

## Chapter 2

# Review of Quantum Mechanics

Quantum mechanics is the most successful physical theory. No phenomenon has yet been found, which contradicts the predictions of quantum mechanics. Quantum mechanics is essential for understanding and modeling carrier transport in nanoelectronic devices. In this chapter basic elements of quantum mechanics are briefly reviewed. For a more comprehensive review, interested readers are referred to standard textbooks, such as Refs. [7, 8, 12, 13].

### 2.1 Historical Background

At the end of the nineteenth century, classical physics offered a rather complete view of most processes in the natural world based on deterministic Newtonian dynamics, Maxwell's equations of electromagnetism, and thermodynamics. In 1900, Thompson (Lord Kelvin) gave a lecture titled *Nineteenth-Century Clouds over the Dynamical Theory of Heat and Light*. He claimed that most problems related to physics had already been solved, except the failure of Michelson-Morley's experiment to measure the velocity of light with respect to an absolute ether, and the problem of black body radiation. The attempt to solve these problems gave birth to Einstein's theories of special and general relativity, and *quantum mechanics*, the latter of which provides a conceptual framework for understanding the physical processes taking place at the atomic scale.

Classical electrodynamics predicts that objects emit radiation, but this idea fails to predict the observed spectrum of light at higher frequencies, which is often referred to as ultraviolet catastrophe. In 1900, Planck supposed that light is not emitted continuously in a constant amount from all matter. He suggested that light is always emitted and absorbed in discrete units referred to as quanta such that each of these energy quanta  $\epsilon$  is proportional to the frequency  $\nu$  with which each individually radiates energy [11]:

$$\epsilon = h\nu , \tag{2.1}$$

where  $h$  is Planck's constant. Based on this assumption, Planck obtained a mathematical equation which described the entire spectrum of black body radiation. In 1905, Einstein explained the photoelectric effect by postulating that light can be divided into a finite number of energy quanta [6], later came to be called photons. It explained why the energy of photo excited electrons was dependent only on the frequency of the incident light and not on its intensity. In 1913, Bohr explained the spectral lines of the hydrogen atom, again by using quantization [3]. The idea that each photon had to consist of energy in terms of quanta was a remarkable achievement, but the concept was strongly resisted at first because it contradicted the wave theory of light that followed naturally from Maxwell's equations. However, Einstein's postulate was confirmed experimentally by Millikan and Compton over the next two decades. Thus it became apparent that light has both wave-like and particle-like properties. In 1924, de Broglie put forward his theory of matter waves by stating that particles can exhibit wave characteristics and vice versa. He suggested that all particles, like electrons, must be transported by a wave into which they are incorporated [4]. With every particle of matter, a wave must be associated:

$$\lambda = \frac{h}{p}, \quad (2.2)$$

where  $\lambda$  is the wavelength and  $p$  is the momentum. Building on de Broglie's approach, modern quantum mechanics was born in 1925, when Heisenberg developed matrix mechanics [9] and Erwin Schrödinger invented wave mechanics and the non-relativistic Schrödinger equation as an approximation to the generalized case of de Broglie's theory [14–17]. Schrödinger subsequently showed that the two approaches were equivalent [18]. Starting around 1927, Paul Dirac started to unify quantum mechanics with special relativity by proposing the Dirac equation for the electron. It predicts electron spin and led Dirac to predict the existence of the positron. He also pioneered the use of operator theory, including the bra-ket notation. During the same period, von Neumann formulated a rigorous mathematical basis for quantum mechanics as the theory of linear operators on Hilbert spaces.

Quantum mechanics was successful at describing non-relativistic systems with fixed numbers of particles, but a new framework was needed to describe systems in which particles can be created or destroyed, for example, the electromagnetic field, considered as a collection of photons. Beginning in 1927, researchers, including Dirac, Pauli, Weisskopf, and Jordan, made attempts to apply quantum mechanics to fields instead of particles, resulting in quantum field theories [5]. Quantizing the classical theory of a single-particle gave rise to a wave function and quantizing a field appeared to be similar to quantizing a theory that was already quantized, leading to the term second quantization in the early literature, which is still used to describe field quantization. Quantum field theory provides a theoretical framework for constructing quantum mechanical models of fields and many-body systems. Interested readers can find further details on the history of quantum mechanics in Ref. [1].

## 2.2 Postulates of Quantum Mechanics

Theories are based on postulates. Postulates are rules of nature, which cannot be proven or derived. Their justification is from the fact that they are consistent with experiment. Classical mechanics is based on two postulates: *the state postulate* and *the time evolution postulate*. In classical mechanics, the change in the state of the system is characterized by a set of dynamical variables. Therefore, initial state of the system specifies the initial conditions of these dynamical variables, and the way the state of the system changes, based on an equation of motion, is described by how the dynamical variables change with time. In classical mechanics the state of a system is described by the positions and velocities of the particles that form the system. Given that the state of a point particle is known at some time  $t_0$ , one can predict its state at any other time  $t$ , by using Newton's second law. Quantum mechanics differs from classical mechanics by the employment of operators rather than dynamical variables. In addition, quantum mechanics involves a new postulate – *the measurement postulate* – that does not have a classical analogue. A more detailed discussion of those postulates follows.

### 2.2.1 Quantum States

The state of a system at any instant of time may be represented by a wave function  $\psi$  which is continuous and differentiable. For example the state of an isolated system at some time  $t$  with a point particle is given by the wave function  $\psi(\mathbf{r}, t)$ . The interpretation of a wave describing a particle was the subject of discussion in early years of quantum mechanics. Born paved the way for the statistical interpretation of the wave function describing a particle. He suggested the term guiding field which determines at every point the probability of finding the particle there. The square of the amplitude of the wave function  $\psi$  gives the probability density  $|\psi|^2 = \psi\psi^*$ , where  $\psi^*$  is the complex conjugate of  $\psi$ . The probability of finding a particle in a certain volume element  $d\mathbf{r}$  at some time  $t$  is therefore given by  $|\psi(\mathbf{r}, t)|^2 d\mathbf{r}$ . The amplitude of  $\psi$  is conventionally normalized:

$$\int_{\mathcal{V}} d\mathbf{r} \psi(\mathbf{r}, t) \psi^*(\mathbf{r}, t) = 1, \quad (2.3)$$

which implies that the particle must be somewhere in space  $\mathcal{V}$ . The wave function can only be normalized if it is square integrable. Bound states, which describe closed systems, are square integrable, whereas for free states this condition is not satisfied. Free states, however, can be normalized by imposing either a periodic or closed boundary condition to the system [7].

