Appendix B

Quantum mechanics

Quantum kinematics

Physical states of a quantum system may be represented by elements of a complex linear vector space, (or more formally, a *Hilbert* space), and are symbolized by a *ket vector* $|\psi\rangle$. The corresponding *bra vector* $\langle\psi|$ denotes the Hermitian conjugate of $|\psi\rangle$. A bra vector $\langle\phi|$ may be applied to a ket vector $|\psi\rangle$ and defines the complex inner product of the two state vectors, $\langle\phi|\psi\rangle$. Properly normalized states satisfy $\langle\psi|\psi\rangle = 1$. If $|\phi\rangle$ and $|\psi\rangle$ are normalized states, then their inner product $\langle\phi|\psi\rangle$ may be interpreted as giving the projection of the state vector $|\psi\rangle$ onto the state $|\phi\rangle$. The funny "bra-ket" names and notation were introduced by Dirac, and give a distinctive and convenient notation for this physically important inner product. The representation of physical states by vectors in a linear space encodes the *superposition principle*: if $|\psi\rangle$ and $|\phi\rangle$ are two possible states of some physical system, then any complex linear combination $\alpha|\psi\rangle + \beta|\phi\rangle$ is also a possible physical state.

Physical observables — i.e., physical quantities which can, in principle, be measured — are represented by Hermitian linear operators. Suppose $\hat{A}$ is such an operator.[1] Being Hermitian, the eigenvalues $\{\alpha_a\}$ of $\hat{A}$ are real, and the corresponding eigenvectors (or "eigenstates") $|v_a\rangle$ are mutually orthogonal (and may be chosen to be normalized). If a physical system is prepared in some state $|\psi\rangle$ and a measurement of the quantity A is performed, the result (of an ideal measurement with negligible experimental error) will yield one of the eigenvalues α_a. If one repeatedly prepares the state $|\psi\rangle$ and measures $\hat{A}$, individual measurements in identically prepared states may yield differing eigenvalues of $\hat{A}$. If this process is repeated many, many times, the fraction p_a of measurements which yield a particular eigenvalue α_a will be given by the absolute square of the projection of the initial state $|\psi\rangle$ onto the corresponding eigenstate $|v_a\rangle$ of the observable,

$$p_a = |\langle v_a|\psi\rangle|^2 \,. \tag{B.1}$$

This is the probability that any single measurement of $\hat{A}$ in the state $|\psi\rangle$ will yield the result α_a. The projection $\langle v_a|\psi\rangle$ is called a *probability amplitude*; physical probabilities are always given by the (absolute) square of the probability amplitude. If repeated measurements of identically prepared

[1] Here and below, carets ($\wedge$) are placed over quantum operators to distinguish them from ordinary numbers — not to indicate unit vectors.

states are averaged together, the mean value of these measurements is

$$\langle \hat{A} \rangle \equiv \sum_a p_a \, \alpha_a = \sum_a \langle \psi | v_a \rangle \, \alpha_a \, \langle v_a | \psi \rangle = \langle \psi | \hat{A} | \psi \rangle \, . \tag{B.2}$$

This is referred to as the *expectation value* of the operator $\hat{A}$ in the state $|\psi\rangle$. Relations (B.1) and (B.2) are the fundamental predictions of quantum mechanics, and serve to connect the mathematical formalism to experimental observations. Quantum mechanics makes no prediction regarding the precise sequence of results obtained from repeated measurements of identically prepared systems, it only predicts the probabilities of different outcomes.

Depending on the system under consideration, the space of states may be finite dimensional or infinite dimensional. The simplest non-trivial quantum system is one with a two dimensional space of states. This can, for example, describe the spin state of a single spin-1/2 particle. Any such spin state can be written as a linear combination of two basis states which may be chosen to represent the spin pointing either up or down along some chosen axis. Denoting these basis states as $|\uparrow\rangle$ and $|\downarrow\rangle$, an arbitrary (normalized) spin state $|\psi\rangle = \alpha|\uparrow\rangle + \beta|\downarrow\rangle$ for some coefficients α and β satisfying $|\alpha|^2 + |\beta|^2 = 1$. Equivalently, the state $|\psi\rangle$ may be represented by the complex two-component vector $\binom{\alpha}{\beta}$, so that $|\uparrow\rangle$ corresponds to $\binom{1}{0}$ and $|\downarrow\rangle$ corresponds to $\binom{0}{1}$.

If one chooses the z-axis as the spin quantization axis, then the operators representing the components of angular momentum (or "spin") in the x, y, and z directions are given by $\hat{J}_1 = \frac{\hbar}{2}\,\sigma_1$, $\hat{J}_2 = \frac{\hbar}{2}\,\sigma_2$, and $\hat{J}_3 = \frac{\hbar}{2}\,\sigma_3$, respectively, where the $\{\sigma_i\}$ denote the 2×2 *Pauli matrices*,

$$\sigma_1 \equiv \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_2 \equiv \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_3 \equiv \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{B.3}$$

In this representation, $\hat{J}_3$ is diagonal and has eigenvalues $\pm\hbar/2$ with corresponding eigenvectors $\binom{1}{0}$ and $\binom{0}{1}$ representing the states $|\uparrow\rangle$ and $|\downarrow\rangle$ with definite projection of spin along the z-axis. Squaring any Pauli matrix gives the 2×2 identity matrix, $\sigma_i^2 = I$, so for any system with spin-1/2, the operator $\hat{J}^2 \equiv \sum_i \hat{J}_i^2 = \frac{3}{4}\,\hbar^2\,\hat{1}$ (where $\hat{1}$ is the identity operator). In other words, every spin state of an object with spin 1/2 is an eigenstate of $\hat{J}^2$ with eigenvalue $\frac{3}{4}\,\hbar^2$.

