Chapter 3
Basic Concepts and Axioms

Abstract The postulates of quantum mechanics are formulated using the mathematical tools of the preceding chapter. First, the axioms related to the quantum kinematics are summarized, dealing with a variety and physical meaning of quantum states at the specified time. They include alternative definitions and interpretations of the wave functions of microobjects as amplitudes of the particle probability distributions in the configuration or momentum spaces. As an illustrative example the electron densities are then discussed. The superposition principle is formulated, and the symmetry implications of indistinguishability of identical particles in quantum mechanics are examined. The links between the quantum states and outcomes of the physical measurements are then surveyed and the physical observables are attributed to quantum mechanical operators, linear and Hermitian, and their specific forms in the position and momentum representations are introduced. The eigenvalues of the quantum mechanical operator are postulated to determine a variety of all possible results of a single experiment measuring the physical property the operator represents, while the operator expectation value represents the average value of this quantity in a very large number of repeated measurements performed on the system in the same quantum state. The eigenstates of the quantum mechanical operator are shown to correspond to the sharply specified value of the physical property under consideration, while other quantum states exhibit distributions of its allowed eigenvalues. The statistical mixtures of quantum states are defined in terms of the density operator and the ensemble averages of physical observables in such mixed states are examined. The simultaneous sharp measurement of several physical observables is linked to the mutual commutation of their operators and the quantum mechanical formulation of the general Principle of Indeterminacy is given. Properties of the electron angular momentum and spin operators are examined.

In the dynamical development, the pictures of time evolution in quantum mechanics are introduced through the alternative time-dependent unitary transformations of the state vectors/operators. The Schrödinger equation is explored in some detail, with the emphasis placed upon the stationary states, time dependence of expectation values, conservation laws, the probability current, and continuity equation. The

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correspondence between the quantum and classical dynamics is established through the Ehrenfest principle. Finally, the rudiments of the Heisenberg and interaction pictures of quantum dynamics are briefly summarized.

3.1 *N*-Electron Wave Functions and Their Probabilistic Interpretation

In the canonical formulation of classical mechanics, the system dynamics is formulated in terms of the Hamilton function $E = H(\boldsymbol{Q}, \boldsymbol{P})$ expressing the system energy E in terms of its generalized coordinates $\boldsymbol{Q} = \{Q_\alpha\}$ and their conjugated momenta $\boldsymbol{P} = \{P_\alpha\}$, $\alpha = 1, 2, \ldots, f$, with f denoting the system number of dynamical *degrees of freedom*. Together these conjugate dynamical variables uniquely specify the system mechanical state. Indeed, the knowledge of $\boldsymbol{Q}(t)$ and $\boldsymbol{P}(t)$ at the specified time $t = t_0$ allows one to determine the exact time evolution of these state parameters, via the Hamilton equations of motion:

$$\dot{Q}_\alpha = \frac{dQ_\alpha}{dt} = \frac{\partial H}{\partial P_\alpha}, \quad \dot{P}_\alpha = \frac{dP_\alpha}{dt} = -\frac{\partial H}{\partial Q_\alpha}, \quad \alpha = 1, 2, \ldots, f. \tag{3.1}$$

Since these are the *first*-order differential equations, their solutions $\{\boldsymbol{Q}(t), \boldsymbol{P}(t)\}$ are uniquely specified when the values of these classical state variables are fixed at $t = t_0$. Thus, knowing the state $\{\boldsymbol{Q}(t_0), \boldsymbol{P}(t_0)\}$ of the classical system at this time, one can in principle predict with certainty the system mechanical state at $t \neq t_0$, i.e., precisely determine the outcome of any measurement at an earlier or later stage of the system time evolution.

As we have argued in Chap. 1, this classical specification of the mechanical state is inapplicable in the quantum theory, due to the simultaneous indeterminacy of coordinates and momenta of microobjects (the Heisenberg principle). Indeed, since the state variables must be precisely specified, either the position coordinates or the components of the canonically conjugated momenta of the system particles should be used to uniquely characterize its quantum state. Therefore, at the given time t, which in the simplest (nonrelativistic) formulation of the quantum theory plays the role of a parameter, the quantum state corresponding to the state vector $|\Psi(t)\rangle$ is represented by the wave functions in either the position or momentum representations,

$$\Psi(\boldsymbol{Q}; t) = \langle \boldsymbol{Q} | \Psi(t) \rangle \quad \text{or} \quad \Psi(\boldsymbol{P}; t) = \langle \boldsymbol{P} | \Psi(t) \rangle; \tag{3.2a}$$

here, the representation basis sets $\{|\boldsymbol{Q}\rangle\}$ and $\{|\boldsymbol{P}\rangle\}$ correspond to the position and momentum eigenstates, respectively, in which these molecular variables are known precisely. For quantum particles these classical state "coordinates" should be also supplemented with all nonclassical, internal (*spin*) degrees of freedom for each particle, $\boldsymbol{\Sigma} = \{\Sigma_k\}$. Therefore, the full specification of the mechanical state of the given quantum system, in either the *position-spin* or *momentum-spin* representations, is embodied in the corresponding wave functions:

$$\Psi(\boldsymbol{Q},\boldsymbol{\Sigma};\, t) = \langle \boldsymbol{Q},\boldsymbol{\Sigma}|\Psi(t)\rangle \quad \text{or} \quad \Psi(\boldsymbol{P},\boldsymbol{\Sigma};\, t) = \langle \boldsymbol{P},\boldsymbol{\Sigma}|\Psi(t)\rangle. \tag{3.2b}$$

Since the theoretical description of the electronic structure of molecules is the main objective of this book, in what follows we shall focus on a general (atomic or molecular) N-electron system, with the list of the (coordinate/momenta)-spin variables in the Cartesian coordinates:

$$\begin{aligned} |\boldsymbol{Q},\boldsymbol{\Sigma}\rangle &\equiv \left|\boldsymbol{q}^N\right\rangle = |\{\boldsymbol{q}_k\}\rangle \equiv \left|\mathcal{Q}^N\right\rangle, \quad \boldsymbol{q}_k = (\boldsymbol{r}_k,\, \sigma_k), \\ |\boldsymbol{P},\boldsymbol{\Sigma}\rangle &\equiv \left|\boldsymbol{u}^N\right\rangle = |\{\boldsymbol{u}_k\}\rangle \equiv \left|\mathcal{P}^N\right\rangle, \quad \boldsymbol{u}_k = (\boldsymbol{p}_k,\, \sigma_k), \quad k = 1,2,\ldots,N; \end{aligned} \tag{3.3}$$

here $\boldsymbol{r}_k = (x_k, y_k, z_k), \boldsymbol{p}_k = (p_{x_k}, p_{y_k}, p_{z_k})$ and σ_k, respectively, denote the continuous position, momentum vectors of kth electron and its discrete spin orientation variable $\sigma_k \in (+½, -½)$ (see Fig. 1.2).

Therefore, the vector space of the N-electron system is spanned by all basis vectors in either the position $\{|\mathcal{Q}^N\rangle\}$ or momentum $\{|\mathcal{P}^N\rangle\}$ representations. In what follows we shall call this vector space the *molecular Hilbert space*. The specific state of such an N-electron system in time t will be denoted by the ket $|\Psi^N(t)\rangle$. Since each basis vector is specified by the three position/momentum coordinates and one spin variable for each electron, the overall dimensionality of either the *position*-spin or *momentum*-spin spaces is $4N$. The basis vectors $|\mathcal{Q}^N\rangle$ and $|\mathcal{P}^N\rangle$ are then identified by corresponding points in these configurational spaces. It should be observed that in the classical mechanics the system state was uniquely specified at the given time by selecting the point in the $6N$-dimensional position–momentum *phase space* of N particles.

Moreover, the corresponding position-spin or momentum-spin data for the atomic nuclei are also required for the complete specification of the molecular state. However, as we shall argue in Part II of this book, due to a huge difference in masses between the (light) electrons and (heavy) nuclei, the dynamics of the former can be to a good approximation described by examining their fast movements in the effective potential generated by the "frozen" nuclear framework, with the fixed positions of nuclei playing the role of parameters in the electronic structure theory. In this *adiabatic approximation* of Born and Oppenheimer the nuclei, sources of the external potential in which electrons move, thus determine the assumed molecular geometry.

After these short preliminaries, we are now in a position to formulate the important postulate of quantum mechanics, due to Born, which provides the physical interpretation of the wave functions of (3.2a) and (3.2b):

Postulate I: The (normalized) quantum mechanical state of the molecular system containing N-electrons in time *t*, $\langle\Psi^N(t)|\Psi^N(t)\rangle \equiv \left\|\Psi^N(t)\right\|^2 = 1$, where $\left\|\Psi^N(t)\right\|$

stands for the norm (“length”) of the state vector, is uniquely specified by the orientation of the state-vector $|\Psi^N(t)\rangle$ in the molecular Hilbert space or equivalently by its equivalent representations (wave functions) in the position or momentum basis sets, respectively,

$$\Psi(\mathcal{Q}^N;\, t) = \langle \mathcal{Q}^N | \Psi^N(t) \rangle \quad \text{or} \quad \Psi(\mathcal{P}^N; t) = \langle \mathcal{P}^N | \Psi^N(t) \rangle. \tag{3.2c}$$

These in general complex-valued functions determine the probability amplitudes of simultaneously observing at this time the specified positions/momenta and spin orientations of all N electrons, with the corresponding probability densities being determined by the squares of the wave function moduli:

$$\begin{aligned}
p(\mathcal{Q}^N; t) &= \left| \langle \mathcal{Q}^N | \Psi^N(t) \rangle \right|^2 = \left| \Psi(\mathcal{Q}^N; t) \right|^2 \equiv P[\mathcal{Q}^N | \Psi^N(t)],\\
\int p(\mathcal{Q}^N; t)\, d\mathcal{Q}^N &= \int \langle \Psi^N(t) | \mathcal{Q}^N \rangle \langle \mathcal{Q}^N | \Psi^N(t) \rangle\, d\mathcal{Q}^N = \langle \Psi^N(t)\, | \Psi^N(t) \rangle = 1;\\
\pi(\mathcal{P}^N; t) &= \left| \langle \mathcal{P}^N | \Psi^N(t) \rangle \right|^2 = \left| \Psi(\mathcal{P}^N; t) \right|^2 \equiv P[\mathcal{P}^N | \Psi^N(t)],\\
\int \pi(\mathcal{P}^N; t)\, d\mathcal{P}^N &= \int \langle \Psi^N(t) | \mathcal{P}^N \rangle \langle \mathcal{P}^N | \Psi^N(t) \rangle\, d\mathcal{P}^N = \langle \Psi^N(t)\, | \Psi^N(t) \rangle = 1.
\end{aligned} \tag{3.4}$$

Here, the generalized “integration” symbol $\int d\mathcal{Q}^N$ actually denotes the definite integrations over the position coordinates and summations over the spin variables of all electrons:

$$\int d\mathcal{Q}^N \equiv \int d\boldsymbol{q}_1 \ldots d\boldsymbol{q}_N \equiv \int d\boldsymbol{r}_1 \ldots d\boldsymbol{r}_N \sum_{\sigma_1} \cdots \sum_{\sigma_N}, \tag{3.5a}$$

The related operation in the momentum-spin space similarly reads:

$$\int d\mathcal{P}^N \equiv \int d\boldsymbol{u}_1 \ldots d\boldsymbol{u}_N \equiv \int d\boldsymbol{p}_1 \ldots d\boldsymbol{p}_N \sum_{\sigma_1} \cdots \sum_{\sigma_N}. \tag{3.5b}$$

In fact, the normalization conditions of this postulate, for the position-spin and momentum-spin probability densities $p(\mathcal{Q}^N; t)$ and $\pi(\mathcal{P}^N; t)$, respectively, express the unit probability of the sure event that at the specified time t all electrons are located somewhere in the physical or momentum spaces, and assume one of its allowed spin orientations. We have also indicated in (3.4) that the probability densities $P[\mathcal{Q}^N | \Psi^N(t)]$ and $P[\mathcal{P}^N | \Psi^N(t)]$ of the particle positions and momenta, respectively, are *conditional* upon the specified quantum state. Indeed, these densities represent the conditional probabilities of observing the basis set events corresponding to the wave function arguments $\mathcal{Q}^N$ or $\mathcal{P}^N$ (*variables*), given the molecular state $|\Psi^N(t)\rangle$ (the *parameter*): $p(\mathcal{Q}^N; t) = P[\mathcal{Q}^N | \Psi^N(t)]$ and $\pi(\mathcal{P}^N; t) = P[\mathcal{P}^N | \Psi^N(t)]$. The normalization relations thus involve the integrations/summations of these conditional probabilities over the *variable* states $\{|\mathcal{Q}^N\rangle\}$ and $\{|\mathcal{P}^N\rangle\}$, respectively, for the fixed *parameter* state $|\Psi^N(t)\rangle$. The integrands of these sum rules thus provide the associated probabilities of the particles being simultaneously found in their specified, infinitesimal ranges of coordinates $d\mathcal{Q}^N = \{d\boldsymbol{r}_k, \sigma_k\}$ or momenta $d\mathcal{P}^N = \{d\boldsymbol{p}_k, \sigma_k\}$, i.e., of the system particles occupying the corresponding volumes of the position or momentum spaces for their specified spin orientations.

This physical interpretation of the quantum mechanical wave functions has far reaching implications for their admissible analytical form. First, the normalization condition excludes the functions which become infinite over a finite region of space, since then Born's interpretation would be untenable. Clearly, the Dirac-delta wave functions of (2.69), which correspond to precise localizations or momenta of electrons, are not excluded since their infinite values extend only over the infinitesimal volumes of space, thus giving rise to the finite normalization integral. However, for the finite, constant probability densities, e.g., $p(\mathcal{Q}^N; t) = const. > 0$, this integral may become infinite, when the movements of electrons are not confined to finite regions of space. In such cases, this density provides only a *relative* measure of probability.

Another implication of the Born probability interpretation is that the wave functions must be single valued. Indeed, $\Psi(\mathcal{Q}^N; t)$[or $\Psi(\mathcal{P}^N; t)$] must generate the *unique* representation of the quantum state $|\Psi^N(t)\rangle$. Additional constraints on their admissible forms are imposed by the form of the quantum mechanical operators. As we have established in Sect. 2.6, the position operator in the momentum representation and the momentum operator in the position representation correspond to differential operators (gradients), e.g., $\hat{\mathbf{p}}(\boldsymbol{r}) = -i\hbar\nabla$. For these operations to be mathematically meaningful, the wave functions on which these observables act must be continuous. Sometimes, the additional condition of the continuous first derivative is also invoked, since the action of the kinetic energy operator of a single particle in the position representation, $\hat{\mathrm{T}}(\boldsymbol{r}) = \hat{\mathbf{p}}^2(\boldsymbol{r})/2m = -(\hbar^2/2m)\Delta$, involves a double differentiation of the wave function embodied in the Laplacian operator $\Delta = \nabla^2$. However, this condition is too severe, since the expectation value of the kinetic energy, when transformed by parts,

$$T = \langle\Psi|\hat{\mathrm{T}}|\Psi\rangle = \int \Psi^*(\boldsymbol{r})\hat{\mathrm{T}}(\boldsymbol{r})\Psi(\boldsymbol{r})d\boldsymbol{r} = (\hbar^2/2m)\int |\nabla\Psi(\boldsymbol{r})|^2 d\boldsymbol{r}, \qquad (3.6)$$

remains well defined even for the discontinuous derivatives of the wave function. For example, such discontinuity is encountered for some excessively ill-behaved potentials $V(\boldsymbol{r})$ of forces acting on the particle, e.g., in the *particle-in-the-box* problem, when it jumps from zero to infinity in an infinitesimal distance.

To summarize, in quantum mechanics only such well-behaved wave functions have the physical meaning of probability amplitudes implied by Postulate I. The Born interpretation thus imposes a restriction on the "acceptable" solutions of the differential equations of quantum mechanics, e.g., the crucial Schrödinger equations for determining the system stationary states and their quantum dynamics. Only such well-behaved wave functions may represent the dynamical states of physical systems.

The constraints of the wave function finiteness, single valuedness, and continuity, supplemented by the boundary conditions appropriate for the physical problem in question, give rise to the *quantization* of physical properties, e.g., the system energy (see Sect. 2.7). Indeed, only for some energy levels, the eigenvalues $\{E_n\}$ of the system Hamiltonian, it is possible to construct the well-behaved eigenfunction. For example, in a system with boundaries, when the movement of particles is confined to some finite region of space, the energy is quantized and the less confining is the potential, the less separation is predicted between the neighboring energy levels.

As a result of the Heisenberg uncertainty principle the physically admissible wave functions may penetrate, i.e., exhibit finite values, in the classically forbidden regions, where the total energy is below the potential energy level, $E < V$, thus generating the nonzero probability of finding a particle in such locations. For example, the motion of the quantum mechanical harmonic oscillator is not confined to the classical region between the turning points of the parabolic Hooke potential, and the quantum particles may tunnel through the finite potential barriers. In these classically-forbidden positions the microparticle formally exhibits the negative kinetic energy. This does not imply, however, that the *average* kinetic energy, represented by the expectation value of (3.6), becomes negative in such states. Indeed, the average value over both the (dominating) region of space, where the kinetic energy is positive, and the classically inaccessible (marginal) regions, where it is negative, is always positive. It should be observed, however, that it would be meaningless to speak of the precise kinetic energy of the localized particle anyway, since its momentum is completely unknown!

