Quantum Mechanics Review

0.1 Wave Functions

A physical state is described by a wavefunction, $\Psi(q_i)$, where the q_i are relevant parameters of the state, for example, (one of, but not both of) (time and position) or (energy and momentum), as well as other measurables, such as angular momentum and spin. $|\Psi(q_i)|^2$ is the probability that a measurement of the coordinate of the state will yield a value q_i. If q_i is a continuous parameter, then $|\Psi(q_i)|^2 dq_i$ is the probability that a measurement of the state will yield a value of q_i in the infinitesimal volume dq_i. Since $|\Psi(q_i)e^{i\alpha}|^2 = |\Psi(q_i)|^2$, a wavefunction is defined only to within a phase factor, and is therefore not unique.

Wavefunctions, like waves, superpose:

$$\Psi(q_i) = A\Psi_1(q_i) + B\Psi_2(q_i) \tag{1}$$

describes a physical state resulting from the superposition of states $\Psi_1(q_i)$ and $\Psi_2(q_i)$. The coefficients A and B are amplitude weights, indicating the relative contribution of the respective states to the superposed state.

Assume instead that two states, $\Psi_1(q_{1i})$ and $\Psi_2(q_{2i})$ are independent (do not interact). The state of this two-state system is described by the wavefunction

$$\Psi(q_{1i},\ q_{2i}) = \Psi_1(q_{1i})\Psi_2(q_{2i}) \tag{2}$$

A state is a probability distribution function, where each possible measurement outcome has a probability of being realized. Quantum mechanics describes the time evolution of these probabilities, typically with a version of Schrödinger's equation ($\hbar = \frac{h}{2\pi} = 1$)

$$\hat{H}\Psi = i\frac{\partial}{\partial t}\Psi \tag{3}$$

0.2 Observables: Operators and Eigenstates

Measurables, x, are associated with linear operators, $\hat{X}$. If the wavefunction is known, possible values of measurements are given by the eigenvalue equation (the arguments of the wavefunction are taken for granted)

$$\hat{X}\Psi = x\psi \tag{4}$$

and the expected (average) value of repeated measurements is given by

$$\bar{x} = \int \Psi^\dagger \hat{X} \Psi dq_i \tag{5}$$

where $\Psi^\dagger$ is the conjugate transpose (adjoint) of Ψ: $\Psi^\dagger = (\Psi^T)^*$.

Common non-relativistic operators are listed in Table 1.

Table 1: Common non-relativistic operators

Position	$\hat{x} = x,\ \hat{y} = y,\ \hat{z} = z$
Momentum	$\hat{p_x} = -i\frac{\partial}{\partial x},\ \hat{p_y} = -i\frac{\partial}{\partial y},\ \hat{p_z} = -i\frac{\partial}{\partial z}$
Angular Momentum	$\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y,\ \hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z,\ \hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x,\ \hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$
	$\hat{L}_x = -i\left(-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right),\ \hat{L}_y = -i\left(-\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right),$
	$\hat{L}_z = -i\frac{\partial}{\partial\phi},\ \hat{L}^2 = -\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$
Kinetic Energy	$\hat{T} = \frac{\hat{p}^2}{2m} = -\frac{1}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) = -\frac{1}{2m}\nabla^2$
Potential Energy	$\hat{V} = V$
Total Energy	$\hat{H} = \hat{T} + \hat{V} = -\frac{1}{2m}\nabla^2 + V$

The set of eigenvalues may be discrete or continuous. Discrete eigenvalues typically arise in bound states, such as a potential well, which leads for the case of a potential well of width a, say, to discrete energy levels $\sim \frac{n}{a}$, where n is an index. The index typically labels the members of the set with subscript as well as the associated eigenstate, for example:

$$\hat{H}\Psi_n = E_n\Psi_n \tag{6}$$

Periodic boundary conditions, such as $\Psi(\phi + 2\pi) = \Psi(\phi)$ also yield discrete eigenvalues such as those for angular momentum.

Eigenstates and their derivatives must be continuous, single-valued, and finite, as measurable quantities (eigenvalues) must be finite and and definite.

If $x_m \neq x_n$ and

$$\int \Psi_n^\dagger \Psi_m dq_i = 0 \tag{7}$$

then Ψ_m and Ψ_n are orthogonal. If any number of eigenstates have the same eigenvalue, then linear combinations of these eigenstates have the same eigenvalue. Such linear combinations can be made orthogonal.

