States: In quantum mechanics the state of a system encodes all knowledge of its physical properties. The set of all possible states is a complex vector space known as its Hilbert space. Figure 1) illustrates the (complex) two-dimensional space for a spin 1/2 particle. We employ Dirac’s bra(c)ket notation in which the state with spin up along $\hat{z}$ is denoted as a “ket”-vector represented by the symbol $|\uparrow\rangle$, $|+\hat{z}\rangle$, or if the context is clear, simply as $|+\rangle$; the spin down state is $|\downarrow\rangle$, $|-\hat{z}\rangle$, or $|\rangle$. We assume these basis states are normalized to have length 1. However, a state vector can be multiplied by an arbitrary complex number $\alpha$ without altering its physical properties. For example $\alpha|+\hat{z}\rangle$ still represents the physical state of spin up along the $+\hat{z}$ axis, even for the case $\alpha = -1$.

One of the strange properties of quantum mechanics is the possibility to create a superposition state such as $|\psi\rangle = \alpha|+\hat{z}\rangle + \beta|-\hat{z}\rangle$. The complex number $\alpha$ represents the amplitude of the projection of $|\psi\rangle$ onto $|+\hat{z}\rangle$ and $\beta$ the amplitude for $|-\hat{z}\rangle$. Geometrically, the amplitude of a state vector $|\psi\rangle$ projected onto a unit vector $|\phi\rangle$ is the dot product of the two vectors, denoted $\langle\phi|\psi\rangle$. The projection itself lies in the direction of $|\phi\rangle$, hence the projection of $|\psi\rangle$ onto a $|\phi\rangle$ is $(\langle\phi|\psi\rangle)|\phi\rangle = (|\phi\rangle\langle\phi||\psi\rangle)$. The useful combination $|\phi\rangle\langle\phi|$ is known as the projector onto $|\phi\rangle$. The symbol $\langle+\phi|$ that is used to perform the inner product is known as a “bra”-vector and is dual to the ket vector $|+\phi\rangle$. The dual to the ket-vector $|\psi\rangle$ is the bra-vector $\langle\psi| \alpha^*\langle+\hat{z}| + \beta^*\langle-\hat{z}|$.

States with mutually exclusive properties, such as $\pm\hat{z}$, are orthogonal. Thus $\langle+\hat{z}| -\hat{z}\rangle = \langle-\hat{z}| +\hat{z}\rangle = 0$. The inner product of a vector with itself is the square of its norm, $||\psi||^2 = \langle\psi|\psi\rangle = |\alpha|^2 + |\beta|^2$. The vector is normalized, i.e. a unit vector, if $||\psi||^2 = 1$. 

Figure 1: Hilbert space of spin 1/2 particle. Horizontal and vertical axes represent the rays $\{\alpha|+\hat{z}\rangle\}$ and $\{\beta|-\hat{z}\rangle\}$ (with $\alpha, \beta \in \mathbb{C}$). The unit circle is the set $|\alpha|^2 + |\beta|^2 = 1$. An arbitrary state vector $|\psi\rangle = \alpha|+\hat{z}\rangle + \beta|-\hat{z}\rangle$. The state $|\psi\rangle$ shown is normalized because it lies on the unit circle.
Operators: Observable properties such as spin, magnetic moment, energy, etc. are represented in quantum mechanics by operators. For example, in a state $|E\rangle$ of known energy $E$, the energy operator (also called the Hamiltonian $H$) acting on the state returns the state itself multiplied by its energy, $H|E\rangle = E|E\rangle$. Thus the state of known energy $|E\rangle$ is an eigenvector of $H$ with eigenvalue $E$. If the state is a superposition of states with different energies, e.g. $|\psi\rangle = \alpha_1|E_1\rangle + \alpha_2|E_2\rangle$, then $H|\psi\rangle = \alpha_1E_1|E_1\rangle + \alpha_2E_2|E_2\rangle$.