The electron density $\rho(\boldsymbol{r})$ of locating any of the system N electrons at point $\boldsymbol{r}$ can be obtained from the N-electron probability density $p(\mathfrak{Q}^N;t)$ of Eq. (3.4) by the appropriate integration/summation over the remaining arguments of the wave function, i.e., over all admissible events satisfying the condition $\boldsymbol{r}_k = \boldsymbol{r}$, $k = 1, 2, \ldots, N$, enforced by the relevant Dirac deltas in the integrand,

$$\begin{aligned}\rho(\boldsymbol{r};t) &= \sum_{k=1}^{N}\int \delta(\boldsymbol{r}_k-\boldsymbol{r})\,p(\mathfrak{Q}^N;t)\,d\mathfrak{Q}^N \\ &\equiv \int \Psi^*(\mathfrak{Q}^N;t)\,\hat{\rho}(\boldsymbol{r})\Psi(\mathfrak{Q}^N;t)\,d\mathfrak{Q}^N = N\int \delta(\boldsymbol{r}_1-\boldsymbol{r})\,p(\mathfrak{Q}^N;t)\,d\mathfrak{Q}^N.\end{aligned} \tag{3.7}$$

In the preceding equation we have introduced the electron density *operator* $\hat{\rho}(\boldsymbol{r}) = \sum_k \delta(\boldsymbol{r}_k - \boldsymbol{r})$ and recognized that due to the indistinguishability of electrons, i.e., impossibility to recognize which electron is which, all contributions in the sum of the first line of the equation must be identical. Indeed, we cannot follow the precise trajectories of the separate electrons, due to the incompatibility of its position and momentum, so that their specific identities (hypothetical labels) remain unknown. Clearly, the integral of the electron density over all locations in space must satisfy the sum rule

$$\int \rho(\boldsymbol{r};t)d\boldsymbol{r} = \int \sum_{k=1}^{N}\left[\int \delta(\boldsymbol{r}_k-\boldsymbol{r})d\boldsymbol{r}\right] p(\mathfrak{Q}^N;t)\,d\mathfrak{Q}^N = N\int p(\mathfrak{Q}^N;t)\,d\mathfrak{Q}^N = N. \tag{3.8}$$

One similarly obtains the corresponding *spin* densities of electrons, of detecting at the specified location $\boldsymbol{r}$ electrons with the specified spin $\sigma = (-½, +½)$, the condition enforced by the corresponding Dirac and Kronecker deltas, which together identify the point $\boldsymbol{q} = (\boldsymbol{r}, \sigma)$ in the four-dimensional position-spin space:

$$\begin{aligned}
\rho(\boldsymbol{q};t) \equiv \rho^{\sigma}(\boldsymbol{r};t) &= \sum_{k=1}^{N} \int \delta(\boldsymbol{r}_k - \boldsymbol{r})\, \delta_{\sigma_k,\sigma} p(\mathbb{Q}^N;t)\, d\mathbb{Q}^N \\
&\equiv \int \Psi^*(\mathbb{Q}^N;t)\, \hat{\rho}(\boldsymbol{q}) \Psi(\mathbb{Q}^N;t)\; d\mathbb{Q}^N \\
&= N_\sigma \int \delta(\boldsymbol{r}_\sigma - \boldsymbol{r})\, p(\mathbb{Q}^N;t)\, d\mathbb{Q}^N, \\
\rho(\boldsymbol{r};t) &= \textstyle\sum_\sigma \rho(\boldsymbol{q};t); \qquad \displaystyle\int \rho(\boldsymbol{q};t)\, d\boldsymbol{r} = N_\sigma; \\
\int \rho(\boldsymbol{q};t)\, d\boldsymbol{q} &= \textstyle\sum_\sigma \displaystyle\int \rho(\boldsymbol{q};t)\, d\boldsymbol{r} = N,
\end{aligned} \tag{3.9}$$

where N_σ stands for the number of electrons exhibiting the spin orientation σ.

In a similar manner, one determines the *many*-electron densities or their respective spin components and the associated operators in the position representation. For example, the spinless *two*-electron density, $\rho_2(\boldsymbol{r}, \boldsymbol{r}'; t)$, of observing one electron (of all N electrons) at $\boldsymbol{r}$ and another electron (of all the remaining $N-1$ electrons) at $\boldsymbol{r}'$ is given by the following expression:

$$\begin{aligned}
\rho_2(\boldsymbol{r},\boldsymbol{r}';t) &= \sum_{k=1}^{N} \sum_{l \neq k} \int \delta(\boldsymbol{r}_k - \boldsymbol{r}) \delta(\boldsymbol{r}_l - \boldsymbol{r}') p(\mathbb{Q}^N;t)\, d\mathbb{Q}^N \\
&\equiv \int \Psi^*(\mathbb{Q}^N;t)\, \hat{\rho}_2(\boldsymbol{r},\boldsymbol{r}') \Psi(\mathbb{Q}^N;t)\; d\mathbb{Q}^N \\
&= N(N-1) \int \delta(\boldsymbol{r}_1 - \boldsymbol{r}) \delta(\boldsymbol{r}_2 - \boldsymbol{r}') p(\mathbb{Q}^N;t)\, d\mathbb{Q}^N, \\
\iint \rho_2(\boldsymbol{r},\boldsymbol{r}';t)\, d\boldsymbol{r}\, d\boldsymbol{r}' &= N(N-1).
\end{aligned} \tag{3.10}$$

Again, this *two*-electron distribution can be decomposed into the spin-resolved components:

$$\begin{aligned}
\rho_2(\boldsymbol{q},\boldsymbol{q}';t) \equiv \rho^{\sigma,\sigma'}(\boldsymbol{r},\boldsymbol{r}';t) &= \sum_{k=1}^{N} \sum_{l \neq k} \int \delta(\boldsymbol{r}_k - \boldsymbol{r}) \delta(\boldsymbol{r}_l - \boldsymbol{r}')\, \delta_{\sigma_k,\sigma} \delta_{\sigma_l,\sigma'} p(\mathbb{Q}^N;t)\, d\mathbb{Q}^N \\
&\equiv \int \Psi^*(\mathbb{Q}^N;t)\, \hat{\rho}_2(\boldsymbol{q},\boldsymbol{q}') \Psi(\mathbb{Q}^N;t)\, d\mathbb{Q}^N, \\
\rho_2(\boldsymbol{r},\boldsymbol{r}';t) &= \sum_{\sigma} \sum_{\sigma'} \rho^{\sigma,\sigma'}(\boldsymbol{r},\boldsymbol{r}';t), \\
\iint \rho_2(\boldsymbol{q},\boldsymbol{q}';t)\, d\boldsymbol{r}\, d\boldsymbol{r}' &= \begin{cases} N_\sigma(N_\sigma - 1), & \sigma' = \sigma \\ N_\sigma N_{\sigma'}, & \sigma' \neq \sigma \end{cases}, \\
\iint \rho_2(\boldsymbol{q},\boldsymbol{q}';t)\, d\boldsymbol{q}\, d\boldsymbol{q}' &= \sum_{\sigma} \sum_{\sigma'} \iint \rho^{\sigma,\sigma'}(\boldsymbol{r},\boldsymbol{r}';t)\, d\boldsymbol{r}\, d\boldsymbol{r}' = N(N-1).
\end{aligned} \tag{3.11}$$

Of interest also is the *pair* density in which the permuted *two*-electron localization events $(\boldsymbol{r}_k = \boldsymbol{r})\wedge(\boldsymbol{r}_l = \boldsymbol{r}')$ and $(\boldsymbol{r}_k = \boldsymbol{r}')\wedge(\boldsymbol{r}_l = \boldsymbol{r})$ are regarded as physically identical and thus counted only once:

$$\begin{aligned} \Gamma(\boldsymbol{r},\boldsymbol{r}';t) &= \int \Psi^*(\boldsymbol{\mathcal{Q}}^N;t)\,\hat{\Gamma}(\boldsymbol{r},\boldsymbol{r}')\Psi(\boldsymbol{\mathcal{Q}}^N;t)\,d\boldsymbol{\mathcal{Q}}^N, \\ \hat{\Gamma}(\boldsymbol{r},\boldsymbol{r}') &= \sum_{k=1}^{N-1}\sum_{l=k+1}^{N}\delta(\boldsymbol{r}_k-\boldsymbol{r})\delta(\boldsymbol{r}_l-\boldsymbol{r}'), \\ \iint \Gamma(\boldsymbol{r},\boldsymbol{r}';t)\,d\boldsymbol{r}\,d\boldsymbol{r}' &= N(N-1)/2 = \binom{N}{2}. \end{aligned} \tag{3.12}$$

This distribution of the physically *indistinguishable* electronic pairs satisfies the pair normalization of the preceding equation (Löwdin 1955a, b), which differs from that adopted for the *two*-electron distribution of (3.10) (McWeeny 1989). This change in the normalization simplifies the expression for the average electron repulsion energy,

$$V_{e,e}(N;t) = \int \Psi^*(\boldsymbol{\mathcal{Q}}^N;t)\hat{\mathrm{V}}_{e,e}(N)\Psi(\boldsymbol{\mathcal{Q}}^N;t)d\boldsymbol{\mathcal{Q}}^N, \tag{3.13}$$

the expectation value of the associated (multiplicative) operator in position representation, $\hat{\mathrm{V}}_{e,e}(N)$, which measures the interelectron Coulomb interaction for the sharply specified locations of all N electrons:

$$\hat{\mathrm{V}}_{e,e}(N) = \sum_{k=1}^{N-1}\sum_{l=k+1}^{N}\frac{1}{|\boldsymbol{r}_k-\boldsymbol{r}_l|} \equiv \sum_{k=1}^{N-1}\sum_{l=k+1}^{N} g(k,l). \tag{3.14}$$

In terms of the above *two*-electron densities, the expectation value of the electron repulsion energy of (3.13) thus reads:

$$\begin{aligned} V_{e,e}(N;t) &= \tfrac{1}{2}\iint |\boldsymbol{r}-\boldsymbol{r}'|^{-1}\rho_2(\boldsymbol{r},\boldsymbol{r}';t)\,d\boldsymbol{r}\,d\boldsymbol{r}' \\ &= \iint |\boldsymbol{r}-\boldsymbol{r}'|^{-1}\Gamma(\boldsymbol{r},\boldsymbol{r}';t)\,d\boldsymbol{r}\,d\boldsymbol{r}'. \end{aligned} \tag{3.15}$$

Clearly, by using the corresponding Kronecker deltas of the spin variables of electrons [see (3.11)], one could similarly define the spin components of the pair density as well.

The extension of these concepts into the corresponding momentum-spin densities is straightforward. For example, the spinless *one*- and *two*-electron densities in the momentum space of N electrons become:

$$\begin{aligned} \pi(\boldsymbol{p};t) &= \sum_{k=1}^{N}\int \delta(\boldsymbol{p}_k-\boldsymbol{p})\,\pi(\boldsymbol{\mathcal{P}}^N;t)\,d\boldsymbol{\mathcal{P}}^N \equiv \int \Psi^*(\boldsymbol{\mathcal{P}}^N;t)\,\hat{\pi}(\boldsymbol{p})\Psi(\boldsymbol{\mathcal{P}}^N;t)\;d\boldsymbol{\mathcal{P}}^N \\ &= N\int \delta(\boldsymbol{p}_1-\boldsymbol{p})\,\pi(\boldsymbol{\mathcal{P}}^N;t)\,d\boldsymbol{\mathcal{P}}^N \equiv NP(\boldsymbol{p};t) \\ &\qquad \int \pi(\boldsymbol{p};t)\,d\boldsymbol{p} = N; \end{aligned} \tag{3.16}$$

$$\begin{aligned}\pi_2(\boldsymbol{p},\boldsymbol{p}';t) &= \sum_{k=1}^{N}\sum_{l\neq k}\int \delta(\boldsymbol{p}_k - \boldsymbol{p})\delta(\boldsymbol{p}_l - \boldsymbol{p}')\pi(\mathcal{P}^N;t)\,d\mathcal{P}^N \\ &\equiv \int \Psi^*(\mathcal{P}^N;t)\,\hat{\pi}_2(\boldsymbol{p},\boldsymbol{p}')\Psi(\mathcal{P}^N;t)\,d\mathcal{P}^N \\ &= N(N-1)\int \delta(\boldsymbol{p}_1 - \boldsymbol{p})\delta(\boldsymbol{p}_2 - \boldsymbol{p}')\pi(\mathcal{P}^N;t)\,d\mathcal{P}^N, \\ \iint \pi_2(\boldsymbol{p},\,\boldsymbol{p}';t)\,d\boldsymbol{p}\,d\boldsymbol{p}' &= N(N-1). \end{aligned} \tag{3.17}$$

Consider now the expectation value of the kinetic energy of N-electrons in the momentum representation,

$$\begin{aligned} T_e(N;t) &= \left\langle \Psi^N(t)\middle|\hat{\mathrm{T}}(N)\middle|\Psi^N(t)\right\rangle \equiv \int \Psi^*(\mathcal{P}^N;t)\,\hat{\mathrm{T}}(\mathcal{P}^N)\Psi(\mathcal{P}^N;t)d\mathcal{P}^N \\ &= \int T(\mathcal{P}^N)\pi(\mathcal{P}^N;t)d\mathcal{P}^N, \end{aligned} \tag{3.18}$$

where the (multiplicative) kinetic energy operator $\hat{\mathrm{T}}(\mathcal{P}^N) = T(\mathcal{P}^N)$ measures the system kinetic energy when the momenta of all N electrons are sharply specified:

$$\hat{\mathrm{T}}(\mathcal{P}^N) = \frac{1}{2m}\sum_{k=1}^{N}\boldsymbol{p}_k^2 \equiv \sum_{k=1}^{N} T(\boldsymbol{p}_k) = T(\mathcal{P}^N) = NT(\boldsymbol{p}). \tag{3.19}$$

Therefore, the expectation value of (3.18) is given by the following mean value expression involving the *one*-electron density in momentum space:

$$T_e(N;t) = N\int T(\boldsymbol{p})\,P(\boldsymbol{p};t)d\boldsymbol{p} = \int T(\boldsymbol{p})\,\pi(\boldsymbol{p};t)d\boldsymbol{p}. \tag{3.20}$$

3.2 Superposition Principle, Expectation Values, and Indistinguishability of Identical Particles

The superposition principle of Sect. 2.2 is formally summarized by another basic axiom of quantum mechanics:

Postulate II: Any combination $|\Psi\rangle = \sum_i C_i|\Psi_i\rangle$ of the admissible quantum states $\{|\Psi_i\rangle\}$, where $\{C_i\}$ denotes generally complex factors, also represents a possible quantum state of the system under consideration. The squares of moduli of these expansion coefficients determine the normalized conditional probabilities $\{P(\Psi_i|\Psi) = |C_i|^2\}$ of observing state Ψ_i given the state Ψ: $\sum_i P(\Psi_i|\Psi) = 1$.

As an illustration let us consider the basis eigenvectors $|\boldsymbol{i}\,\rangle = \{|\Psi_i\rangle \equiv |a_i\rangle\}$ of the quantum observable $\hat{\mathrm{A}}$ (2.55a), which for reasons of simplicity we assume to correspond to the discrete spectrum of eigenvalues $\{a_i\}$. Expanding a general state vector $|\Psi\rangle$ in this basis set (2.48a) then gives the following components of its (column) vector representation: $\boldsymbol{\Psi}(\boldsymbol{i}) = \langle \boldsymbol{i}|\Psi\rangle = \{C_i = \langle\Psi_i|\Psi\rangle\} \equiv \boldsymbol{C}$. Hence [see (2.39)], the corresponding conditional probabilities read:

$$\begin{aligned} P(\Psi_i|\Psi) &= |C_i|^2 = C_iC_i^* = \langle\Psi_i|\Psi\rangle\langle\Psi|\Psi_i\rangle = \langle\Psi_i|\hat{\mathrm{P}}_\Psi|\Psi_i\rangle \\ &= C_i^*C_i = \langle\Psi|\Psi_i\rangle\langle\Psi_i|\Psi\rangle = \langle\Psi|\hat{\mathrm{P}}_i|\Psi\rangle = P(\Psi|\Psi_i). \end{aligned} \tag{3.21}$$

It follows from this equation that the conditional probabilities between two quantum states can be considered as the expectation values in the *variable* state of the projection operator onto the *reference* state, which plays the role of a parameter. Their normalization then directly follows from the basis set closure of (2.41a):

$$\Sigma_i P(\Psi_i|\Psi) = \langle\Psi|\sum_i \hat{\mathrm{P}}_i|\Psi\rangle = \langle\Psi|\Psi\rangle = 1. \tag{3.22}$$

As we shall see in Sect. 3.3, the conditional probabilities of (3.21) also reflect relative frequencies of possible outcomes $\{a_i = \langle\Psi_i|\hat{\mathrm{A}}|\Psi_i\rangle\}$ of the experiments measuring the physical quantity A. Indeed, the eigenvector representation of $\hat{\mathrm{A}}$ is given by the diagonal matrix $\mathbf{A} = \langle\boldsymbol{i}|\hat{\mathrm{A}}|\boldsymbol{i}\rangle = \{A_{m,n} = \langle\Psi_m|\hat{\mathrm{A}}|\Psi_n\rangle = a_m\delta_{m,n}\}$. Therefore, the statistical average (expectation) value $\langle A\rangle$ in state $|\Psi\rangle$ is given by the relevant mean value expression:

$$\langle A\rangle = \Sigma_m P(\Psi_m|\Psi)\,a_m = \Sigma_m\Sigma_n C_m^*\,A_{m,n}\,C_n = \langle\Psi|\boldsymbol{i}\rangle\langle\boldsymbol{i}|\hat{\mathrm{A}}|\boldsymbol{i}\rangle\langle\boldsymbol{i}|\Psi\rangle = \langle\Psi|\hat{\mathrm{A}}|\Psi\rangle. \tag{3.23}$$

We have already encountered such a statistical (ensemble) interpretation in (2.97), when defining the probability $W(E_n|\Psi)$ of observing the specified energy level E_n in the given quantum state $|\Psi\rangle$.

In the case of a degenerate eigenvalue a_i the probability of observing it in state $|\Psi\rangle$ is given by the sum of contributions $P(\Psi_{i,j}|\Psi)$ originating from all independent component states for this eigenvalue, $\{|\Psi_{i,j}\rangle = |i_j\rangle,\ j = 1,\ 2,\ g\}$ [see (2.58)]: $P(a_i) = \sum_{j=1}^{g} |\langle i_j|\Psi\rangle|^2$.