The state of a classical particle can be completely described by its position and momentum, which can be mathematically represented by a point in a phase space. In a classical system with  $N$  particles, the phase-space is in general  $6N$ -dimensional.

In quantum mechanical systems, however, any state can be mathematically represented as a vector in a *Hilbert* space. A Hilbert space  $\mathcal{H}$  is a vector space over  $\mathcal{C}$  ( $\mathcal{H} \rightarrow \mathcal{C} \times \mathcal{C}$ ) on which an inner product  $\langle | \rangle$  is defined that satisfies the following conditions for all  $f, g$ , and  $h$  on  $\mathcal{H}$  and  $\alpha$  and  $\beta$  in  $\mathcal{C}$ :

- Symmetry:  $\langle f | g \rangle = \langle g | f \rangle^*$ .
- Linearity:  $\langle \alpha f + \beta g | h \rangle = \alpha \langle f | h \rangle + \beta \langle g | h \rangle$ .
- Positivity:  $f \neq 0, \langle f | f \rangle > 0$ .

In addition  $\mathcal{H}$  should be complete with respect to the norm defined by

$$\|f\| = \sqrt{\langle f | f \rangle} . \quad (2.4)$$

For describing states in Hilbert space, bra-ket notation is considered as a standard notation. This notation was introduced by Dirac and is also known as *Dirac notation*. A state is represented by the *ket*  $|\psi\rangle$ . This state is an abstract vector in a Hilbert space. A dual or adjoint-space state is represented by the *bra*  $\langle\psi|$ . There is a one-to-one correspondence between the elements of the ket space and those of the related bra space. For every element of the ket space, there is a corresponding element in the bra space. These elements are related by the *adjoint* operation

$$\langle\psi| \equiv |\psi\rangle^* . \quad (2.5)$$

The expression  $\int d\mathbf{r} \phi^* \psi$  is considered as an inner product of wave functions  $\psi$  and  $\phi$  and is interpreted as the probability amplitude for the state  $\psi$  to collapse into the state  $\phi$ . Usually a shorthand notation is used

$$\langle\phi|\psi\rangle = \int d\mathbf{r} \phi^* \psi . \quad (2.6)$$

In the Dirac Notation, the normalization condition reads

$$\langle\psi|\psi\rangle = 1 . \quad (2.7)$$

While, by orthogonality

$$\langle\psi|\phi\rangle = 0 . \quad (2.8)$$

For any two kets from a countable orthonormal set indexed by integers, we may write

$$\langle v_m | v_n \rangle = \delta_{m,n} , \quad (2.9)$$

where  $\delta_{i,j}$  is the Kronecker delta function. Using a complete orthonormal set of kets  $|v_n\rangle$  as a basis in Hilbert space, one can expand any state in terms of these basis vectors:

$$|\psi\rangle = \sum_n c_n |v_n\rangle, \quad c_n = \langle v_n | \psi \rangle. \quad (2.10)$$

By writing  $\langle v_n | \psi \rangle = \psi_n$ , one can represent  $|\psi\rangle$  as a column vector with respect to the set of basis states:

$$|\psi\rangle = \begin{bmatrix} \psi_1 \\ \psi_2 \\ \vdots \end{bmatrix}. \quad (2.11)$$

To obtain a vector representation of a bra, one can form the inner product of two arbitrary states as

$$\langle \phi | \psi \rangle = \sum_n \langle \phi | v_n \rangle \langle v_n | \psi \rangle. \quad (2.12)$$

Using the notation  $\phi_n = \langle v_n | \phi \rangle$  and knowing that  $\langle \phi | v_n \rangle = \langle v_n | \phi \rangle^*$  one obtains  $\langle \phi | v_n \rangle = \phi_n^*$  and hence

$$\langle \phi | \psi \rangle = \sum_n \phi_n^* \psi_n, \quad (2.13)$$

which can be written as

$$\langle \phi | \psi \rangle = [\phi_1^* \ \phi_2^* \ \dots] \begin{bmatrix} \psi_1 \\ \psi_2 \\ \vdots \end{bmatrix}. \quad (2.14)$$

Here one can make an identification of the bra vector  $\langle \phi |$  as a row vector, which is the complex conjugate of its corresponding ket vector:

$$\langle \phi | = [\phi_1^* \ \phi_2^* \ \dots]. \quad (2.15)$$

In Eq. (2.10) the summation is for discrete states. In many systems which would include, for example, a free particle, one has a continuous set of states. In such systems the discrete index  $n$  and summation in Eq. (2.10) are replaced by a continuous variable and integral, respectively. For a continuous set of complete kets indexed by the continuous variables  $x$  and  $x'$ , the orthogonality relation is written as

$$\langle x | x' \rangle = \delta(x - x'). \quad (2.16)$$

Here  $\delta(x - x')$  is the Dirac delta function, which is an analogue to the Kronecker delta function. The Hilbert space of a point particle without spin degree of freedom can be spanned by the spatial coordinate  $|\mathbf{r}\rangle$ , where  $\mathbf{r}$  extends over the set of all points in space. Since there are infinitely many vectors in the basis, this is an

infinite-dimensional Hilbert space. Using this basis set, an arbitrary state  $|\psi\rangle$  can be represented by

$$|\psi\rangle = \int d\mathbf{r} c(\mathbf{r})|\mathbf{r}\rangle . \quad (2.17)$$

The coefficients  $c(\mathbf{r})$  in Eq. (2.17) are simply the value of the wave function at each point  $\mathbf{r}$ ,  $c(\mathbf{r}) = \psi(\mathbf{r})$ . In Dirac notation, the wave function in the coordinate space is represented by

$$\psi(\mathbf{r}) \equiv \langle \mathbf{r} | \psi \rangle , \quad (2.18)$$

that is, its projection on the  $\mathbf{r}$  basis.

