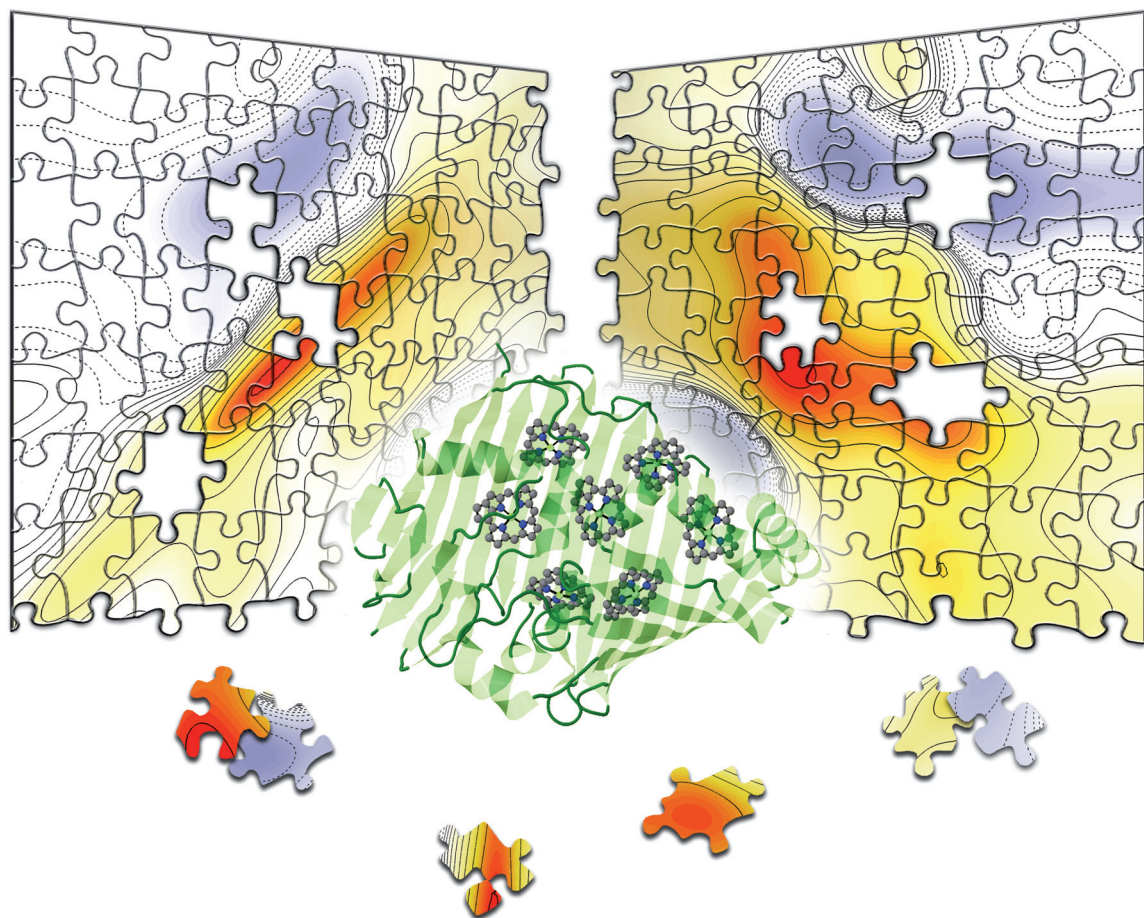


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# Molecular Excitation Dynamics and Relaxation

Quantum Theory and Spectroscopy





*Leonas Valkunas,  
Darius Abramavicius, and  
Tomáš Mančal*

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and Relaxation**

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and Tomáš Mančal*

# **Molecular Excitation Dynamics and Relaxation**

Quantum Theory and Spectroscopy

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## Cover Picture

Rephasing and non-rephasing two-dimensional spectra calculated for the Fenna–Matthews–Olson complexes at zero population time ( $T = 0$ ), see Chapter 17 for details.

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## Preface

Classical mechanics is known for its ability to describe the dynamics of macroscopic bodies. Their behavior in the course of time is usually represented by classical trajectories in the real three-dimensional space or in the so-called phase space defined by characteristic coordinates and momenta, which together determine the degrees of freedom of the body under consideration. For the description of the dynamics of a microscopic system, however, quantum mechanics should be used. In this case, the system dynamics is qualified by the time evolution of a complex quantity, the wavefunction, which characterizes the maximum knowledge we can obtain about the quantum system. In terms of the quantum mechanical description, coordinates and momenta cannot be determined simultaneously. Their values should satisfy the Heisenberg uncertainty principle. At the interface between the classical world in which we live and the world of microscopic systems, this type of description is inherently probabilistic. This constitutes the fundamental differences between classical and quantum descriptions of the system dynamics. In principle, however, both classical and quantum mechanics describe a reversible behavior of an isolated system in the course of time.