The superposition principle can be straightforwardly extended into the continuous basis sets $|\boldsymbol{x}\rangle = \{|x\rangle\}$, e.g., the position and momentum representations of Sect. 2.6: any continuous combination [see (2.17)] also represents a possible quantum state of the system with $\{P(x|\Psi) = |c(x)|^2\}$ now providing the conditional probability density of observing $|x\rangle$ given $|\Psi\rangle$, and hence also of all its physical observables in the reference state $|\Psi\rangle$, with the relevant normalization condition $\int P(x|\Psi)\,dx = 1$. Indeed, since $\{c(x)\} = \boldsymbol{\Psi}(\boldsymbol{x}) = \langle \boldsymbol{x}|\Psi\rangle$ (continuous column-vector),

$$\int P(x|\Psi)dx = \int \langle\Psi|x\rangle\langle x|\Psi\rangle dx = \langle\Psi|\boldsymbol{x}\rangle\langle\boldsymbol{x}|\Psi\rangle = \langle\Psi|\Psi\rangle = 1, \tag{3.24}$$

where we have used the closure relation of (2.41b). Best illustration of this continuous version of the superposition principle is Postulate I itself. Indeed, as implied by (2.70) and (3.2c), the wave functions in the position and momentum representations constitute the expansion coefficients in the basis sets consisting of the eigenstates of the position and momentum operators, respectively, and hence the squares of their moduli are in fact the conditional probabilities of observing in $|\Psi^N(t)\rangle$ the sharply specified locations and momenta of the system constituent particles:

$$P[\mathcal{Q}^N|\Psi(t)] = |\Psi(\mathcal{Q}^N;t)|^2 = p(\mathcal{Q}^N;t), \quad P[\mathcal{P}^N|\Psi(t)] = |\Psi(\mathcal{P}^N;t)|^2 = \pi(\mathcal{P}^N;t). \tag{3.25}$$

Consider next the expression for the average kinetic energy (3.6) of a spinless particle, corresponding to the quantum observable $\hat{\mathrm{T}} = \hat{\mathbf{p}}^2(\boldsymbol{r})/2m$. The relevant expansion is again that in terms of the eigenstates $\{|\boldsymbol{p}\rangle\}$ of the particle momentum (2.75), $c(\boldsymbol{p}) = \Psi(\boldsymbol{p}) = \langle\boldsymbol{p}|\Psi\rangle$, which also mark the eigenstates of $\hat{\mathrm{T}}$ corresponding to the eigenvalues $\{T(\boldsymbol{p}) = \boldsymbol{p}^2/2m\}$. The associated conditional probability density is therefore the momentum density of (3.16), $P(\boldsymbol{p}|\Psi) = |\Psi(\boldsymbol{p})|^2 = \pi(\boldsymbol{p})$, which gives rise to the following mean value expression for the expectation value of the kinetic energy in state $|\Psi\rangle$ [see also (3.20)]:

$$\langle T\rangle_\Psi = \int T(\boldsymbol{p})P(\boldsymbol{p}|\Psi)\,d\boldsymbol{p} = \int T(\boldsymbol{p})\,\pi(\boldsymbol{p})\,d\boldsymbol{p}. \tag{3.26}$$

In the mixed basis set case, $|\boldsymbol{m}\rangle = (\{|\alpha\rangle\}, \{|y\rangle\})$, the expansion is generated by the identity projector of (2.41c). The squares of expansion coefficients, $\{C_\alpha = \langle\alpha|\Psi\rangle\}$ and $\{c(x) = \langle x|\Psi\rangle\}$, thus determine the corresponding conditional probabilities of observing the representation discrete and continuous eigenvalues, respectively,

$$P(\alpha|\Psi) = |\langle\alpha|\Psi\rangle|^2 \quad \text{and} \quad P(y|\Psi) = |\langle y|\Psi\rangle|^2, \tag{3.27}$$

with the normalization condition [see the closure relation of (2.41c)]:

$$\sum_\alpha P(\alpha|\Psi) + \int P(y|\Psi)dy = \langle\Psi|\boldsymbol{m}\rangle\langle\boldsymbol{m}|\Psi\rangle = \langle\Psi|\Psi\rangle = 1. \tag{3.28}$$

An important property of the wave functions of identical particles is embodied in their symmetry properties with respect to the operation exchanging the spin-position (or momentum-position) variables of two particles. The physical meaning of the quantum state is not affected by such an operation since the identical particles, e.g., electrons in a molecule, are indistinguishable due to the basic inability to follow their classical trajectories in quantum mechanics (the Heisenberg Principle of Indeterminacy). Therefore, should we mentally associate some labels distinguishing electrons at the specified time, their identity afterwards would be still completely unknown. Clearly, the objective laws of quantum mechanics cannot depend upon such a subjective act of attributing these identity labels to electrons.

This physical invariance with respect to exchanging two identical particles, say electrons k and l, symbolized by the associated permutation operator $\hat{\mathrm{X}}(k,l)$, is also reflected by the symmetry of the system Hamiltonian $\hat{\mathrm{H}}(\boldsymbol{\mathcal{Q}}^N)$ with respect to such an operation [see (2.104)],

$$\begin{aligned}&\hat{\mathrm{X}}(k,l)\,\hat{\mathrm{H}}(\boldsymbol{\mathcal{Q}}^N)\hat{\mathrm{X}}(k,l)^{-1} = \hat{\mathrm{H}}(\boldsymbol{\mathcal{Q}}^N) \quad \text{or}\\ &\hat{\mathrm{X}}(k,l)\,\hat{\mathrm{H}}(\boldsymbol{\mathcal{Q}}^N) = \hat{\mathrm{H}}(\boldsymbol{\mathcal{Q}}^N)\,\hat{\mathrm{X}}(k,l).\end{aligned} \tag{3.29}$$

The conservation in such an operation of the probability densities of Postulate I,

$$\begin{aligned}&p(\boldsymbol{q}_1,\ldots\boldsymbol{q}_k,\ldots,\boldsymbol{q}_l,\ldots,\boldsymbol{q}_N;t) = p(\boldsymbol{q}_1,\ldots\boldsymbol{q}_l,\ldots,\boldsymbol{q}_k,\ldots,\boldsymbol{q}_N;t) \quad \text{or}\\ &\pi(\boldsymbol{u}_1,\ldots\boldsymbol{u}_k,\ldots,\boldsymbol{u}_l,\ldots,\boldsymbol{u}_N;t) = \pi(\boldsymbol{u}_1,\ldots\boldsymbol{u}_l,\ldots,\boldsymbol{u}_k,\ldots,\boldsymbol{u}_N;t),\end{aligned} \tag{3.30}$$

thus requires preservation of the squares of the moduli of the associated wave functions. It is assured, when the wave functions themselves are either symmetrical or antisymmetrical with respect to such a permutation of two identical particles:

$$\begin{aligned}&\hat{\mathrm{X}}(k,l)\Psi(\boldsymbol{\mathcal{Q}}^N;t) = \pm\Psi(\boldsymbol{\mathcal{Q}}^N;t) \equiv X_\xi\Psi(\boldsymbol{\mathcal{Q}}^N;t) \quad \text{or}\\ &\hat{\mathrm{X}}(k,l)\Psi(\boldsymbol{\mathcal{P}}^N;t) = \pm\Psi(\boldsymbol{\mathcal{P}}^N;t) \equiv X_\xi\Psi(\boldsymbol{\mathcal{P}}^N;t).\end{aligned} \tag{3.31}$$

Thus, in view of the commutation relation (3.29), $[\hat{\mathrm{H}}(\boldsymbol{\mathcal{Q}}^N),\hat{\mathrm{X}}(k,l)] = 0$, the eigenfunctions of the Hamiltonian of a system of identical particles also satisfy the simultaneous eigenvalue problem (3.31) (see Sect. 2.5) of the particle exchange operator $\hat{\mathrm{X}}(k,l)$, which exhibits only two eigenvalues: $X_\xi = \pm 1$. This symmetry or antisymmetry feature of the wave function reflects the identity of the particles involved. This permutational symmetry of quantum states is conserved in time.

These symmetry properties of the admissible wave functions of identical particles can be summarized in the following postulate of Pauli:

Postulate III: The physical wave functions of the system of identical particles must be either symmetric or antisymmetric with respect to the permutation of their position-spin $\{\boldsymbol{q}_k\}$ or momentum-spin $\{\boldsymbol{u}_k\}$ variables. Those particles for which the wave functions are symmetric are called bosons and those for which they are antisymmetric are called fermions.

Thus, the elementary particles existing in nature are divided into two categories: the particles corresponding to $X = +1$, i.e., the symmetric wave functions, called *bosons*, and those associated with $X = -1$, i.e., the antisymmetric wave functions, called *fermions*. All currently known particles obey the following *empirical* rule related to their spin quantum number S (see Sect. 1.4): particles of *half*-integral spin (e.g., electrons, positrons, protons, neutrons, muons) are fermions, while those of the integral spin (e.g., photons, mesons) are bosons. It also holds for the composite particles such as the atomic nuclei, which are known to be composed of nucleons (neutrons and protons), which are fermions. Thus, the spin of the nucleus as a whole, is reflected by the parity of the number of nucleons: the nuclei with an even number of fermions, e.g., ^{4}He isotope, are bosons, while those containing an odd number of nucleons, e.g., ^{3}He isotope, are fermions, since the resultant spin of such composite particles is integral in the first case and *half*-integral in the other case.

There are also macroscopic consequences of the particle spin identity in the statistical mechanics, which predicts the physical properties of systems composed of a very large number of particles as averages over the ensembles corresponding to alternative thermodynamic equilibria. The statistical weight of a macroscopic state is then proportional to a number of the microscopic states, through which it can be realized, a variety of which strongly depends on the particle identity.

In the classical, *Maxwell–Boltzmann statistics*, the identical particles were in fact treated as if they are different. Indeed, the microscopic states with identical list of states of individual (identical) particles were considered distinct, when the permutation of particles among these states was different. In the quantum statistical mechanics the above symmetrization postulate intervenes, so that an admissible microscopic state is now solely identified by the enumeration of individual particle states which form it, their actual ordering being insignificant. This gives rise to different predictions compared with those resulting from the classical statistical mechanics.

The consequence of the antisymmetrization rule for the wave function of fermions implies that two identical fermions cannot “occupy” the same quantum state, a restriction known as the *Pauli Exclusion Principle*. There are no such occupation restrictions implied by the symmetrization rule for bosons, so that an individual state is accessible to any number of such integral spin particles. Different statistical averages result: the bosons obey the *Bose–Einstein statistics*, while fermions – the *Fermi–Dirac statistics*, which explains the nomenclature adopted to distinguish these two categories of quantum particles. Thermodynamic differences between them are amplified at low temperatures: the *Bose condensation* is observed for systems composed of identical bosons, with particles accumulating in the lowest energy individual states; by the Pauli exclusion rule this effect is prohibited in systems of identical fermions.

All physical predictions for quantum objects are expressed in terms of the probability amplitudes (see Postulate I), which represent the scalar products of two state vectors, or matrix elements of an operator. The symmetrization requirement of Postulate III causes special *interference effects* between the so-called "direct" and "exchange" processes, to appear in the conditional probabilities (see Postulate II) of specific outcomes of experiments performed on systems of identical particles. The formal postulates related to measurement processes, single or repeated, performed on quantum systems are the subject of the next section.

3.3 Results of Physical Measurements

In this section, we shall further elaborate on the physical implications of the mathematical concepts of the quantum mechanical description, which has been introduced in the preceding chapter, by specifically addressing the link between this abstract formalism and the results of measurements. As in previous sections we shall focus on the position and momentum wave functions and the associated operators representing the physical properties of the microsystems. In what follows both the results of a single experiment and the average values of a large number of repetitions of the same experiment performed on systems in the same initial quantum state will be tackled by the corresponding postulates of quantum mechanics.

3.3.1 Classical Observables in Position and Momentum Representations

As we have already remarked in Sect. 2.5, each physical quantity A is represented in quantum mechanics by its linear and Hermitian operator $\hat{\mathrm{A}}$, the eigenvalue problem of which plays the fundamental role in predicting the outcomes of physical measurements. This correspondence is formalized in terms of the following axiom:

Postulate IV.1: To every mechanical quantity A there corresponds in quantum mechanics the associated operator $\hat{\mathrm{A}}$ called an observable. It has to be linear, to satisfy the requirements of the Superposition Principle (Postulate II), and Hermitian (self-adjoint), for its eigenvalues to be real. Their eigenvectors form the bases in the vector space of all quantum states of the physical system.

The prescription for constructing the position/momentum representations of the quantum mechanical observables are known as the *Jordan rules*. Consider the classical quantities, which can be expressed as functions of the particle positions and momenta, $A = A(\{\boldsymbol{r}_k\},\{\boldsymbol{p}_k\})$, or equivalently in terms of the conjugated Cartesian coordinates, $A = A(\{x_\alpha\}, \{p_\beta\})$. The Jordan rules summarize the results of Sect. 2.6 by attributing to such functions the corresponding functions of the position and momentum operators:

$$\hat{\mathrm{A}} = A(\{\hat{\mathbf{r}}_k\}, \{\hat{\mathbf{p}}_k\}) \quad \text{or} \quad \hat{\mathrm{A}} = A(\{\hat{\mathrm{x}}_\alpha\}, \{\hat{\mathrm{p}}_\beta\}). \tag{3.32}$$

In the *position representation* $\{\boldsymbol{r}_k\} = \{x_\alpha\}$, the coordinate operator $\hat{\mathrm{x}}_\alpha$ denotes the multiplication by x_α, $\hat{\mathrm{x}}_\alpha = x_\alpha$. Similarly for any function of the particle coordinates, e.g., the position vector $\boldsymbol{r} = x\boldsymbol{i} + y\boldsymbol{j} + z\boldsymbol{k}$ or the potential energy $V(\{x_\alpha\})$, there corresponds the associated multiplicative operators:

$$\begin{aligned} \hat{\mathbf{r}}(\boldsymbol{r}) &= \hat{\mathrm{x}}\,\boldsymbol{i} + \hat{\mathrm{y}}\,\boldsymbol{j} + \hat{\mathrm{z}}\,\boldsymbol{k} = x\boldsymbol{i} + y\boldsymbol{j} + z\boldsymbol{k} = \boldsymbol{r}, \\ \hat{\mathrm{V}}(\{x_\alpha\}) &= V(\{\hat{\mathrm{x}}_\alpha\}) = V(\{x_\alpha\}), \text{etc.} \end{aligned} \tag{3.33}$$

The elementary momentum operators in this representation,

$$\hat{\mathbf{p}}_k(\boldsymbol{r}_k) = -i\hbar\nabla_{\boldsymbol{r}_k} \equiv -i\hbar\nabla_k, \quad \hat{\mathrm{p}}_\alpha(x_\alpha) = -i\hbar\partial/\partial x_\alpha, \tag{3.34}$$

similarly determine the quantum mechanical operator of any function of the particle momenta, e.g., the kinetic energy $T = T(\{\boldsymbol{p}_k\}) = \sum_k \boldsymbol{p}_k{}^2/2m_k$:

$$\hat{\mathrm{T}}(\{\boldsymbol{r}_k\}) = T(\{\hat{\mathbf{p}}_k(\boldsymbol{r}_k)\}) = \Sigma_k \hat{\mathbf{p}}_k^2(\boldsymbol{r}_k)/2m_k = -\sum_k \frac{\hbar^2}{2m_k}\Delta_k. \tag{3.35}$$

These rules are sufficient to generate the quantum operator in the position representation for any physical quantity encountered in the classical mechanics, e.g., that of the orbital angular momentum of a single particle:

$$\begin{aligned} \boldsymbol{l} = \boldsymbol{r} \times \boldsymbol{p} &= \begin{vmatrix} \boldsymbol{i} & \boldsymbol{j} & \boldsymbol{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} \to \hat{\mathbf{l}}(\{x_\alpha\}) = \boldsymbol{i}\hat{\mathrm{l}}_x + \boldsymbol{j}\hat{\mathrm{l}}_y + \boldsymbol{k}\hat{\mathrm{l}}_z \\ &= -i\hbar \begin{vmatrix} \boldsymbol{i} & \boldsymbol{j} & \boldsymbol{k} \\ x & y & z \\ \partial/\partial x & \partial/\partial y & \partial/\partial z \end{vmatrix}, \end{aligned} \tag{3.36}$$

or the operator attributed to the system Hamilton function $H(\{\hat{\mathbf{r}}_k\}, \{\hat{\mathbf{p}}_k(r_k)\}) = E(\{\hat{\mathbf{r}}_k\}, \{\hat{\mathbf{p}}_k(\boldsymbol{r}_k)\}) = \hat{\mathrm{H}}(\{x_\alpha\})$, the system Hamiltonian in the position representation:

$$\hat{\mathrm{H}}(\{x_\alpha\}) = \hat{\mathrm{T}}(\{x_\alpha\}) + \hat{\mathrm{V}}(\{x_\alpha\}) = -\sum_k \frac{\hbar^2}{2m_k}\Delta_k + V(\{x_\alpha\}), \tag{3.37}$$

where the Laplacian $\Delta_k = \nabla_k^2 = \partial^2/\partial x_k^2 + \partial^2/\partial y_k^2 + \partial^2/\partial z_k^2$.

These rules can be straightforwardly transcribed into the associated prescriptions for the *momentum representation* $\{\boldsymbol{p}_k\} = \{p_\alpha\}$, in which (see again Sect. 2.6) $\hat{\mathrm{p}}_\alpha = p_\alpha$, or $\hat{\mathbf{p}}(\boldsymbol{p}) = \hat{\mathrm{p}}_x\boldsymbol{i} + \hat{\mathrm{p}}_y\boldsymbol{j} + \hat{\mathrm{p}}_z\boldsymbol{k} = p_x\boldsymbol{i} + p_y\boldsymbol{j} + p_z\boldsymbol{k} = \boldsymbol{p}$, and

$$\hat{\mathrm{x}}_\alpha(p_\alpha) = i\hbar\partial/\partial p_\alpha \quad \text{or} \quad \hat{\mathbf{r}}_k(\boldsymbol{p}_k) = i\hbar\nabla_{\boldsymbol{p}_k}. \tag{3.38}$$

Therefore, in this representation the kinetic energy corresponds to the multiplicative operator $\hat{\mathrm{T}}(\{\boldsymbol{p}_k\}) = T(\{\boldsymbol{p}_k\}) = \sum_k \boldsymbol{p}_k{}^2/2m_k$, while the potential energy function generates the associated differential operator:

$$\hat{\mathrm{V}}(\{\hat{\mathrm{x}}_\alpha(p_\alpha)\}) = V(\{i\hbar\partial/\partial p_\alpha\}). \tag{3.39}$$

3.3.2 Possible Outcomes of a Single Measurement

In accordance with the discussion in Sect. 2.5 the possible outcomes of individual measurements of the physical quantity A are related to its quantum mechanical operator $\hat{\mathrm{A}}$ via the

Postulate IV.2: The result of a single measurement of the physical quantity A is one of the eigenvalues $\{a_i\}$ of its observable $\hat{\mathrm{A}}$ in the eigenvalue problem (2.55a). In position/momentum representations, it reads:

$$\hat{\mathrm{A}}(\{x_\alpha\})\Psi_i(\{x_\alpha\}) = a_i\Psi_i(\{x_\alpha\}), \quad \hat{\mathrm{A}}(\{p_\alpha\})\Psi_i(\{p_\alpha\}) = a_i\Psi_i(\{p_\alpha\}), \tag{3.40}$$

where $\Psi_i(\{x_\alpha\})$ and $\Psi_i(\{p_\alpha\})$ denote the corresponding eigenfunctions associated with the eigenvalue a_i.