In principle the wave function can be expressed in terms of any complete set of eigenstates. By choosing different sets of basis functions, one can arrive at a number of different representations of the same state. The eigenstates of any Hermitian operator form a complete basis in Hilbert space, see Sect. 2.2.2. The eigenstates of the momentum operator (see Eq. (2.49)), which are represented by the ket  $|\mathbf{p}\rangle$ , are plane waves in coordinate-space [7]

$$\langle \mathbf{r} | \mathbf{p} \rangle = c(\mathbf{p}) e^{i\mathbf{p} \cdot \mathbf{r} / \hbar} . \quad (2.19)$$

The normalization constant  $c(\mathbf{p})$  can be obtained by using the orthonormality of the momentum eigenstates:

$$\begin{aligned} \langle \mathbf{p} | \mathbf{p}' \rangle &= \delta(\mathbf{p} - \mathbf{p}') = \int d\mathbf{r} \langle \mathbf{p} | \mathbf{r} \rangle \langle \mathbf{r} | \mathbf{p}' \rangle , \\ &= \int d\mathbf{r} c^*(\mathbf{p}) e^{-i\mathbf{p} \cdot \mathbf{r} / \hbar} c(\mathbf{p}') e^{i\mathbf{p}' \cdot \mathbf{r} / \hbar} , \\ &= c^*(\mathbf{p}) c(\mathbf{p}') \int d\mathbf{r} e^{-i(\mathbf{p} - \mathbf{p}') \cdot \mathbf{r} / \hbar} , \\ &= |c(\mathbf{p})|^2 (2\pi\hbar)^3 \delta(\mathbf{p} - \mathbf{p}') . \end{aligned} \quad (2.20)$$

Thus  $|c(\mathbf{p})|^2 = 1/(2\pi\hbar)^3$ . The eigenstates of the momentum operator in coordinate representation can be written as

$$\langle \mathbf{r} | \mathbf{p} \rangle = \frac{1}{(2\pi\hbar)^{3/2}} e^{i\mathbf{p} \cdot \mathbf{r} / \hbar} . \quad (2.21)$$

If one picks the eigenstates of the momentum operator as a set of basis functions, the resulting wave function  $\psi(\mathbf{p})$  is said to be the wave function in momentum space:

$$\psi(\mathbf{p}) \equiv \langle \mathbf{p} | \psi \rangle . \quad (2.22)$$

The interpretation of the wave function in momentum space is that  $|\psi(\mathbf{p})|^2 d\mathbf{p}$  is the probability to find the momentum in the range  $[\mathbf{p}, \mathbf{p} + d\mathbf{p}]$ . The momentum representation of a wave function is very closely related to the Fourier transform and the concept of frequency domain. Since a quantum mechanical particle has a frequency proportional to the momentum (Eq. (2.2)), describing the particle as a sum of its momentum components is equivalent to describing it as a sum of frequency components, which is a Fourier transform:

$$\begin{aligned}\psi(\mathbf{r}) &= \langle \mathbf{r} | \psi \rangle = \int d\mathbf{p} \langle \mathbf{r} | \mathbf{p} \rangle \langle \mathbf{p} | \psi \rangle = \int d\mathbf{p} \langle \mathbf{r} | \mathbf{p} \rangle \psi(\mathbf{p}) , \\ &= \frac{1}{(2\pi\hbar)^{3/2}} \int d\mathbf{p} e^{i\mathbf{p}\cdot\mathbf{r}/\hbar} .\end{aligned}\quad (2.23)$$

Here  $\langle \mathbf{r} | \mathbf{p} \rangle$  represents the momentum eigenstate in coordinate space, which is a plane wave, see Eq. (2.21). Similarly one can write

$$\begin{aligned}\psi(\mathbf{p}) &= \langle \mathbf{p} | \psi \rangle = \int d\mathbf{r} \langle \mathbf{p} | \mathbf{r} \rangle \langle \mathbf{r} | \psi \rangle , \\ &= \frac{1}{(2\pi\hbar)^{3/2}} \int d\mathbf{r} e^{-i\mathbf{p}\cdot\mathbf{r}/\hbar} \psi(\mathbf{r}) .\end{aligned}\quad (2.24)$$

It is often practical to use wave vectors defined as  $\mathbf{k} = \mathbf{p}/\hbar$ . Conventional momenta are denoted by  $\mathbf{p}, \mathbf{p}', \mathbf{P}$  and wave vectors are represented by  $\mathbf{k}, \mathbf{K}, \mathbf{q}$ . The wave function for the state with the wave vector  $\mathbf{k}$  becomes

$$\langle \mathbf{r} | \mathbf{k} \rangle = \frac{1}{(2\pi)^{3/2}} e^{i\mathbf{k}\cdot\mathbf{r}} , \quad (2.25)$$

with the normalization condition

$$\langle \mathbf{k}' | \mathbf{k} \rangle = \delta(\mathbf{k}' - \mathbf{k}) . \quad (2.26)$$

Equation (2.24) can be expressed in  $\mathbf{k}$ -space as

$$\psi(\mathbf{k}) = \frac{1}{(2\pi)^{3/2}} \int d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} \psi(\mathbf{r}) . \quad (2.27)$$

For some applications it is more convenient to assume periodic boundary conditions for  $\mathbf{k}$  enclosed in a huge box taken to be a cube with sides  $L$  and volume  $\mathcal{V} = L^3$ , yielding the wave function

$$\langle \mathbf{r} | \mathbf{k} \rangle = \frac{1}{\sqrt{\mathcal{V}}} e^{i\mathbf{k}\cdot\mathbf{r}} . \quad (2.28)$$

The normalization then reads

$$\begin{aligned}\langle \mathbf{k}' | \mathbf{k} \rangle &= \int_{\mathcal{V}} d\mathbf{r} \langle \mathbf{k}' | \mathbf{r} \rangle \langle \mathbf{r} | \mathbf{k} \rangle, \\ &= \frac{1}{\mathcal{V}} \int_{\mathcal{V}} d\mathbf{r} e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}} = \delta_{\mathbf{k}, \mathbf{k}'}.\end{aligned}\quad (2.29)$$

Boundary conditions imposed at the edges of the box, allow only discrete values for each component of the wave vector:

$$k_x = \frac{2\pi}{L}n_x, \quad k_y = \frac{2\pi}{L}n_y, \quad k_z = \frac{2\pi}{L}n_z. \quad (2.30)$$