Irreversibility of time evolution is a property found in the dynamics of open systems. No realistic system is isolated; it is always subjected to coupling to its environment, which in most cases cannot be considered as a negligible factor. The theory of open quantum systems plays a major role in determining the dynamics and relaxation of excitations induced by an external perturbation. A typical external perturbation is caused by the interaction of a system with an electromagnetic field. In resonance conditions, when the characteristic transition frequencies of the system match the frequencies of the electromagnetic field, the energy is transferred from the field to the system and the system becomes excited. The study of the response of material systems to various types of external excitation conditions is the main objective of spectroscopy. Spectroscopy, in general, is an experimental tool to monitor the features and properties of the system based on the measurement of its response. More complicated spectroscopic experiments study the response which mirrors the dynamics of excitation and its relaxation.

Together with the widely used conventional spectroscopic approaches, two-dimensional coherent spectroscopic methods were developed recently, and they have been applied for studies of the excitation dynamics in various molecular

systems, such as photosynthetic pigment–protein complexes, molecular aggregates, and polymers. Despite the complexity of the temporal evolution of the two-dimensional spectra, some of these spectra demonstrate the presence of vibrational and electronic coherence on the subpicosecond timescale and even picosecond timescale. Such observations demonstrate the interplay between the coherent behavior of the system, which might be considered in terms of conventional quantum mechanics, and the irreversibility of the excitation dynamics due to the interaction of the system with its environment.

From the general point of view, quantum mechanics is the basic approach for considering various phenomena in molecular systems. However, a typical description must be based on a simplified model, where specific degrees of freedom are taken into consideration, and the rest of them are attributed to an environment or bath. This is the usual approach used for open quantum systems. Thus, complexity of the molecular system caused by some amount of interacting molecules has to be specifically taken into account by describing the quantum behavior of the system. For this purpose the concept of excitons is usually invoked.

As can be anticipated, this area of research covers a very broad range of fields in physics and chemistry. Having this in mind, we have divided this book into two parts. Part One, being more general, describes the basic principles and theoretical approaches which are necessary to describe the excitation dynamics and relaxation in quantum systems interacting with the environment. These theoretical approaches are then used for the description of spectroscopic observables in Part Two.

Consequently, we have many different readers of this book in mind. First of all, the book addresses undergraduate and graduate students in theoretical physics and chemistry, molecular chemical physics, quantum optics and spectroscopy. For this purpose the basic principles of classical physics, quantum mechanics, statistical physics, and stochastic processes are presented in Part One. Special attention is paid to the interface of classical and quantum physics. This includes discussion on the decoherence and entanglement problems, the projection operator, and stochastic classical and quantum problems. These processes are especially relevant in small molecular clusters, often serving as primary natural functioning devices. Therefore, the adiabatic description of molecules, the concept of Frenkel and Wannier–Mott excitons, charge-transfer excitons, and problems of exciton self-trapping and trapping are also presented. This knowledge helps understand other chapters in this book, especially in Part Two, which is more geared toward graduate students and professionals who are interested in spectroscopy. Since different approaches to the problem are widely used to describe the problem of coherence, various methods used for the description are also discussed. Possible modern approaches for observation of the processes determining the excitation dynamics and relaxation in molecular systems are discussed in Part Two, which is mainly devoted to the theoretical description of the spectroscopic observations. For this purpose the response function formalism is introduced. Various spectroscopic methods are discussed, and the results demonstrating the possibility to distinguish the coherent effects on the excitation dynamics are also presented.

We would like to thank our colleagues and students for their contribution. First of all we mention Vytautas Butkus, who produced almost all the figures in this book and who pushed us all the time to proceed with the book. He was also involved in the theoretical analysis of the two-dimensional spectra of molecular aggregates. We are also grateful to our students, Vytautas Balevicius Jr., Jevgenij Chmeliov, Andrius Gelzinis, Jan Olsina, and others, who were involved in solving various theoretical models. We are thankful to our colleagues and collaborators, the discussions with whom were very stimulating and helped in understanding various aspects in this rapidly developing field of science. Especially we would like to express our appreciation to our colleagues Shaul Mukamel and Graham R. Fleming, who were initiators of two-dimensional coherent electronic spectroscopy and who have inspired our research. We also thank our wives and other members of our families for patience, support, and understanding while we were taking precious time during holidays and vacations to write this book.