Since the set of eigenvectors $\{|\Psi_i\rangle\}$ of the quantum mechanical observable $\hat{\mathrm{A}}$ forms the complete basis in the system vector space (see Sect. 2.5), any state $|\Psi\rangle$ can be expressed as their combination, with the squares of the moduli of the expansion coefficients determining the conditional probabilities of observing $|\Psi_i\rangle$ in state $|\Psi\rangle$ (Postulate II):

$$|\Psi\rangle = \Sigma_i|\Psi_i\rangle\langle\Psi_i|\Psi\rangle = \Sigma_i|\Psi_i\rangle C_i, \quad P(\Psi_i|\Psi) = |C_i|^2 \leq 1. \tag{3.41}$$

The $P(\Psi_i|\Psi) = 1$, and hence $\{P(\Psi_{j\neq i}|\Psi) = 0\}$, marks the eigenvector itself, $|\Psi\rangle = |\Psi_i\rangle$, when we know with certainty that the eigenvalue a_i (nondegenerate) has been observed. Therefore, a general combination of the preceding equation is reduced after the measurement of A to a single eigenvector of $\hat{\mathrm{A}}$, the one corresponding to the observed eigenvalue. This "contraction" of $|\Psi\rangle$ into $|\Psi_i\rangle$ marks the irreversible intervention of the measuring device. Indeed, as we have emphasized in Chap. 1, any experiment performed on the microobject inadvertently modifies its state.

This contraction of a combination of eigenstates into its single member has to be modified in the case of the degenerate eigenvalue a_i of the physical quantity A. Such a result of the experiment implies that the state immediately after the measurement is now the normalized projection $\left(\langle\Psi|\hat{\mathrm{P}}(a_i)|\Psi\rangle\right)^{-1/2}\hat{\mathrm{P}}(a_i)|\Psi\rangle$ of the initial state $|\Psi\rangle$ into the eigensubspace associated with a_i, $\{|\Psi_{i,j}\rangle = |i_j\rangle, j = 1, 2, g\}$, which is effected by the subspace projector $\hat{\mathrm{P}}(a_i) = \sum_{j=1}^{g} |i_j\rangle\langle i_j|$.

In quantum mechanics the set of eigenvalues $\{a_i\}$ thus determines the spectrum of all possible outcomes of the single measurement of A. Since the eigenvalues of the square of the observable $\hat{\mathrm{A}}^2$ are given by the squares of eigenvalues of $\hat{\mathrm{A}}$, for the same set of eigenstates,

$$\hat{\mathrm{A}}^2|\Psi_i\rangle = a_i\hat{\mathrm{A}}|\Psi_i\rangle = {a_i}^2|\Psi_i\rangle, \tag{3.42}$$

the square of the dispersion in A, ${\sigma_A}^2 = \langle A^2\rangle - \langle A\rangle^2$ [see (3.23)], observed in the repeated measurements of A in the eigenstate $|\Psi_i\rangle$, represented by the eigenfunctions $\Psi_i(\{x_\alpha\})$ or $\Psi_i(\{p_\alpha\})$, identically vanishes:

$${\sigma_A}^2 = \langle A^2\rangle_i - {\langle A\rangle_i}^2 = \langle\Psi_i|\hat{\mathrm{A}}^2|\Psi_i\rangle - \langle\Psi_i|\hat{\mathrm{A}}|\Psi_i\rangle^2 = {a_i}^2 - {a_i}^2 = 0. \tag{3.43}$$

Therefore, in the eigenstate of $\hat{\mathrm{A}}$ the physical quantity A is sharply specified, and each single measurement of this physical property in this state always gives the same result a_i, as reflected by the conditional probabilities: $P(\Psi_i|\Psi_i) = 1$ and $P(\Psi_{j\neq i}|\Psi_i) = 0$.

As we have already demonstrated in (2.60), the eigenstates corresponding to different eigenvalues are automatically orthogonal. However, for the degenerate eigenvalues, several eigenstates correspond to the same eigenvalue (2.58), so they have to be orthogonalized to safeguard their linear independence. This orthogonalization is performed by taking appropriate linear combinations of generally nonorthogonal state vectors, which satisfy the conditions of their mutual orthogonality.

As schematically shown in Fig. 3.1, the prescription to make any pair of degenerate state vectors to be mutually "perpendicular" is not unique. Thus, the specific orthogonalization scheme can be selected for reasons of convenience. For the sake of simplicity consider two normalized state vectors $|\boldsymbol{a}_i\rangle = \{|i_1\rangle, |i_2\rangle\}$ of the *doubly* degenerate eigenvalue a_i, $g = 2$, which define the *overlap* matrix of their scalar products:

$$\mathbf{S} = \langle\boldsymbol{a}_i|\boldsymbol{a}_i\rangle = \{\langle i_j|i_{j'}\rangle; j, j' = 1, 2\} \equiv \begin{bmatrix} 1 & S \\ S & 1 \end{bmatrix}, \tag{3.44}$$

where for definiteness we assume $S > 0$. In the (nonsymmetric) *Schmidt orthogonalization* scheme (see Fig. 3.1) of transforming the original vectors $\{|i_1\rangle, |i_2\rangle\}$ to the mutually orthogonal set $|\bar{\boldsymbol{a}}_i\rangle = \{|\bar{i}_1\rangle, |\bar{i}_2\rangle\}$, one leaves one of these vectors unchanged, say $|\bar{i}_1\rangle = |i_1\rangle$, and "rotates" the other, $|\bar{i}_2\rangle = \mathcal{N}_2(|i_2\rangle + C|i_1\rangle)$, where $\mathcal{N}_2$ is the normalization constant and C denotes the mixing coefficient, until the two vectors become mutually orthogonal: $\langle i_1|\bar{i}_2\rangle = 0$. This condition then gives $C = -S$, while the normalization $\langle\bar{i}_2|\bar{i}_2\rangle = 1$ implies $\mathcal{N}_2 = (1 - S^2)^{-1/2}$, and hence

$$|\bar{i}_2\rangle = (1 - S^2)^{-1/2}(|i_2\rangle - |i_1\rangle S) = \mathcal{N}_2(|i_2\rangle - |i_1\rangle\langle i_1|i_2\rangle) = \mathcal{N}_2(|i_2\rangle - \hat{\mathrm{P}}_i|i_2\rangle). \tag{3.45a}$$

This expression can be straightforwardly extended to a general case of the normalized state vector $|\psi\rangle$ Schmidt orthogonalized with respect to the given subspace $|\boldsymbol{\varphi}\rangle = (|\varphi_1\rangle, |\varphi_2\rangle, \ldots, |\varphi_r\rangle)$ of the orthonormal states:

$$|\bar{\psi}\rangle = \mathcal{N}\Big[|\psi\rangle - \sum_{i=1}^{r} |\varphi_i\rangle\langle\varphi_i \mid \psi\rangle\Big] = \mathcal{N}\big[|\psi\rangle - \hat{\mathrm{P}}_{\boldsymbol{\varphi}}|\psi\rangle\big]. \tag{3.45b}$$

Alternatively, as also shown in the figure, one could manipulate the two nonorthogonal vectors simultaneously in a symmetrical way, so that both orthogonalized vectors $|\tilde{\boldsymbol{a}}_i\rangle = \{|\tilde{i}_1\rangle, |\tilde{i}_2\rangle\}$, strongly resemble their initial, nonorthogonal analogs. In the *Löwdin orthogonalization* scheme, this transformation is effected through the symmetric matrix $\mathbf{S}^{-1/2}$, $|\tilde{\boldsymbol{a}}_i\rangle = |\boldsymbol{a}_i\rangle\mathbf{S}^{-1/2}$, defined by the eigenvalue problem of the overlap matrix $\mathbf{S}$, i.e., its diagonalization in the orthogonal transformation:

$$\mathbf{O}^{\mathrm{T}}\mathbf{S}\mathbf{O} = \mathbf{s} = \{s_m\delta_{m,n}\},\ \mathbf{S}^{-1/2} = \mathbf{O}\mathbf{s}^{-1/2}\mathbf{O}^{\mathrm{T}},\ \mathbf{s}^k = \{(s_m)^k\delta_{m,n}\},\ \mathbf{O}\mathbf{O}^{\mathrm{T}} = \mathbf{I}. \tag{3.46}$$

Indeed, the orthogonality of the symmetrically rotated vectors $|\tilde{\boldsymbol{a}}_i\rangle$ then directly follows from the orthogonal transformation $\mathbf{O}$ which diagonalizes the overlap matrix:

$$\langle\tilde{\boldsymbol{a}}_i|\tilde{\boldsymbol{a}}_i\rangle = \mathbf{S}^{-1/2}\langle\boldsymbol{a}_i|\boldsymbol{a}_i\rangle\,\mathbf{S}^{-1/2} = \mathbf{S}^{-1/2}\mathbf{S}\,\mathbf{S}^{-1/2} = \mathbf{S}^0 = \mathbf{I}. \tag{3.47}$$

These matrix equations apply to any number of the orthogonalized vectors or wave functions. In the latter case, the overlap matrix is defined to be the corresponding integrals between nonorthogonal functions, e.g., $\boldsymbol{\chi}(\boldsymbol{r}) = \{\chi_t(\boldsymbol{r})\}$ (row vector), when $\mathbf{S}_{\boldsymbol{\chi}} = \langle\boldsymbol{\chi}|\boldsymbol{\chi}\rangle = \{S_{r,t} = \int\chi_r^{\,*}(\boldsymbol{r})\chi_t(\boldsymbol{r})\,d\boldsymbol{r}\}$: $\tilde{\boldsymbol{\chi}}(\boldsymbol{r}) = \boldsymbol{\chi}(\boldsymbol{r})\mathbf{S}_{\boldsymbol{\chi}}^{\ -1/2}$.

The specific forms of these matrices for the metric of (3.44) read:

$$\begin{aligned}
&\mathbf{s} = \begin{bmatrix} 1+S & 0 \\ 0 & 1-S \end{bmatrix} = \begin{bmatrix} s_1 & 0 \\ 0 & s_2 \end{bmatrix}, \quad \mathbf{O} = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix}, \\
&\mathbf{S}^{-1/2} = \begin{bmatrix} a & b \\ b & a \end{bmatrix}, \quad a = \frac{1}{2}\left(\frac{1}{\sqrt{s_1}} + \frac{1}{\sqrt{s_2}}\right), \quad b = \frac{1}{2}\left(\frac{1}{\sqrt{s_1}} - \frac{1}{\sqrt{s_2}}\right).
\end{aligned} \tag{3.48}$$

3.3.3 Expectation Value of Repeated Measurements and Heisenberg Uncertainty Principle

The average result of the repeated measurements of A in quantum mechanics, performed on the system in the same initial quantum state $|\Psi\rangle$, has already

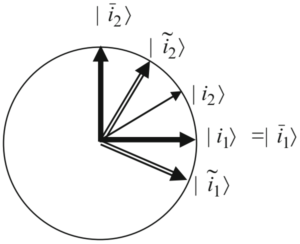

Fig. 3.1 The diagrammatic representation of the mutually nonorthogonal state vectors $\{|i_1\rangle, |i_2\rangle\}$, and the two sets of their orthogonalized (mutually "perpendicular") analogs: the Schmidt (nonsymmetrically) orthogonalized vectors $|\bar{\boldsymbol{a}}_i\rangle = \{|\bar{i}_1\rangle, |\bar{i}_2\rangle\}$, and the Löwdin (symmetrically) orthogonalized vectors $|\tilde{\boldsymbol{a}}_i\rangle = \{|\tilde{i}_1\rangle, |\tilde{i}_2\rangle\}$. The two sets are related by the unitary (rotation) transformation $\mathbf{U} = \langle \bar{\boldsymbol{a}}_i | \tilde{\boldsymbol{a}}_i \rangle$: $|\tilde{\boldsymbol{a}}_i\rangle = |\bar{\boldsymbol{a}}_i\rangle \mathbf{U}$

been established in (3.23). It can be formally stated in the form of a separate postulate:

Postulate IV.3: The statistically average result of a very large number $m \to \infty$ of repeated measurements of the physical quantity A performed on the microsystem in the same initial state $|\Psi\rangle$ is given by the expectation value of its quantum mechanical operator $\hat{\mathrm{A}}$:

$$\begin{aligned}\langle A\rangle_\Psi &= \sum_i P(\Psi_i|\Psi)\, a_i = \langle \Psi|\hat{\mathrm{A}}|\Psi\rangle = \int \Psi^*(\mathcal{Q}^N;t)\,\hat{\mathrm{A}}(\mathcal{Q}^N)\Psi(\mathcal{Q}^N;t)\ d\mathcal{Q}^N \\ &= \int \Psi^*(\mathcal{P}^N;t)\,\hat{\mathrm{A}}(\mathcal{P}^N)\Psi(\mathcal{P}^N;t) d\mathcal{P}^N.\end{aligned} \tag{3.49}$$

It has been demonstrated in (3.43) that in the eigenstate $|\Psi_i\rangle$ this quantity is sharply specified with $\langle A\rangle_{\Psi_i} = a_i$, $\langle A^2\rangle_{\Psi_i} = a_i^2$, etc. The same conclusion applies to all physical observables which commute with $\hat{\mathrm{A}}$, since all these operators have a common set of eigenvectors (see Sect. 2.5). However, in a general quantum state of (3.41), one will detect a dispersion in the measured values of A, with a statistically distributed results $\{a_i\}$ appearing with frequencies $\{m_i = mP(\Psi_i|\Psi)\}$ proportional to the conditional probabilities $\{P(\Psi_i|\Psi)\}$ of observing the specified eigenstates (see caption of Fig. 1.1).

We are now in a position to provide a general formulation of the Heisenberg Principle of Indeterminacy in quantum mechanics (see Chap. 1). As specific measures of the simultaneous accuracies of the physical quantities A and B we adopt their dispersions (standard deviations), $\sigma_X = \langle (X - \langle X\rangle)^2\rangle^{½} = (\langle X^2\rangle - \langle X\rangle^2)^{½}$, $X = A, B$, with the corresponding expressions in terms of the quantum mechanical expectation values:

$$\sigma_X{}^2 = \langle X^2\rangle_\Psi - \langle X\rangle_\Psi^2 = \langle \Psi|(\hat{\mathrm{X}} - \langle X\rangle_\Psi)^2|\Psi\rangle \equiv \langle \Psi|\hat{\Delta}_X^2|\Psi\rangle, \quad X = A, B. \tag{3.50}$$

We further observe that the displacement operators $\hat{\Delta}_A$ and $\hat{\Delta}_B$ are both Hermitian, as are the observables $\hat{A}$ and $\hat{B}$ themselves, and the following commutator identity is satisfied:

$$[\hat{A}, \hat{B}] = [\hat{\Delta}_A, \hat{\Delta}_B], \tag{3.51}$$

since the average values $\langle X \rangle_\Psi$ (numbers) commute with every operator [see (2.34)].

We shall now demonstrate that the following inequality is satisfied by the simultaneous indeterminacies of the physical quantities A and B:

$$\sigma_A{}^2 \sigma_B{}^2 \geq -\frac{1}{4} \langle \Psi | [\hat{A}, \hat{B}] | \Psi \rangle^2. \tag{3.52}$$

It constitutes the quantum mechanical formulation of the Heisenberg Uncertainty Principle, which indeed predicts the simultaneous sharp specification of the commuting observables.

In order to prove this inequality let us introduce the physically meaningful, i.e., exhibiting a finite norm, auxiliary state vector $|\Phi(\lambda)\rangle$ depending on real parameter λ:

$$|\Phi(\lambda)\rangle = (\lambda \hat{\Delta}_A - i \hat{\Delta}_B) |\Psi\rangle. \tag{3.53}$$

The square of its norm (positive) then determines the quadratic function $f(\lambda)$:

$$\begin{aligned} \langle \Phi(\lambda) | \Phi(\lambda) \rangle = \| \Phi(\lambda) \|^2 &= \langle \Psi | (\lambda \, \hat{\Delta}_A - i \hat{\Delta}_B)^\dagger (\lambda \, \hat{\Delta}_A - i \hat{\Delta}_B) | \Psi \rangle \\ &= \langle \Psi | (\lambda \, \hat{\Delta}_A + i \, \hat{\Delta}_B)(\lambda \, \hat{\Delta}_A - i \, \hat{\Delta}_B) | \Psi \rangle \\ &= \langle \Psi | (\lambda^2 \hat{\Delta}_A^2 - i\lambda \, [\hat{\Delta}_A, \hat{\Delta}_B] + \hat{\Delta}_B^2) | \Psi \rangle \\ &= \sigma_A{}^2 \lambda^2 - i \langle \Psi | [\hat{A}, \hat{B}] | \Psi \rangle \lambda + \sigma_B{}^2 \\ &\equiv a\lambda^2 + b\lambda + c > 0. \end{aligned} \tag{3.54}$$

For $a = \sigma_A{}^2 > 0$ this inequality can be satisfied only when there are no solutions of the associated quadratic equation $a\lambda^2 + b\lambda + c = 0$, i.e., when $\varDelta = b^2 - 4\,ac < 0$ or

$$-\langle \Psi | [\hat{A}, \hat{B}] | \Psi \rangle^2 < 4\, \sigma_A^2 \sigma_B^2, \tag{3.55}$$

which completes the proof.

Consider the illustrative example of the position–momentum relation (1.7). In position representation (3.34), $\hat{A} = x, \hat{B} = -i\hbar \partial / \partial x$, so that their commutator acting on the continuous function $f(x)$ gives:

$$[\hat{A}, \hat{B}] f = -i\hbar x (\partial f / \partial x) + i\hbar x (\partial f / \partial x) + i\hbar f = i\hbar f \quad \text{or} \quad [\hat{x}, \hat{p}_x] = i\hbar. \tag{3.56}$$

Thus, these two physical quantities are incompatible, with the limit of the product of their lowest (simultaneous) inaccuracies being determined by (3.52):

$$\sigma_x \sigma_{p_x} > \frac{1}{2}\hbar. \tag{3.57}$$

These predictions agree with the constant (position-independent) probability of finding a particle at the specified location in space in the state described by the basis function $u_{\boldsymbol{p}}(\boldsymbol{r})$ (2.76), corresponding to the sharply specified momentum: $\sigma_{\boldsymbol{p}} \to 0$. It indeed implies that all localization events are then equally probable, i.e., we are then completely ignorant about the particle position: $\sigma_{\boldsymbol{r}} \to \infty$. In accordance with the Heisenberg principle of (3.57) only the infinite position indeterminacy gives the finite product when multiplied by the infinitesimal momentum uncertainty $\sigma_{\boldsymbol{p}} \to 0$.