In macroscopic systems, the distance between two adjacent wave vectors is very small. If one has to sum a function  $f(\mathbf{k})$  over allowed wave vectors, one can substitute the sum with integral, yielding the practical rule

$$\sum_{\mathbf{k}} f(\mathbf{k}) \rightarrow \frac{L^3}{(2\pi)^3} \int d\mathbf{k} f(\mathbf{k}) = \frac{\mathcal{V}}{(2\pi)^3} \int d\mathbf{k} f(\mathbf{k}). \quad (2.31)$$

### 2.2.2 Operators

An operator,  $\hat{O}$ , is a mathematical entity which transforms one state into another

$$\hat{O}|\psi\rangle = |\phi\rangle. \quad (2.32)$$

By expanding the state  $|\psi\rangle$  in terms of some basis set  $|v_n\rangle$ , one can write

$$|\phi\rangle = \hat{O}|\psi\rangle = \hat{O} \sum_n |v_n\rangle \langle v_n | \psi \rangle = \sum_n \hat{O} |v_n\rangle \langle v_n | \psi \rangle. \quad (2.33)$$

By multiplying both sides by the bra  $\langle v_m |$  one obtains

$$\langle v_m | \phi \rangle = \sum_n \langle v_m | \hat{O} | v_n \rangle \langle v_n | \psi \rangle, \quad (2.34)$$

which can be written as

$$\phi_m = \sum_n O_{mn} \psi_n, \quad (2.35)$$

with

$$O_{mn} = \langle v_m | \hat{O} | v_n \rangle. \quad (2.36)$$



Equation (2.35) can be written as a matrix equation

$$\begin{bmatrix} \phi_1 \\ \phi_2 \\ \phi_3 \\ \vdots \end{bmatrix} = \begin{bmatrix} O_{11} & O_{12} & O_{13} & \dots \\ O_{21} & O_{22} & O_{23} & \dots \\ O_{31} & O_{32} & O_{33} & \dots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix} \begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \vdots \end{bmatrix}, \quad (2.37)$$

where the operator  $\hat{O}$  is represented by a matrix

$$\hat{O} = \begin{bmatrix} O_{11} & O_{12} & O_{13} & \dots \\ O_{21} & O_{22} & O_{23} & \dots \\ O_{31} & O_{32} & O_{33} & \dots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix}. \quad (2.38)$$

The quantities  $O_{mn}$  are known as the matrix elements of the operator  $\hat{O}$  with respect to the basis set  $|\nu_n\rangle$ . If a different set of basis states is employed, the state vectors and operators remain the same, but the column or row vector, or matrix representing the state vector or operator, respectively, will change. Thus to give any meaning to a row vector, a column vector, or a matrix, it is essential that the basis states be known. An important part of quantum mechanics is the mathematical formalism that deals with transforming between different sets of basis states. For this purpose the *projection operator* plays an important role. This operator can be formed by the outer product of a ket and a bra. The outer product of a ket and a bra generates an operator:

$$\hat{P} = |\mu\rangle\langle\nu|. \quad (2.39)$$

If applied to a vector, it projects the vector onto the state  $|\nu\rangle$  and generates a new vector in parallel to  $|\mu\rangle$  with a magnitude equal to the projection:

$$\hat{P}|\psi\rangle = \langle\nu|\psi\rangle|\mu\rangle. \quad (2.40)$$

Given a complete set of orthonormal basis states  $|\nu_n\rangle$  any state  $|\psi\rangle$  can be written as (see Eq. (2.10))

$$|\psi\rangle = \sum_n |\nu_n\rangle\langle\nu_n|\psi\rangle, \quad (2.41)$$

which implies that

$$\hat{I} = \sum_n |\nu_n\rangle\langle\nu_n|, \quad (2.42)$$

**Table 2.1** Physical observables and their corresponding quantum mechanical operators.  $\mathbf{e}_x$  is the unit vector along the  $x$ -direction

Observable name	Observable symbol	Operator symbol	Operator operation
Position	$\mathbf{r}$	$\hat{\mathbf{r}}$	Multiplication by $\mathbf{r}$
Momentum	$\mathbf{p}$	$\hat{\mathbf{p}}$	$-i\hbar \left( \mathbf{e}_x \frac{\partial}{\partial x} + \mathbf{e}_y \frac{\partial}{\partial y} + \mathbf{e}_z \frac{\partial}{\partial z} \right)$
Kinetic energy	$T$	$\hat{T}$	$-\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)$
Potential energy	$V(\mathbf{r})$	$\hat{V}(\mathbf{r})$	Multiplication by $V(\mathbf{r})$
Total energy	$E$	$\hat{H}$	$\hat{T} + V(\mathbf{r})$
Orbital angular momentum	$L_x$	$\hat{L}_x$	$-i\hbar \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right)$
	$L_y$	$\hat{L}_y$	$-i\hbar \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right)$
	$L_z$	$\hat{L}_z$	$-i\hbar \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$

where  $\hat{I}$  represents an identity operator. By applying the identity operator from the left and right side

$$\begin{aligned}
 \hat{I} \hat{O} \hat{I} &= \sum_{m,n} |v_m\rangle \langle v_m| \hat{O} |v_n\rangle \langle v_n| , \\
 &= \sum_{m,n} O_{mn} |v_m\rangle \langle v_n| .
 \end{aligned} \tag{2.43}$$

Classical dynamical variables, such as position and momentum, are represented in quantum mechanics by linear *Hermitian* operators, which act on the wave function. An operator  $\hat{O} : \mathcal{H} \rightarrow \mathcal{H}$  in Hilbert space is called Hermitian or self-adjoint if  $\hat{O} = \hat{O}^\dagger$ , which is equivalent to (see Sect. 2.2.3)

$$\langle \phi | \hat{O} \psi \rangle = \langle \hat{O} \phi | \psi \rangle , \tag{2.44}$$

where  $|\phi\rangle$  and  $|\psi\rangle$  are arbitrary states. Hermitian operators have the following properties:

- The eigenvalues are always real.
- The eigenstates can always be chosen so that they are normalized and mutually orthogonal; in other words, an orthonormal set.
- Their eigenstates form a *complete* set. This implies that any state can be written as some linear combination of the eigenstates.

