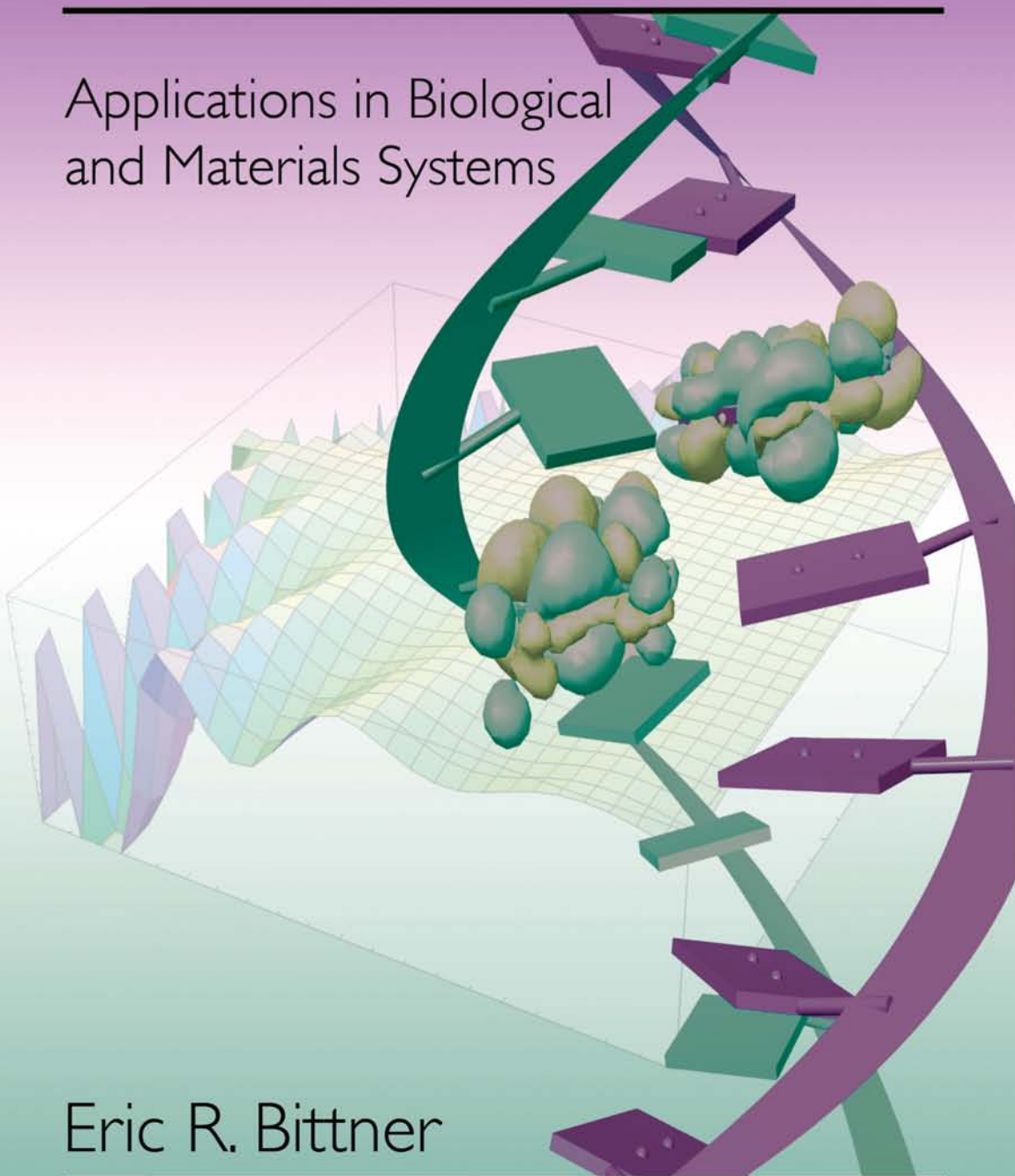


QUANTUM DYNAMICS

Applications in Biological
and Materials Systems



Eric R. Bittner



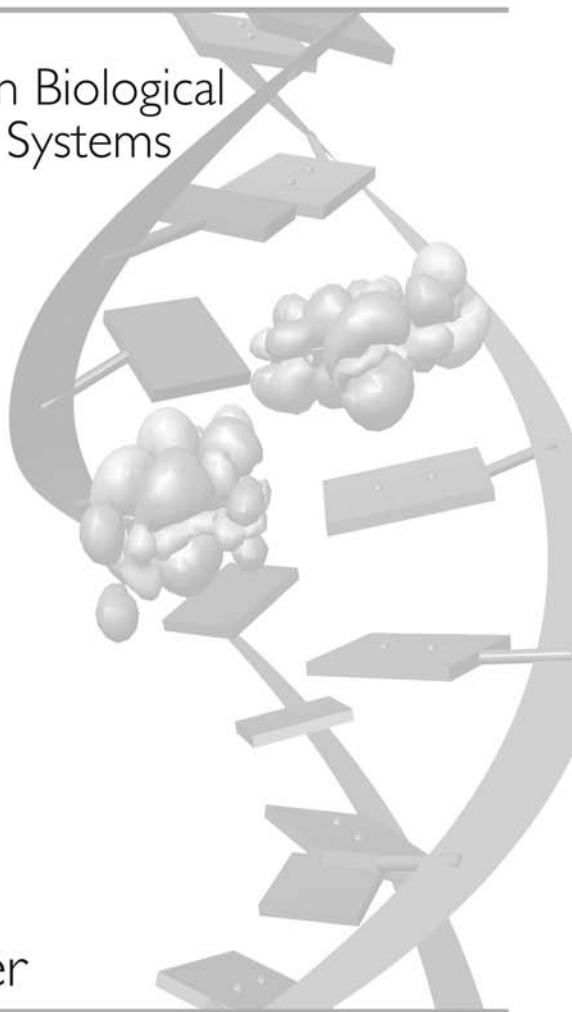
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Preface

Why do we need another book on quantum mechanics? Go to any university library and you're bound to find hundreds of textbooks on this subject. A number are truly outstanding and nearly everyone has a favorite. In my case, I very much like Cohen-Tannoudji's two-volume text, although Merzbach, Feynman, and Hibbs and Landau and Lifshitz hold their own places of honor on my bookshelf. So, why go through the bother and effort of trying to say something new? The majority of leading texts focus upon the solution of Schrödinger's equation for a handful of solvable problems. Some will venture into the realm of scattering theory and most will have a good presentation of second quantization. However, the discussion of time-dependent quantum dynamics is typically limited to the spread of a Gaussian wave packet, the dispersionless evolution of a Gaussian in a parabolic potential, and time-dependent perturbation theory leading to Fermi's golden rule.

This book grew out of the need to fill a glaring gap between the standard quantum mechanics textbooks and more specialized texts. It has evolved out of a series of lecture notes for a course on this topic that I have presented intermittently over the past decade, and it has grown out of my own attempts to study the underlying physics of quantum relaxation dynamics as applied to chemical systems. For certain, this book draws from a variety of deep wells.

One significant focus of modern chemical physics is the experimental detection of quantum dynamical processes that occur in chemical systems, typically in a condensed phase environment. With the rapid advance of multiphonon spectroscopies, we are beginning to probe some of nature's most important processes, such as the light-harvesting mechanism in photosynthetic systems or the mechanism of photo-damage to DNA. We have also turned these tools to study similar ultrafast processes in nanoscale materials that may eventually be used for artificial photosynthetic systems, electronic switches, or light sources. Understanding these systems requires an in-depth knowledge of time-dependent quantum mechanics beyond what is presented in a typical graduate-level course.