Ψ can be represented as a linear combination of eigenstates:

$$\Psi = \sum_k c_i \Psi_k \tag{8}$$

in the case of discrete eigenstates. The coefficients c_i weight the probability that a measurement will yield Ψ_k: $P_k = |c_k|^2$, so that $\sum_k |c_k|^2 = 1$.

In the case of continuous eigenstates,

$$\Psi = \int c(x)\Psi_x dx \tag{9}$$

and $dP = |c(x)|^2 dx$ is the probability of measuring x in the infinitesimal volume dx, and $\int |c(x)|^2 dx = 1$.

Orthonormality (orthogonal and normalized to 1) of wavefunctions is summarized as

$$\int \Psi_j^\dagger \Psi_k dq_i = \delta_{jk} \tag{10}$$

for discrete eigenstates, and

$$\int \Psi_{x'}^\dagger \Psi_x dx = \delta(x' - x) \tag{11}$$

for continuous eigenstates.

Sets of operators whose eigenvalues (observable) can be measured simultaneously with "infinite" precision are commutative, $\hat{Y}\hat{X} = \hat{X}\hat{Y}$,[1] or, more formally, in terms of commutator algebra,

$$[\hat{Y},\ \hat{X}] = \hat{Y}\hat{X} - \hat{X}\hat{Y} = 0 \tag{12}$$

Obviously, the eigenvales of non-commutative operators cannot be simultaneously measured with precision. These are referred to as complementary properties.

This is a statement of Heisenberg's uncertainty principle

$$dx dp_x \approx 1 \tag{13}$$

which implies that the momentum uncertainty of a particle constrained to a region dx is $dp \approx 1/dx$, and that the position of a particle that has undergone a momentum change of dp can be resolved to no better than $dx \approx 1/dp$.

Problem

Calculate $[\hat{x},\ \hat{p}_x]$ (recall that operators act on wavefunctions), and show that a coordinate of a position and the respective coordinate of the momentum do not commute.

A similar uncertainty principle relates uncertainties in time and energy:

$$dt dE \approx 1 \tag{14}$$

which has consequences for lifetimes and widths of resonances and other bound systems.

In Table 2 are listed representative complementary and non-complementary properties.

0.2.1 Hamiltonian Eigenstates

When the potential V is independent of time, as it is frequently quantum mechanical interactions. Ψ can be factorized into time-dependent and time-independent parts,

$$\Psi(\mathbf{r}, t) = \phi(t)\psi(\mathbf{r}) \tag{15}$$

Equations 3 and 6 combine to describe the time dependence of the wavefunction

$$i\frac{\partial}{\partial t}\Psi_n = E_n \Psi_n \tag{16}$$

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[1] Recall that operators "act" on wavefunctions in order: $\hat{Y}\hat{X}\Psi$ says that $\hat{X}$ operates on Ψ first, and then $\hat{Y}$ operates on the outcome of that operation, $\hat{X}\Psi$.

Table 2: Representative complementary (do not commute) and non-complementary (commuting) properties. Some entries (e.g., x) imply all three coordinates. $\mathbf{J} = \mathbf{L} + \mathbf{S}$.

Commute	Do Not Commute
x	x, p_x
p_x	t, E
x, p_j, p_k	L_x
L_x, p_x	L_x, p_y
L_x, L^2	
x, L_x	
L^2, S^2, J^2, J_z	

which, in terms of Equation 15, has the solution

$$\Psi(\mathbf{r}, t) = \psi_n(\mathbf{r}) e^{-iE_n t} \tag{17}$$

The general state equation is the linear combination of these solutions for all n:

$$\Psi(\mathbf{r}, t) = \sum_n c_n \psi(\mathbf{r}) e^{-iE_n t} \tag{18}$$

The problem then is to determine $\psi(\mathbf{r})$ for specific potentials.

Problem

Show that the wavefunctions of a particle of mass m in a one-dimensional box of length L and infinitely high walls, that is

$$V(x) = \begin{cases} 0, & 0 \leq x \leq L \\ \infty, & \text{Otherwise} \end{cases}$$

are

$$\Psi_n(x, t) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) e^{-iE_n t}$$

where

$$E_n = \frac{n^2 \pi^2}{2mL^2}$$

and $n \geq 1$.