Vilnius, Prague  
November 2012

*Leonas Valkunas*  
*Darius Abramavicius*  
*Tomáš Mančal*





**Part One**  
**Dynamics and Relaxation**



# 1

## Introduction

Photoinduced dynamics of excitation in molecular systems are determined by various interactions occurring at different levels of their organization. Depending on the perturbation conditions, the excitation in solids and molecular aggregates may lead to a host of photoinduced dynamics, from coherent and incoherent energy migration to charge generation, charge transfer, crystal lattice deformation, or reorganization of the environmental surroundings. The theoretical description of all these phenomena therefore requires one to treat part of the molecular system as an open system subject to external perturbation. Since perfect insulation of any system from the rest of the world is practically unattainable, the theory of open systems plays a major role in any realistic description of experiments on molecular systems.

In classical physics, the dynamics of an open system is reflected in the temporal evolution of its parameters, leading to a certain fixed point in the corresponding phase space. This fixed point corresponds to a thermodynamic equilibrium, with the unobserved degrees of freedom determining the thermodynamic bath. Many situations in molecular physics allow one to apply a classical or semiclassical description of the evolution of the perturbation-induced excitation in an open system. Often, the influence of the large number of degrees of freedom can be efficiently simulated by stochastic fluctuations of some essential parameters of the system. Such fluctuations may lead to transitions between several stable fixed points in the phase space of the system, or, in a semiclassical situation, to transitions between several states characterized by different energies.

Apart from classical fluctuations, a genuine quantum description might be required when entanglement between constituents of the system has to be considered. This is especially essential for systems with energy gaps larger than the thermal energy, which is an energy characteristic of the bath defined by macroscopic degrees of freedom. Only a full quantum description then leads to proper formation of a thermal equilibrium.

Indeed it is impossible to switch off fluctuations completely. Even if we place a system in a complete vacuum and isolate it from some light sources, there still exist background vacuum fluctuations of the electromagnetic field. Even at zero temperature these fluctuations affect the quantum system, and the resulting spontaneous

emission emerges. All these fluctuations cause decay of excited states and establish thermal equilibrium and stochasticity “in the long run.”

The first part of this book presents a coarse-grained review of the knowledge which is needed for a description of excitation dynamics and relaxation in molecular systems. Basic topics of classical physics which are directly related to the main issue of this book are presented in Chapter 2. It is worthwhile mentioning that concepts of classical physics are also needed for better understanding of the basic behavior of quantum systems. The electromagnetic field, which is responsible for electronic excitations, can usually be well described in terms of classical electrodynamics. Thus, the main principles of this theory and the description of the field–matter interaction are also introduced in Chapter 2. The concept and main applicative features of stochastic dynamics are presented in Chapter 3. Markov processes, the Fokker–Planck equation, and diffusive processes together with some relationships between these descriptions and purely stochastic dynamics are also described in Chapter 3. The basic concepts of quantum mechanics, which is the fundamental theory of the microworld, are presented in Chapter 4. Together with its main postulates and equations, some typical model quantum systems with exact solutions are briefly discussed. The density matrix and second quantization of the vibrations and electromagnetic field are briefly introduced as well. Special attention is paid in this book to consideration of molecular aggregates. The adiabatic approximation, the exciton concept, Frenkel excitons, Wannier–Mott excitons, and charge-transfer excitons are described together with vibronic interactions, the self-trapping problem, and the exciton trapping problem in Chapter 5. Chapter 6 is devoted to a discussion of decoherence and entanglement concepts. The problem of measurements in quantum mechanics and the relative state interpretation are also discussed. The basics of statistical physics are then presented in Chapter 7. The relationship between the statistical approach and thermodynamics is briefly outlined, and standard statistics used for descriptions of classical and quantum behavior are presented. The harmonic oscillator model of the system–bath interaction is described in Chapter 8. In Chapter 9 we describe the projection operator technique together with the concept of the reduced density matrix and its master equations. The path integral technique is then discussed in Chapter 10 together with the stochastic Schrödinger equation approach and the so-called hierarchical equations of motions. Excitation dynamics and relaxation in some model systems are discussed in Chapter 11.

## 2

### Overview of Classical Physics

In this chapter we will review some of the most important concepts of classical physics. Despite the eminent role played by quantum mechanics in the description of molecular systems, classical physics provides an important conceptual and methodological background to most of the theories presented in later chapters and to quantum mechanics itself. Often classical or semiclassical approximations are indispensable to make a theoretical treatment of problems in molecular physics feasible. In the limited space of this chapter we have no intention to provide a complete review as we assume that the reader is familiar with most of the classical concepts. Specialized textbooks are recommended to the interested reader in which the topics presented in this chapter are treated with full rigor (e.g., [1–4]).