Regarding scope and level, I deliberately chose not to include much detail on solving the standard models for the harmonic oscillator, hydrogen atom, quantized angular momentum, and so forth. These appear in all standard textbooks and I saw little need to rework these models here. A truly comprehensive text would fill at least two complete bookshelves. However, I do rely upon such models for bases and approximations, and I summarize the essential features (eigenstates, spectrum, and so on) as needed. I assume that the reader is familiar with the essential theory of quantum mechanics as presented in a typical undergraduate-level physical chemistry course, and we have used this material in our first-year graduate quantum chemistry course at the University of Houston. My assumption is that students are acquainted with the notion of quantization and its role in molecular spectroscopy. Applications and codes for further illustration can be found on the accompanying Web site (http://k2.chem.uh.edu/quantum_dynamics). A solutions manual is also available for download.

Much of this was committed to text over the course of my sabbatical at Cambridge in 2007, and I wish to thank all the students, postdocs, and colleagues who helped track down typos, clarify sessions, provide figures, and so on. I thank the editors at CRC/Taylor & Francis for keeping me on target to complete this. I also thank the postdocs and graduate students in my group for contributing figures, proofreading, and working problems.

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Cambridge, U.K. & Houston, Texas

About the Author

Eric Bittner is currently the John and Rebecca Moores Distinguished Professor of chemical physics at the University of Houston. He received his PhD from the University of Chicago in 1994 and was a National Science Foundation Postdoctoral Fellow at the University of Texas at Austin and at Stanford University before moving to the University of Houston in 1997. His accolades include an NSF Career Award and a Guggenheim Fellowship. He has also held visiting appointments at the University of Cambridge, the *École Normale Supérieure*, Paris, and at Los Alamos National Lab. His research is focused in the areas of quantum dynamics as applied to organic polymer semiconductors, object linking and embedding directory services (OLEDS), solar cells, and energy transport in biological systems.

1 Survey of Classical Mechanics

Quantum mechanics is in many ways the cumulation of many hundreds of years of work and thought about how mechanical things move and behave. Since ancient times, scientists have wondered about the structure of matter and have tried to develop a generalized and underlying theory that governs how matter moves at all length scales.

For ordinary objects, the rules of motion are very simple. By ordinary, I mean objects that are more or less on the same length and mass scale as you and I, say (conservatively) 10^{-7} m to 10^6 m and 10^{-25} g to 10^8 g moving at less than 20% of the speed of light. On other words, almost everything you can see and touch and hold obeys what are called *classical* laws of motion. The term *classical* means that that the basic principles of this class of motion have their foundation in antiquity. Classical mechanics is an extremely well-developed area of physics. While you may think that because classical mechanics has been studied extensively for hundreds of years there really is little new development in this field, it remains a vital and extremely active area of research. Why? Because the majority of universe “lives” in a dimensional realm where classical mechanics is extremely valid. Classical mechanics is the workhorse for atomistic simulations of fluids, proteins, and polymers. It provides the basis for understanding chaotic systems. It also provides a useful foundation of many of the concepts in quantum mechanics.

Quantum mechanics provides a description of how matter behaves at very small length and mass scales, that is, the realm of atoms, molecules, and below. It has been developed over the past century to explain a series of experiments on atomic systems that could not be explained using purely classical treatments. The advent of quantum mechanics forced us to look beyond the classical theories. However, it was not a drastic and complete departure. At some point, the two theories must correspond so that classical mechanics is the limiting behavior of quantum mechanics for macroscopic objects. Consequently, many of the concepts we will study in quantum mechanics have direct analogs to classical mechanics: momentum, angular momentum, time, potential energy, kinetic energy, and action.

Much as classical music is cast in a particular style, classical mechanics is based upon the principle that the motion of a body can be reduced to the motion of a point particle with a given mass m , position x , and velocity v . In this chapter, we will review some of the concepts of classical mechanics which are necessary for studying quantum mechanics. We will cast these in forms whereby we can move easily back and forth between classical and quantum mechanics. We will first discuss Newtonian motion and cast this into the Lagrangian form. We will then discuss the principle of least action and Hamiltonian dynamics and the concept of phase space.

1.1 NEWTON'S EQUATIONS OF MOTION

1.1.1 NEWTON'S POSTULATES

Why do things move? Why does an apple fall from a tree? This is usually the first sort of problem we face in trying to study the motion and dynamics of particles and develop laws of nature that are independent of a particular situation.

We understand the concept of *force*. We all have pushed, pulled, or thrown something. Those actions require an action or force from the muscles in our body. Newton proposed a set of basic rules or postulates which he thought could describe the rules that all objects obey under the influence of any kind of force.

Postulate 1.1

Law of Inertia: A free particle always moves without acceleration.

That is, a particle that is not under the influence of an outside force moves along a straight line at constant speed, or remains at rest.

Postulate 1.2

Law of Motion: The rate of change of an object's momentum is equal to the force acting upon it.

$$\frac{d\vec{p}}{dt} = \vec{F} \quad (1.1)$$

This is equivalent to $\vec{F} = m\vec{a}$ where $\vec{a} = d\vec{v}/dt$ is the acceleration. Note that in Newton's first postulate, we assume that the mass does not change with time.

Postulate 1.3

Law of Action: For every action, there is an equal and opposite reaction.

$$\vec{F}_{12} = -\vec{F}_{21} \quad (1.2)$$

This is to say that if particle 1 pushes on particle 2 with force F , then particle 2 pushes on particle 1 with a force $-F$. In SI units, the unit of force is the Newton, $1N = 1kg \cdot m \cdot s^{-2}$.

Newton's *Principia* set the theoretical basis of mathematical mechanics and analysis of physical bodies. The equation that force equals mass times acceleration is the fundamental equation of classical mechanics. Stated mathematically,

$$m\ddot{x} = f(x) \quad (1.3)$$

The dots refer to differentiation with respect to time. We will use this notion for time derivatives. We may also use x' or dx/dt as well. So,

$$\ddot{x} = \frac{d^2x}{dt^2} \quad (1.4)$$

For now we are limiting ourselves to one particle moving in one dimension. For motion in more dimensions, we need to introduce vector components. In Cartesian

coordinates, Newton's equations are

$$m\ddot{x} = f_x(x, y, z) \quad (1.5)$$

$$m\ddot{y} = f_y(x, y, z) \quad (1.6)$$

$$m\ddot{z} = f_z(x, y, z) \quad (1.7)$$

where the force vector $\vec{f}(x, y, z)$ has components in all three dimensions and varies with location. We can also define a position vector $\vec{x} = (x, y, z)$ and velocity vector $\vec{v} = (\dot{x}, \dot{y}, \dot{z})$. We can also replace the second-order differential equation with two first-order equations

$$\dot{x} = v_x \quad (1.8)$$

$$\dot{v}_x = f_x/m \quad (1.9)$$

These, along with the initial conditions $x(0)$ and $v(0)$, are all that are needed to solve for the motion of a particle with mass m given a force f . We could have chosen two endpoints as well and asked, What path must the particle take to get from one point to the next? Let us consider some elementary solutions.