In quantum mechanics the operators are also called observable operators, or just observables. Table 2.1 shows common dynamical variables and their corresponding quantum mechanical operators. The wave function of a particle,  $\psi(\mathbf{r})$ , represents the probability density of finding the particle at some position  $\mathbf{r}$ . Therefore, the

expectation value (see Sect. 2.2.3) of a measurement of the position of the particle is  $\langle \mathbf{r} \rangle = \int d\mathbf{r} \mathbf{r} |\psi|^2$ . Accordingly, the quantum mechanical operator corresponding to position is  $\hat{\mathbf{r}}$ , where

$$\hat{\mathbf{r}}\psi(\mathbf{r}) = \mathbf{r}\psi(\mathbf{r}) . \quad (2.45)$$

It can be shown that the eigenstates of the position operator, represented in position basis, are Dirac delta functions [7]:

$$\langle \mathbf{r} | \mathbf{r}' \rangle = \delta(\mathbf{r} - \mathbf{r}') . \quad (2.46)$$

The momentum operator can be derived from infinitesimal translations. The translation operator  $\hat{T}(\epsilon)$ , where  $\epsilon$  represents the length of the translation, satisfies

$$\begin{aligned} \hat{T}(\epsilon)|\psi\rangle &= \int d\mathbf{r} \hat{T}(\epsilon)|\mathbf{r}\rangle \langle \mathbf{r} | \psi \rangle , \\ &= \int d\mathbf{r} |\mathbf{r} + \epsilon\rangle \langle \mathbf{r} | \psi \rangle = \int d\mathbf{r} |\mathbf{r}\rangle \langle \mathbf{r} - \epsilon | \psi \rangle , \\ &= \int d\mathbf{r} |\mathbf{r}\rangle \psi(\mathbf{r} - \epsilon) . \end{aligned} \quad (2.47)$$

Assuming the wave function is differentiable, for infinitesimal values of  $\epsilon$ , one has  $\psi(\mathbf{r} - \epsilon) = \psi(\mathbf{r}) - \epsilon d\psi/d\mathbf{r}$ . Therefore, the translation operator can be written as

$$\hat{T}(\epsilon) = 1 - \epsilon \frac{d}{d\mathbf{r}} = 1 - \frac{i}{\hbar} \epsilon \left( -i\hbar \frac{d}{d\mathbf{r}} \right) . \quad (2.48)$$

As the momentum is the generator of translation, the relation between translation and momentum operators is  $T(\epsilon) = 1 - i\epsilon \hat{\mathbf{p}}/\hbar$ , therefore, the momentum operator can be written as

$$\hat{\mathbf{p}} = -i\hbar \frac{d}{d\mathbf{r}} . \quad (2.49)$$

In classical mechanics, angular momentum is defined as  $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ . This can be carried over to quantum mechanics by reinterpreting  $\mathbf{r}$  as the position operator and  $\mathbf{p}$  as the momentum operator.  $\hat{\mathbf{L}}$  is then an operator, called the *orbital angular momentum* operator.  $\hat{\mathbf{L}}$  is a vector operator  $\hat{\mathbf{L}} = (\hat{L}_x, \hat{L}_y, \hat{L}_z)$  with

$$\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \quad \hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z, \quad \hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x . \quad (2.50)$$

However, there is another type of angular momentum, called *spin angular momentum* (more often shortened to spin), represented by the spin operator  $\hat{\mathbf{S}}$ , see Sect. 2.3. Spin is an intrinsic property of a particle, unrelated to any sort of motion in space. Thus total angular momentum becomes  $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$ . Conservation of angular

momentum states that  $\hat{\mathbf{J}}$  for a closed system is conserved. However,  $\hat{\mathbf{L}}$  and  $\hat{\mathbf{S}}$  are not generally conserved. For example, the spin-orbit interaction allows angular momentum to transfer back and forth between  $\hat{\mathbf{L}}$  and  $\hat{\mathbf{S}}$ , with the total  $\hat{\mathbf{J}}$  remaining constant.

It should be noted that the product of two operators in general does commute  $\hat{A}\hat{B} - \hat{B}\hat{A} \neq 0$ . Two operators commute if, and only if  $\hat{A}\hat{B} - \hat{B}\hat{A} = 0$ . This expression is usually called *commutator* and is written as

$$[\hat{A}, \hat{B}]_- = \hat{A}\hat{B} - \hat{B}\hat{A} . \quad (2.51)$$

In analogy an *anti-commutator* relation is defined as

$$[\hat{A}, \hat{B}]_+ = \hat{A}\hat{B} + \hat{B}\hat{A} . \quad (2.52)$$

If two operators commute with each other, they have simultaneous eigenstates implying that they can be measured together, see Sect. 2.2.3. For instance,

$$[\hat{x}, \hat{p}_x]_- |\psi\rangle = x \frac{-i\hbar \partial}{\partial x} |\psi\rangle - \frac{-i\hbar \partial x}{\partial x} |\psi\rangle = i\hbar |\psi\rangle . \quad (2.53)$$

This indicates that position and momentum operators along the same direction do not have common eigenstates, whereas position and momentum along different directions commute with each other:

$$\begin{aligned} [\hat{x}, \hat{p}_x]_- &= [\hat{y}, \hat{p}_y]_- = [\hat{z}, \hat{p}_z]_- = i\hbar , \\ [\hat{x}, \hat{p}_y]_- &= [\hat{x}, \hat{p}_z]_- = [\hat{y}, \hat{p}_x]_- = [\hat{y}, \hat{p}_z]_- = [\hat{z}, \hat{p}_x]_- = [\hat{z}, \hat{p}_y]_- = 0 . \end{aligned} \quad (2.54)$$

Using the commutation relations of position and momentum, one can show that the components of the orbital angular momentum satisfy the following relations

$$[\hat{L}_x, \hat{L}_y]_- = i\hbar \hat{L}_z , \quad [\hat{L}_y, \hat{L}_z]_- = i\hbar \hat{L}_x , \quad [\hat{L}_z, \hat{L}_x]_- = i\hbar \hat{L}_y . \quad (2.55)$$

Like any vector, a magnitude can be defined for the orbital angular momentum operator  $\hat{L}^2 \equiv \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$ .  $\hat{L}^2$  is a quantum operator that commutes with the components of  $\hat{\mathbf{L}}$ :

$$[\hat{L}^2, \hat{L}_x]_- = [\hat{L}^2, \hat{L}_y]_- = [\hat{L}^2, \hat{L}_z]_- = 0 . \quad (2.56)$$

### 2.2.3 Measurements and Expectation Values

The measurement postulate provides the bridge between the wave function, which is an abstract object and cannot be probed directly, and actual measurements.