3.3.4 Ensemble Averages in Mixed States

Only certain idealized systems, isolated from their environment, are completely described by a single state vector $|\Psi\rangle$ or a single wave function $\Psi(x)$. The wave function of an isolated system depends only on its internal coordinates x and carries the maximum information about the state of the microsystem available in quantum physics. The full specification of quantum state of the microobject is through the state vector belonging to the basis set of the simultaneous eigenvectors of the system complete set of the mutually commuting observables $\{\hat{\mathrm{A}}, \hat{\mathrm{B}}, \ldots\}$, which diagonalize the matrix representations of these operators, $|\Psi\rangle \in \{|\Psi_n\rangle = |a_k, b_l, \ldots\rangle\}$. Their eigenvalues $(a_k, b_l, \ldots)$ then provide the complete identification of the direction of the state vector $|a_k, b_l, \ldots\rangle$ in the molecular Hilbert space.

However, microobjects can be coupled to their surroundings. For example, the particles at constant temperature are in contact with the thermostat (heat "bath") and the open systems, exhibiting fluctuating (fractional, continuously changing) number of particles, are coupled to the external particle "reservoir(s)." The state of the closed system *interacting* with its environment will also depend on the external degrees of freedom describing the latter. Therefore, the formalism of quantum mechanics must also admit all intermediate stages of an imprecise definition of the system state, which cannot be linked to a single state vector (wave function). Such generalized states are called the *mixed states*, while the systems with the specified wave function are said to be in the *pure state*.

As in statistical mechanics, the incomplete information about the system calls for the concept of an *ensemble* of quantum states, in which the admissible pure states appear with some probability. The ensemble consists of a very large number of replicas of the same system. For example, a system in the thermodynamic equilibrium at temperature T has a probability of being in its energy eigenstate $|E_n\rangle$ proportional to $\exp(-E_n/k_B T)$, where k_B is the Boltzmann constant. This probability describes the frequency of such a state among members of the *canonical* ensemble. Similarly, the systems in the *grand-canonical* ensemble describing the system in thermodynamic equilibrium with the heat bath at temperature T and the particle reservoir characterized by the chemical potential μ will exhibit the probability proportional to $\exp(\mu N_i - E_{n,i})/k_B T$ of observing the eigenvalue $E_{n,i}$ of the Hamitonian $\hat{\mathrm{H}}(N_i)$, for the specified (integral) number of electrons N_i.

Therefore, such an imprecise definition of the quantum mechanical state can be interpreted as the statistical mixture of the admissible states $\{|\psi_1\rangle, |\psi_2\rangle, \ldots\}$ of the system replicas in the ensemble, which appear with the associated (*external*) probabilities $\{p_1, p_2, \ldots\}$, $\sum_\alpha p_\alpha = 1$. The individual states in the mixture do not have to be orthogonal, e.g., in the grand ensemble, when we mix eigenstates of different Hamiltonians, but they are always assumed to be normalized.

The statistical mixture should not be confused with the expansion of a single wave function $|\Phi\rangle$ in the (orthonormal) basis set, say $\{|\Psi_n\rangle\}$,

$$|\Phi\rangle = \sum_n |\Psi_n\rangle\langle\Psi_n|\Phi\rangle = \sum_n |\Psi_n\rangle c_n, \tag{3.58}$$

where $|c_n|^2$ generates the conditional probability $P(\Psi_n|\Phi)$ of observing in state $|\Phi\rangle$ the physical attributes of $|\Psi_n\rangle$. Indeed, this does not imply that $|\Phi\rangle$ is the mixture of $|\Psi_1\rangle$ with the probability $P(\Psi_1|\Phi)$, and $|\Psi_2\rangle$ with the probability $P(\Psi_2|\Phi)$, etc. The square of the modulus of $\Phi(x)$, which generates the probability distribution $\rho(x) = \Phi^*(x)\Phi(x)$, then includes the crucial *interference* terms between different basis functions, $c_n^* c_m \Psi_n^*(x)\Psi_m(x)$, which are not present in the statistical mixture of the same basis functions. Thus, the probability weighted sum of distributions $\{\rho_n(x) = \Psi_n^*(x)\Psi_n(x)\}$, generated by each state in the basis set, $\rho_{ens.}(x) = \sum_n p_n \rho_n(x)$, cannot reproduce the true probability density $\rho(x)$. In other words, it is not possible to describe a statistical mixture by an "average" state vector in the form of the combination of states of (3.58): $\rho_{ens.}(x) \neq \rho(x)$.

The two levels of probabilities are thus involved in determining the results of measurements performed on systems in their mixed quantum states. On one hand, there is the *intrinsic* quantum mechanical probability of finding in each (pure) state $|\psi_\alpha\rangle$ a specific eigenvalue a_k of the observable $\hat{\mathrm{A}}$, $\hat{\mathrm{A}}|\Psi_k\rangle = a_k|\Psi_k\rangle$, given by the square of the modulus of the expansion coefficient $C_{k,\alpha} = \langle\Psi_k|\psi_\alpha\rangle$, $P_{k,\alpha} = |C_{k\alpha}|^2$ (Postulate II), which determines the quantum mechanical *expectation value*

$$\langle A\rangle_\alpha = \langle\psi_\alpha|\hat{\mathrm{A}}|\psi_\alpha\rangle = \sum_k a_k P_{k,\alpha}. \tag{3.59}$$

Notice that these eigenstates generate the diagonal representation of $\hat{\mathrm{A}}$, $\mathbf{A}^{(\boldsymbol{\Psi})} = \left\{A_{m,n} = \langle\Psi_m|\hat{\mathrm{A}}|\Psi_n\rangle = a_n\delta_{m,n}\right\}$.

On the other hand, the additional level of the *external* probabilities $\{p_\alpha\}$ of observing the individual states $\{|\psi_\alpha\rangle\}$ in the ensemble intervenes in the mixed quantum mechanical states. They define the associated *density operator* given by the sum of the externally weighted projections onto the quantum states being mixed,

$$\hat{\mathrm{D}} = \sum_{\alpha} |\psi_{\alpha}\rangle p_{\alpha} \langle \psi_{\alpha}| = \sum_{\alpha} p_{\alpha} \hat{\mathrm{P}}_{\alpha}, \tag{3.60a}$$

Its matrix representation in the basis set of eigenstates of $\hat{\mathrm{A}}$,

$$\mathbf{D}^{(\boldsymbol{\Psi})} = \{D_{m,n} = \langle \Psi_m|\hat{\mathrm{D}}|\Psi_n\rangle = \sum_{\alpha} \langle \Psi_n|\psi_{\alpha}\rangle p_{\alpha} \langle \psi_{\alpha}|\Psi_m\rangle\}, \tag{3.60b}$$

determines the *ensemble* average value of A:

$$\begin{aligned} A_{ens.} &= \sum_{\alpha} p_{\alpha} \langle A\rangle_{\alpha} = \sum_{\alpha} p_{\alpha} \{\sum_{k} a_k P_{k,\alpha}\} \\ &= \sum_{n}\sum_{m} \left\{ \sum_{\alpha} \langle \Psi_n|\psi_{\alpha}\rangle p_{\alpha} \langle \psi_{\alpha}|\Psi_m\rangle \right\} \langle \Psi_m|\hat{\mathrm{A}}|\Psi_n\rangle \\ &= \sum_{n}\sum_{m} \langle \Psi_n|\hat{\mathrm{D}}|\Psi_m\rangle \langle \Psi_m|\hat{\mathrm{A}}|\Psi_n\rangle \equiv \sum_{n}\sum_{m} D_{n,m} A_{m,n} \\ &\equiv \mathrm{tr}[\mathbf{D}^{(\boldsymbol{\Psi})} \mathbf{A}^{(\boldsymbol{\Psi})}] = \sum_{n} \langle \Psi_n|\hat{\mathrm{D}}\,\hat{\mathrm{A}}|\Psi_n\rangle \equiv \mathrm{tr}(\hat{\mathrm{D}}\,\hat{\mathrm{A}}) \\ &= \mathrm{tr}[\mathbf{A}^{(\boldsymbol{\Psi})} \mathbf{D}^{(\boldsymbol{\Psi})}] = \sum_{m} \langle \Psi_m|\hat{\mathrm{A}}\,\hat{\mathrm{D}}|\Psi_m\rangle = \mathrm{tr}(\hat{\mathrm{A}}\,\hat{\mathrm{D}}). \end{aligned} \tag{3.60c}$$

The Hermitian (nonidempotent!) density operator $\hat{\mathrm{D}}$ involves the probability weighted projections $\{\{\hat{\mathrm{P}}_{\alpha}\}\}$ onto the individual states being mixed, while the *trace* operation (tr) denotes the summation of all diagonal elements of the matrix representations of operators in the adopted basis. It also follows from the definition of $\hat{\mathrm{D}}$ that its expectation value in state $|\Phi\rangle$

$$\langle \Phi|\hat{\mathrm{D}}|\Phi\rangle = \sum_{\alpha} p_{\alpha} \langle \psi_{\alpha}|\Phi\rangle \langle \Phi|\psi_{\alpha}\rangle = \sum_{\alpha} p_{\alpha}\, P(\psi_{\alpha}|\Phi) \geq 0, \tag{3.61}$$

and hence $\hat{\mathrm{D}}$ is a positive operator.

It can be also verified that the trace of the product of operators is invariant with respect to the cyclic permutations of factors in the product [see (3.60c)],

$$\mathrm{tr}\,(\mathbf{AB}\ldots\mathbf{CD}) = \mathrm{tr}(\mathbf{DAB}\ldots\mathbf{C}),\ \text{etc.}, \tag{3.62}$$

and to a change $\boldsymbol{\Psi} \to \boldsymbol{\Phi}$ in the (orthonormal) basis set:

$$\begin{aligned} \mathrm{tr}\,\hat{\mathrm{A}} &= \sum_{n} \langle \Psi_n|\hat{\mathrm{A}}|\Psi_n\rangle \equiv \mathrm{tr}\mathbf{A}_{\boldsymbol{\Psi}} \\ &= \sum_{n}\sum_{m}\sum_{m'} \langle \Psi_n|\Phi_m\rangle \langle \Phi_m|\hat{\mathrm{A}}|\Phi_{m'}\rangle \langle \Phi_{m'}|\Psi_n\rangle \\ &= \sum_{n}\sum_{m}\sum_{m'} \langle \Phi_{m'}|\Psi_n\rangle \langle \Psi_n|\Phi_m\rangle \langle \Phi_m|\hat{\mathrm{A}}|\Phi_{m'}\rangle \\ &= \sum_{m}\sum_{m'} \langle \Phi_{m'}|\Phi_m\rangle \langle \Phi_m|\hat{\mathrm{A}}|\Phi_m\rangle \\ &= \sum_{m} \langle \Phi_m|\hat{\mathrm{A}}|\Phi_m\rangle \equiv \mathrm{tr}\,\mathbf{A}_{\boldsymbol{\Phi}}, \end{aligned} \tag{3.63}$$

where we have used the closure relations $\sum_m |\Phi_m\rangle\langle\Phi_m| = \sum_n |\Psi_n\rangle\langle\Psi_n| = 1$ and the orthonormality of basis functions $\langle\Phi_{m'}|\Phi_m\rangle = \delta_{m,m'}$. One also observes that

$$\begin{aligned}\mathrm{tr}\,\hat{\mathrm{D}} &= \sum_n \langle\Psi_n|\hat{\mathrm{D}}|\Psi_n\rangle = \sum_\alpha\sum_n p_\alpha\langle\psi_\alpha|\Psi_n\rangle\langle\Psi_n|\psi_\alpha\rangle \\ &= \sum_\alpha p_\alpha\langle\psi_\alpha|\psi_\alpha\rangle = \sum_\alpha p_\alpha = 1.\end{aligned} \tag{3.64}$$

Obviously, the pure state, e.g., $|\psi_\alpha\rangle$, can be viewed as the limiting case of the ensemble, when $p_\alpha = 1$ and $\{p_{\beta\neq\alpha} = 0\}$, so that $\hat{\mathrm{D}} = \hat{\mathrm{P}}_\alpha$. Only in the pure quantum state the density operator is idempotent, $\hat{\mathrm{D}}^2 = \hat{\mathrm{D}}$ (idempotency of $\hat{\mathrm{P}}_\alpha$), so that $\mathrm{tr}\hat{\mathrm{D}}^2 = \mathrm{tr}\hat{\mathrm{D}} = 1$. The corresponding inequality for the mixed state reads: $\mathrm{tr}\hat{\mathrm{D}}^2 < 1$.

When describing parts of a physical system the concept of the *partial trace* emerges. Assume that the global system, (1) + (2), consists of distinct subsystems (1) and (2), described by their associated Hilbert spaces $\mathcal{H}(1) = \{|\Psi_i(1)\rangle\}$ and $\mathcal{H}(2) = \{|\Phi_m(2)\rangle\}$, the tensor product of which spans the Hilbert space of the system as a whole:

$$\mathcal{H}(1,2) = \{|\Psi_i(1)\rangle|\Phi_m(2)\rangle \equiv |\Psi_i(1)\Phi_m(2)\rangle\} = \mathcal{H}(1)\otimes\mathcal{H}(2). \tag{3.65}$$

We now introduce the partial traces of the system density operator $\hat{\mathrm{D}}$, which define the effective density operators for each subsystem: $\hat{\mathrm{D}}(1)$ and $\hat{\mathrm{D}}(2)$. This is effected by contractions of the matrix representation of $\hat{\mathrm{D}}$ in $\mathcal{H}(1, 2)$,

$$\mathbf{D}(1,2) = \{\langle\Psi_i(1)\Phi_m(2)|\hat{\mathrm{D}}|\Psi_{i'}(1)\Phi_{m'}(2)\rangle \equiv D_{i,m;i',m'}(1,2)\}, \tag{3.66}$$

by partial trace summations over $m = m'$ in one subsystem or $i = i'$ of the other subsystem:

$$\begin{aligned}\mathbf{D}(1) &= \sum_m \langle\Psi_i(1)\Phi_m(2)|\,\hat{\mathrm{D}}\,|\Psi_{i'}(1)\Phi_m(2)\rangle \equiv \mathrm{tr}_2\mathbf{D}(1,2) \equiv \{\,D_{i,i'}(1)\},\\ \mathbf{D}(2) &= \sum_i \langle\Psi_i(1)\Phi_m(2)|\,\hat{\mathrm{D}}\,|\Psi_i(1)\Phi_{m'}(2)\rangle \equiv \mathrm{tr}_1\mathbf{D}(1,2) \equiv \{\,D_{m,m'}(2)\}\ .\end{aligned} \tag{3.67}$$

Let $A(1)$ be a physical quantity of subsystem (1) with the corresponding observable $\hat{\mathrm{A}}(1)$ acting in $\mathcal{H}(1)$, which is represented in $\mathcal{H}(1, 2)$ by the matrix:

$$\begin{aligned}\mathbf{A}^{1,2}(1) &= \{\langle\Psi_i(1)\Phi_m(2)|\hat{\mathrm{A}}(1)|\Psi_{i'}(1)\Phi_{m'}(2)\rangle \equiv A_{i,m;i',m'}(1)\\ &= \langle\Psi_i(1)|\hat{\mathrm{A}}(1)|\Psi_{i'}(1)\rangle\langle\Phi_m(2)|\Phi_{m'}(2)\rangle = A_{i,i'}(1)\delta_{m,m'}(2)\}\\ &\equiv \mathbf{A}(1)\otimes\mathbf{I}(2).\end{aligned} \tag{3.68}$$

The ensemble average value of $A(1)$ [see (3.60a)–(3.60c)] now reads:

$$\begin{aligned} A_{ens}(1) &= \mathrm{tr}[\mathbf{D}(1,2)\mathbf{A}^{1,2}(1)] \\ &= \sum_i\sum_m[\sum_{i'}\sum_{m'}D_{i,m;i',m'}(1,2)A_{i',m';i,m}(1)] \\ &= \sum_i\sum_m[\sum_{i'}\sum_{m'}D_{i,m;i',m'}(1,2)A_{i',i}(1)\delta_{m',m}(2)] \\ &= \sum_i\sum_{i'}[\sum_m D_{i,m;i',m}(1,2)]A_{i',i}(1)] \\ &= \sum_i\sum_{i'}[\sum_m D_{i,i'}(1)A_{i',i}(1)] \\ &= \mathrm{tr}[\mathbf{D}(1)\mathbf{A}(1)]. \end{aligned} \tag{3.69}$$

Therefore, the partial trace concept enables one to calculate the ensemble average of the subsystem quantity $A(1)$ as if this part of the whole physical system were isolated in the effective mixed state of (1) in the system as a whole, defined by the density operator $\mathbf{D}(1)$, which already involves the partial trace over the states of the other subsystem.