First, the case in which $f = 0$ and $\ddot{x} = 0$. Thus, $v = \dot{x} = \text{const.}$ So, unless there is an applied force, the velocity of a particle will remain unchanged.

Second, we consider the case of a linear force $f = -kx$. This is restoring force for a spring and such force laws are termed *Hooke's law* and k is termed the *force constant*. Our equations are

$$\dot{x} = v_x \quad (1.10)$$

$$\dot{v}_x = -k/mx \quad (1.11)$$

or $\ddot{x} = -(k/m)x$. So we want some function which is its own second derivative multiplied by some number. The cosine and sine functions have this property, so let us try

$$x(t) = A \cos(at) + B \sin(bt) \quad (1.12)$$

Taking time derivatives,

$$\dot{x}(t) = -aA \sin(at) + bB \cos(bt) \quad (1.13)$$

$$\ddot{x}(t) = -a^2A \cos(at) - b^2B \sin(bt) \quad (1.14)$$

So we get the required result if $a = b = \sqrt{k/m}$, leaving A and B undetermined. Thus, we need two initial conditions to specify these coefficients. Let us pick $x(0) = x_o$ and $v(0) = 0$. Thus, $x(0) = A = x_o$ and $B = 0$. Notice that the term $\sqrt{k/m}$ has units of angular frequency,

$$\omega = \sqrt{\frac{k}{m}} \quad (1.15)$$

So, our equations of motion are

$$x(t) = x_o \cos(\omega t) \quad (1.16)$$

$$v(t) = -x_o\omega \sin(\omega t) \quad (1.17)$$

Let us now consider a two-dimensional example where we have a particle launched upwards at some initial velocity and we wish to predict where it will land. We shall neglect frictional forces.

The equations of motion in each direction are as follows. In the vertical direction,

$$m\ddot{y} = -mg \quad (1.18)$$

where g is the gravitational constant and the force $-mg$ is the attractive force due to gravity. In x , we have

$$m\ddot{x} = 0 \quad (1.19)$$

since there are no net forces acting in the x direction. Hence, we can solve the x equation immediately since $\dot{v}_x = 0$ and thus, $x(t) = v_x(0)t + x_o = v_o t \cos(\phi)$. For the y equation, denote $v_y = \dot{y}$,

$$m \frac{d}{dt} v_y = -mg \quad (1.20)$$

Integrating, $v_y = -gt + \text{const}$. Evaluating this at $t = 0$, $v_y(0) = v_o \sin(\phi) = \text{const}$. Thus,

$$v_y(t) = -gt + v_o \sin(\phi) \quad (1.21)$$

This we can integrate as

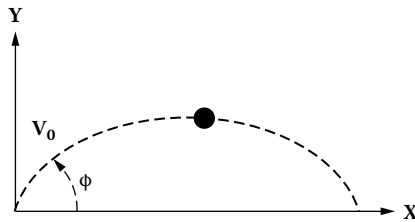
$$\int dy = \int (-gt + v_o \sin(\phi)) dt \quad (1.22)$$

that is,

$$y = v_o \sin(\phi)t - \frac{g}{2}t^2 \quad (1.23)$$

So the trajectory in y is parabolic. To determine the point of impact, we seek the roots of the equation

$$\left(v_o \sin(\phi)t - \frac{g}{2}t^2 \right) = 0 \quad (1.24)$$



Either $t = 0$ or

$$t_I = \frac{2}{g} v_o \sin(\phi) \quad (1.25)$$

We can now ask this question: What angle do we need to point our cannon to hit a target X meters away? In time t_I the cannon ball will travel a distance $x = v_o \cos(\phi)t_I$. Substituting our expression for the impact time:

$$X = v_o^2 \cos(\phi) \frac{2}{g} \sin(\phi) = \frac{v_o^2 \sin(2\phi)}{g} \quad (1.26)$$

Thus,

$$\sin(2\phi) = \frac{g}{v_o^2} X \quad (1.27)$$

One can also see that the maximum range is obtained when $\phi = \pi/4$.

1.2 LAGRANGIAN MECHANICS

1.2.1 THE PRINCIPLE OF LEAST ACTION

The most general form of the law governing the motion of a mass is the principle of least action or Hamilton's principle. The basic idea is that every mechanical system is described by a single function of coordinate, velocity, and time: $L(x, \dot{x}, t)$ and that the motion of the particle is such that certain conditions are satisfied. That condition is that the time integral of this function

$$S = \int_{t_o}^{t_f} L(x, \dot{x}, t) dt \quad (1.28)$$

takes the least possible value given a path that starts at x_o at the initial time and ends at x_f at the final time.

Let us take $x(t)$ to be a function for which S is minimized. This means that S must increase for any variation about this path, $x(t) + \delta x(t)$. Since the endpoints are specified, $\delta x(0) = \delta x(t) = 0$ and the change in S upon replacement of $x(t)$ with $x(t) + \delta x(t)$ is

$$\delta S = \int_{t_o}^{t_f} L(x + \delta x, \dot{x} + \delta \dot{x}, t) dt - \int_{t_o}^{t_f} L(x, \dot{x}, t) dt = 0 \quad (1.29)$$

This is zero because S is a minimum. Now, we can expand the integrand in the first term

$$L(x + \delta x, \dot{x} + \delta \dot{x}, t) = L(x, \dot{x}, t) + \left(\frac{\partial L}{\partial x} \delta x + \frac{\partial L}{\partial \dot{x}} \delta \dot{x} \right) \quad (1.30)$$

Thus, we have

$$\int_{t_o}^{t_f} \left(\frac{\partial L}{\partial x} \delta x + \frac{\partial L}{\partial \dot{x}} \delta \dot{x} \right) dt = 0 \quad (1.31)$$

Since $\delta \dot{x} = d\delta x/dt$ and integrating the second term by parts

$$\delta S = \left[\frac{\partial L}{\partial \dot{x}} \delta x \right]_{t_o}^{t_f} + \int_{t_o}^{t_f} \left(\frac{\partial L}{\partial x} - \frac{d}{dt} \frac{\partial L}{\partial \dot{x}} \right) \delta x dt = 0 \quad (1.32)$$

The surface term vanishes because of the condition imposed above. This leaves the integral. It too must vanish and the only way for this to happen is if the integrand itself vanishes. Thus we have

$$\frac{\partial L}{\partial x} - \frac{d}{dt} \frac{\partial L}{\partial \dot{x}} = 0 \quad (1.33)$$

L is known as the Lagrangian. Before moving on, we consider the case of a free particle. The Lagrangian in this case must be independent of the position of the particle since a freely moving particle defines an inertial frame. Since space is isotropic, L must depend upon only the magnitude of v and not its direction. Hence,

$$L = L(v^2) \quad (1.34)$$

Since L is independent of x , $\partial L / \partial x = 0$, so the Lagrange equation is

$$\frac{d}{dt} \frac{\partial L}{\partial v} = 0 \quad (1.35)$$

So, $\partial L / \partial v = \text{const}$, which leads us to conclude that L is quadratic in v . In fact,

$$L = \frac{1}{m} v^2 \quad (1.36)$$

which is the *kinetic energy* for a particle

$$T = \frac{1}{2} m v^2 = \frac{1}{2} m \dot{x}^2 \quad (1.37)$$

For a particle moving in a potential field V , the Lagrangian is given by

$$L = T - V \quad (1.38)$$

L has units of energy and gives the difference between the energy of motion and the energy of location.