In classical mechanics, it is implicitly assumed that the accuracy of a measurement is only limited by the accuracy of the measurement device, which, at least in principle, can be improved indefinitely. In addition, it is assumed that, at least ideally, measurements can be made such that they do not significantly affect the system. In quantum mechanics, the outcome of a measurement is, however, probabilistic. If the wave function of a quantum mechanical system is known, one can only predict the probability of a measurement, rather than the outcome itself. It is a fundamental limitation of quantum mechanical systems and has nothing to do with experimental limitations or the accuracy of measurement devices. Furthermore, there is no way to avoid the effect of the measurement on the system. Assuming  $u_n$  and  $|u_n\rangle$  represent the eigenvalues and eigenstates of  $\hat{O}$ , respectively, such that  $\hat{O}|u_n\rangle = u_n|u_n\rangle$ , then

- The outcome of the measurement is always one of the eigenvalues of  $\hat{O}$ ,
- The probability for measuring the eigenvalue  $u_n$  is given by  $p_n = |\langle u_n|\psi\rangle|^2$ ,
- If the measurement gives the value  $u_n$ , after the measurement the state of the system will collapse to the corresponding eigenstate,  $|u_n\rangle$ .

In a quantum mechanical system, the only possible measurement outcomes are equal to the eigenvalues of the operator representing the observable, and the probability of measuring this value is given by the absolute value squared of the inner product of the quantum state with the operator's corresponding eigenstate. If two Hermitian operators commute, there is a complete set of eigenstates that is common to both. Under this condition it is possible to measure both quantities simultaneously with certainty. If they do not commute, one of the measurements alters the other measurement outcome.

Quantum mechanics shows an inherent statistical behavior. The measured outcome of an experiment will generally not be the same if the experiment is repeated several times. Quantum mechanics does not, in fact, predict the result of individual measurements, but only their statistical mean. This predicted mean value is called the expectation value. If a state of a system is described by the wave function  $\psi(\mathbf{r}, t)$  the average of any physical observable  $\hat{O}$  is given by

$$\langle O \rangle = \langle \psi | \hat{O} | \psi \rangle = \int d\mathbf{r} \psi^*(\mathbf{r}, t) \hat{O} \psi(\mathbf{r}, t) , \quad (2.57)$$

where  $\langle O \rangle$  represent the expectation value. This integral can be interpreted as the average value that one would expect to obtain over a large number of runs of the experiment. As stated before, any quantum mechanical operator  $\hat{O}$  associated with a measurable property must be linear and Hermitian. Physically, the Hermitian property is necessary in order for the eigenvalues or measurement values to be constrained to real numbers.

As discussed earlier, if two physical quantities correspond to commuting Hermitian operators, they have a common set of eigenstates. In these eigenstates both quantities have precise values at the same time and they can be measured simultaneously. However, if two operators do not commute, in general one cannot

specify both values precisely. In this case the *uncertainty principle* requires that if one measures one of them more accurately, one increasingly loses track of the other. For example, the energy and momentum of a free particle can both be specified exactly, whereas position and momentum along one direction cannot be specified simultaneously. To quantify how accurately physical quantities can be measured together one can use the *mean square deviation*. The deviation from the mean value of a quantum mechanical operator  $\hat{O}$  is defined as  $\Delta\hat{O} = \hat{O} - \langle O \rangle$ . The mean square deviation is, therefore, expressed as

$$\Delta O^2 = \langle \psi | (\Delta\hat{O})^2 | \psi \rangle = \int d\mathbf{r} \psi^*(\mathbf{r}, t) (\Delta\hat{O})^2 \psi(\mathbf{r}, t). \quad (2.58)$$

One may consider two physical quantities described by Hermitian operators  $\hat{A}$  and  $\hat{B}$ . It can be shown that the mean values of the square of deviation are related as [7]

$$\Delta A^2 \Delta B^2 \geq \left( \frac{1}{2i} \langle [\hat{A}, \hat{B}]_- \rangle \right)^2. \quad (2.59)$$

This is *Heisenberg's uncertainty principle* [10] in its most general form. It indicates that two physical quantities cannot be simultaneously measured without uncertainty if their corresponding operators do not commute. The commutator of the position and momentum operators along the same direction is  $[\hat{x}, \hat{p}_x]_- = i\hbar$ . As a result, the uncertainty relation for these quantities is obtained as

$$\Delta x \Delta p_x \geq \frac{\hbar}{2}. \quad (2.60)$$

A similar relation holds between energy and time:

$$\Delta E \Delta t \geq \frac{\hbar}{2}. \quad (2.61)$$

In the special theory of relativity, a coordinate in space-time is specified by a 4-vector consisting of position and time. Knowing that  $E = i\hbar\partial/\partial t$  one obtains the commutator  $[\hat{E}, t] = i\hbar$ . Therefore, by employing Eq. (2.59) one can achieve the uncertainty relation for energy and time [7]. In non-relativistic theory, however, time is considered as an independent variable of which dynamical variables are functions. In this context,  $\Delta t$  is not the standard deviation of a collection of time measurements. The *time-energy uncertainty principle* is a statement about how statistical uncertainty in the energy controls the time scale for a change in the system [8]. If the initial state of a system is an energy eigenstate, then the system remains stationary and  $\Delta E = 0$ , which forces  $\Delta t \rightarrow \infty$ , implying that the physical attributes of the state never change.

### 2.2.4 Schrödinger Equation

The Schrödinger equation replaces Newton's second law as the fundamental equation of motion. Given that the state of the system at some initial time  $t_0$ , this equation predicts the state of the system at another time  $t$ . Time-dependent Schrödinger equation is written as

$$i\hbar \frac{\partial}{\partial t} \Psi = \hat{H} \Psi , \quad (2.62)$$

The Hamiltonian operator  $\hat{H}$  replaces the classical Hamiltonian, which gives the total energy in terms of the particle position and momentum. Using the corresponding operators from Table 2.1, one obtains

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) , \quad (2.63)$$

where  $\nabla^2$  is the Laplacian. Mathematically the time-dependent Schrödinger equation is a linear, second order, partial differential equation. Any linear differential equation allows for the superposition of its solutions. This implies that, if  $\psi_1$  and  $\psi_2$  are solutions of the Schrödinger equation, then any linear combination of  $\psi_1$  and  $\psi_2$  are solutions as well:

$$\Psi(\mathbf{r}, t) = C_1 \psi_1(\mathbf{r}, t) + C_2 \psi_2(\mathbf{r}, t) , \quad (2.64)$$

where,  $C_1$  and  $C_2$  are some constants. This property is called *superposition*.

