Chapter 1 of Atkins, "Molecular Quantum Mechanics", 5th edition.

Mathematical framework of non-relativistic quantum mechanics

The unified mathematical framework of quantum mechanics has emerged as a generalization of a large number of partially successful attempts at creating a physical theory of microscopic processes. At the time of writing, no violations of quantum mechanical equations of motion have ever been observed, although it is clear that quantum mechanics (in which space is a container) is fundamentally incompatible with the general theory of relativity (in which space is a participant). The following statements may be viewed as a summary of one-dimensional non-relativistic quantum mechanics from the mathematical perspective:

1. Any quantum system can be described by a complex-valued function, called *wavefunction*, of co-ordinates and time. Such functions populate a Hilbert space, called the *state space* of the system. The norm and the scalar product on this space are defined as:

$$\left\| f(x) \right\| = \sqrt{\int f^*(x) f(x)\, dx} \qquad \left\langle f(x) \middle| g(x) \right\rangle = \int f^*(x) g(x)\, dx$$

   where the star denotes complex conjugation and the integration is carried out over all coordinates of the system. Wavefunctions of physical systems are continuous and have an infinite number of continuous derivatives.

2. The *expectation value* (defined as the average outcome of many repeated experiments) of an observable property $O(t)$ of a quantum system with a wavefunction $\psi(x,t)$ is related to the wavefunction in the following way:

$$O(t) = \left\langle \psi(x,t) \middle| \hat{O} \middle| \psi(x,t) \right\rangle = \int \psi^*(x,t)\, \hat{O} \psi(x,t)\, dx$$

   where $\hat{O}$ is a linear operator. Simple commonly occurring operators are coordinate $\hat{x}$, momentum $\hat{p}$ and kinetic energy $\hat{T}$:

$$\hat{x} = x \qquad \hat{p} = -i\frac{\partial}{\partial x} \qquad \hat{T} = \frac{1}{2m}\frac{\partial^2}{\partial x^2}$$

   Operators of physical observables are Hermitian, *i.e.* $\left\langle \hat{O}f(x,t) \middle| g(x,t) \right\rangle = \left\langle f(x,t) \middle| \hat{O}g(x,t) \right\rangle$, for all wavefunctions f and g. It may be shown that eigenvalues of such operators are real and their eigenfunctions belonging to different eigenvalues are orthogonal.

3. The wavefunction obeys the *time-dependent Schrödinger equation*:

$$\frac{\partial}{\partial t}\middle| \psi(x,t) \right\rangle = -i\hat{H}(x,t) \middle| \psi(x,t) \right\rangle$$

   where $\hat{H}(x,t)$ is the operator that corresponds to the energy of the system. By analogy with classical mechanics it is called *Hamiltonian*. Its eigenvalues are known in chemistry as *energy levels* and its eigenfunctions, in the case of molecular quantum systems, are called *orbitals*. A passable derivation for the Schrödinger equation may be built on the philosophical principle of causality and the theory of Lie groups. A rigorous derivation does not, at the moment, appear to exist.

4. The absolute square of the wavefunction $\left|\psi\left(x,t\right)\right|^{2}$ is the *probability density* of the system being found at the coordinate x at time t. The probability theory requirement for the sum total of all probabilities to be equal to 1

$$\int \left|\psi\left(x,t\right)\right|^{2} dx = 1$$

then yields the *normalization condition* for the wavefunction:

$$\left\|\psi\left(x,t\right)\right\| = 1$$

5. A measurement of an observable property O performed on a system in a state described by an eigenfunction $\left|\varphi_{k}\right\rangle$ of the corresponding operator $\hat{O}$

$$\hat{O}\left|\varphi_{k}\right\rangle = \lambda_{k}\left|\varphi_{k}\right\rangle$$

yields the corresponding eigenvalue λ_{k} with the probability of 1. A measurement of O performed on a system that is described by a linear combination of eigenfunctions of $\hat{O}$:

$$\left|\psi\right\rangle = a_{1}\left|\varphi_{1}\right\rangle + a_{2}\left|\varphi_{2}\right\rangle + a_{3}\left|\varphi_{3}\right\rangle + \ldots$$

yields λ_{1} with probability $\left|a_{1}\right|^{2}$, λ_{2} with probability $\left|a_{2}\right|^{2}$ and so on. The normalization condition for linear combinations of wavefunctions is therefore $\left|a_{1}\right|^{2} + \left|a_{2}\right|^{2} + \left|a_{3}\right|^{2} + \ldots = 1$.

Quantum mechanics is often described as strange and counter-intuitive. That is not the case – the properties listed above are in many ways natural for Hilbert spaces. The only real requirement is good working knowledge of the relevant areas of mathematics.