This leads to the equations of motion:

$$\frac{d}{dt} \frac{\partial L}{\partial v} = \frac{\partial L}{\partial x} \quad (1.39)$$

Substituting $L = T - V$ yields

$$m \dot{v} = - \frac{\partial V}{\partial x} \quad (1.40)$$

which is identical to Newton's equations given above once we identify the force as the minus of the derivative of the potential. For the free particle, $v = \text{const}$. Thus,

$$S = \int_{t_o}^{t_f} \frac{m}{2} v^2 dt = \frac{m}{2} v^2 (t_f - t_o) \quad (1.41)$$

You may be wondering at this point why we needed a new function and derived all this from some minimization principle. The reason is that for some systems we

have constraints on the type of motion they can undertake. For example, there may be bonds, hinges, and other mechanical hindrances that limit the range of motion a given particle can take. The Lagrangian formalism provides a mechanism for incorporating these extra effects in a consistent and correct way. In fact we will use this principle later in deriving a variational solution to the Schrödinger equation by constraining the wave function solutions to be orthonormal.

Lastly, it is interesting to note that $v^2 = (dl/dt)^2 = (dl)^2/(dt)^2$ is the square of the element of an arc in a given coordinate system. Thus, within the Lagrangian formalism it is easy to convert from one coordinate system to another. For example, in Cartesian coordinates: $dl^2 = dx^2 + dy^2 + dz^2$. Thus, $v^2 = \dot{x}^2 + \dot{y}^2 + \dot{z}^2$. In cylindrical coordinates, $dl = dr^2 + r^2 d\phi^2 + dz^2$, we have the Lagrangian

$$L = \frac{1}{2}m(\dot{r}^2 + r^2\dot{\phi}^2 + \dot{z}^2) \quad (1.42)$$

and for spherical coordinates, $dl^2 = dr^2 + r^2 d\theta^2 + r^2 \sin^2 \theta d\phi^2$; hence,

$$L = \frac{1}{2}m(\dot{r}^2 + r^2\dot{\theta}^2 + r^2 \sin^2 \theta \dot{\phi}^2) \quad (1.43)$$

1.2.2 EXAMPLE: THREE-DIMENSIONAL HARMONIC OSCILLATOR IN SPHERICAL COORDINATES

Here we take the potential energy to be a function of r alone (isotropic)

$$V(r) = kr^2/2 \quad (1.44)$$

Thus, the Lagrangian in Cartesian coordinates is

$$L = \frac{m}{2}(\dot{x}^2 + \dot{y}^2 + \dot{z}^2) + \frac{k}{2}r^2 \quad (1.45)$$

Since $r^2 = x^2 + y^2 + z^2$, we could easily solve this problem in Cartesian space since

$$L = \frac{m}{2}(\dot{x}^2 + \dot{y}^2 + \dot{z}^2) + \frac{k}{2}(x^2 + y^2 + z^2) \quad (1.46)$$

$$= \left(\frac{m}{2}\dot{x}^2 + \frac{k}{2}x^2 \right) + \left(\frac{m}{2}\dot{y}^2 + \frac{k}{2}y^2 \right) + \left(\frac{m}{2}\dot{z}^2 + \frac{k}{2}z^2 \right) \quad (1.47)$$

and we see that the system is separable into three independent oscillators. To convert to spherical polar coordinates, we use

$$x = r \sin(\phi) \cos(\theta) \quad (1.48)$$

$$y = r \sin(\phi) \sin(\theta) \quad (1.49)$$

$$z = r \cos(\theta) \quad (1.50)$$

and the arc length given above

$$L = \frac{m}{2}(\dot{r}^2 + r^2\dot{\theta}^2 + r^2 \sin^2 \theta \dot{\phi}^2) - \frac{k}{2}r^2 \quad (1.51)$$

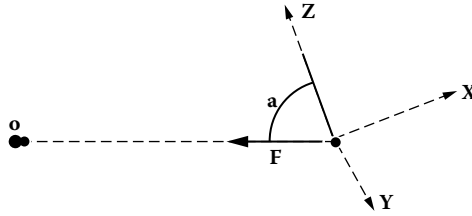


FIGURE 1.1 Vector diagram for motion in central forces. The particle's motion is along the Z axis, which lies in the plane of the page.

The equations of motion are

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{\phi}} - \frac{\partial L}{\partial \phi} = \frac{d}{dt} mr^2 \sin^2 \theta \dot{\phi} = 0 \quad (1.52)$$

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{\theta}} - \frac{\partial L}{\partial \theta} = \frac{d}{dt} (mr^2 \dot{\theta}) - mr^2 \sin \theta \cos \theta \dot{\phi} = 0 \quad (1.53)$$

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{r}} - \frac{\partial L}{\partial r} = \frac{d}{dt} (m\dot{r}) - mr\dot{\theta}^2 - mr \sin^2 \theta \dot{\phi}^2 + kr = 0 \quad (1.54)$$

We now prove that the motion of a particle in a central force field lies in a plane containing the origin. The force acting on the particle at any given time is in a direction toward the origin. Now, place an arbitrary Cartesian frame centered about the particle with the z axis parallel to the direction of motion as sketched in Figure 1.1. Note that the y axis is perpendicular to the plane of the page, and hence, there is no force component in that direction. Consequently, the motion of the particle is constrained to lie in the zx plane, that is the plane of the page, and there is no force component that will take the particle out of this plane.

Let us make a change of coordinates by rotating the original frame to a new one whereby the new z' is perpendicular to the plane containing the initial position and velocity vectors. In Figure 1.1, this new z' axis would be perpendicular to the page and would contain the y axis we placed on the moving particle. In terms of these new coordinates, the Lagrangian will have the same form as previously since our initial choice of axis was arbitrary. However, now we have some additional constraints. Because the motion is now constrained to lie in the $x'y'$ plane, $\theta' = \pi/2$ is a constant, and $\dot{\theta} = 0$. Thus $\cos(\pi/2) = 0$ and $\sin(\pi/2) = 1$ in the previous equations. From the equations for ϕ we find

$$\frac{d}{dt} mr^2 \dot{\phi} = 0 \quad (1.55)$$

or

$$mr^2 \dot{\phi} = \text{const} = p_{\phi} \quad (1.56)$$

This we can put into the equation for r

$$\frac{d}{dt}(m\dot{r}) - m r \dot{\phi}^2 + kr = 0 \quad (1.57)$$

$$\frac{d}{dt}(m\dot{r}) - \frac{p_\phi^2}{mr^3} + kr = 0 \quad (1.58)$$

where we notice that $-p_\phi^2/mr^3$ is the centrifugal force. Taking the last equation, multiplying by $\dot{r}$, and then integrating with respect to time gives

$$\dot{r}^2 = -\frac{p_\phi^2}{m^2 r^2} - kr^2 + b \quad (1.59)$$

that is,

$$\dot{r} = \sqrt{-\frac{p_\phi^2}{m^2 r^2} - kr^2 + b} \quad (1.60)$$

Integrating once again with respect to time,

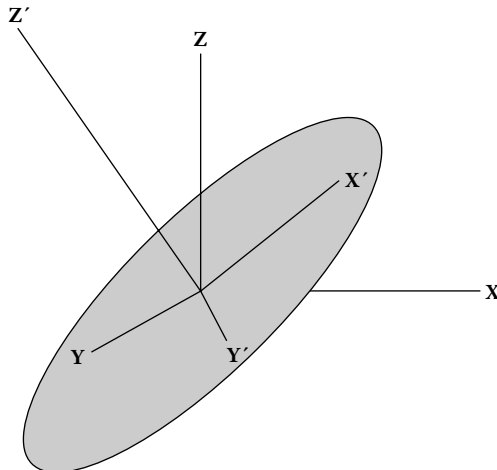
$$t - t_o = \int \frac{r dr}{\dot{r}} \quad (1.61)$$