If the potential energy does not explicitly depend on time, one can solve the Schrödinger equation by separating the variables. Under this condition the wave function is assumed to be the product of a function of time and a function of position  $\Psi(\mathbf{r}, t) = \psi(\mathbf{r})\theta(t)$ . Substituting this relation in Eq. (2.62) and dividing both side by  $\psi(\mathbf{r}, t)$  the Schrödinger equation can be reformulated as

$$i\hbar \frac{1}{\theta(t)} \frac{\partial \theta(t)}{\partial t} = \frac{\hat{H} \psi(\mathbf{r})}{\psi(\mathbf{r})} = E . \quad (2.65)$$

The term on the left hand side of Eq. (2.65) is a function of time only, whereas the second term depends on the positions only. As time and position are independent variables, this relation holds only if both sides are constant. This constant is denoted by  $E$  and has a unit of energy. Therefore, the Schrödinger equation can be written as two decoupled equations. The solution of the time-dependent equation is simply given by  $\theta(t) = \exp(-iEt/\hbar)$  and the other equation, which is called the *time-independent* Schrödinger, reads as

$$\hat{H} \psi(\mathbf{r}) = E \psi(\mathbf{r}) . \quad (2.66)$$

Finally, the total wave function of the system is given by

$$\Psi(\mathbf{r}, t) = \psi(\mathbf{r}) \exp(-iEt/\hbar) . \quad (2.67)$$

## 2.3 Spin

Spin is one of two types of angular momentum in quantum mechanics, the other being orbital angular momentum, which is the quantum-mechanical counterpart to the classical notion of angular momentum. Spin is an intrinsic form of angular momentum carried by elementary particles. All elementary particles of a given kind have the same magnitude of spin angular momentum, which is indicated by assigning the particle a spin quantum number. Pauli was the first to propose the concept of spin. In 1925, Kronig, Uhlenbeck, and Goudsmit suggested a physical interpretation of particles spinning around their own axis. When Paul Dirac derived his relativistic quantum mechanics in 1928, electron spin was an essential part of it. There is a theorem in relativistic quantum field theory called *spin-statistics*, proven by Heisenberg. It says that any particle with integer spin, such as a photon, should obey Bose-Einstein statistics, while any particle with half-odd spin, such as an electron, should obey Fermi-Dirac statistics. The half-spin property of electrons results in the Pauli exclusion principle, which in turn underlies the periodic table of chemical elements.

### 2.3.1 Spinors and Pauli Equation

The existence of spin angular momentum is inferred from experiments, such as the Stern-Gerlach experiment, in which particles are observed to possess angular momentum that cannot be accounted for by orbital angular momentum alone. Spin is like a vector quantity that has a definite magnitude and also has a *direction*. Experiments suggest the existence of a spin vector  $\hat{\mathbf{S}} = (\hat{S}_x, \hat{S}_y, \hat{S}_z)$  that should be an angular momentum vector operator. Therefore, the components of  $\hat{\mathbf{S}}$  should obey the same commutation relation as the components of the orbital angular momentum:

$$[\hat{S}_x, \hat{S}_y]_- = i\hbar\hat{S}_z, \quad [\hat{S}_y, \hat{S}_z]_- = i\hbar\hat{S}_x, \quad [\hat{S}_z, \hat{S}_x]_- = i\hbar\hat{S}_y. \quad (2.68)$$

Furthermore, the components of the spin operator should be Hermitian ( $\hat{S}_i = \hat{S}_i^\dagger$ ) to guarantee that their expectation values are real. However, spins are not strictly vectors, and they are instead described as a related quantity: a *spinor*. For the representation of the operators, it is common to use *Pauli matrices*  $\sigma_i$  [7]:

$$\hat{S}_x = \frac{1}{2}\hbar\hat{\sigma}_x, \quad \hat{S}_y = \frac{1}{2}\hbar\hat{\sigma}_y, \quad \hat{S}_z = \frac{1}{2}\hbar\hat{\sigma}_z. \quad (2.69)$$



Thus the commutation relations Eq. (2.68) take the following form

$$[\hat{\sigma}_x, \hat{\sigma}_y]_- = 2i\hat{\sigma}_z, \quad [\hat{\sigma}_y, \hat{\sigma}_z]_- = 2i\hat{\sigma}_x, \quad [\hat{\sigma}_z, \hat{\sigma}_x]_- = 2i\hat{\sigma}_y. \quad (2.70)$$

Based on possible orientations, spin components have only two eigenvalues  $\pm\hbar/2$  that are generally referred to as *spin-up* and *spin-down*. Therefore, the spin matrices should be  $2 \times 2$  matrices. It is common to take the  $z$ -direction as the direction of the quantization. Then the  $z$  axis is the axis which the orientation of the spin is related to. Matrix  $\hat{\sigma}_z$  is diagonal in its eigenstates representation and has the eigenvalues  $\pm 1$  as diagonal elements and  $\hat{\sigma}_z^2 = \mathbb{1}$ , where  $\mathbb{1}$  represents  $2 \times 2$  identity matrix. The matrices  $\hat{\sigma}_x$  and  $\hat{\sigma}_y$  take similar form in their eigenstate representation. As an identity matrix remains unchanged under the change of representation, the identity  $\hat{\sigma}_x^2 = \hat{\sigma}_y^2 = \hat{\sigma}_z^2 = \mathbb{1}$  holds in general. Using this identity relation and Eq. (2.70), the matrices  $\hat{\sigma}_x$  and  $\hat{\sigma}_y$  in the eigenstate representation of  $\hat{\sigma}_z$  are obtained as [7]

$$\hat{\sigma}_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \quad \hat{\sigma}_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \quad \hat{\sigma}_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}. \quad (2.71)$$