Time-dependent and time-independent Schrödinger equations

In the case when the Hamiltonian is time-independent, the formal variable separation procedure may be applied to the Schrödinger equation in general (it also works in the time-dependent Hamiltonian case, but the derivation is longer and less elegant):

$$\frac{\partial}{\partial t}\left|\psi\left(x,t\right)\right\rangle = -i\hat{H}\left(x\right)\left|\psi\left(x,t\right)\right\rangle \qquad \left|\psi\left(x,t\right)\right\rangle = \sum_{km} a_{km} f_{k}\left(x\right) g_{m}\left(t\right) \qquad (1)$$

Where $\hat{H}\left(x\right)$ indicates that the Hamiltonian is *acting on* functions of the variable x. To simplify notation, we will eventually drop the $\left(x\right)$ bracket. After using the generic $f\left(x\right)g\left(t\right)$ ansatz, we get:

$$\frac{\partial}{\partial t} f\left(x\right) g\left(t\right) = -i\hat{H}\left(x\right) f\left(x\right) g\left(t\right) \quad \Rightarrow \quad \frac{i}{g\left(t\right)}\frac{\partial}{\partial t} g\left(t\right) = \frac{1}{f\left(x\right)}\hat{H}\left(x\right) f\left(x\right) \qquad (2)$$

By the same argument as in the previous lecture, both terms must be independently equal to a constant. Because the Hamiltonian is the energy operator, that constant has the dimension of energy:

$$\begin{cases} \dfrac{i}{g\left(t\right)}\dfrac{\partial}{\partial t} g\left(t\right) = E \\[2ex] \dfrac{1}{f\left(x\right)}\hat{H}f\left(x\right) = E \end{cases} \quad \Rightarrow \quad \begin{cases} \dfrac{\partial}{\partial t} g\left(t\right) = -iEg\left(t\right) \\[2ex] \hat{H}f\left(x\right) = Ef\left(x\right) \end{cases} \quad \Rightarrow \quad \psi\left(x,t\right) = \sum_{k} a_{k} f_{k}\left(x\right) e^{-iE_{k}t} \qquad (3)$$

The equation in this system that involves the Hamiltonian:

$$\hat{H}f\left(x\right) = Ef\left(x\right) \qquad (4)$$

is often called the *time-independent Schrödinger equation*. It is clear that this is simply an eigensystem problem for the Hamiltonian operator. We have solved exactly such problem a few lectures ago for the harmonic oscillator. Some confusion can occur here because many textbooks use $|\psi(x)\rangle$ to denote the coordinate part of the full wavefunction $|\psi(x,t)\rangle$:

$$\hat{H}|\psi(x)\rangle = E|\psi(x)\rangle \tag{5}$$

Based on the methods for solving partial differential equations that have been introduced in the previous lecture, the flowchart for solving the full Schrödinger equation can be summarised as follows:

1. Separate the variables as shown in Equations (2) and (3).

2. Solve the eigensystem problem for the Hamiltonian operator and apply the boundary conditions to obtain $f_k(x)$ and E_k.

3. Assemble the general solution shown in Equation (3) and obtain the coefficients a_k from the initial condition.

Very few instances of the Schrödinger equation have analytical solutions. Those solutions tend to be complicated and often involve numerically difficult functions, sums and integrals. Modern quantum mechanics operates almost exclusively using matrix representations.

Matrix representations

Choosing a particular basis set of orthogonal and normalized functions $\{g_k(x)\}$ transforms the time-independent Schrödinger equation into a matrix-vector equation:

$$\hat{H}|\psi(x)\rangle = E|\psi(x)\rangle \qquad |\psi(x)\rangle = \sum_k a_k |g_k(x)\rangle$$

$$\Downarrow$$

$$\hat{H}\sum_k a_k |g_k(x)\rangle = E\sum_k a_k |g_k(x)\rangle$$

$$\Downarrow$$

$$\left\{\sum_k a_k \langle g_m(x)|\hat{H}|g_k(x)\rangle = E\sum_k a_k \langle g_m(x)|g_k(x)\rangle\right\}_m$$

$$\Downarrow$$

$$\left\{\sum_k H_{mk} a_k = E a_m\right\}_m$$

$$\Downarrow$$

$$\mathbf{H}\vec{a} = E\vec{a}$$

where $\vec{a}$ is a vector with elements a_k and $\mathbf{H}$ is a matrix with elements $H_{mk} = \langle g_m(x)|\hat{H}|g_k(x)\rangle$. This representation is equivalent to the differential equation formalism, but with a significant complication that matrices and vectors are usually infinite-dimensional and cannot be stored in a computer. In practice, however, most functions in the infinite $\{g_k(x)\}$ set correspond to inaccessibly high energies and can therefore be ignored. The resulting finite-dimensional matrix equations are easily solved on modern computers – this is the primary working formalism of modern quantum chemistry.

Interpretations of quantum mechanics

Almost anything that one could put in writing about what quantum mechanics "actually means" is arguable. The primary problem appears to be in the human concept of *meaning* – recognition, valuation, emotional association and incorporation into the knowledge framework that a person already holds. Quantum mechanics does not appear to "mean" anything recognizable to a lay person in the terms that the human brain had evolved to use. Scientists themselves interpret quantum theory using its mathematical properties, which are well understood and currently used with great effect in research and engineering.

This does not prevent the "philosophers of physics" from making attempts at interpreting quantum theory, but very few of their propositions are not dismissed by the actual physics community as ludicrous. Some lingering misconceptions had been created by the physicists themselves: *e.g.* the "measurement paradox" is not a paradox at all, but a collision of approximations between quantum and classical physics. For the purposes of this course we shall subscribe to the *instrumentalist interpretation* of quantum mechanics that is based on David Mermin's famous *dictum*: "shut up and calculate".

Week 32 workshop exercises

Monk and Munro, 2nd edition: chapter 25, problem 25.9; chapter 26, problems 26.7, 26.9, 26.10; chapter 29, problems 29.1-29.3, 29.7-29.10.

Steiner, 2nd edition: section 14.8, problem 8.

Extra difficulty exercises for the brave

Steiner, 2nd edition: section 14.8, problems 12-15.