0.2.2 Momentum Eigenstates

As for the spatial factor, $psi(x, y, z)$, operating on it with the momentum operators will result in determining momentum eigenvalues. For example,

$$\hat{p}_x \psi(x, y, z) = p_x \psi(x, y, z) \tag{19}$$

which is also a partial differential equation,

$$-i\frac{\partial}{\partial x}\psi(x,y.z) \tag{20}$$

The solutions of these (realizing that coordinates are independent) are

$$\psi_{p_x}(x,y,z) = e^{ip_x x}\chi(y,z) \tag{21}$$

Each coordinate would give the similar results, leading to

$$\psi_p(\mathbf{r}) = Ce^{i(p_x x+p_y y+p_z z)} = Ce^{i\mathbf{p}\cdot\mathbf{r}} \tag{22}$$

where the coeffient C is chosen to normalize ψ:

$$\iiint C^2\psi^\dagger_{p'}\psi_p dxdydz = \delta(p'-p) \tag{23}$$

Since, $\int_{-\infty}^{+\infty} e^{ikx}dx = 2\pi\delta(k)$,

$$C = \frac{1}{(2/pi)^{3/2}} \tag{24}$$

A general solution is found by superposing momentum eigenstates ($dp_x dp_y dp_z = d^3p$):

$$\psi(\mathbf{r}) = \int c(\mathbf{p})\psi_p(\mathbf{r})d^3p = \frac{1}{(2\pi)^{3/2}}\int c(\mathbf{p})e^{i\mathbf{p}\cdot\mathbf{r}}d^3p \tag{25}$$

This indicates that $\psi_p(\mathbf{r})$ and $c(\mathbf{p})$ are Fourier transforms of one another.

Combining Equations 17, 22, and 24, gives a solution to the free-particle wavefunction:

$$\Psi(E,\mathbf{p}) = \frac{1}{(2\pi)^{3/2}}e^{-i(Et-\mathbf{p}\cdot\mathbf{r})} \tag{26}$$

0.2.3 Angular Momentum Eigenstates

Quantum systems exhibit two types of angular momentum, orbital and spin. It is impossible, in quantum mechanics, to measure simultaneously the three components of angular momentum, just the total (squared) and one projection (typically chosen as the z-component. Measurements of these yield discrete (quantized) values.

The magnitude-squared of the orbital momentum, L^2, yields values

$$\hat{L}^2\Psi = l(l+1)\Psi \tag{27}$$

where l is a non-negative integer starting from 0.

For a given, fixed, angular momentum, l, there will be $2l+1$ possible projections onto, as is usually the case, the L_z axis. The eigenvalue of $\hat{L}_z$ is typically designated m, and so, $-l \le m \le l$, with $\Delta m = 1$.

The eigenvalue equation for this projection

$$\hat{L}_z\Psi = m\Psi \tag{28}$$

becomes, in polar coordinates (which can be separated),

$$-i\frac{\partial}{\partial\phi}\Psi(r,\theta,\phi)=m\Psi(r,\theta,\phi) \tag{29}$$

with solutions

$$\Psi(r,\theta,\phi)=e^{im\phi}f(r,\theta) \tag{30}$$

The integer quantization of angular momentum follows from the standard periodic boundary conditions $\Psi(\phi+2\pi)=\Psi(\phi)$.

The magnitude of the angular momentum (squared) and projection commute [see Table 2], and so l and m are simultaneously measureable. The consequent θ,ϕ dependence is given by spherical harmonics $Y_l^m(\theta,\phi)$:

$$\Psi(r,\theta,\phi)=f(r)Y_l^m(\theta,\phi) \tag{31}$$

a few of which are given below:

$Y_0^0=\frac{1}{\sqrt{4\pi}}$

$Y_1^0=\sqrt{\frac{3}{4\pi}}\cos\theta$, $Y_1^{\pm1}=\mp\sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm i\phi}$

$Y_2^0=\sqrt{\frac{5}{16\pi}}(3\cos^2\theta-1)$, $Y_2^{\pm1}=\mp\sqrt{\frac{15}{8\pi}}\cos\theta\sin\theta e^{\pm i\phi}$, $Y_2^{\pm2}=\sqrt{\frac{15}{32\pi}}\sin^2\theta e^{\pm2i\phi}$

Quantum objects can in principle obtain different values of orbital angular momentum, but each object has a single characteristic intrinsic angular momentum, called spin (even though nothing is spinning).