The unit matrix together with the Pauli matrices span the space of two-dimensional matrices. By taking spin into account, a further degree of freedom can be assigned to a particle. For describing this degree of freedom, one should additionally introduce the component of the spin in the  $z$ -direction  $S_z$  as an argument of the wave function. As  $S_z$  takes only two values, the wave function with spin can be mathematically described by a vector-like object known as *spinor*. The two components of the spinor are  $\psi_\uparrow(\mathbf{r}) = \psi(\mathbf{r}, +\frac{1}{2}\hbar)$  and  $\psi_\downarrow(\mathbf{r}) = \psi(\mathbf{r}, -\frac{1}{2}\hbar)$ , while the total wave function is written as [13]

$$\Psi = \begin{bmatrix} \psi_\uparrow(\mathbf{r}) \\ \psi_\downarrow(\mathbf{r}) \end{bmatrix} = \psi_\uparrow(\mathbf{r}) \begin{bmatrix} 1 \\ 0 \end{bmatrix} + \psi_\downarrow(\mathbf{r}) \begin{bmatrix} 0 \\ 1 \end{bmatrix} = \psi_\uparrow(\mathbf{r})\chi_\uparrow + \psi_\downarrow(\mathbf{r})\chi_\downarrow, \quad (2.72)$$

where the spin wave functions indicate only the state of spin, spin-up or spin-down, and  $\chi$  are unit spinors:

$$\chi_\uparrow = \begin{bmatrix} 1 \\ 0 \end{bmatrix}, \quad \chi_\downarrow = \begin{bmatrix} 0 \\ 1 \end{bmatrix}. \quad (2.73)$$

The spinors in Eq. (2.73) are the eigenstates of  $\hat{\sigma}_z$ . One can write the total wave function as  $\psi(\mathbf{r})\chi_\sigma$ , where  $\sigma = \{\uparrow, \downarrow\}$  is the spin index. In Dirac notation, spin states can be represented by the kets  $|\uparrow\rangle$  and  $|\downarrow\rangle$ .

Particles with spin can have a magnetic dipole moment. The magnetic moment  $\mu$  of a spin-half particle with charge  $e$ , mass  $m$ , and spin angular momentum  $\hat{\mathbf{S}}$ , is

$$\hat{\boldsymbol{\mu}} = -g_s \frac{e}{2m} \hat{\mathbf{S}} = -\mu_B \hat{\boldsymbol{\sigma}}, \quad (2.74)$$

where  $\mu_B = e\hbar/(2m)$  and the dimensionless quantity  $g_s$  is called the spin g-factor and is approximately equal to 2 for electrons. Since spin interacts with magnetic fields, the electron gains additional potential energy in the presence of a magnetic field  $\Delta E = -\hat{\boldsymbol{\mu}} \cdot \mathbf{B}$ . Therefore, the Hamiltonian of an electron with spin takes the form

$$\hat{H}\Psi = \left[ \hat{H}_0 + \mu_B \hat{\boldsymbol{\sigma}} \cdot \mathbf{B} \right] \Psi, \quad (2.75)$$

where  $H_0$  is the spin-independent part of the Hamiltonian,  $\Psi$  is the spinor wave function, and the second term on the right hand side is called the Zeeman term. Equation (2.75) is referred to as *Pauli equation*.

### 2.3.2 Spin-Orbit Coupling

*Spin-orbit coupling* is the interaction of a particle's spin with its motion. One of the known example of this effect is that spin-orbit interaction causes shifts in an electron's atomic energy level due to electromagnetic interaction between the electron's spin and the magnetic field generated by the electron's orbit around the nucleus. Spin-orbit coupling can be viewed as the Zeeman term due to an effective magnetic field. In the framework of the electron that moves with velocity  $\mathbf{v}$  relative to an electric field  $\mathbf{E}$ , it sees a magnetic field due to *relativistic effects*. In other words, the moving electron experiences a magnetic field in its rest frame that arises from the Lorentz transformation of the static electric field; this field will affect the electron spin and is given by

$$\mathbf{B} = -\frac{\mathbf{v} \times \mathbf{E}}{c^2 \sqrt{1 - v^2/c^2}} \approx -\frac{\mathbf{v} \times \mathbf{E}}{c^2} = \frac{\mathbf{E} \times \mathbf{p}}{mc^2}, \quad (2.76)$$

where terms of order  $(v/c)^2$  and higher order terms are neglected. The energy of the electron in this field, due to its magnetic moment  $\boldsymbol{\mu}$ , is

$$\Delta E_{\text{SOC}} = -\boldsymbol{\mu} \cdot \mathbf{B} = -\frac{e}{m} \hat{\mathbf{S}} \cdot \mathbf{B} = -\frac{e}{m^2 c^2} \hat{\mathbf{S}} \cdot (\mathbf{E} \times \hat{\mathbf{p}}). \quad (2.77)$$

The spin-orbit interaction potential consists of two parts. The Larmor part is connected to the interaction of the magnetic moment of the electron with the magnetic field of the nucleus in the co-moving frame of the electron. The second contribution is related to Thomas precession. Equation (2.77) takes care of the former contribution. The electron's curved trajectory is taken into account in the Thomas precession correction. In 1926, Llewellyn Thomas relativistically recomputed the doublet separation in the fine structure of the atom [19]. The net effect of *Thomas precession* is the reduction of the Larmor interaction energy by factor 1/2, which came to be known as the Thomas half. In case of centrally

symmetric electrical fields – for example, the orbital motion of an electron in the electric field of an atomic nucleus – one has

$$\mathbf{E} = -\frac{1}{e} \frac{\mathbf{r}}{r} \frac{dU}{dr}. \quad (2.78)$$

Using Eq. (2.78), the definition of the angular momentum of a particle  $\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}$ , and reducing the interaction potential due to Thomas precession, one can write the spin-orbit coupling Hamiltonian as

$$\hat{H}_{\text{soc}} = -\frac{e}{2m^2c^2} \hat{\mathbf{S}} \cdot \left( -\frac{1}{e} \frac{\mathbf{r}}{r} \frac{dU}{dr} \times \hat{\mathbf{p}} \right) = \frac{1}{2m^2c^2} \frac{1}{r} \frac{dU}{dr} \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = \xi \hat{\mathbf{L}} \cdot \hat{\mathbf{S}}, \quad (2.79)$$

where the spin-orbit coupling constant  $\xi$  varies in the range 1.25–250 meV for various materials and orbitals. As spin-orbit coupling provides a way to manipulate the spin of electrons with electric field, it plays an important role in spintronics [2].

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