The angular momentum of any quantum mechanical system is quantized in either integer or half-integer multiples of $\hbar$. A system with angular momentum j has a $2j+1$ dimensional space of spin states. The projection of angular momentum along some chosen spin quantization axis, say the z-axis, can take on $2j+1$ possible values: $j, j-1, \cdots, -(j-1), -j$ (times $\hbar$). These are the eigenvalues of the angular momentum operator $\hat{J}_3$. Different components of angular momentum do not commute, and hence are not simultaneously diagonalizable. Rather, they satisfy the commutation relation

$$[\hat{J}_i,\, \hat{J}_j] = i\hbar\,\epsilon_{ijk}\,\hat{J}_k \, , \tag{B.4}$$

where the antisymmetric symbol ϵ_{ijk} is $+1$ if (ijk) is an even permutation of (123), -1 if (ijk) is an odd permutation of (123), and 0 otherwise. The square of the angular momentum $\hat{J}^2 \equiv \sum_i \hat{J}_i^2$ does commute with the individual angular momentum components. For a system with angular momentum j, $\hat{J}^2$ is proportional to the identity operator,

$$\hat{J}^2 = j(j+1)\,\hbar^2\,\hat{1} \, . \tag{B.5}$$

Hence, specifying the spin j of a system is equivalent to specifying the eigenvalue of $\hat{J}^2$.

In many circumstances (including multi-particle systems like atoms or molecules) one is interested in a quantum system containing two or more subsystems. Suppose a system has two subsystems, A and B. The angular momentum of the total system is the sum of the angular momenta of the subsystems, $\vec{J}^{\rm tot} = \vec{J}^A + \vec{J}^B$. Suppose subsystem A is known to have spin j^A, and subsystem B has spin j^B. Hence $(\vec{J}^A)^2 = j^A(j^A+1)$ and $(\vec{J}^B)^2 = j^B(j^B+1)$. One can show that the total spin $j^{\rm tot}$ of the combined system must be one of the values $\{j_{\rm min},\, j_{\rm min}{+}1,\, \cdots,\, j_{\rm max}{-}1,\, j_{\rm max}\}$ where

$$j_{\rm min} = |j^A - j^B|\,, \qquad j_{\rm max} = j^A + j^B\,. \tag{B.6}$$

Any system which moves (in ordinary 3-dimensional space) will have an infinite dimensional space of states. In such systems, the position $\vec{X}$ and momentum $\vec{P}$ are basic quantum operators. Position operators mutually commute, $[\hat{X}_i, \hat{X}_j] = 0$, and hence may be simultaneously diagonalized. One may introduce a basis of position eigenstates $\{|\vec{x}\rangle\}$ satisfying the delta-function orthonormality relation,

$$\langle\vec{x}|\vec{y}\rangle = \delta^3(\vec{x}-\vec{y})\,, \tag{B.7}$$

and corresponding completeness relation

$$\hat{1} = \int d^3x\, |\vec{x}\rangle\langle\vec{x}|\,. \tag{B.8}$$

An arbitrary quantum state $|\psi\rangle$ (with no additional degrees of freedom) may be represented as a superposition of position eigenstates,

$$|\psi\rangle = \int d^3x\, |\vec{x}\rangle\, \Psi(\vec{x})\,. \tag{B.9}$$

The amplitude $\Psi(\vec{x})$ is the *position space wavefunction*, equal to the projection of the given state $|\psi\rangle$ onto position eigenstates, $\Psi(\vec{x}) \equiv \langle\vec{x}\,|\psi\rangle$. Momentum operators also mutually commute, $[\hat{P}_i, \hat{P}_j] = 0$, and may be simultaneously diagonalized. It is convenient to define a basis of momentum eigenstates $\{|\vec{p}\rangle\}$ to satisfy the orthonormality relation

$$\langle\vec{p}|\vec{p}\,'\rangle = (2\pi\hbar)^3\delta^3(\vec{p}-\vec{p}\,')\,, \tag{B.10}$$

so the corresponding completeness relation takes the form

$$\hat{1} = \int \frac{d^3p}{(2\pi\hbar)^2}\, |\vec{p}\rangle\langle\vec{p}|\,. \tag{B.11}$$