$$= \int \frac{r dr}{\sqrt{-\frac{p_\phi^2}{m^2} - kr^4 + br^2}} \quad (1.62)$$

$$= \frac{1}{2} \int \frac{dx}{\sqrt{a + bx + cx^2}} \quad (1.63)$$

where $x = r^2$, $a = -p_\phi^2/m^2$, b is the constant of integration, and $c = -k$. This is a standard integral and we can evaluate it to find

$$r^2 = \frac{1}{2\omega} (b + A \sin(\omega(t - t_o))) \quad (1.64)$$



where

$$A = \sqrt{b^2 - \frac{\omega^2 p_\phi^2}{m^2}} \quad (1.65)$$

What we see then is that r follows an elliptical path in a plane determined by the initial velocity.

This example also illustrates another important point that has tremendous impact on molecular quantum mechanics, namely, that the angular momentum about the axis of rotation is conserved. We can choose any axis we want. In order to avoid confusion, let us define χ as the angular rotation about the body-fixed Z' axis and ϕ as angular rotation about the original Z axis. So our conservation equations are

$$mr^2 \dot{\chi} = p_\chi \quad (1.66)$$

about the Z' axis and

$$mr^2 \sin \theta \dot{\phi} = p_\phi \quad (1.67)$$

for some arbitrary fixed Z axis. The angle θ will also have an angular momentum associated with it, $p_\theta = mr^2 \dot{\theta}$, but we do not have an associated conservation principle for this term since it varies with ϕ . We can connect p_χ with p_θ and p_ϕ about the other axis via

$$p_\chi d\chi = p_\theta d\theta + p_\phi d\phi \quad (1.68)$$

Consequently,

$$mr^2 \dot{\chi}^2 d\chi = mr^2 (\dot{\phi} \sin \theta d\phi + \dot{\theta} d\theta) \quad (1.69)$$

Here we see that the the angular momentum vector remains fixed in space in the absence of any external forces. Once an object starts spinning, its axis of rotation remains pointing in a given direction unless something acts upon it (torque); in essence, in classical mechanics we can fully specify L_x , L_y , and L_z as constants of the motion since $d\vec{L}/dt = 0$. In a later chapter, we will cover the quantum mechanics of rotations in much more detail. In the quantum case, we will find that one cannot make such a precise specification of the angular momentum vector for systems with low angular momentum. We will, however, recover the classical limit in the end as we consider the limit of large angular momenta.

1.3 CONSERVATION LAWS

We just encountered one extremely important concept in mechanics, namely, that some quantities are conserved if there is an underlying symmetry. Next, we consider a conservation law arising from the homogeneity of time. For a closed dynamical system, the Lagrangian does not explicitly depend upon time. Thus we can write

$$\frac{dL}{dt} = \frac{\partial L}{\partial x} \dot{x} + \frac{\partial L}{\partial \dot{x}} \ddot{x} \quad (1.70)$$

Replacing $\partial L/\partial x$ with Lagrange's equation, we obtain

$$\frac{dL}{dt} = \dot{x} \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{x}} \right) + \frac{\partial L}{\partial \dot{x}} \ddot{x} \quad (1.71)$$

$$= \frac{d}{dt} \left(\dot{x} \frac{\partial L}{\partial \dot{x}} \right) \quad (1.72)$$

Now, rearranging this a bit,

$$\frac{d}{dt} \left(\dot{x} \frac{\partial L}{\partial \dot{x}} - L \right) = 0 \quad (1.73)$$

So, we can take the quantity in the parenthesis to be a constant, and

$$E = \left(\dot{x} \frac{\partial L}{\partial \dot{x}} - L \right) = \text{const} \quad (1.74)$$

is an integral of the motion. This is the *energy* of the system. L can be written in the form $L = T - V$ where T is a quadratic function of the velocities, and using Euler's theorem on homogeneous functions:

$$\dot{x} \frac{\partial L}{\partial \dot{x}} = \dot{x} \frac{\partial T}{\partial \dot{x}} = 2T \quad (1.75)$$

This gives

$$E = T + V \quad (1.76)$$

which says that the energy of the system can be written as the sum of two different terms: the kinetic energy or energy of motion and the potential energy or the energy of location.

One can also prove that linear momentum is conserved when space is homogeneous. That is, when we can translate our system, some arbitrary amount ε and our dynamical quantities must remain unchanged. We will prove this in the problem sets.

1.3.1 CONSERVATIVE FORCES

A conservative force has nothing to do with its particular political bend. In a loose sense, it is a force in which the total energy is conserved. More precisely, a conservative force acts in such a way that the potential energy of an object does not depend upon the path taken by the object. Recall that work is force times the distance moved. More precisely, work is an integral of the force along a given line or trajectory. In one dimension

$$W = \int_a^b F(x) dx \quad (1.77)$$

where a and b are beginning and end of the path. In multiple dimensions, we have to extend this concept so that the integral is taken along some arbitrary path.

Suppose we have a curve, C , connecting two points either on a plane or in a volume. This curve may twist and bend, but it is fixed at the two endpoints and our integral must be taken along C from one endpoint to the other. First, let us cut C into N short straight segments of length Δs_i so that the segments $\{\Delta s_1 \cdots \Delta s_N\}$ make up a piecewise continuous approximation for C . The work performed along any one of the segments can be approximated as

$$W_i = \Delta s_i F(x_i, y_i, z_i) \quad (1.78)$$

Consequently, the total work in moving along C is approximately

$$W \approx \sum_i^N \Delta s_i F(x_i, y_i, z_i) \quad (1.79)$$

Taking $\Delta s_i \rightarrow 0$ and $N \rightarrow \infty$, we can write the work performed in moving along path C as

$$W = \lim_{\Delta s_i \rightarrow 0} \sum_i^N \Delta s_i F(x_i, y_i, z_i) = \int_C F(s) ds \quad (1.80)$$

Now, suppose the force can be written as the gradient of some scalar potential function

$$F = \nabla G \quad (1.81)$$

and that our curve C can be parametrized via a single variable t . For example, t could be the length traveled along C or the time. Thus,

$$\frac{dG}{dt} = \nabla G \frac{ds}{dt} = F(s(t)) \frac{ds}{dt} \quad (1.82)$$

Inserting this into the work integral,

$$W = \int_C F(s) ds = \int_C F(s(t)) \frac{ds}{dt} dt = \int_C \frac{dG}{dt} dt = G(a) - G(b) \quad (1.83)$$

where a and b are the two endpoints. As you can see, the integral now depends only upon the two endpoints and does not depend upon the particular details of path C .