#### 2.1

##### Classical Mechanics

Classical mechanics, as the oldest discipline of physics, has provided the formal foundation for most of the other branches of physics. Perhaps with the exception of phenomenological thermodynamics, there is no theory with a similar general validity and success that does not owe its foundations to mechanics. Classical mechanics reached its height with its Lagrangian and Hamiltonian formulations. These subsequently played a very important role in the development of statistical and quantum mechanics.

In classical mechanics, the physical system is described by a set of idealized material points (point-sized particles) in space which interact with each other by a specific set of forces. The coordinates and velocities of all particles fully describe the state of the system of the particles. The three laws formulated by Newton fully describe the properties of motion of this system. The first law states that the particle moves at a constant speed in a predefined direction if it is not affected by a force. The second law relates the change of motion of the particle due to the presence of external forces. The third law defines the symmetry of all forces: particle  $a$  acts on particle  $b$  with the same force as particle  $b$  acts on particle  $a$ .

The dynamics of the system of  $N$  particles is described by a set of differential equations [1, 2, 4]:

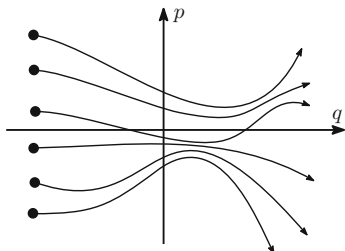
$$m_i \ddot{\mathbf{r}}_i = \sum_j \mathbf{F}_{ij}(\mathbf{r}_1 \dots \mathbf{r}_N). \quad (2.1)$$

Here  $m_i$  is the mass of the  $i$ th particle and  $\mathbf{F}_{ij}$  is the force created by the  $j$ th particle acting on the  $i$ th particle. The velocity of the  $i$ th particle is given by a time derivative of the coordinate  $\dot{\mathbf{r}}_i$ . For a problem formulated in three spatial dimensions the particle momenta  $\mathbf{p}_i = m_i \dot{\mathbf{r}}_i$  together with the coordinates  $\mathbf{r}_i$  create a  $6N$ -dimensional *phase space* in the three-dimensional real space.

The real phase space is often smaller due to specific symmetries, resulting in certain conservation laws. For instance, if the points describe some finite body, which is at rest, the center of mass of all points may be fixed. In that case the dimension of the phase space effectively decreases by six (three coordinates and three momenta corresponding to a center of mass equal to zero). If additionally the body is rigid, we are left with three dimensional phase space, characterizing orientation of the body (e.g. three Euler angles).

A single point in the phase space defines an instantaneous state of the system. The notion of the system's state plays an important role in quantum physics; thus, it is also useful to introduce this type of description in classical physics. The motion of the system according to Newton's laws draws a trajectory in the phase space. In the absence of external forces, the energy of the system is conserved, and the trajectory therefore corresponds to a particular energy value. Different initial conditions draw different trajectories in the phase space as shown schematically in Figure 2.1. The phase space trajectories never intersect or disappear. Later in the discussion of statistical mechanics this notion is used to describe the microcanonical ensemble of an isolated system.

Note that in Newton's equation, (2.1), we can replace  $t$  by  $-t$  and the equation remains the same. Thus, the Newtonian dynamics is invariant to an inversion of the time axis, and the dynamics of the whole system is reversible. This means that Newton's equation for a finite isolated system with coordinate-related pairwise forces has no preferred direction of the time axis. Because energy is conserved, the whole system does not exhibit any damping effects. The damping is often introduced phenomenologically. In order to achieve irreversible dynamics using a



**Figure 2.1** Motion of the system in a phase space starting with different initial conditions.

microscopic description, one has to introduce an infinitely large system so that the observable part is a small open subsystem of the whole. In such a subsystem the damping effects occur naturally from statistical arguments. Various treatments of open systems are described in subsequent chapters.

### 2.1.1

#### Concepts of Theoretical Mechanics: Action, Lagrangian, and Lagrange Equations

Some problems in mechanics can be solved exactly. The feasibility of such an exact solution often depends crucially on our ability to express the problem in an appropriate coordinate system. Let us find now a more general way of expressing mechanical equations of motion that would have the same general form in an arbitrary system of coordinates, and would therefore allow a straightforward transformation from one coordinate system to another. This new form of the representation of Newton's equations is called the Lagrangian formulation of mechanics.