3.4 Angular Momentum and Spin Operators

In (3.36) we have used the Jordan rules to generate the quantum mechanical observable $\hat{\mathbf{l}}(\{x_\alpha\}) = -i\hbar\boldsymbol{r}\times\nabla$ corresponding in the position representation to the particle angular momentum $\boldsymbol{l} = \boldsymbol{r}\times\boldsymbol{p}$, e.g., that of the electron moving around nucleus in an atom. This equation also defines the associated component operators, obtained by expanding the determinant of the vector product:

$$\begin{aligned} \hat{\mathrm{l}}_{\mathrm{x}} &= \hat{\mathrm{y}}\hat{\mathrm{p}}_z - \hat{\mathrm{z}}\hat{\mathrm{p}}_y = -i\hbar(y\partial/\partial z - z\partial/\partial y), \\ \hat{\mathrm{l}}_{\mathrm{y}} &= \hat{\mathrm{z}}\hat{\mathrm{p}}_x - \hat{\mathrm{x}}\hat{\mathrm{p}}_z = -i\hbar(z\partial/\partial x - x\partial/\partial z), \\ \hat{\mathrm{l}}_{\mathrm{z}} &= \hat{\mathrm{x}}\hat{\mathrm{p}}_y - \hat{\mathrm{y}}\hat{\mathrm{p}}_x = -i\hbar(x\partial/\partial y - y\partial/\partial x). \end{aligned} \tag{3.70}$$

They give rise to the following commutation relations:

$$[\hat{\mathrm{l}}_x,\hat{\mathrm{l}}_y] = i\hbar\hat{\mathrm{l}}_z, \quad [\hat{\mathrm{l}}_y,\hat{\mathrm{l}}_z] = i\hbar\hat{\mathrm{l}}_x, \quad [\hat{\mathrm{l}}_z,\hat{\mathrm{l}}_x] = i\hbar\hat{\mathrm{l}}_y, \; [\hat{\mathbf{l}}^2,\hat{\mathrm{l}}_x] = [\hat{\mathbf{l}}^2,\hat{\mathrm{l}}_y] = [\hat{\mathbf{l}}^2,\hat{\mathrm{l}}_z] = 0. \tag{3.71}$$

It thus follows from the first three relations of this equation that for the finite angular momentum $|\boldsymbol{l}| > 0$ its three components cannot be simultaneously determined precisely; clearly, for $|\boldsymbol{l}| = 0$ they are all vanishing: $l_x = l_y = l_z = 0$. The remaining relations indicate that only the length $|\boldsymbol{l}| = (\boldsymbol{l}^2)^{1/2}$ of the angular momentum and one of its components, say l_z, can be simultaneously sharply defined. Indeed, the analysis of the quantized eigenvalue problems of these operators, which can be found in any textbook of quantum mechanics, gives:

$$\boldsymbol{l}^2 = l(l+1)\hbar^2, \quad l = 0, 1, 2, \ldots; \quad l_z = m\hbar, \quad m = -l, -l+1, \ldots, 0, \ldots, l-1, l. \tag{3.72}$$

The commutation relations can be straightforwardly derived using the commutator identities of (2.34) and the known commutators involving the position $\{\hat{\mathrm{x}}_i\}$ and momentum $\{\hat{\mathrm{p}}_i\}$ observables [see (3.56)]:

$$[\hat{\mathrm{x}}_i, \hat{\mathrm{x}}_j] = [\hat{\mathrm{p}}_i, \hat{\mathrm{p}}_j] = 0, \quad [\hat{\mathrm{x}}_i, \hat{\mathrm{p}}_j] = i\hbar\delta_{i,j}. \tag{3.73}$$

For example,

$$\begin{aligned}[\hat{\mathrm{l}}_x, \hat{\mathrm{l}}_y] &= \hat{\mathrm{l}}_x\hat{\mathrm{l}}_y - \hat{\mathrm{l}}_y\hat{\mathrm{l}}_x = [\hat{\mathrm{y}}\hat{\mathrm{p}}_z - \hat{\mathrm{z}}\hat{\mathrm{p}}_y,\ \hat{\mathrm{z}}\hat{\mathrm{p}}_x - \hat{\mathrm{x}}\hat{\mathrm{p}}_z] \\ &= [\hat{\mathrm{y}}\hat{\mathrm{p}}_z,\ \hat{\mathrm{z}}\hat{\mathrm{p}}_x] + [\hat{\mathrm{z}}\hat{\mathrm{p}}_y,\ \hat{\mathrm{x}}\hat{\mathrm{p}}_z] \\ &= (\hat{\mathrm{x}}\hat{\mathrm{p}}_y - \hat{\mathrm{y}}\hat{\mathrm{p}}_x)[\hat{\mathrm{z}}, \hat{\mathrm{p}}_z] = i\hbar\hat{\mathrm{l}}_z.\end{aligned} \tag{3.74}$$

However, the origin of the spin angular momenta (see Sect. 1.4) is not classical, so that the Jordan rules do not apply in constructing their operators. Consider a single electron as an example. We shall now derive the matrix representations of the spin operator $\hat{\mathbf{s}} = \boldsymbol{i}\hat{\mathrm{s}}_x + \boldsymbol{j}\hat{\mathrm{s}}_y + \boldsymbol{j}\hat{\mathrm{s}}_z$ in the basis set of the two allowed spin states $|\boldsymbol{\xi}\rangle \equiv (|\alpha\rangle, |\beta\rangle)$ (see Fig. 1.2) by postulating that these nonclassical angular momentum operators satisfy the same commutator relations as their classical analogs:

$$[\hat{\mathrm{s}}_x, \hat{\mathrm{s}}_y] = i\hbar\hat{\mathrm{s}}_z, \quad [\hat{\mathrm{s}}_y, \hat{\mathrm{s}}_z] = i\hbar\hat{\mathrm{s}}_x, \quad [\hat{\mathrm{s}}_z, \hat{\mathrm{s}}_x] = i\hbar\hat{\mathrm{s}}_y, \ [\hat{\mathbf{s}}^2, \hat{\mathrm{s}}_x] = [\hat{\mathbf{s}}^2, \hat{\mathrm{s}}_y] = [\hat{\mathbf{s}}^2, \hat{\mathrm{s}}_z] = 0. \tag{3.75}$$

In other words, we again recognize that, as in the classical case, only the length and one of the components of the spin angular momentum can be simultaneously specified. This is exactly what is observed in the experiment (see Fig. 1.2).

We first observe that the two spin states of an electron are then represented by the associated spin wave functions (column vectors):

$$\begin{aligned}&\boldsymbol{\alpha}(\boldsymbol{\xi}) = \langle\boldsymbol{\xi}|\alpha\rangle = \{\langle\sigma|\alpha\rangle\} = \begin{bmatrix}1\\0\end{bmatrix}, \quad \boldsymbol{\beta}(\boldsymbol{\xi}) = \langle\boldsymbol{\xi}|\beta\rangle = \{\langle\sigma|\beta\rangle\} = \begin{bmatrix}0\\1\end{bmatrix}, \\ &\langle\beta|\alpha\rangle = \sum_\sigma \langle\beta|\sigma\rangle\langle\sigma|\alpha\rangle = \boldsymbol{\beta}^\dagger(\boldsymbol{\xi})\,\boldsymbol{\alpha}(\boldsymbol{\xi}) = 0, \\ &\langle\alpha|\alpha\rangle = \sum_\sigma \langle\alpha|\sigma\rangle\langle\sigma|\alpha\rangle = \boldsymbol{\alpha}^\dagger(\boldsymbol{\xi})\,\boldsymbol{\alpha}(\boldsymbol{\xi}) = \langle\beta|\beta\rangle = \sum_\sigma \langle\beta|\sigma\rangle\langle\sigma|\beta\rangle = \boldsymbol{\beta}^\dagger(\boldsymbol{\xi})\boldsymbol{\beta}(\boldsymbol{\xi}) = 1.\end{aligned} \tag{3.76}$$

To simplify notation, we introduce the dimensionless Pauli operator,

$$\hat{\boldsymbol{\sigma}} = 2\hat{\mathbf{s}}/\hbar = \boldsymbol{i}\hat{\sigma}_x + \boldsymbol{j}\hat{\sigma}_y + \boldsymbol{j}\hat{\sigma}_z, \tag{3.77}$$

in terms of which the first three commutation relations of (3.75) read:

$$[\hat{\sigma}_x, \hat{\sigma}_y] = 2i\hat{\sigma}_z, \quad [\hat{\sigma}_y, \hat{\sigma}_z] = 2i\hat{\sigma}_x, \quad [\hat{\sigma}_z, \hat{\sigma}_x] = 2i\hat{\sigma}_y. \tag{3.78}$$

The same relations must be satisfied by the matrix representations of the spin components $\{\hat{\sigma}_i\}$ in the basis $|\boldsymbol{\xi}\rangle$, called the Pauli matrices.

Since $[\hat{\boldsymbol{\sigma}}^2, \hat{\sigma}_z] = 0$, these two operators are represented by the diagonal matrices in this basis set $|\boldsymbol{\xi}\rangle$ of their common eigenvectors:

$$\hat{\boldsymbol{\sigma}}^2|\alpha\rangle = 3|\alpha\rangle, \quad \hat{\boldsymbol{\sigma}}^2|\beta\rangle = 3|\beta\rangle; \quad \hat{\sigma}_z|\alpha\rangle = |\alpha\rangle, \quad \hat{\sigma}_z|\beta\rangle = -|\beta\rangle.$$

These matrices include the corresponding eigenvalues as diagonal elements:

$$\boldsymbol{\sigma}^2 = \langle\boldsymbol{\xi}|\hat{\boldsymbol{\sigma}}^2|\boldsymbol{\xi}\rangle = \begin{bmatrix} 3 & 0 \\ 0 & 3 \end{bmatrix} \quad \text{and} \quad \boldsymbol{\sigma}_z = \langle\boldsymbol{\xi}|\hat{\sigma}_z|\boldsymbol{\xi}\rangle = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}. \tag{3.79}$$

In order to determine the Pauli matrices representing the remaining spin components,

$$\boldsymbol{\sigma}_x = \langle\boldsymbol{\xi}|\hat{\sigma}_x|\boldsymbol{\xi}\rangle = \begin{bmatrix} a_{1,1} & a_{1,2} \\ a_{2,1} & a_{2,2} \end{bmatrix} \quad \text{and} \quad \boldsymbol{\sigma}_y = \langle\boldsymbol{\xi}|\hat{\sigma}_y|\boldsymbol{\xi}\rangle = \begin{bmatrix} b_{1,1} & b_{1,2} \\ b_{2,1} & b_{2,2} \end{bmatrix}, \tag{3.80}$$

we first use two commutation relations of (3.78):

$$[\boldsymbol{\sigma}_x, \boldsymbol{\sigma}_z] = -2i\boldsymbol{\sigma}_y \Rightarrow \begin{bmatrix} 0 & -2a_{1,2} \\ 2a_{2,1} & 0 \end{bmatrix} = -2i\begin{bmatrix} b_{1,1} & b_{1,2} \\ b_{2,1} & b_{2,2} \end{bmatrix}, \tag{3.81}$$

$$[\boldsymbol{\sigma}_y, \boldsymbol{\sigma}_z] = 2i\boldsymbol{\sigma}_x \Rightarrow \begin{bmatrix} 0 & -2b_{1,2} \\ 2b_{2,1} & 0 \end{bmatrix} = 2i\begin{bmatrix} a_{1,1} & a_{1,2} \\ a_{2,1} & a_{2,2} \end{bmatrix}. \tag{3.82}$$

Hence, $a_{1,1} = a_{2,2} = b_{1,1} = b_{2,2} = 0$, $b_{1,2} = -ia_{1,2}$, $b_{2,1} = ia_{2,1}$. The remaining two matrix elements then result from the third commutation rule,

$$[\boldsymbol{\sigma}_x, \boldsymbol{\sigma}_y] = 2i\boldsymbol{\sigma}_z \Rightarrow 2i\begin{bmatrix} a_{1,2}a_{2,1} & 0 \\ 0 & -a_{1,2}a_{2,1} \end{bmatrix} = 2i\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, \tag{3.83}$$

which implies $a_{1,2}a_{2,1} = 1$. Therefore, by setting $a_{1,2} = a_{2,1} = 1$, one arrives at the following explicit forms of the Pauli matrices in (3.80):

$$\boldsymbol{\sigma}_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad \text{and} \quad \boldsymbol{\sigma}_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}. \tag{3.84}$$

Their nondiagonal character reflects the fact that these observables are not sharply defined simultaneously with the two spin parameters defining the basis set $|\boldsymbol{\xi}\rangle$.

It thus directly follows from these explicit representations of the Pauli operators that their actions on the spin functions of (3.76) give:

$$\boldsymbol{\sigma}_x\boldsymbol{\alpha} = \boldsymbol{\beta},\ \ \boldsymbol{\sigma}_x\boldsymbol{\beta} = \boldsymbol{\alpha};\ \ \boldsymbol{\sigma}_y\boldsymbol{\alpha} = i\boldsymbol{\beta},\ \ \boldsymbol{\sigma}_y\boldsymbol{\beta} = -i\boldsymbol{\alpha};\ \ \boldsymbol{\sigma}_z\boldsymbol{\alpha} = \boldsymbol{\alpha},\ \ \boldsymbol{\sigma}_z\boldsymbol{\beta} = -\boldsymbol{\beta}. \tag{3.85}$$

3.5 Pictures of Time Evolution

After establishing the basic concepts of the quantum *kinematics*, dealing with the quantum objects at the given time $t = t_0$, we now turn to alternative formulations of the quantum *dynamics*, which determines the evolution of the microsystems in time. The possibility of such different formulations arises because the basic mathematical entities of the theory, such as state vectors and operators, are not directly accessible to physical measurement. As we have seen in the preceding sections of this chapter, only the eigenvalues of the quantum observables and the scalar products of state vectors have direct experimental implications. They respectively determine the spectrum of all possible outcomes of single measurements of the physical quantity to which the operator corresponds and their associated probabilities in a very large number of repetitions of experiments carried on the same quantum state of the physical system in question. Therefore, as long as these experimental predictions remain the same, the alternative formulations of the quantum dynamics, called state *pictures*, remain acceptable and fully equivalent physical theories.

As we have seen in Sect. 2.7, the unitary operators $\hat{\mathrm{U}}$, for which $\hat{\mathrm{U}}^\dagger = \hat{\mathrm{U}}^{-1}$, have the desired property of not affecting the eigenvalues of the transformed operators $\hat{\mathrm{A}}' = \hat{\mathrm{U}}\hat{\mathrm{A}}\hat{\mathrm{U}}^\dagger$ and the scalar products between the transformed vectors $|\Psi'\rangle = \hat{\mathrm{U}}|\Psi\rangle$ and $|\Phi'\rangle = \hat{\mathrm{U}}|\Phi\rangle : \langle\Phi'|\Psi'\rangle = \langle\Phi|\hat{\mathrm{U}}^\dagger\hat{\mathrm{U}}|\Psi\rangle = \langle\Phi|\Psi\rangle$. The range of unitary operators is not limited to their time-independent form, which we have examined in Sect. 2.7, giving rise to different descriptions of the quantum object at the specified time $t = t_0$. The unitary transformations can be also used to express a change of quantum states with time, i.e., the alternative dynamical pictures of quantum mechanics.

For example, in the *Schrödinger* (*S*) picture, when the spectrum of the operator eigenvalues does not depend on time, one uses the time-independent operators $\hat{\mathrm{A}} \equiv \hat{\mathrm{A}}_S$ so that the evolution of quantum objects in time is embodied in the time-dependent state vector $|\Psi_S(t)\rangle$, generated from the initial state $|\Psi(t_0)\rangle$ by the action of the unitary operator $\hat{\mathrm{U}}(t-t_0)$ of the time evolution $t_0 \to t$ of $|\Psi(t_0)\rangle$:

$$\begin{aligned} &|\Psi_S(t)\rangle = \hat{\mathrm{U}}(t-t_0)|\Psi(t_0)\rangle, \quad \hat{\mathrm{U}}(t-t_0)^\dagger = \hat{\mathrm{U}}(t-t_0)^{-1} \equiv \hat{\mathrm{U}}(t_0-t), \\ &\hat{\mathrm{U}}(t-t_0)\hat{\mathrm{U}}(t_0-t) = 1 \quad \text{and} \quad \hat{\mathrm{U}}(0) = 1, \end{aligned} \tag{3.86}$$

where the inverse evolution $t \to t_0$ of $|\Psi_S(t)\rangle$ recovers the state vector at $t = t_0$:

$$\hat{\mathrm{U}}(t_0-t)|\Psi_S(t)\rangle = |\Psi(t_0)\rangle. \tag{3.87}$$

It also directly follows from the unitary character of the time evolution operator that the normalization of state vectors is conserved in time:

$$\langle\Psi_S(t)|\Psi_S(t)\rangle = \langle\Psi(t_0)|\hat{\mathrm{U}}(t-t_0)^\dagger\hat{\mathrm{U}}(t-t_0)|\Psi(t_0)\rangle = \langle\Psi(t_0)|\Psi(t_0)\rangle. \tag{3.88}$$

In the *Heisenberg* (*H*) *picture,* the state vectors do not change in time, but the operators become time dependent. Therefore, the operator of the inverse time evolution in (3.86) marks the unitary transformation of $|\Psi_S(t)\rangle$ into the time-independent vector of the Heisenberg picture: $|\Psi(t_0)\rangle \equiv |\Psi_H\rangle$. The time-dependent operators are then given by the transformation:

$$\hat{\mathrm{A}}_H(t) = \hat{\mathrm{U}}(t_0-t)\hat{\mathrm{A}}_S\hat{\mathrm{U}}(t_0-t)^{-1} = \hat{\mathrm{U}}(t_0-t)\hat{\mathrm{A}}_S\hat{\mathrm{U}}(t-t_0). \tag{3.89}$$

When the quantum object is composed of interacting subsystems, its time-independent energy operator of the Schrödinger picture, the Hamiltonian $\hat{\mathrm{H}}$, can be partitioned into the contribution representing the energy of the noninteracting subsystems, $\hat{\mathrm{H}}_0$, and their mutual interaction, $\hat{\mathrm{V}}$,

$$\hat{\mathrm{H}} = \hat{\mathrm{H}}_0 + \hat{\mathrm{V}}. \tag{3.90}$$

The quantum dynamics of such composite systems can be best expressed in the *Interaction* (*I*) picture*,* in which both the state vectors and operators are time dependent. The relevant time-dependent unitary operator, which transforms these mathematical entities from the above Schrödinger picture, depends solely on $\hat{\mathrm{H}}_0$:

$$\hat{\mathrm{S}}(t) = \exp\left(\frac{i}{\hbar}\hat{\mathrm{H}}_0 t\right). \tag{3.91}$$

Here, the exponential operator is defined by its power series expansion:

$$\hat{\mathrm{B}}(t) \equiv \exp\left(\hat{\mathrm{A}}t\right) = \sum_{n=0}^{\infty}\frac{\left(\hat{\mathrm{A}}t\right)^n}{n!}, \tag{3.92a}$$

giving rise to the time derivative:

$$\frac{d\hat{\mathrm{B}}(t)}{dt} = \sum_{n=0}^{\infty} \frac{nt^{n-1}\hat{\mathrm{A}}^{n}}{n!} = \hat{\mathrm{A}} \sum_{n=1}^{\infty} \frac{(\hat{\mathrm{A}}t)^{n-1}}{(n-1)!} = \hat{\mathrm{A}} \sum_{m=0}^{\infty} \frac{(\hat{\mathrm{A}}t)^{m}}{m!} = \hat{\mathrm{A}}\exp(\hat{\mathrm{A}}t). \tag{3.92b}$$

The state vectors and operators in the I-picture of Quantum Mechanics are defined by the following transformations of their corresponding S-picture analogs:

$$|\Psi_I(t)\rangle = \hat{\mathrm{S}}(t)|\Psi_S(t)\rangle, \quad \hat{\mathrm{A}}_I(t) = \hat{\mathrm{S}}(t)\hat{\mathrm{A}}_S\hat{\mathrm{S}}(t)^{-1}. \tag{3.93}$$

In the remaining part of this chapter we shall explore in some detail the time evolution of quantum states in the Schrödinger picture and examine some of its physical implications. In the final Sect. 3.7 we summarize the related dynamical equations in the alternative pictures of quantum dynamics.