Suppose an object starts at point A and moves about some arbitrary closed path P such that after some time it is again at point A . It may still be moving, but the net work done on the object is exactly zero. That is, for a conservative force

$$W = \oint \vec{F}(s) \cdot d\vec{s} = 0 \quad (1.84)$$

Although most forces encountered in molecular systems are conservative, many are not, particularly those that depend upon velocity. For such forces, the three criteria are not mathematically equivalent. For example, a magnetic force will satisfy the first requirement, but its curl is not defined and it cannot be written as the gradient of a

potential. However, the magnetic force $F = q\vec{v} \times \vec{B}$ can be counted as conservative since the force acts perpendicular to the velocity vector $\vec{v}$ and as such the work is always zero. Nonconservative forces often arise when we neglect or exclude various degrees of freedom. For example, for Brownian motion, the Brownian particle feels a random kick and a viscous drag. These forces arise from the microscopic motion of the surrounding atoms and molecules in the liquid. If we were to treat their motions explicitly, the force acting on the Brownian particle would be conservative. Treating the forces and interactions statistically makes for a far simpler description at the cost of introducing a nonconservative force.

Example: Let us take for an example a force given by $F(x, y) = (x + y)$ and let us compute the work along three different paths. First, a path C_1 from the origin to $(1, 1)$; second, along a path C_2 from $(0, 0)$ to $(1, 0)$ then to $(1, 1)$; and finally along a curved parabolic path C_3 given by $y = x^2$ from the origin to $(1, 1)$. Along C_1 , we take s as the distance traveled along C_1 so that $x = s/\sqrt{2}$ and $y = s/\sqrt{2}$. Thus,

$$W_1 = \int_{C_1} (x + y)ds = \sqrt{2} \int_0^{\sqrt{2}} s ds = \sqrt{2} \quad (1.85)$$

Moving on to C_2 , it is easier to break this into two segments. Along the segment from $(0,0)$ to $(1,0)$, $x = s$ and $y = 0$. Thus,

$$W_2^{(1)} = \int_0^1 s ds = \frac{1}{2} \quad (1.86)$$

Along the next segment from $(1, 0)$ to $(1, 1)$, $x = 1$ and $y = s$, so we integrate

$$W_2^{(2)} = \int_0^1 (1 + s)ds = \frac{3}{2} \quad (1.87)$$

then add $W_2 = W_2^{(1)} + W_2^{(2)} = 2$. Finally, along the parabolic path, let $x = s$ and $y = s^2$ and we integrate

$$W_3 = \int_0^1 (s + s^2)ds = \frac{5}{6} \quad (1.88)$$

Clearly, we are not dealing with a conservative force in this case! In fact, in most cases, line integrals depend upon the path taken.

1.4 HAMILTONIAN DYNAMICS

Hamiltonian dynamics is a further generalization of classical dynamics and provides a crucial link with quantum mechanics. Hamilton's function, H , is written in terms of the particle's position and momentum, $H = H(p, q)$. It is related to the Lagrangian via

$$H = \dot{x}p - L(x, \dot{x}) \quad (1.89)$$

Taking the derivative of H with respect to x ,

$$\frac{\partial H}{\partial x} = -\frac{\partial L}{\partial x} = -\dot{p} \quad (1.90)$$

Differentiation with respect to p gives

$$\frac{\partial H}{\partial p} = \dot{q} \quad (1.91)$$

These last two equations give the conservation conditions in the Hamiltonian formalism. If H is independent of the position of the particle, then the generalized momentum, p , is constant in time. If the potential energy is independent of time, the Hamiltonian gives the total energy of the system,

$$H = T + V \quad (1.92)$$

It is often easier and more convenient to express Newton's equations of motion as two first-order differential equations rather than a single second-order differential equation. Both are equally valid. However, it is far easier to obtain equations of motion in other coordinate systems than the x, y, z Cartesian coordinates we work with as a more general set of equations. For this, we define a more general quantity for the energy of a system,

$$H = T(v_1, v_2, \dots, v_N) + V(q_1, q_2, \dots, q_N) \quad (1.93)$$

where T is the kinetic energy that depends upon the velocities of the N particles in the system and V is the potential energy describing the interaction between all the particles and any external forces. V is the energy of position whereas T is the energy of motion. For a single particle moving in three dimensions,

$$T = \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2) \quad (1.94)$$

If we write the momentum as $p_x = mv_x$, then

$$T = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) \quad (1.95)$$

Notice that we can also define the momentum as the velocity derivative of T :

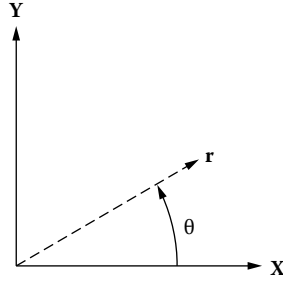
$$p_x = \frac{\partial T}{\partial v_x} \quad (1.96)$$

This defines a generalized momentum such that q_x is the conjugate coordinate to p_x and (q_x, p_x) are a pair of conjugate variables. This relation between T and p_x is important since we can define the canonical momentum in any coordinate frame. In the Cartesian frame, $p_x = mv_x$. However, in other frames, this will not be so simple.

We can also define the following relations:

$$\frac{\partial H}{\partial p_i} = \frac{\partial T}{\partial p_i} = \frac{p_i}{m} = \frac{\partial q_i}{\partial t} \quad (1.97)$$

$$\frac{\partial H}{\partial q_i} = \frac{\partial V}{\partial q_i} = -F_i = -\frac{\partial(mv_i)}{\partial t} \quad (1.98)$$



where i now denotes a general coordinate (not necessarily x, y, z). In short, we can write the following equations of motion:

$$\frac{\partial H}{\partial p_i} = \frac{\partial q_i}{\partial t} \quad (1.99)$$

$$-\frac{\partial H}{\partial q_i} = \frac{\partial p_i}{\partial t} \quad (1.100)$$

These hold in any coordinate frame and are termed *Hamilton's equations*.

Example: Hamilton's Equations in Polar Coordinates

Let us consider the transformation between polar and two-dimensional Cartesian coordinates, x and y .

$$x = r \cos \theta \quad \text{and} \quad y = r \sin \theta \quad (1.101)$$

Our Hamiltonian in x, y coordinates is

$$H = \frac{m}{2} (v_x^2 + v_y^2) + V(x, y) \quad (1.102)$$

Thus,

$$v_x = \frac{dx}{dt} = v_r \cos \theta - v_\theta r \sin \theta \quad (1.103)$$

$$v_y = \frac{dy}{dt} = v_r \sin \theta + v_\theta r \cos \theta \quad (1.104)$$

$$v^2 = v_x^2 + v_y^2 = v_r^2 + v_\theta^2 r^2 \quad (1.105)$$

Thus,

$$H = \frac{m}{2} (v_r^2 + v_\theta^2 r^2) + V(r, \theta) \quad (1.106)$$

We can now proceed to write this in terms of the conjugate variables,

$$p_r = \frac{\partial T}{\partial v_r} = m v_r \quad (1.107)$$

$$p_\theta = \frac{\partial T}{\partial v_\theta} = m v_\theta r^2 \quad (1.108)$$

Note that p_θ is the *angular momentum* of the system. Thus, we can write

$$H = \frac{1}{2m} \left(p_r^2 + \frac{p_\theta^2}{r^2} \right) + V(r, \theta) \quad (1.109)$$

Next, consider the case where $V(r, \theta)$ has no angular dependence. Thus,

$$\frac{\partial p_r}{\partial t} = -\frac{\partial H}{\partial r} = \frac{p_\theta^2}{mr^3} - \frac{\partial V}{\partial r} \quad (1.110)$$

$$\frac{\partial p_\theta}{\partial t} = -\frac{\partial H}{\partial \theta} = -\frac{\partial V}{\partial \theta} = 0 \quad (1.111)$$

$$\frac{\partial r}{\partial t} = \frac{\partial H}{\partial p_r} = \frac{p_r}{m} \quad (1.112)$$

$$\frac{\partial \theta}{\partial t} = \frac{\partial H}{\partial p_\theta} = \frac{p_\theta}{mr^2} \quad (1.113)$$

