \mu \omega^2 (r - r_0)^2 = \epsilon,$$

where  $\epsilon$  is some constant. What use has this?

**1-6. The classical harmonic oscillator.** The potential energy of a one-dimensional harmonic oscillator is given by

$$\Phi(x) = \frac{1}{2} m \omega^2 x^2.$$

The initial value problem (with  $x(0) = x_0$  and  $\dot{x}(0) = v_0$ ) has been solved in Eq. (1.5). Show explicitly that the total energy is conserved.

**1-7. Time derivative of an observable (commutator).** Suppose we have an observable and associated operator  $A$ . Show that the time derivative of the expectation value of the observable is given by

$$\frac{d\langle A \rangle}{dt} = \frac{1}{i\hbar} \int d^3r \Psi^*(\mathbf{r}, t) (A\mathcal{H} - \mathcal{H}A) \Psi(\mathbf{r}, t).$$

The integral is also written briefly as the commutator of  $A$  with  $\mathcal{H}$ :  $[A, \mathcal{H}]$ . (Hint: Use the Schrödinger equation. Perform a partial integration and use the fact that  $\Psi = 0$  at infinity.)



**1-8. Time dependence of the wave function.** Using Eq. (1.66) and the Schrödinger equation, show that the time dependence of the coefficients  $a_n(t)$  is given by

$$a_n(t) = a_n(0) \exp(-iE(n)t/\hbar).$$

Calculate  $\langle \mathcal{H} \rangle$ .

**1-9. The quantummechanical particle in a box.** Suppose a particle is enclosed in a cubic box of length  $L$  at each side. The eigenfunctions of the Hamiltonian then should obey

$$-\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi_n(\mathbf{r}) = \epsilon(n) \psi_n(\mathbf{r}),$$

with boundary conditions

$$\begin{aligned} \psi_n(0, y, z) &= \psi_n(L, y, z) = 0 \\ \psi_n(x, 0, z) &= \psi_n(x, L, z) = 0 \\ \psi_n(x, y, 0) &= \psi_n(x, y, L) = 0. \end{aligned}$$

Show that the eigenvalues are given by

$$\epsilon(n_x, n_y, n_z) = \frac{\hbar^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2),$$

where  $n_x$ ,  $n_y$ , and  $n_z$  are positive integer numbers.

**1-10. The quantummechanical harmonic oscillator.** In this exercise we will study the Hamiltonian eigenfunctions  $\psi_n$  and eigenvalues  $\epsilon(n)$  of the quantummechanical harmonic oscillator. The eigenfunctions and -values must obey Eq. (1.77). We have already seen that the function

$$\psi_0(x) = C_0 \exp(-ax^2),$$

with  $a = m\omega/(2\hbar)$ , is a correct eigenfunction with eigenvalue  $\epsilon(0) = \frac{1}{2}\hbar\omega$ . Next try

$$\psi_1(x) = P_1(x) \exp(-ax^2),$$

with  $P_1(x)$  a polynomial of degree 1 (of the form  $c_0 + c_1x$ ). Then try

$$\psi_2(x) = P_2(x) \exp(-ax^2),$$

with  $P_2(x)$  a polynomial of degree 2 (of the form  $c_0 + c_1x + c_2x^2$ ). Show that the eigenvalues are  $\frac{3}{2}\hbar\omega$  and  $\frac{5}{2}\hbar\omega$ , respectively, in agreement with the general result

$$\epsilon(n) = \left( n + \frac{1}{2} \right) \hbar\omega.$$

**1-11. Degeneracy of the energy levels of a 3d particle in a box and harmonic oscillator.** Using the result of Problem 1-9, calculate the degeneracy  $\Omega$  of each energy level of a three-dimensional particle in a box with an energy lower or equal to  $14 \times \frac{h^2}{8mL^2}$ . (Hint: how many realisations are there to make the sum  $n_x^2 + n_y^2 + n_z^2 = M$  with  $M$  a positive integer?) How will the general result of Problem 1-10 look like for the energy of a three-dimensional harmonic oscillator? Calculate the degeneracy  $\Omega$  of each energy level of a 3d harmonic oscillator with an energy lower or equal to  $\frac{11}{2}\hbar\omega$ .