Let us start with Newton's law, (2.1), in the following form:

$$\sum_i (\mathbf{F}_i - m_i \ddot{\mathbf{r}}_i) = 0. \quad (2.2)$$

Here we sum up over all particles in the system, and  $\mathbf{F}_i = \sum_j \mathbf{F}_{ij}$  is the total force acting on the  $i$ th particle. With a given initial condition, the whole trajectory  $\mathbf{r}_i(t)$  of the  $i$ th particle satisfies (2.2). At every point of the trajectory, we can imagine a small displacement of the trajectory  $\delta \mathbf{r}_i(t)$  from  $\mathbf{r}_i(t)$  to  $\mathbf{r}_i(t) + \delta \mathbf{r}_i(t)$ , that is, an infinitesimal variation. We multiply each term of the sum in (2.2) by  $\delta \mathbf{r}_i(t)$  and integrate it over time from  $t_1$  to  $t_2$ . The right-hand side of the equation remains zero. On the left-hand side we assume that the force can be expressed by means of a gradient of the potential  $V$  as  $\mathbf{F}_i = -\partial V / \partial \mathbf{r}_i$ , so we get

$$\int_{t_1}^{t_2} dt \left( \sum_i \frac{\partial V}{\partial \mathbf{r}_i} + m_i \ddot{\mathbf{r}}_i \right) \cdot \delta \mathbf{r}_i(t) = 0. \quad (2.3)$$

The first term on the left-hand side of (2.3) can obviously be written as a variation of an integral over the potential:

$$\int_{t_1}^{t_2} dt \sum_i \frac{\partial V}{\partial \mathbf{r}_i} \cdot \delta \mathbf{r}_i(t) = \delta \int_{t_1}^{t_2} V dt. \quad (2.4)$$

The second term on the left-hand side can be turned into a variation as well. We apply integration by parts and interchange the variation with the derivative to obtain

$$\int_{t_1}^{t_2} dt m_i \ddot{\mathbf{r}}_i \cdot \delta \mathbf{r}_i = [m_i \dot{\mathbf{r}}_i \cdot \delta \mathbf{r}_i]_{t_1}^{t_2} - \int_{t_1}^{t_2} dt m_i \dot{\mathbf{r}}_i \cdot \delta \dot{\mathbf{r}}_i. \quad (2.5)$$

By assuming now that variation of the trajectory  $\delta \mathbf{r}_i(t)$  is zero at times  $t_1$  and  $t_2$ , that is,  $\delta \mathbf{r}_i(t_1) = 0$  and  $\delta \mathbf{r}_i(t_2) = 0$  for all  $i$ , we set the first term on the right-hand side to zero. Therefore, (2.3) reads

$$\delta \int_{t_1}^{t_2} dt \left( \sum_i \frac{1}{2} m_i |\dot{\mathbf{r}}_i|^2 - V \right) = 0. \quad (2.6)$$

Here we used the rules of variation of a product, and we multiplied the equation obtained by  $-1$ . Now, the first term denotes the total kinetic energy of the system. The second term is the full potential energy. Thus, the variation of the kinetic energy must be anticorrelated with the variation of the potential energy. This result is also implied by the conservation of the total energy.

We next denote the kinetic energy term  $\sum_i 1/2 m_i |\dot{\mathbf{r}}_i|^2$  by  $T$ , and introduce two new functions:

$$S = \int_{t_1}^{t_2} L dt, \quad (2.7)$$

where

$$L = T - V. \quad (2.8)$$

Here,  $S$  denotes the *action functional* or simply the *action*. The scalar function  $L$  is the *Lagrangian function*, or the *Lagrangian*. The whole mechanics therefore reduces to the variational problem

$$\delta S = 0, \quad (2.9)$$

also known as the *Hamilton principle*. According to this principle, the trajectories  $\mathbf{r}_i(t)$ , which satisfy Newton's laws of motion, correspond to an extremum of the action functional  $S$ . In Chapter 10, we will see that the action functional plays an important role in the path integral representations of quantum mechanics.

This formulation is independent of any specific choice of coordinates. Trajectories  $\mathbf{r}_i(t)$  can also be expressed in terms of coordinates different from the original Cartesian coordinates  $\mathbf{r}$ . Let us have the Lagrangian expressed in terms of generalized coordinates  $\{q_i\} = \{q_1, q_2, \dots, q_{3N}\}$  and their time derivatives  $\{\dot{q}_i\}$ , where  $N$  is the number of particles. The variational problem, (2.9), then leads to

$$\int_{t_1}^{t_2} dt \left( \frac{\partial L}{\partial q_i} \delta q_i + \frac{\partial L}{\partial \dot{q}_i} \delta \dot{q}_i \right) = 0. \quad (2.10)$$

By integrating the second term by parts under the assumption that  $\delta q_i(t_1) = \delta q_i(t_2) = 0$  as done for (2.6), we obtain

$$\int_{t_1}^{t_2} dt \left[ \frac{\partial L}{\partial q_i} - \frac{d}{dt} \left( \frac{\partial L}{\partial \dot{q}_i} \right) \right] \delta q_i = 0. \quad (2.11)$$



This can only be satisfied for an arbitrary value of  $\delta q_i$  if

$$\frac{d}{dt} \left( \frac{\partial}{\partial \dot{q}_i} L \right) - \frac{\partial}{\partial q_i} L = 0. \quad (2.12)$$

Equation (2.12) is the famous *Lagrange equation* of classical mechanics in a form independent of the choice of the coordinate system.