Notice that p_θ does not change in time; that is, the angular momentum is a constant of the motion. The radial force we obtain from $\partial p_r / \partial t = F_r$ is

$$F_r = \frac{p_\theta^2}{mr^3} - \frac{\partial V}{\partial r} \quad (1.114)$$

The first term is constant (since $p_\theta = \text{const}$) and represents the radial force produced by the angular momentum. It always points *outward* toward larger values of r and is termed the *centrifugal force*. The second term is the force due to the attraction between the moving object and the origin. It could be the gravitational forces, the Coulombic force between charged particles, and so forth. Using the expression for p_θ (Equation 1.111), we can also write the force equation as

$$F_r = \frac{(mv_\theta r^2)^2}{mr^3} - \frac{\partial V}{\partial r} = mv_\theta^2 r - \frac{\partial V}{\partial r} \quad (1.115)$$

If the two forces counterbalance each other, then the net force is $F_r = 0$ and we have

$$mv_\theta^2 r = \frac{\partial V}{\partial r} \quad (1.116)$$

Since $v_\theta = \dot{\theta} = \text{const}$, $\theta = \omega t + \text{const}$. Where ω is the angular velocity and using $v_\theta = \omega r$, we can write

$$m\omega^2 r = \frac{\partial V}{\partial r} \quad (1.117)$$

Finally, we note that the linear velocity is related to the angular velocity by $\omega = vr$,

$$\frac{mv^2}{r} = \frac{\partial V}{\partial r} \quad (1.118)$$

Hence we have a relation between the kinetic energy T and the potential energy V for a centro-symmetric system:

$$mv^2 = 2T = r \frac{\partial V}{\partial r} \quad (1.119)$$

This relation is extremely useful in deriving the classical orbital motion for Coulomb-bound charges as in the hydrogen atom or for planetary motion.

1.4.1 PHASE PLANE ANALYSIS

Often we cannot determine the closed-form solution to a given problem and we need to turn to more approximate methods or even graphical methods. Here, we will look at an extremely useful way to analyze a system of equations by plotting their time derivatives.

First, let us look at the oscillator we just studied. We can define a vector $s = (\dot{x}, \dot{v}) = (v, -k/mx)$ and plot the vector field. Figure 1.2 shows how to do this in Mathematica. The superimposed curve is one trajectory and the arrows give the “flow” of trajectories on the phase plane.

We can examine more complex behavior using this procedure. For example, the simple pendulum obeys the equation $\ddot{x} = -\omega^2 \sin x$. This can be reduced to two first-order equations: $\dot{x} = v$ and $\dot{v} = -\omega^2 \sin(x)$.

We can approximate the motion of the pendulum for small displacements by expanding the pendulum’s force about $x = 0$:

$$-\omega^2 \sin(x) = -\omega^2 \left(x - \frac{x^3}{6} + \cdots \right) \quad (1.120)$$

For small x , the cubic term is very small, and we have

$$\dot{v} = -\omega^2 x = -\frac{k}{m}x \quad (1.121)$$

which is the equation for harmonic motion. So, for small initial displacements, we see that the pendulum oscillates back and forth with an angular frequency ω . For large initial displacements, $x_o = \pi$, or if we impart some initial velocity on the system $v_o > 1$, the pendulum does not oscillate back and forth but undergoes librational motion (spinning!) in one direction or the other.

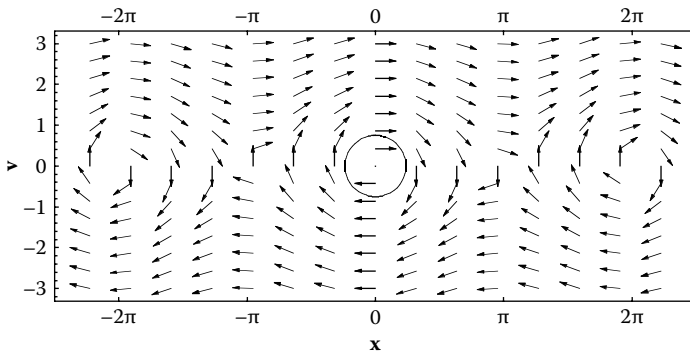


FIGURE 1.2 Tangent field for simple pendulum with $\omega = 1$. The superimposed curve is a linear approximation to the pendulum motion.

1.4.2 INTERACTION BETWEEN A CHARGED PARTICLE AND AN ELECTROMAGNETIC FIELD

We consider here a free particle with mass m and charge e in an electromagnetic field. The Hamiltonian is

$$H = p_x \dot{x} + p_y \dot{y} + p_z \dot{z} - L \quad (1.122)$$

$$= \dot{x} \frac{\partial L}{\partial \dot{x}} + \dot{y} \frac{\partial L}{\partial \dot{y}} + \dot{z} \frac{\partial L}{\partial \dot{z}} - L \quad (1.123)$$

Our goal is to write this Hamiltonian in terms of momenta and coordinates.

For a charged particle in a field, the force acting on the particle is the Lorentz force. Here it is useful to introduce a vector and scalar potential and to work in centimeter-gram-second (cgs) units

$$\vec{F} = \frac{e}{c} \vec{v} \times (\vec{\nabla} \times \vec{A}) - \frac{e}{c} \frac{\partial \vec{A}}{\partial t} - e \vec{\nabla} \phi \quad (1.124)$$

The force in the x direction is given by

$$\begin{aligned} F_x = \frac{d}{dt} m \dot{x} &= \frac{e}{c} \left(\dot{y} \frac{\partial A_y}{\partial x} + \dot{z} \frac{\partial A_z}{\partial x} \right) \\ &\quad - \frac{e}{c} \left(\dot{y} \frac{\partial A_x}{\partial y} + \dot{z} \frac{\partial A_x}{\partial z} + \frac{\partial A_x}{\partial t} \right) - e \frac{\partial \phi}{\partial x} \end{aligned} \quad (1.125)$$

with the remaining components given by cyclic permutation. Since

$$\frac{dA_x}{dt} = \frac{\partial A_x}{\partial t} + \dot{x} \frac{\partial A_x}{\partial x} + \dot{y} \frac{\partial A_x}{\partial y} + \dot{z} \frac{\partial A_x}{\partial z} \quad (1.126)$$

with the force in x given by

$$F_x = \frac{e}{c} \left(\dot{x} \frac{\partial A_x}{\partial x} + \dot{y} \frac{\partial A_x}{\partial y} + \dot{z} \frac{\partial A_x}{\partial z} \right) - \frac{e}{c} \vec{v} \cdot \vec{A} - e \phi \quad (1.127)$$

and we find that the Lagrangian is

$$L = \frac{1}{2} m \dot{x}^2 + \frac{1}{2} m \dot{y}^2 + \frac{1}{2} m \dot{z}^2 + \frac{e}{c} \vec{v} \cdot \vec{A} - e \phi \quad (1.128)$$

where ϕ is a velocity independent and static potential.