For a spin-1/2 particle, states with spin up or down along the $\hat{z}$ axis are eigenstates of the $z$-component of spin, $S_z$, so that $S_z|\pm\hat{z}\rangle = \pm(h/2)|\pm\hat{z}\rangle$. Taking the kets $|\pm\hat{z}\rangle$ as a basis, we can represent the spin operator as a $2 \times 2$ matrix,

$$S_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$ 

The 3-dimensional spin vector operator can be expressed as $S = (\hbar/2)\vec{\sigma}$, where $\vec{\sigma}$ is a vector of Pauli matrices with components

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$ 

Particles cannot simultaneously possess definite values of the spin along different axes because of the lack of commutation between different Pauli matrices. For example, $\sigma_x\sigma_z \neq \sigma_z\sigma_x$. You can check that the superposition state $|\psi\rangle = (|+\hat{z}\rangle + |-\hat{z}\rangle)/\sqrt{2}$ is an eigenstate of $S_x$ with eigenvalue $+h/2$, but it is not an eigenstate of $S_z$. This seeming contradiction shows that we cannot specify the $\hat{x}$ and $\hat{z}$ properties simultaneously; they are incompatible.

We will often consider electrons coupled with magnetic fields via their magnetic moments $\mathbf{m} = -g\mu_B\mathbf{S}/\hbar$. Here the $-$ sign enters because of the negative charge on the electron, $g \approx 2$ is the $g$-factor, and $\mu_B = e\hbar/2mc$ is the Bohr magneton. The energy of a magnetic moment in an applied magnetic field $\mathbf{B}$ is $-\mathbf{m} \cdot \mathbf{B}$, hence the Hamiltonian for an electron in a magnetic field $\mathbf{B} = B\hat{z}$ is

$$H = \mu_B B \sigma_z.$$
where the $g \approx 2$ has canceled against the $1/2$ from the electron spin. Note that spin up ($m$ opposite to $B$) has high energy $+\mu_B B$ and spin down has low energy $-\mu_B B$.

Any operator $\mathcal{A}$ can be represented as a matrix in an orthonormal basis. Let $\{|m]\}$ be a complete basis for the Hilbert space. Then we can express the identity operator as

$$I = \sum_m |m\rangle\langle m|$$

and we can write

$$\mathcal{A} = I\mathcal{A}I = \sum_m |m\rangle\langle m| \sum_n |n\rangle\langle n| = \sum_{mn} |m\rangle A_{mn} \langle n|$$

where $A_{mn} = \langle m|\mathcal{A}|n\rangle$ is the matrix element of $\mathcal{A}$ between states $|m\rangle$ and $|n\rangle$. In particular $\mathcal{A}$ can be represented as a diagonal matrix in the basis of normalized eigenvectors $\{|v_j\rangle\}$ with the corresponding eigenvalues $\{\lambda_j\}$ along the diagonal. Alternatively, we may form the projectors $|v_j\rangle\langle v_j|$ and write a projective decomposition of the operator as

$$\mathcal{A} = \sum_j \lambda_j |v_j\rangle\langle v_j| = \sum_j |v_j\rangle \lambda_j \langle v_j|.$$

The eigenvector $|v_j\rangle$ represents the state in which the physical property $\mathcal{A}$ takes the value $\lambda_j$.

**Probability:** According to the probabilistic rule of Born, the probability that a state $|\psi\rangle$ possesses the value $\lambda_j$ of a physical observable $\mathcal{A}$ is the squared norm of the projection of $|\psi\rangle$ onto $|v_j\rangle$,

$$\text{Pr} (A = \lambda_j) = |\langle v_j|\psi\rangle|^2.$$

Here we assume that both $|\psi\rangle$ and $|v_j\rangle$ are normalized; otherwise we would need to divide by their squared norms.

For example, in the normalized state $|\psi\rangle = \alpha|+\hat{z}\rangle + \beta|{-}\hat{z}\rangle$ the probability that the moment is up equals $|\alpha|^2$, and the probability the moment is down equals $|\beta|^2$. Since the moment
must be either up or down, we confirm that \( \langle \psi | \psi \rangle = |\alpha|^2 + |\beta|^2 = 1 \). Consider a state such as \( |\psi\rangle = (|\hat{z}\rangle + |-\hat{z}\rangle)/\sqrt{2} \). This state has 50% probability to be up in the \( \hat{z} \) direction, and 50% probability to be down. Curiously, as shown in the previous section, this particular state has also 100% probability to have its moment in the positive \( \hat{x} \) direction.