There is some flexibility in choosing a particular form of the Lagrangian. If we define a new Lagrangian  $L'$  by adding a total time derivative of a function of coordinates,

$$L'(q_i, \dot{q}_i, t) = L(q_i, \dot{q}_i, t) + \frac{d}{dt} f(q_i, t), \quad (2.13)$$

the equations of motion remain unchanged. The corresponding action integral  $S'$  is

$$\begin{aligned} S' &= \int_{t_1}^{t_2} dt L + \int_{t_1}^{t_2} dt \frac{d}{dt} f(q_i, t) \\ &= \int_{t_1}^{t_2} dt L + f(q_i(t_2), t_2) - f(q_i(t_1), t_1), \end{aligned} \quad (2.14)$$

where the last two terms do not contribute to a variation with fixed points at times  $t_1$  and  $t_2$ . By means of (2.13), the Lagrangian can sometimes be converted into a form more convenient for description of a particular physical situation. We will give an example of such a situation in Section 2.4.3.

### 2.1.2

#### Hamilton Equations

A more symmetric formulation of mechanics can be achieved by introducing generalized momenta  $p_i$  as conjugate quantities of coordinates  $q_i$ . So far the independent variables of the Lagrangian were  $q_i$  and  $\dot{q}_i$ . Now we will define the generalized momentum corresponding to the coordinate  $q_i$  as

$$p_i = \frac{\partial}{\partial \dot{q}_i} L. \quad (2.15)$$

It can be easily shown that in Cartesian coordinates the momentum  $p_i = m\dot{q}_i$  is conjugate to the coordinate  $r_i$ . Let us investigate the variation of the Lagrangian:

$$\delta L = \sum_i \frac{\partial L}{\partial q_i} \delta q_i + \sum_i \frac{\partial L}{\partial \dot{q}_i} \delta \dot{q}_i. \quad (2.16)$$

First, from (2.12) and (2.15) we obtain a very symmetric expression:

$$\delta L = \sum_i \dot{p}_i \delta q_i + \sum_i p_i \delta \dot{q}_i, \quad (2.17)$$

which can also be written as

$$\delta L = \sum_i \dot{p}_i \delta q_i + \delta \left( \sum_i p_i \dot{q}_i \right) - \sum_i \dot{q}_i \delta p_i . \quad (2.18)$$

This in turn can be written in such a way that we have a variation of a certain function on the left-hand side and an expression with variations of  $p_i$  and  $q_i$  only on the right-hand side:

$$\delta \left( \sum_i p_i \dot{q}_i - L \right) = \sum_i \dot{q}_i \delta p_i - \sum_i \dot{p}_i \delta q_i . \quad (2.19)$$

The expression on the left-hand side,

$$H = \sum_i p_i \dot{q}_i - L , \quad (2.20)$$

must therefore be a function of parameters  $p_i$  and  $q_i$  only, that is,  $H = H(p_i, q_i)$ . By taking its formal variation and using (2.19), we arrive at

$$\delta H = \sum_i \frac{\partial H}{\partial q_i} \delta q_i + \sum_i \frac{\partial H}{\partial p_i} \delta p_i = \sum_i \dot{q}_i \delta p_i - \sum_i \dot{p}_i \delta q_i . \quad (2.21)$$

Comparing the coefficients of variations of  $\delta q_i$  and  $\delta p_i$ , we get two independent equations:

$$\dot{p}_i = - \frac{\partial H}{\partial q_i} \quad (2.22)$$

and

$$\dot{q}_i = \frac{\partial H}{\partial p_i} . \quad (2.23)$$

Equations (2.22) and (2.23) are known as the canonical or *Hamilton equations* of classical mechanics. We usually call the momentum  $p_i$  the *canonically conjugated momentum* only to the coordinate  $q_i$ . The Hamilton equations represent mechanics in a very compact and elegant way by the set of first-order differential equations.

The Hamiltonian or Lagrangian formalism applies to systems with gradient forces, that is, those which are given by derivatives of potentials. This assumption is true when considering gravitational, electromagnetic, and other fundamental forces. However, frictional forces often included phenomenologically in the mechanical description of dynamic systems cannot be given as gradients of some friction potential. Thus, the Hamiltonian description cannot describe friction phenomena. The microscopic relaxation theory and openness of the dynamic system are required to obtain a theory with the relaxation phenomena.