3.6 Schrödinger Picture: Dynamics of Wave Functions and Density Operators

Let us determine the explicit form of the unitary operator $\hat{\mathrm{U}}(t - t_0)$ of (3.86). The relevant *equation of motion* for quantum states in this dynamical picture is the subject of

Postulate V: The time evolution of the state vector $|\Psi_S(t)\rangle \equiv |\Psi(t)\rangle$ is governed by the Schrödinger equation:

$$i\hbar \frac{d|\Psi(t)\rangle}{dt} = \hat{\mathrm{H}}|\Psi(t)\rangle, \tag{3.94}$$

where the Hamiltonian $\hat{\mathrm{H}}$ is the observable associated with the system total energy.

The corresponding wave equations, either in the position-spin or the momentum-spin representations, determine the dynamics of the associated wave functions:

$$i\hbar \frac{d\Psi(\mathcal{Q}^N, t)}{dt} = \hat{\mathrm{H}}(\mathcal{Q}^N)\Psi(\mathcal{Q}^N, t) \quad \text{or} \quad i\hbar \frac{d\Psi(\mathcal{P}^N, t)}{dt} = \hat{\mathrm{H}}(\mathcal{P}^N)\Psi(\mathcal{P}^N, t). \tag{3.95}$$

Substituting (3.86) into (3.94) gives:

$$\left[i\hbar \frac{d\hat{\mathrm{U}}(t - t_0)}{dt} - \hat{\mathrm{H}}\,\hat{\mathrm{U}}(t - t_0)\right]|\Psi(t_0)\rangle = 0 \text{ or } i\hbar \frac{d\hat{\mathrm{U}}(t - t_0)}{dt} = \hat{\mathrm{H}}\,\hat{\mathrm{U}}(t - t_0). \tag{3.96}$$

The formal solution of this differential equation is thus given by the following evolution operator [see also (3.92a) and (3.92b)]:

$$\hat{\mathrm{U}}(t-t_0) = \exp\left(-\frac{i}{\hbar}(t-t_0)\hat{\mathrm{H}}\right) \equiv \exp\left(-\frac{i}{\hbar}\tau\,\hat{\mathrm{H}}\right) \equiv \hat{\mathrm{U}}(\tau). \tag{3.97}$$

Hence, the operator of the reverse evolution, from t to t_0,

$$\hat{\mathrm{U}}(\tau)^{\dagger} = \hat{\mathrm{U}}(\tau)^{-1} = \exp\left(\frac{i}{\hbar}\tau\,\hat{\mathrm{H}}\right) = \hat{\mathrm{U}}(-\tau). \tag{3.98}$$

It can be easily verified by the differentiation with respect to time, using the derivative (3.92b) of the exponential operator (3.92a), that the action of this unitary operator is equivalent to the dynamical Schrödinger equation (3.94).

We now briefly examine the implications of Schrödinger's time evolution for the mixed states. The unitary character of the time evolution operator then directly implies that if the system at the initial time $t = t_0$ has probability p_k of being in the state $|\psi_\alpha\rangle = |\psi_\alpha(t_0)\rangle$, then, at a subsequent time t, it has the same probability of being in the evolved state $|\psi_\alpha(t)\rangle$. Indeed, the density operator at time t [see (3.60a)–(3.60c)],

$$\hat{\mathrm{D}}(t) = \sum_\alpha p_\alpha(t)|\psi_\alpha(t)\rangle\langle\psi_\alpha(t)| = \sum_\alpha p_\alpha(t)\hat{\mathrm{P}}_\alpha(t), \tag{3.99}$$

gives

$$p_\alpha(t) = \langle\psi_\alpha(t)|\hat{\mathrm{D}}(t)|\psi_\alpha(t)\rangle = \langle\psi_\alpha|\hat{\mathrm{D}}|\psi_\alpha\rangle = p_\alpha, \tag{3.100}$$

since the matrix elements of operators are invariants of the unitary transformations.

Before we examine the *equation of motion* for $\hat{\mathrm{D}}(t) = \sum_\alpha p_\alpha \hat{\mathrm{P}}_\alpha(t)$ let us first derive it for the projection operator $\hat{\mathrm{P}}_\alpha(t)$ onto the pure state $|\psi_\alpha(t)\rangle$. Using the Schrödinger equation (3.94) for $|\psi_\alpha(t)\rangle$ and its Hermitian conjugate gives:

$$\begin{aligned}\frac{d}{dt}\hat{\mathrm{P}}_\alpha(t) &= \left(\frac{d|\psi_\alpha(t)\rangle}{dt}\right)\langle\psi_\alpha(t)| + |\psi_\alpha(t)\rangle\left(\frac{d\langle\psi_\alpha(t)|}{dt}\right)\\ &= \frac{1}{i\hbar}\left(\hat{\mathrm{H}}|\psi_\alpha(t)\rangle\langle\psi_\alpha(t)| - |\psi_\alpha(t)\rangle\langle\psi_\alpha(t)|\hat{\mathrm{H}}\right) = \frac{1}{i\hbar}[\hat{\mathrm{H}},\hat{\mathrm{P}}_\alpha(t)].\end{aligned} \tag{3.101}$$

Multiplying the preceding equation by $p_\alpha(t) = p_\alpha$ and summing over all states in the statistical mixture of $\hat{\mathrm{D}}(t)$ gives the related dynamics of the density operator itself:

$$i\hbar\frac{d}{dt}\hat{\mathrm{D}}(t) = [\hat{\mathrm{H}},\hat{\mathrm{D}}(t)]. \tag{3.102}$$

3.6.1 Energy Representation and Stationary States

The explicit form of the time-dependent wave function

$$\Psi(\mathcal{Q}^N; t - t_0) \equiv \Psi(\mathcal{Q}^N; \tau) = \exp\left(-\frac{i}{\hbar}\hat{\mathrm{H}}(\mathcal{Q}^N)\tau\right)\Psi(\mathcal{Q}^N; t_0), \tag{3.103}$$

can be obtained in the energy representation of Sect. 2.7, i.e., for the orthonormal basis set of the eigenfunctions $\left\{\psi_n(\mathcal{Q}^N) = \left\langle \mathcal{Q}^N \mid \psi_n \right\rangle\right\}$ of the system Hamiltonian $\hat{\mathrm{H}}(\mathcal{Q}^N) = \left\langle \mathcal{Q}^N \middle| \hat{\mathrm{H}} \middle| \mathcal{Q}^N \right\rangle$:

$$\hat{\mathrm{H}}(\mathcal{Q}^N)\ \psi_n(\mathcal{Q}^N) = E_n\, \psi_n(\mathcal{Q}^N). \tag{3.104}$$

Indeed, by expanding the wave function in this energy basis set,

$$\begin{aligned} \Psi(\mathcal{Q}^N; t_0) &= \sum_n C_n\ \psi_n(\mathcal{Q}^N), \\ C_n = \langle \psi_n \mid \Psi(t_0) \rangle &= \int \psi_n^*(\mathcal{Q}^N)\Psi(\mathcal{Q}^N; t_0)\ d\mathcal{Q}^N, \end{aligned} \tag{3.105}$$

and using the power series for the exponential evolution operator (3.92a) and its derivative (3.92b), one finds the wave function after the time interval $\tau = t - t_0$:

$$\begin{aligned} \Psi(\mathcal{Q}^N; \tau) &= \sum_{k=0}^{\infty} \frac{1}{k!}\left(-\frac{i}{\hbar}\hat{\mathrm{H}}(\mathcal{Q}^N)\,\tau\right)^k \sum_n C_n\, \psi_n(\mathcal{Q}^N) \\ &= \sum_n C_n\, \psi_n(\mathcal{Q}^N) \sum_{k=0}^{\infty} \frac{1}{k!}\left(-\frac{i}{\hbar}E_n\tau\right)^k \\ &= \sum_n C_n \exp\left(-\frac{i}{\hbar}E_n\tau\right)\psi_n(\mathcal{Q}^N) \\ &\equiv \sum_n u_n(\tau)\, \psi_n(\mathcal{Q}^N) \equiv \sum_n C_n\, \Psi_n(\mathcal{Q}^N; \tau). \end{aligned} \tag{3.106}$$

In the preceding expansion, the time-dependent wave function is expressed in terms of the time-dependent eigenfunctions of the Hamiltonian,

$$\begin{aligned} \Psi_n(\mathcal{Q}^N; \tau) &= \psi_n(\mathcal{Q}^N) \exp\left(-\frac{i}{\hbar}E_n\tau\right) \equiv \psi_n(\mathcal{Q}^N) \exp(-i\omega_n\tau) \\ &= \left\langle \mathcal{Q}^N \mid \Psi_{E_n}(\tau) \right\rangle, \end{aligned} \tag{3.107}$$

which represent the *stationary states* of the system, for its sharply specified energies $\{E_n\}$. Such states are given by the product of the time-independent *amplitude* $\psi_n(\mathcal{Q}^N)$, determined by the eigenvalue problem of (3.104), and the time-dependent *phase* factor $\exp(-i\omega_n\tau)$, which does not contribute to the associated (time independent) probability distribution,

$$p_n(\boldsymbol{\mathfrak{Q}}^N;\tau) = \left|\psi_n(\boldsymbol{\mathfrak{Q}}^n)\exp\left(-\frac{i}{\hbar}E_n\tau\right)\right|^2 = |\psi_n(\boldsymbol{\mathfrak{Q}}^n)|^2 = \psi_n^*(\boldsymbol{\mathfrak{Q}}^n)\psi_n(\boldsymbol{\mathfrak{Q}}^n), \tag{3.108}$$

which is seen to be determined solely by the state amplitude.

The time-dependent coefficients $\{u_n(\tau) = \langle\psi_n \mid \Psi(\tau)\rangle = C_n\exp(-i\omega_n\tau\}$ in (3.106) provide the energy representation of state $|\Psi(\tau)\rangle$. Since the conditional probability $P(\psi_n|\Psi(\tau)) = |u_n(\tau)|^2 = |C_n|^2$, we thus conclude that the time evolution of the state vector in the S-picture represents its "rotation" in the Hilbert space, which conserves in time the probabilities of observing the system stationary states. We also observe that for the combination of (3.106) to retain the stationary character it must be limited only to the subspace corresponding to a single degenerate eigenvalue E_n, with all its components thus exhibiting the same phase factor.

To summarize, the stationary states, in which the system energy is sharply defined, are distinguished by several special features. The energy determines uniquely the time-dependent factor of the wave function, so that the probability distribution and its current (see Section 3.6.3) are time independent. Moreover, the expectation values of any physical observable $\hat{\mathrm{A}}(\boldsymbol{\mathfrak{Q}}^N)$, which does not depend on time explicitly, are conserved:

$$\langle A\rangle = \int \Psi_n^*(\boldsymbol{\mathfrak{Q}}^N;\tau)\hat{\mathrm{A}}(\boldsymbol{\mathfrak{Q}}^N)\Psi_n(\boldsymbol{\mathfrak{Q}}^N;\tau)\,d\boldsymbol{\mathfrak{Q}}^N = \int \psi_n^*(\boldsymbol{\mathfrak{Q}}^N)\hat{\mathrm{A}}(\boldsymbol{\mathfrak{Q}}^N)\psi_n(\boldsymbol{\mathfrak{Q}}^N)\,d\boldsymbol{\mathfrak{Q}}^N = const. \tag{3.109}$$

These average values thus become sharply defined, equal to a single eigenvalue of $\hat{\mathrm{A}}(\boldsymbol{\mathfrak{Q}}^N)$, $\langle A\rangle = a_i$, when the latter commutes with the system Hamiltonian. Also, when these two observables do not commute, the conditional probability $P(\varphi_j|\Psi_n)$ of finding a given eigenvalue a_j, where $\varphi_j(\boldsymbol{\mathfrak{Q}}^N)$ represents the eigenstate of $\hat{\mathrm{A}}(\boldsymbol{\mathfrak{Q}}^N)$,

$$\hat{\mathrm{A}}(\boldsymbol{\mathfrak{Q}}^N)\,\varphi_k(\boldsymbol{\mathfrak{Q}}^N) = a_k\,\varphi_k(\boldsymbol{\mathfrak{Q}}^N)\,, \tag{3.110}$$

given by the square of the modulus of the relevant expansion coefficient, the projection of Ψ_n into φ_k, also remains constant in time:

$$P(\varphi_j|\Psi_n) = \left|\int \varphi_j^*(\boldsymbol{\mathfrak{Q}}^N)\Psi_n(\boldsymbol{\mathfrak{Q}}^N;\tau)\;d\boldsymbol{\mathfrak{Q}}^N\right|^2 = const. \tag{3.111}$$

The Schrödinger equation emphasizes the crucial role of the system energy operator in determining the system dynamics, similar to that played by the Hamilton function in classical mechanics [see (3.1)]. In general, the precise specification of the system energy does not identify the stationary quantum state uniquely. Indeed, for this to be the case one also requires the eigenvalues $\boldsymbol{a} = \{a_i\}$ of the complete set of the commuting observables $\{\hat{\mathrm{A}}_i\}$, which also commute with the system Hamiltonian (see Sect. 2.5):

$$[\hat{\mathrm{H}}, \hat{\mathrm{A}}_i] = [\hat{\mathrm{A}}_i, \hat{\mathrm{A}}_j] = 0, \quad i,j = 1, 2, \ldots, s. \tag{3.112}$$

Together with the sharply defined energy E_n they provide the complete description of their common eigenvectors:

$$\hat{\mathrm{H}}|E_n, \boldsymbol{a}\rangle = E_n|E_n, \boldsymbol{a}\rangle, \quad \{\hat{\mathrm{A}}_i|E_n, \boldsymbol{a}\rangle = a_i|E_n, \boldsymbol{a}\rangle\}. \tag{3.113}$$

It follows from (3.102) that in the energy representation the dynamics of the diagonal elements of the density operator $\hat{\mathrm{D}}(\tau), D_{n,n}(\tau) = \langle\psi_n|\hat{\mathrm{D}}(\tau)|\psi_n\rangle$, representing the *population* of state $|\psi_n\rangle$ in the ensemble, predicts:

$$i\hbar\frac{d}{d\tau}D_{n,n}(\tau) = \langle\psi_n|\hat{\mathrm{H}}\hat{\mathrm{D}}(\tau) - \hat{\mathrm{D}}(\tau)\hat{\mathrm{H}}|\psi_n\rangle = E_n\langle\psi_n|\hat{\mathrm{D}}(\tau) - \hat{\mathrm{D}}(\tau)|\psi_n\rangle = 0. \tag{3.114}$$

For its *off*-diagonal matrix element $D_{m,n}(\tau) = \langle\psi_m|\hat{\mathrm{D}}(\tau)|\psi_n\rangle$, representing *coherences* between states $|\psi_m\rangle$ and $|\psi_n\rangle$ in the ensemble, one similarly finds:

$$\begin{aligned} i\hbar\frac{d}{dt}D_{m,n}(\tau) &= \langle\psi_m|\hat{\mathrm{H}}\hat{\mathrm{D}}(\tau) - \hat{\mathrm{D}}(\tau)\hat{\mathrm{H}}|\psi_n\rangle \\ &= (E_m - E_n)\langle\psi_n|\hat{\mathrm{D}}(\tau)|\psi_n\rangle \\ &= (E_m - E_n)D_{m,n}(\tau) \end{aligned} \tag{3.115a}$$

or

$$\frac{d}{d\tau}[\ln D_{m,n}(\tau)] = -\frac{i}{\hbar}(E_m - E_n). \tag{3.115b}$$

Therefore, in the stationary-state representation $D_{n,n}(\tau) = const.$ and

$$D_{m,n}(\tau) = \exp\left(-\frac{i}{\hbar}(E_m - E_n)\tau\right)D_{m,n}(0). \tag{3.116}$$

In the remaining part of this section we shall explore some physical implications of the dynamical Schrödinger equation.

3.6.2 Time Dependence of Expectation Values and Ehrenfest Principle

Since the Schrödinger equation (3.94) is of the first order in t, the state $|\Psi(t)\rangle$ at any subsequent time $t > t_0$ is uniquely determined given the initial state $|\Psi(t_0)\rangle$. Therefore, there is no indeterminacy in the free evolution of quantum systems. The irreversibility arises only in an act of measurement, which unpredictably modifies the system state. Thus, between the two measurements the evolution of quantum states is perfectly deterministic.

It also follows from the linear and homogeneous character of this equation that its solutions are linearly superposable. More specifically, the linear combination at the initial time $|\Psi(t_0)\rangle = C_1|\Psi_1(t_0)\rangle + C_2|\Psi_2(t_0)\rangle$ becomes $|\Psi(t)\rangle = C_1|\Psi_1(t)\rangle + C_2|\Psi_2(t)\rangle$ at $t > t_0$, so that the correspondence between $|\Psi(t_0)\rangle$ and $|\Psi(t)\rangle$ is marked by preservation of the coefficients before their components during time evolution. Another manifestation of this property is the conservation in time of the ensemble probabilities (3.100).

Next, let us examine the time evolution of the mean (expectation) values of the physical observables. As we have already observed in (3.88), the preservation in time of the state normalization is assured by the unitary character of the time evolution operator of (3.86). Thus, in the mean value of the physical quantity A, which in general case may explicitly depend on time, $\hat{\mathrm{A}} = \hat{\mathrm{A}}(t)$, only the explicit time dependency of the wave function and that of the observable do matter, since the implicit dependence through the coordinates (or momenta) has already been eliminated by integration in the expectation value of (3.109). Using the relevant Hilbert space expression and the Schrödinger equation (3.94) then gives:

$$\begin{aligned}\frac{d\langle\Psi(t)|\hat{\mathrm{A}}(t)|\Psi(t)\rangle}{dt} &= \left(\frac{d}{dt}\langle\Psi(t)|\right)\hat{\mathrm{A}}|\Psi(t)\rangle + \langle\Psi(t)|\hat{\mathrm{A}}\left(\frac{d}{dt}|\Psi(t)\rangle\right) + \langle\Psi(t)|\frac{\partial\hat{\mathrm{A}}}{\partial t}|\Psi(t)\rangle \\ &= \frac{1}{i\hbar}\langle\Psi(t)|[\hat{\mathrm{A}},\hat{\mathrm{H}}]|\Psi(t)\rangle + \langle\Psi(t)|\frac{\partial\hat{\mathrm{A}}}{\partial t}|\Psi(t)\rangle \equiv \frac{1}{i\hbar}\langle[\hat{\mathrm{A}},\hat{\mathrm{H}}]\rangle + \left\langle\frac{\partial\hat{\mathrm{A}}}{\partial t}\right\rangle.\end{aligned} \tag{3.117}$$

Therefore, for the physical observables, which do not depend explicitly on time,

$$\frac{d\langle A\rangle}{dt} = \frac{i}{\hbar}\langle[\hat{\mathrm{H}},\hat{\mathrm{A}}]\rangle, \tag{3.118}$$

and hence the observable commuting with the Hamiltonian represents the system *constant of motion*.