Since we know the probability to have a certain property (e.g. the value of the energy or the magnetic moment) we can calculate the expectation value of the property. This is the probability-weighted average of possible values and is also the predicted average if the property were to be measured repeatedly in multiple instances of the same state. Let \( \{v_j\} \) be the set of possible values and \( \text{Pr}(v_j) \) be their probabilities, then the expectation value

\[
\langle v \rangle = \sum_j v_j \text{Pr}(v_j).
\]

For example, the possible electron magnetic moments along \( \hat{z} \) are \( m_z = \pm \mu_B \) and the average moment is

\[
\langle m_z \rangle = (|\beta|^2 - |\alpha|^2)\mu_B.
\]

Since the energy \( E = -m_z B \), the expectation value of the Hamiltonian is

\[
\langle H \rangle = (|\alpha|^2 - |\beta|^2)\mu_B B = -\langle m_z \rangle B.
\]

In general we can use the projective decomposition of the operator \( A \) to evaluate the average of \( A \) in any state \( |\psi\rangle \). Since the probability of eigenvalue \( \lambda_j \) is

\[
\text{Pr}(\lambda_j) = |\langle v_j | \psi \rangle|^2 = \langle \psi | v_j \rangle \langle v_j | \psi \rangle,
\]

then summing over all eigenvectors results in

\[
\langle A \rangle = \sum_j \langle \psi | v_j \rangle \lambda_j \langle v_j | \psi \rangle \equiv \langle \psi | A | \psi \rangle.
\]

A separate type of probability enters if we lack information about the state of the system. Say we prepare the system in such a way that it enters state \( |\psi\rangle \) with probability \( P_\psi \) but it enters a different orthogonal state \( |\phi\rangle \) with probability \( P_\phi \). We refer to the individual states \( |\psi\rangle \) and \( |\phi\rangle \) as pure states, and the combination as a mixed state. In a mixed state, the average value of any observable is the probability-weighted average of the individual pure
state expectation values. In the pure states $|\psi\rangle$ and $|\phi\rangle$ the expectation values are $\langle \psi | A | \psi \rangle$ and $\langle \phi | A | \phi \rangle$. Hence, in the mixed state, the expectation value $\langle A \rangle = P_\psi \langle \psi | A | \psi \rangle + P_\phi \langle \phi | A | \phi \rangle$.

**Density operator:** Another way to calculate expectation values, that will generalize nicely to quantum statistical mechanics, is through the use of a *density operator*. Given a normalized quantum state $|\psi\rangle$, we call the projector $\rho = |\psi\rangle\langle \psi |$ the density operator of the pure state $|\psi\rangle$. If we wish we can represent $\rho$ as a matrix in some orthonormal basis basis $\{|m\rangle\}$. Write $|\psi\rangle = \sum_m c_m |m\rangle$ with $c_m = \langle m | \psi \rangle$ and $\langle \psi | = \sum_n c_n^* \langle n |$ with $c_n^* = \langle \psi | n \rangle$ so that $\rho = \sum_{mn} c_m c_n^* |n\rangle\langle m|$ has matrix elements $\rho_{mn} = \langle m | n \rangle = c_m c_n^*$. Notice that $\text{Tr} \rho = \sum_m |c_m|^2 = 1$, which always holds for density operators, and also $\rho^2 = \rho$ (because $\rho$ is a projector) so that $\text{Tr} \rho^2 = 1$, which holds only for pure states.

To evaluate the expectation value of an observable, $A$, consider

$$\langle A \rangle_\rho = \langle \psi | A | \psi \rangle$$

$$= \sum_{mn} \langle \psi | m \rangle A_{mn} \langle n | \psi \rangle$$

$$= \sum_{mn} \langle n | \psi \rangle \langle \psi | m \rangle A_{mn}$$

$$= \sum_n \left( \sum_m \rho_{mn} A_{mn} \right)$$

$$= \text{Tr} (\rho A).$$

Now, consider a mixed state $\rho = \sum_k p_k |\psi_k\rangle\langle \psi_k |$, where $0 < p_k < 1$ is the probability to be in the $k^{th}$ orthogonal pure state $|\psi_k\rangle$. Note that $\text{Tr} (\rho) = \sum_k p_k = 1$, however $\rho^2 \neq \rho$ and $\text{Tr} (\rho^2) = \sum_k p_k^2 < 1$ in a mixed state. As the expectation value of $A$ is given by the average of pure state expectation values $\text{Tr} (|\psi_k\rangle\langle \psi_k | A)$ weighted by the probabilities $p_k$, we have