An arbitrary quantum state $|\psi\rangle$ may also be represented as a superposition of momentum eigenstates,

$$|\psi\rangle = \int \frac{d^3p}{(2\pi\hbar)^3}\, |\vec{p}\rangle\, \widetilde{\Psi}(\vec{p})\,, \tag{B.12}$$

where the *momentum space wavefunction* $\widetilde{\Psi}(\vec{p})$ is the projection of the given state $|\psi\rangle$ onto momentum eigenstates, $\widetilde{\Psi}(\vec{p}) \equiv \langle\vec{p}\,|\psi\rangle$. Corresponding components of position and momentum do not commute,

$$[\hat{P}_i, \hat{X}_j] = \frac{\hbar}{i}\,\delta_{ij}\,, \tag{B.13}$$

and hence cannot be simultaneously diagonalized. This non-vanishing commutator leads to the *uncertainty relation* $\Delta x_i\,\Delta p_j \geq \frac{1}{2}\hbar\,\delta_{ij}$, where $\Delta x_i \equiv \left[\langle\hat{X}_i^2\rangle - \langle\hat{X}_i\rangle^2\right]^{1/2}$ is the uncertainty (or standard deviation) of $\hat{X}_i$ in some given quantum state, and $\Delta p_j \equiv \left[\langle\hat{P}_j^2\rangle - \langle\hat{P}_j\rangle^2\right]^{1/2}$ is the analogous uncertainty of $\hat{P}_j$ in the same state.

The overlap between position and momentum eigenstates is given by an exponential phase factor,

$$\langle \vec{x}|\vec{p}\rangle = e^{i\vec{p}\cdot\vec{x}/\hbar}\,. \tag{B.14}$$

In other words, the position space wavefunction of the state $|\vec{p}\rangle$ with definite momentum is a plane wave, $e^{i\vec{p}\cdot\vec{x}/\hbar}$. More generally, position and momentum space wavefunctions of any state $|\psi\rangle$ are related via Fourier transforms,

$$\widetilde{\Psi}(\vec{p}) = \int d^3x\, \langle\vec{p}|\vec{x}\rangle\langle\vec{x}|\psi\rangle = \int d^3x\, e^{-i\vec{p}\cdot\vec{x}/\hbar}\,\Psi(\vec{x})\,, \tag{B.15}$$

$$\Psi(\vec{x}) = \int \frac{d^3p}{(2\pi\hbar)^3}\,\langle\vec{x}|\vec{p}\rangle\langle\vec{p}|\psi\rangle = \int \frac{d^3p}{(2\pi\hbar)^3}\; e^{i\vec{p}\cdot\vec{x}/\hbar}\,\widetilde{\Psi}(\vec{p})\,. \tag{B.16}$$

Quantum dynamics

The state of a quantum system will evolve with time. If $|\psi(0)\rangle$ denotes the state of some quantum system at time $t = 0$, then the state $|\psi(t)\rangle$ of the system at some later time t is the solution of the linear evolution equation

$$i\hbar\,\frac{d}{dt}\,|\psi(t)\rangle = \hat{H}(t)\,|\psi(t)\rangle\,, \tag{B.17}$$

known as the *time dependent Schrodinger equation*, with the specified initial condition $|\psi(0)\rangle$. The linear operator $\hat{H}(t)$ is called the *Hamiltonian*; acting on any state at time t, $\hat{H}(t)$ yields the time derivative of the state (times $i\hbar$). The Hamiltonian must be Hermitian, $\hat{H}^\dagger = \hat{H}$, which implies that its eigenvalues are real. If the Hamiltonian has no explicit time dependence, $\hat{H}(t) = \hat{H}$, then the solution of the Schrodinger equation (B.17) involves an exponential of the Hamiltonian,[2]

$$|\psi(t)\rangle = e^{-i\hat{H}t/\hbar}\,|\psi(0)\rangle\,. \tag{B.18}$$

The exponential $\hat{U}(t) \equiv e^{-i\hat{H}t/\hbar}$ is the *time evolution operator*; the Hermiticity of the Hamiltonian implies that (for real values of t) the time evolution operator is unitary, $\hat{U}(t)^{-1} = \hat{U}(t)^\dagger = \hat{U}(-t)$.

In addition to defining time evolution, the Hamiltonian is also the operator which represents the *energy* of a quantum system. Eigenvalues $\{E_a\}$ of the Hamiltonian are called *energy levels*. The corresponding eigenstates $\{|v_a\rangle\}$ satisfy the *time independent Schrodinger equation*

$$\hat{H}\,|v_a\rangle = E_a\,|v_a\rangle\,. \tag{B.19}$$

If an initial state equals some eigenstate of the Hamiltonian, $|\psi(0)\rangle = |v_a\rangle$, then the state merely acquires an overall phase factor under time evolution,

$$|\psi(t)\rangle = e^{-iE_at/\hbar}\,|v_a\rangle\,. \tag{B.20}$$

Such states are called *stationary states*. The expectation value of any quantum operator in such a state is independent of time.

[2]The exponential of an Hermitian operator (or matrix) is defined by the exponential of its eigenvalues in a basis where the operator is diagonal. If an Hermitian operator $\hat{A}$ has eigenvalues α_a and corresponding eigenvectors $|v_a\rangle$, then $e^{\hat{A}} \equiv \sum_a |v_a\rangle\, e^{\alpha_a}\, \langle v_a|$.