## 2.1.3

**Classical Harmonic Oscillator**

Let us consider a one-dimensional case describing the movement of a particle along coordinate  $x$ . Correspondingly the potential is defined as  $V(x)$ . The force acting on the particle is then  $F(x) = -\text{grad } V = -\partial/\partial x V(x)$ , and according to Newton's laws we can write the equation of motion as

$$m\ddot{x} = -\frac{\partial}{\partial x} V(x). \quad (2.24)$$

In the Lagrange formulation we can define the Lagrangian as the difference of kinetic and potential energies, getting for a particle with mass  $m$

$$L = m\frac{\dot{x}^2}{2} - V(x). \quad (2.25)$$

From (2.12) it follows that  $\partial/\partial \dot{x} L = m\dot{x}$ ,  $\partial/\partial x L = -\partial/\partial x V(x)$ , and thus

$$\frac{d}{dt}(m\dot{x}) + \frac{\partial}{\partial x} V(x) = 0, \quad (2.26)$$

which is equivalent to the Newton's equation as demonstrated in the previous sections.

Similarly, we can write the Hamiltonian

$$H = \frac{p^2}{2m} + V(x), \quad (2.27)$$

where the momentum  $p = m\dot{x}$ . In this case the Hamilton equations of motion read

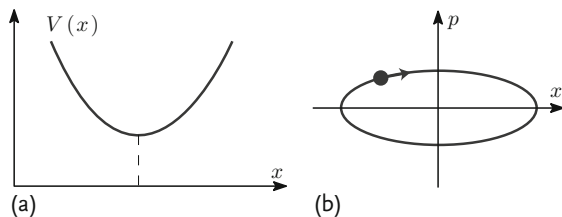
$$\dot{p} = -\frac{\partial}{\partial x} V(x), \quad (2.28)$$

$$\dot{x} = \frac{p}{m}. \quad (2.29)$$

Again we get the same set of equations of motion, which means that the dynamics is equivalent whatever type of description is chosen. However, the Hamiltonian formulation gives one clue about the number of independent variables. In this case we obtain two equations for variables  $x$  and  $p$ , the coordinate and the momentum, respectively. Thus, in the context of dynamic equations, it is a two-dimensional system (two-dimensional phase space).

We can easily solve the equations of motion when the potential surface has a parabolic form as shown in Figure 2.2. In this case the dynamics corresponds to the time evolution of the harmonic oscillator with the potential defined by  $V(x) = kx^2/2$ . Then the equation of motion is

$$m\ddot{x} + kx = 0, \quad (2.30)$$



**Figure 2.2** Parabolic potential of the harmonic oscillator (a), and the two-dimensional phase space of the oscillator (b). The trajectory is the ellipse or the circle.

and the solution is given by

$$x(t) = A \cos(\omega t) + B \sin(\omega t), \quad (2.31)$$

which yields

$$\omega^2 = k/m. \quad (2.32)$$

Let us take the initial condition  $x(0) = x_0$ ,  $\dot{x}(0) = \dot{x}_0$ . We then get  $A = x_0$  and  $B = \dot{x}_0/\omega$ . The final solution is then

$$x(t) = x_0 \cos(\omega t) + \frac{\dot{x}_0}{\omega} \sin(\omega t). \quad (2.33)$$

We thus find that the frequency of the oscillator is described by the stiffness of the force parameter  $k$  and the mass of the particle  $m$ . Keeping this in mind, we can write the potential energy as

$$V(x) = m\omega^2 \frac{x^2}{2}. \quad (2.34)$$

The oscillator equation can be given in somewhat more convenient form by introducing dimensionless parameters. Let us take Hamiltonian (2.27) and denote  $m\omega^2 l^2 = \alpha\omega$ , where  $l$  is some typical length of the oscillation and  $\alpha$  is a constant. Denoting  $y = x/l$  and  $z = p/(m\omega l)$  or  $z = \dot{y}/\omega$ , we get the Hamiltonian in a symmetric form where the coordinate and the momentum are dimensionless:

$$H = \frac{1}{2} \alpha \omega (y^2 + z^2). \quad (2.35)$$

Later we will find that this form of the Hamiltonian is equivalent to the Hamiltonian of the quantum harmonic oscillator and the constant  $\alpha$  is associated with the reduced Planck constant.

The solution of the dynamic equations can now be written as

$$y(t) = \text{Re} \left( \frac{x_0}{l} + \frac{\dot{x}_0}{i l \omega} \right) e^{i\omega t}, \quad (2.36)$$

$$z(t) = -\text{Im} \left( \frac{x_0}{2l} + \frac{\dot{x}_0}{2il\omega} \right) e^{i\omega t}, \quad (2.37)$$

which shows that the phase space defined by the  $y$  and  $z$  axes corresponds to the complex plane and a point  $x_0/l + \dot{x}_0/(il\omega)$  in this space draws a circle. In the following we often face the application of classical or quantum oscillators. The latter is described in Section 4.6.1.