Continuing on, the Hamiltonian is

$$H = \frac{m}{2} (\dot{x}^2 + \dot{y}^2 + \dot{z}^2) + e \phi \quad (1.129)$$

$$= \frac{1}{2m} ((m\dot{x})^2 + (m\dot{y})^2 + (m\dot{z})^2) + e \phi \quad (1.130)$$

The velocities, $m\dot{x}$, are derived from the Lagrangian via the canonical relation

$$p = \frac{\partial L}{\partial \dot{x}} \quad (1.131)$$

From this we find,

$$m\dot{x} = p_x - \frac{e}{c}A_x \quad (1.132)$$

$$m\dot{y} = p_y - \frac{e}{c}A_y \quad (1.133)$$

$$m\dot{z} = p_z - \frac{e}{c}A_z \quad (1.134)$$

and the resulting Hamiltonian is

$$H = \frac{1}{2m} \left[\left(p_x - \frac{e}{c}A_x \right)^2 + \left(p_y - \frac{e}{c}A_y \right)^2 + \left(p_z - \frac{e}{c}A_z \right)^2 \right] + e\phi \quad (1.135)$$

We see here an important concept relating the velocity and the momentum. In the absence of a vector potential, the velocity and the momentum are parallel. However, when a vector potential is included, the actual velocity of a particle is no longer parallel to its momentum and is in fact deflected by the vector potential.

1.4.3 TIME DEPENDENCE OF A DYNAMICAL VARIABLE

One of the important applications of Hamiltonian mechanics is in the dynamical evolution of a variable that depends upon p and q , $G(p, q)$. The total derivative of G is

$$\frac{dG}{dt} = \frac{\partial G}{\partial t} + \frac{\partial G}{\partial q}\dot{q} + \frac{\partial G}{\partial p}\dot{p} \quad (1.136)$$

From Hamilton's equations, we have the canonical definitions

$$\dot{q} = \frac{\partial H}{\partial p}, \quad \dot{p} = -\frac{\partial H}{\partial q} \quad (1.137)$$

Thus,

$$\frac{dG}{dt} = \frac{\partial G}{\partial t} + \frac{\partial G}{\partial q} \frac{\partial H}{\partial p} - \frac{\partial G}{\partial p} \frac{\partial H}{\partial q} \quad (1.138)$$

$$\frac{dG}{dt} = \frac{\partial G}{\partial t} + \{G, H\} \quad (1.139)$$

where $\{A, B\}$ is called the Poisson bracket of two dynamical quantities, G and H :

$$\{G, H\} = \frac{\partial G}{\partial q} \frac{\partial H}{\partial p} - \frac{\partial G}{\partial p} \frac{\partial H}{\partial q} \quad (1.140)$$

We can also define a linear operator $\mathcal{L}$ as generating the Poisson bracket with the Hamiltonian:

$$\mathcal{L}G = \frac{1}{i}\{H, G\} \quad (1.141)$$

so that if G does not depend explicitly upon time,

$$G(t) = \exp(i\mathcal{L}t)G(0) \quad (1.142)$$

where $\exp(i\mathcal{L}t)$ is the propagator that carried $G(0)$ to $G(t)$.

Also, note that if $\{G, H\} = 0$, then $dG/dt = 0$ so that G is a constant of the motion. This too, along with the construction of the Poisson bracket, has considerable importance in the realm of quantum mechanics.

1.4.4 VIRIAL THEOREM

Finally, we turn our attention to a concept that has played an important role in both quantum and classical mechanics. Consider a function G that is a product of linear momenta and coordinate,

$$G = pq \quad (1.143)$$

The time derivative is simply

$$\frac{G}{dt} = q\dot{p} + p\dot{q} \quad (1.144)$$

Now, let us take a *time average* of both sides of this last equation:

$$\left\langle \frac{d}{dt}pq \right\rangle = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T \left(\frac{d}{dt}pq \right) dt \quad (1.145)$$

$$= \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T d(pq) \quad (1.146)$$

$$= \lim_{T \rightarrow \infty} \frac{1}{T} ((pq)_T - (pq)_0) \quad (1.147)$$

If the trajectories of the system are bounded, both p and q are periodic in time and are therefore finite. Thus, the average must vanish as $T \rightarrow \infty$ giving

$$\langle p\dot{q} + q\dot{p} \rangle = 0 \quad (1.148)$$

Since $p\dot{q} = 2T$ and $\dot{p} = -F$, we have

$$\langle 2T \rangle = -\langle qF \rangle \quad (1.149)$$

In Cartesian coordinates this leads to

$$\langle 2T \rangle = -\left\langle \sum_i x_i F_i \right\rangle \quad (1.150)$$

For a conservative system $F = -\nabla V$. Thus, if we have a centro-symmetric potential given by $V = Cr^n$, it is easy to show that

$$\langle 2T \rangle = n\langle V \rangle \quad (1.151)$$

For the case of the harmonic oscillator, $n = 2$ and $\langle T \rangle = \langle V \rangle$. So, for example, if we have a total energy equal to kT in this mode, then $\langle T \rangle + \langle V \rangle = kT$ and $\langle T \rangle = \langle V \rangle = kT/2$. Moreover, for the interaction between two opposite charges separated by r , $n = -1$ and

$$\langle 2T \rangle = -\langle V \rangle \quad (1.152)$$

1.4.5 ANGULAR MOMENTUM

We noted above that if we have a radial force, then the angular velocity and angular momentum are constants of the motion. In general, the angular momentum is defined as the cross product between a radial vector locating the particle and its linear momentum

$$\vec{M} = \vec{r} \times \vec{p} \quad (1.153)$$

Cross products are equivalent to taking the determinant of a matrix

$$\vec{M} = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} \quad (1.154)$$

where $\hat{i}$, $\hat{j}$, and $\hat{k}$ are the unit vectors along the x , y , z axes. Evaluating the determinant gives

$$\vec{M} = \hat{i}(yp_z - zp_y) - \hat{j}(xp_z - zp_x) + \hat{k}(xp_y - yp_x) \quad (1.155)$$

$$= \hat{i}M_x + \hat{j}M_y + \hat{k}M_z \quad (1.156)$$

For motion in the x - y plane, the only term that remains is the M_z term, indicating that the angular momentum vector points perpendicular to the plane of rotation,

$$M_z = (xp_y - yp_x) = m(xv_y - yv_x) \quad (1.157)$$

Since we have noted that the angular momentum is a constant of the motion, we must have $dM_z/dt = 0$. Let us check:

$$\frac{dM_z}{dt} = m(v_x v_y - v_y v_x + x a_y - y a_x) \quad (1.158)$$

where $a_x = \dot{v}_x$ is the acceleration in x . Thus,

$$\frac{dM_z}{dt} = (x F_y - y F_x) \quad (1.159)$$

If the force is radial, $F_x = F_r \cos(\theta)$ and $F_y = F_r \sin(\theta)$. Likewise, $x = r \cos(\theta)$ and $y = r \sin(\theta)$. Putting this into the equations, we have

$$\frac{dM_z}{dt} = r F_r (\sin(\theta) \cos(\theta) - \sin(\theta) \cos(\theta)) = 0 \quad (1.160)$$

Taking $\theta = \omega t$ as above where ω is the angular frequency, and using $v_x = -r\omega \sin(\omega t)$ and $v_y = +r\omega \cos(\omega t)$, we can also write

$$M = m(v_x y - v_y x) = mvr(\sin^2(\omega t) + \cos^2(\omega t)) = mvr \quad (1.161)$$