Thermal Physics 2: Quantum Mechanics Review

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 α 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 α represents the amplitude of the projection of $|\psi\rangle$ onto $|+\hat{z}\rangle$ and β 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 $\langle\psi| = \alpha^*\langle+\hat{z}| + \beta^*\langle-\hat{z}|$.

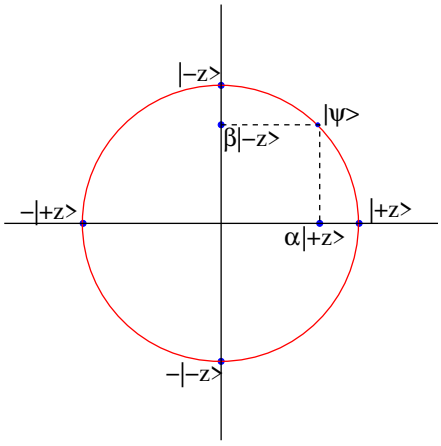

Figure 1: Hilbert space of spin 1/2 particle. Horizontal and vertical axes represent the rays $\{\alpha|+\hat{z}\rangle\}$ and $\{\beta|-\hat{z}\rangle\}$ (with $\alpha, \beta \in \mathbb{C}$). The unit circle is the set $|\alpha|^2 + |\beta|^2 = 1$. An arbitrary state vector $|\psi\rangle = \alpha|+\hat{z}\rangle + \beta|-\hat{z}\rangle$. The state $|\psi\rangle$ shown is normalized because it lies on the unit circle.

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, $||\psi\rangle|^2 = \langle\psi|\psi\rangle = |\alpha|^2 + |\beta|^2$. The vector is normalized, *i.e.* a unit vector, if $||\psi\rangle|^2 = 1$.

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 multipled 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 $H|\psi\rangle = \alpha_1 E_1|E_1\rangle + \alpha_2 E_2|E_2\rangle$.

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 $S_z|\pm\hat{z}\rangle = \pm(\hbar/2)|\pm\hat{z}\rangle$. Taking the kets $|\pm\hat{z}\rangle$ as a basis, we can represent the spin operator as a 2×2 matrix,

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

The 3-dimensional spin vector operator can be expressed as $\mathbf{S} = (\hbar/2)\vec{\sigma}$, 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 $+\hbar/2$, 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 ($\mathbf{m}$ opposite to $\mathbf{B}$) 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 $\{|m\rangle\}$ 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

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

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 λ_j.

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

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

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 $\Pr(v_j)$ be their probabilities, then the expectation value

$$\langle v\rangle = \sum_j v_j \Pr(v_j).$$

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 $\mathcal{A}$ to evaluate the average of $\mathcal{A}$ in any state $|\psi\rangle$. Since the probability of eigenvalue λ_j is

$$\Pr(\lambda_j) = |\langle v_j|\psi\rangle|^2 = \langle\psi|v_j\rangle\langle v_j|\psi\rangle,$$

then summing over all eigenvectors results in

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

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_ψ but it enters a different orthogonal state $|\phi\rangle$ with probability P_ϕ. 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 $\langle\psi|\mathcal{A}|\psi\rangle$ and $\langle\phi|\mathcal{A}|\phi\rangle$. Hence, in the mixed state, the expectation value $\langle\mathcal{A}\rangle = P_\psi\langle\psi|\mathcal{A}|\psi\rangle + P_\phi\langle\phi|\mathcal{A}|\phi\rangle$.

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 ρ 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 $\rho_{mn} = \langle m|\rho|n\rangle = c_m c_n^*$. Notice that Tr $\rho = \sum_m |c_m|^2 = 1$, which always holds for density operators, and also $\rho^2 = \rho$ (because ρ is a projector) so that Tr $\rho^2 = 1$, which holds only for pure states.

To evaluate the expectation value of an observable, $\mathcal{A}$, consider

$$\begin{aligned}
\langle\mathcal{A}\rangle_\rho &= \langle\psi|\mathcal{A}|\psi\rangle \\
&= \sum_{mn}\langle\psi|m\rangle A_{mn}\langle n|\psi\rangle \\
&= \sum_{mn}\langle n|\psi\rangle\langle\psi|m\rangle A_{mn} \\
&= \sum_n\left(\sum_m \rho_{nm}A_{mn}\right) \\
&= \text{Tr }(\rho\mathcal{A}).
\end{aligned}$$

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 Tr $(\rho) = \sum_k p_k = 1$, however $\rho^2 \neq \rho$ and Tr $(\rho^2) = \sum_k p_k^2 < 1$ in a mixed state. As the expectation value of $\mathcal{A}$ is given by the average of pure state expectation values Tr $(|\psi_k\rangle\langle\psi_k|\mathcal{A})$ weighted by the probabilities p_k, we have

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

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 $c_n(t) = c_n(0)e^{-iE_nt/\hbar}$.

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 *in*dependent 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

$$\mathbf{P} = \frac{\hbar}{i}\nabla$$

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 $\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}$ with energy $E(\mathbf{k}) = \hbar^2|\mathbf{k}|^2/2m$, and the time dependent Schrödinger equation has plane wave solutions

$$\psi_{\mathbf{k}}(\mathbf{r}, t) = e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}$$

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

Sometimes we will apply special boundary conditions (*e.g.* confinement to a box, or periodic boundaries), in which case the allowed values of $\mathbf{k}$ (and hence $E(\mathbf{k})$) 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 ψ 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

$$V(x) = \frac{1}{2}Kx^2 = \frac{1}{2}m\omega^2 x^2$$

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

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