$$\langle A \rangle_\rho = \text{Tr} (\rho A),$$

as before.
Schrödinger equation: The Schrödinger equation

\[ i\hbar \frac{\partial}{\partial t} |\psi\rangle = H|\psi\rangle \]

governs the time evolution of the quantum state \( |\psi\rangle \), where \( H \) is the Hamiltonian. If \( |\psi\rangle \) is an eigenstate of the Hamiltonian with energy \( E \equiv \hbar \omega \), then the Schrödinger equation has the simple solution

\[ |\psi\rangle(t) = e^{-i\omega t} |\psi\rangle(0). \]

If \( |\psi\rangle \) is not an energy eigenstate, then it can be expanded in a basis of energy eigenstates,

\[ |\psi\rangle = \sum_n c_n(t) |n\rangle \]

where \( |n\rangle \) obey \( H|n\rangle = E_n|n\rangle \) and \( c_n(t) = c_n(0)e^{-iE_n t/\hbar} \).

Note that the condition for \( |\psi\rangle \) to be an energy eigenstate is

\[ H|\psi\rangle = E|\psi\rangle. \]

This equation is known as the time independent Schrödinger equation. If the Hamiltonian \( H \) can be expressed as an ordinary matrix (e.g. as for a spin 1/2 system) then it becomes an ordinary eigenvalue equation. In other cases the Hamiltonian can be a differential operator, and the time independent Schrödinger equation becomes a differential equation. For example, for a particle of mass \( m \) moving continuously in a potential \( V(\mathbf{r}) \), the Hamiltonian is

\[ H = \frac{\mathbf{P}^2}{2m} + V(\mathbf{r}) \]

where

\[ \mathbf{P} = \frac{i\hbar}{\hbar} \nabla \]

is the momentum operator, and \( \mathbf{P}^2 = -\hbar^2 \nabla^2 \). The quantum state \( |\psi\rangle \) becomes a wavefunction \( \psi(\mathbf{r}) = \langle \mathbf{r}|\psi\rangle \), with \( \rho(\mathbf{r}) = |\psi(\mathbf{r})|^2 \) the probability density for the particle at position \( \mathbf{r} \).
Free particle motion occurs when the potential vanishes. In this case the time independent Schrödinger equation has solutions of the form \( \psi_k(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} \) with energy \( E(k) = \frac{\hbar^2 |k|^2}{2m} \), and the time dependent Schrödinger equation has plane wave solutions

\[ \psi_k(\mathbf{r}, t) = e^{i(k \cdot \mathbf{r} - \omega t)} \]

where \( \omega = \frac{E(k)}{\hbar} \). Notice that we have a continuum of possible states, indexed by the wavevector \( k \), with the dispersion relation \( \omega(k) \).

Sometimes we will apply special boundary conditions (e.g. confinement to a box, or periodic boundaries), in which case the allowed values of \( k \) (and hence \( E(k) \)) become quantized. For a particle confined to a box via the potential

\[ V(x) = \begin{cases} 0 & 0 < x < L \\ +\infty & \text{else,} \end{cases} \]

the eigenstates are \( \psi(x) = \sqrt{2/L} \sin(k_n x) \). Here \( k_n = n\pi/L \), with \( n \) a positive integer, so that \( \psi \) vanishes at \( x = 0 \) and \( L \). With periodic boundary conditions such that \( \psi(x + L) = \psi(x) \), the eigenstates are \( \sqrt{1/L} e^{ik_n x} \) with \( k_n = 2\pi/L \) and \( n \) an integer. In both cases the energies are \( E_n = \hbar^2 k_n^2 / 2m \).

The simple harmonic oscillator, characterized by the potential

\[ V(x) = \frac{1}{2} K x^2 = \frac{1}{2} m \omega^2 x^2 \]

is another important example. In this case the wavefunctions take the form of Gaussians multiplied by Hermite polynomials, and the energies are quantized as

\[ E_n = (n + 1/2)\hbar \omega. \]