## 2.2

### Classical Electrodynamics

For our introduction to classical electrodynamics, the microscopic Maxwell–Lorentz equations provide a convenient starting point. They enable us to view matter as an ensemble of charged particles, as opposed to the continuum view of macroscopic electrodynamics. The microscopic electric and magnetic fields are usually denoted by  $\mathbf{E}$  and  $\mathbf{B}$ , respectively. Let us assume that there are particles with charges  $q_i$  located at points  $\mathbf{r}_i$  in space. The density of charge and the density of current can be then defined as

$$\varrho(\mathbf{r}) = \sum_i q_i \delta(\mathbf{r} - \mathbf{r}_i), \quad \mathbf{j}(\mathbf{r}) = \sum_i q_i \dot{\mathbf{r}}_i \delta(\mathbf{r} - \mathbf{r}_i). \quad (2.38)$$

The Maxwell–Lorentz equations for the fields in a vacuum read [3, 5]

$$\nabla \cdot \mathbf{E} = \frac{\varrho(\mathbf{r})}{\epsilon_0}, \quad (2.39)$$

$$\nabla \cdot \mathbf{B} = 0, \quad (2.40)$$

$$\nabla \times \mathbf{E} = -\frac{\partial}{\partial t} \mathbf{B}, \quad (2.41)$$

$$\nabla \times \mathbf{B} = \frac{1}{c^2} \frac{\partial}{\partial t} \mathbf{E} + \mu_0 \frac{\partial}{\partial t} \mathbf{j}. \quad (2.42)$$

We introduced the usual constants – vacuum permittivity  $\epsilon_0$ , magnetic permeability  $\mu_0$ , and the speed of light in a vacuum  $c$ , which are all related through  $c = 1/\sqrt{\epsilon_0\mu_0}$ .  $\nabla \cdot$  denotes divergence, and  $\nabla \times$  is the curl operator as described in Appendix A.1.

The same equations are valid for the microscopic and macroscopic cases. The difference is only in the charge and current densities, which in the macroscopic case are assumed to be continuous functions of space, while in the microscopic case the charge and current densities are given as a collection of microscopic points and their velocities.

## 2.2.1

**Electromagnetic Potentials and the Coulomb Gauge**

For the subsequent discussion, it is advantageous to introduce the *vector potential*  $\mathbf{A}$  which determines the magnetic field through the following relation:

$$\mathbf{B} = \nabla \times \mathbf{A} . \quad (2.43)$$

The magnetic field given by such an expression automatically satisfies the second Maxwell–Lorentz equation, (2.40). Since for any scalar function  $\chi$  we have the identity  $\nabla \times (\nabla\chi) = 0$ , the vector potential is defined up to the so-called *gauge function*  $\chi$ , and the transformation

$$\mathbf{A} \rightarrow \mathbf{A} + \nabla\chi \quad (2.44)$$

does not change the magnetic field.

The same identity allows us to rewrite the third Maxwell–Lorentz equation, (2.41), in a more convenient form. Applying definition (2.43) to (2.41), we obtain

$$\nabla \times \left( \mathbf{E} + \frac{\partial}{\partial t} \mathbf{A} \right) = 0 , \quad (2.45)$$

which can be satisfied by postulating a *scalar potential*  $\phi$  through

$$-\nabla\phi = \mathbf{E} + \frac{\partial}{\partial t} \mathbf{A} . \quad (2.46)$$

It is easy to see that if  $\mathbf{A}$  is transformed by (2.44), the simultaneous transformation

$$\phi \rightarrow \phi - \frac{\partial}{\partial t} \chi \quad (2.47)$$

keeps (2.46) satisfied. The transformation composed of (2.44) and (2.47) is known as the *gauge transformation*, and the Maxwell–Lorentz equations are invariant with respect to this transformation. This phenomenon is denoted as gauge invariance.

The freedom in the choice of  $\mathbf{A}$  and  $\phi$  can be used to transform Maxwell–Lorentz equations into a form convenient for a particular physical situation. Here we will use the well-known *Coulomb gauge*, which is useful for separating the radiation part of the electromagnetic field from the part associated with charges. The Coulomb gauge is defined by the condition

$$\nabla \cdot \mathbf{A} = 0 , \quad (2.48)$$

which can always be satisfied [6].

## 2.2.2

**Transverse and Longitudinal Fields**

The Maxwell–Lorentz equations provide a complete description of the system of charges and electromagnetic fields, including their mutual interaction. In most of