Consider the illustrative example of a motion in one dimension, in the potential $V(x)$, of the spinless particle described by the Hamiltonian $\hat{\mathrm{H}}(x) = V(x) + \hat{\mathrm{p}}_x^2/2m$.

We first examine the time dependence of the particle average position $\langle x \rangle$. Using (2.34) and (3.56) in the preceding equation gives:

$$\frac{d\langle x\rangle}{dt} = \frac{i}{\hbar}\left\langle [\hat{\mathrm{H}}, \hat{\mathrm{x}}]\right\rangle = \frac{i}{2m\hbar}\left\langle [\hat{\mathrm{p}}_x^2, \hat{\mathrm{x}}]\right\rangle = \frac{i}{2m\hbar}\langle [\hat{\mathrm{p}}_x[\hat{\mathrm{p}}_x, \hat{\mathrm{x}}] + [\hat{\mathrm{p}}_x, \hat{\mathrm{x}}]\hat{\mathrm{p}}_x\rangle = \frac{\langle p_x\rangle}{m}. \quad (3.119)$$

Therefore, the relation between the expectation values of the position and momentum is the same as that between their classical analogs: $v_x = dx/dt = p_x/m$.

One similarly arrives at the second Newton's law of classical dynamics, $dp_x/dt = F_x = -dV(x)/dx$, where F_x stands for the force acting on the particle, by examining the time evolution of $\langle p_x \rangle$:

$$\frac{d\langle p_x\rangle}{dt} = \frac{i}{\hbar}\left\langle [\hat{\mathrm{H}}, \hat{\mathrm{p}}_x]\right\rangle = \frac{i}{\hbar}\langle [V(x), \hat{\mathrm{p}}_x]\rangle = \frac{i}{\hbar}\left\langle i\hbar\frac{\partial V}{\partial x}\right\rangle = -\left\langle \frac{\partial V}{\partial x}\right\rangle = \langle F_x\rangle. \quad (3.120)$$

Accordingly, for the movement of a quantum particle in three dimensions, in the potential $V(\boldsymbol{r})$ generating the classical force field $\boldsymbol{F}(\boldsymbol{r}) = -\nabla V(\boldsymbol{r})$, one finds

$$\frac{d\langle \boldsymbol{p}\rangle}{dt} = -\langle \nabla V\rangle = \langle \boldsymbol{F}\rangle. \quad (3.121)$$

This correspondence between the quantum relations in terms of the expectation (mean) values of physical quantities and the associated equations of classical mechanics expresses the *Ehrenfest principle* of quantum mechanics. In any quantum state $|\Psi\rangle$ the time dependencies of the expectation values of the position and momentum operators are seen to follow the corresponding relations between the associated classical quantities. This rule complements the related Correspondence Principle of Bohr (see Chap. 1) that the quantum description becomes classical in the limit of high energies and very large quantum numbers, when one can safely neglect the finite value of the quantum of action: $\hbar \to 0$.

3.6.3 Probability Current and Continuity Equation

Let us again assume the system composed of a single (spinless) particle. In the position representation, the state $|\psi(t)\rangle$ is represented by the normalized wave function $\psi(\boldsymbol{r};\, t) = \langle \boldsymbol{r}|\psi(t)\rangle$ which generates the probability density

$$p(\boldsymbol{r}; t) = |\psi(\boldsymbol{r}, t)|^2 = \langle \psi(t)|\boldsymbol{r}\rangle\langle \boldsymbol{r}|\psi(t)\rangle \equiv \langle \psi(t)|\hat{\rho}(\boldsymbol{r})|\psi(t)\rangle = \rho(\boldsymbol{r}; t). \quad (3.122)$$

It directly follows from the Schrödinger equation (3.94) that the square of the norm of the wave function, i.e., the integral of $p(\boldsymbol{r},\, t)$ over the whole physical space, remains constant in time and equal to 1 for the normalized quantum state. This does not imply, however, that $p(\boldsymbol{r}, t)$ is also locally conserved over time. Indeed, the stream of probability may transport the particles from one region of space to another. It is our goal in this section to establish the appropriate expression for the local probability current.

It should be recalled that in the electromagnetism the charge (volume) density $\rho_{el}(\boldsymbol{r}; t)$ is linked to the flux of the vector current density $\boldsymbol{J}_{el}(\boldsymbol{r}; t)$ through the local continuity equation,

$$\frac{\partial}{\partial t}\rho_{el}(\boldsymbol{r};t) = -\nabla \cdot \boldsymbol{J}_{el}(\boldsymbol{r};t), \tag{3.123}$$

where the left-hand part of the equation expresses the net change of the density in the fixed, infinitesimal volume around $\boldsymbol{r}$, and the right-hand part represents the flux across the surface, which defines this volume element. We are now searching for an analogous equation expressing the local probability balance in the quantum mechanics, i.e., the appropriate definition of the probability current $\boldsymbol{j}(\boldsymbol{r}; t)$. The negative divergence of this yet unknown vector will then measure the flux of particles leaving the local volume element.

The system Hamiltonian in the position representation,

$$\hat{\mathrm{H}}(\boldsymbol{r}) = V(\boldsymbol{r}) + \frac{\hat{\mathbf{p}}^2(\boldsymbol{r})}{2m} = V(\boldsymbol{r}) - \frac{\hbar^2}{2m}\Delta, \tag{3.124}$$

with the real potential $V(\boldsymbol{r})$ for $\hat{\mathrm{H}}(\boldsymbol{r})$ to be Hermitian, gives the dynamical Schrödinger equation in the form:

$$i\hbar\frac{\partial\psi(\boldsymbol{r};t)}{\partial t} = V(\boldsymbol{r})\,\psi(\boldsymbol{r};t) - \frac{\hbar^2}{2m}\Delta\psi(\boldsymbol{r};t). \tag{3.125}$$

Multiplying, from the left, both sides of this equation by $\psi^*(\boldsymbol{r}; t)$, and of the complex conjugate Schrödinger equation by $\psi(\boldsymbol{r}; t)$, subtracting the resulting equations and dividing by $i\hbar$ then give:

$$\frac{\partial[\psi^*\psi]}{\partial t} = -\frac{\hbar}{2mi}[\psi^*\Delta\psi - \psi\Delta\psi^*]. \tag{3.126}$$

This equation can be then transformed into the continuity-type equation (3.123),

$$\frac{\partial}{\partial t}p(\boldsymbol{r};t) = -\nabla \cdot \boldsymbol{j}(\boldsymbol{r};t), \tag{3.127}$$

with the probability current

$$\begin{aligned}\boldsymbol{j}(\boldsymbol{r};t) &= \frac{\hbar}{2mi}[\psi^*(\boldsymbol{r};t)\nabla\psi(\boldsymbol{r};t) - \psi(\boldsymbol{r};t)\nabla\psi^*(\boldsymbol{r};t)] \\ &= \frac{1}{m}\mathrm{Re}[\psi^*(\boldsymbol{r};t)\frac{\hbar}{i}\nabla\psi(\boldsymbol{r};t)],\end{aligned} \tag{3.128}$$

$$\begin{aligned}\nabla\cdot\boldsymbol{j} &= \frac{\hbar}{2mi}[(\nabla\psi^*)\cdot(\nabla\psi) + \psi^*(\nabla^2\psi) - (\nabla\psi)\cdot(\nabla\psi^*) - \psi(\nabla^2\psi^*)] \\ &= \frac{\hbar}{2mi}[\psi^*\Delta\psi - \psi\,\Delta\psi^*].\end{aligned}$$

The form of the probability current (3.128) indicates that it is determined by the expectation (mean) value in state $|\psi(t)\rangle$ of the Hermitian operator

$$\hat{\mathbf{j}}(\boldsymbol{r}) = \frac{1}{2m}[|\boldsymbol{r}\rangle\langle\boldsymbol{r}|\hat{\mathbf{p}} + \hat{\mathbf{p}}|\boldsymbol{r}\rangle\langle\boldsymbol{r}|], \tag{3.129}$$

which represents the symmetrized product of operators for the probability density, $\hat{\rho}(\boldsymbol{r}) = |\boldsymbol{r}\rangle\langle\boldsymbol{r}|$, and particle velocity, $\hat{\mathbf{v}} = \hat{\mathbf{p}}/m$. Indeed, such a product is also associated with the physical meaning of the current density vector of a classical fluid.

To conclude this section, let us express the complex wave function $\psi(\boldsymbol{r}, t)$ in terms of its (real) modulus $R(\boldsymbol{r}; t)$ and phase $\Phi(\boldsymbol{r}; t)$:

$$\psi(\boldsymbol{r},t) = R(\boldsymbol{r};t)\exp[i\Phi(\boldsymbol{r};t)]. \tag{3.130}$$

It then directly follows from (3.122) and (3.128) that

$$\begin{aligned}&p(\boldsymbol{r};t) = R^2(\boldsymbol{r};t) \quad \text{and} \\ &\boldsymbol{j}(\boldsymbol{r};t) = \frac{\hbar}{m}R^2(\boldsymbol{r};t)\nabla\Phi(\boldsymbol{r};t) = p(\boldsymbol{r};t)\nabla[\frac{\hbar}{m}\Phi(\boldsymbol{r};t)].\end{aligned} \tag{3.131}$$

3.7 Heisenberg and Interaction Pictures of Quantum Dynamics

We conclude this short outline of the formal framework of quantum dynamics with a summary of the relevant *equations of motion* in the H- and I-pictures of Sect. 3.5. As we have already indicated in (3.89) the operators $\{\hat{A}_H\}$ in the Heisenberg picture generally depend on time, even if their analogs in the Schrödinger picture $\{\hat{A}_S\}$ do not. However, for the conservative system, the Hamiltonian $\hat{H}_S$ of which does not depend on time, and an observable $\hat{A}_S$ representing a constant of motion (commuting with $\hat{\mathrm{H}}_S$), the evolution operator $\hat{\mathrm{U}}(t-t_0) \equiv \hat{\mathrm{U}}(\tau)$ of (3.97) commutes with $\hat{\mathrm{A}}_S$ so that

$$\hat{\mathrm{A}}_H(\tau) = \hat{\mathrm{U}}^{-1}(\tau)\hat{\mathrm{A}}_S\hat{\mathrm{U}}(\tau) = \hat{\mathrm{U}}^{-1}(\tau)\hat{\mathrm{U}}(\tau)\hat{\mathrm{A}}_S = \hat{\mathrm{A}}_S. \tag{3.132}$$

The operators for such physical properties are thus equal in both dynamical pictures, and in particular $\hat{\mathrm{H}}_H = \hat{\mathrm{H}}_S$.

For an arbitrary observable $\hat{\mathrm{A}}_S(\tau)$ one finds using (3.96), its adjoint, and (3.89):

$$\begin{aligned}\frac{d}{dt}\hat{\mathrm{A}}_H(\tau) = \frac{1}{i\hbar}\Big[\, &\hat{\mathrm{U}}^{-1}(\tau)\hat{\mathrm{A}}_S(\tau)\hat{\mathrm{H}}_S(\tau)\hat{\mathrm{U}}(\tau) - \hat{\mathrm{U}}^{-1}(\tau)\hat{\mathrm{H}}_S(\tau)\hat{\mathrm{A}}_S(\tau)\hat{\mathrm{U}}(\tau)\Big] \\ &+ \hat{\mathrm{U}}^{-1}(\tau)\frac{d\hat{\mathrm{A}}_S(\tau)}{dt}\hat{\mathrm{U}}(\tau).\end{aligned} \tag{3.133}$$

Inserting next the unity factor $\hat{\mathrm{U}}(\tau)\hat{\mathrm{U}}^{-1}(\tau) = 1$ between $\hat{\mathrm{H}}_S$ and $\hat{\mathrm{A}}_S$ in the first two terms of the right hand side in the preceding equation finally gives

$$\begin{aligned}\frac{d}{dt}\hat{\mathrm{A}}_H(\tau) = \frac{1}{i\hbar}\Big\{ &[\hat{\mathrm{U}}^{-1}(\tau)\hat{\mathrm{A}}_S(\tau)\hat{\mathrm{U}}(\tau)]\,[\hat{\mathrm{U}}^{-1}\hat{\mathrm{H}}_S(\tau)\hat{\mathrm{U}}(\tau)] \\ &-[\hat{\mathrm{U}}^{-1}(\tau)\hat{\mathrm{H}}_S(\tau)\hat{\mathrm{U}}(\tau)]\,[\hat{\mathrm{U}}^{-1}(\tau)\hat{\mathrm{A}}_S(\tau)\hat{\mathrm{U}}(\tau)]\Big\} + \hat{\mathrm{U}}^{-1}(\tau)\frac{d\hat{\mathrm{A}}_S(\tau)}{dt}\hat{\mathrm{U}}(\tau)\end{aligned} \tag{3.134}$$

and hence

$$i\hbar\frac{d}{d\tau}\hat{\mathrm{A}}_H(\tau) = [\hat{\mathrm{A}}_H(\tau), \hat{\mathrm{H}}_H(\tau)] + i\hbar\left(\frac{d}{d\tau}\hat{\mathrm{A}}_S(\tau)\right)_H. \tag{3.135}$$

It was Schrödinger who first discovered the dynamical equation bearing his name. The subsequent Heisenberg picture has established the evolution of matrices representing operators $\{\hat{\mathrm{A}}_H(t)\}$, hence the name *Matrix Mechanics* (see Chap. 1), to be later shown to be fully equivalent to the Schrödinger *Wave Mechanics*.

For the physical observables $\hat{\mathrm{A}}_S$, which do not depend explicitly on time, the last term in (3.135) vanishes. Moreover, since the expectation value is invariant to the unitary transformation linking the two pictures,

$$\langle A(t)\rangle = \langle\Psi_S(t)|\hat{\mathrm{A}}_S|\Psi_S(t)\rangle = \langle\Psi_H|\hat{\mathrm{A}}_H(t)|\Psi_H\rangle. \tag{3.136}$$

Since in the last term only the operator depends on time

$$\begin{aligned}\frac{d}{dt}\langle A(t)\rangle &= \langle \Psi_H|\frac{d\hat{\mathrm{A}}_H(t)}{dt}|\Psi_H\rangle = \frac{1}{i\hbar}\langle \Psi_H|[\hat{\mathrm{A}}_H(\tau),\hat{\mathrm{H}}_H(\tau)]|\Psi_H\rangle \\ &= \frac{1}{i\hbar}\langle \Psi_S(t)|[\hat{\mathrm{A}}_S,\hat{\mathrm{H}}_S]|\Psi_S(t)\rangle = \frac{i}{\hbar}\left\langle[\hat{\mathrm{H}},\hat{\mathrm{A}}]\right\rangle_S,\end{aligned} \tag{3.137}$$

where we have again recognized that commutators and expectation values are invariants of the unitary transformation between the two pictures.

We have thus recovered (3.118) for the time evolution of expectation values in the Schrödinger dynamics. Notice, however, that (3.135) is more general than (3.118), providing the relation between *operators*, instead of their *expectation values*. Indeed, an advantage of the Heisenberg picture is that it gives rise to equations which are formally similar to those in classical mechanics. For example, the Heisenberg picture generalization of the Ehrenfest principle relations of (3.119) and (3.120) reads:

$$\frac{d\hat{\mathrm{x}}_H(t)}{dt} = \frac{\hat{\mathrm{p}}_{x,H}(t)}{m} \quad \text{and} \quad \frac{d\hat{\mathrm{p}}_{x,H}(t)}{dt} = -\frac{\partial V(\hat{\mathrm{x}}_H,t)}{\partial \hat{\mathrm{x}}_H}. \tag{3.138}$$

Finally, let us examine the equation of motion in the interaction picture introduced in Sect. 3.5, with the unitary operator of (3.91), determined by the noninteracting Hamiltonian $\hat{\mathrm{H}}_0$, now transforming the vectors and operators of the Schrödinger picture into their interaction picture analogs. Substituting the reverse transformation to that of (3.93),

$$|\Psi_S(t)\rangle = \hat{\mathrm{S}}^{-1}(t)|\Psi_I(t)\rangle = \exp\left(-\frac{i}{\hbar}\hat{\mathrm{H}}_0 t\right)|\Psi_I(t)\rangle, \tag{3.139}$$

into the Schrödinger equation (3.94) gives the corresponding dynamical equation in the *I*-picture:

$$i\hbar\frac{d|\Psi_I(t)\rangle}{dt} = \hat{\mathrm{V}}_I|\Psi_I(t)\rangle, \tag{3.140a}$$

with the time evolution now governed by the transformed interaction part $\hat{\mathrm{V}}$ of the Hamiltonian (3.90):

$$\hat{\mathrm{V}}_I = \hat{\mathrm{S}}(t)\hat{\mathrm{V}}\hat{\mathrm{S}}^{-1}(t) = \exp\left(\frac{i}{\hbar}\hat{\mathrm{H}}_0 t\right)\hat{\mathrm{V}}\exp\left(-\frac{i}{\hbar}\hat{\mathrm{H}}_0 t\right). \tag{3.140b}$$

Therefore, in the interaction picture, the time dependence of operators (3.93) reads:

$$\hat{\mathrm{A}}_I(t) = \hat{\mathrm{S}}(t)\hat{\mathrm{A}}_S\hat{\mathrm{S}}^{-1}(t) = \exp\left(\frac{i}{\hbar}\hat{\mathrm{H}}_0 t\right)\hat{\mathrm{A}}\exp\left(-\frac{i}{\hbar}\hat{\mathrm{H}}_0 t\right), \tag{3.141}$$

where the observable $\hat{\mathrm{A}} = \hat{\mathrm{A}}_S$ is time independent. It can be also expressed by the equivalent expression obtained by the differentiation with respect to time of the preceding equation [see also (3.92a) and (3.92b)]:

$$i\hbar \frac{d}{dt}\hat{\mathrm{A}}_I(t) = [\hat{\mathrm{A}}_I(t), \hat{\mathrm{H}}_0]. \tag{3.142}$$

Therefore, in the interaction picture both state vectors and operators are changing with time: the time evolution of the former is described by the Schrödinger-like (3.140a) and (3.140b), while the latter evolve in time in accordance with the Heisenberg-like (3.142). This form of quantum dynamics thus represents an intermediate level between the Schrödinger and Heisenberg pictures in treating dynamics of quantum objects. Operators depend on time as do operators in the Heisenberg picture for the noninteracting physical system described by the noninteracting Hamiltonian $\hat{\mathrm{H}}_0$, while the Schrödinger-like time dependence of the state vectors (or wave functions) is determined solely by the interaction operator $\hat{\mathrm{V}}_I$.

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