0.2.4 Spin

The intrinsic spin is measured, like orbital angular momentum, as magnitude-squared

$$\hat{S}^2\Psi=s(s+1)\Psi \tag{32}$$

where s can be 0, a positive integer, or a positive half-integers, and projection (again, usually along the z-axis),

$$\hat{S}_z\Psi=m_s\Psi \tag{33}$$

The eigenvalue m_s can be any of $2s+1$ integer values, ranging from $-s$ to $+s$.

For a spin-$\frac{1}{2}$ particle, the $2\left(\frac{1}{2}\right)+1=2$ projections are usually referred to as up (↑) or down (↓).

The spin projection operators are the 2×2 Pauli matrices:

$$\hat{S}_x=\frac{1}{2}\begin{pmatrix}0&1\\1&0\end{pmatrix}\qquad\hat{S}_y=\frac{1}{2}\begin{pmatrix}0&-i\\i&0\end{pmatrix}\qquad\hat{S}_z=\frac{1}{2}\begin{pmatrix}1&0\\0&-1\end{pmatrix} \tag{34}$$

S_z has eigenvalues $\pm\frac{1}{2}$ associated respectively with eigenstates

$$s_{z,\mathrm{up}}=\begin{pmatrix}1\\0\end{pmatrix}\qquad s_{z,\mathrm{down}}=\begin{pmatrix}0\\1\end{pmatrix} \tag{35}$$

Spin-$\frac{1}{2}$ and other half-integer spin indistinguishable objects are classified as fermions (obeying Fermi-Dirac statistics). They are anti-symmetric under permutations of pairs: $\Psi(1,2)=-\Psi(2,1)$. This anti-symmetry implies that no two fermions can occupy the same quantum state. If $\Psi(1)=\Psi(2)$, then $\Psi(1)\Psi(2)=\Psi(2)\Psi1$.

But by Fermi-Dirac statistics, $\Psi(1)\Psi(2) = -\Psi(2)\Psi 1$. Therefore, $\Psi(1)\Psi(2) = \Psi(2)\Psi 1 = 0$: it can't exist, $\Psi(1) \neq \Psi(2)$.

Note that a composite system with an even number of fermions has integer spin; a composite system with an odd number of fermions has half-integer spin.

Indistinguishable objects with integer spin are classified as bosons (obeying Bose-Einstein statistics). They are symmetric under interchange: $\Psi(1,2) = \Psi(2,1)$. Any number of bosons can occupy the same state, and a composite system of any number of bosons is a boson.

0.3 Hydrogen Atom

The hydrogen atom is an example of a non-relativistic bound system, in which an electron is bound to a proton by the Coulomb interaction, $-\frac{e^2}{r^2}$. The potential energy V, in the non-relativistic Hamiltonian operator, $\bar{H} = -\frac{1}{2m}\nabla^2 + V$, is $V(r) = -\frac{e^2}{r}$. The mass term, m, is the mass of the electron. The proton, being $\sim$ 2000 times more massive, can be, to a good approximation, considered stationary, so the resulting wavefunction is essentially that of the electron in a spherically-symmetric finite well.

The complete solution of Schrödinger's equation, $\Psi_{n,l,m}(r, \theta, \phi, t)$, with this potential is quite complicated, including among its terms spherical harmonics and associated Laguerre polynomials. A key parameter of the expression is the so-called Bohr radius,

$$a = \frac{4\pi}{me^2} \tag{36}$$

whose value is approximately that of a typical atomic radius, or, in more familiar units, about 0.53×10^{-8} cm = 0.5 Å.

Normalizable solutions are possible only when the total energy of the system is quantized

$$E_n = -\frac{me^4}{32\pi^2 n^2} = -\frac{\alpha^2 m}{2n^2} \tag{37}$$

where n is the principal quantum number (any positive integer), which designates and determines the state energy. The fine structure constant, $\alpha = \frac{e^2}{4\pi}$, is related to the fundamental charge and has a value of about $\frac{1}{137}$.

Another number, l, labeling the wavefunction, specifies the total orbital angular momentum, as we've seen. It is an integer with values that range from 0 to $n-1$.

The final wavefunction label is m, which, as explained above, gives the z-component of the orbital angular momentum. These, too, are integers, $2l+1$ of them ranging from $-l$ to l.

Note that for each n, the election may have n different values of total orbital momentum, each of which can have $2l+1$ different projections onto the z-axis. The nth energy level, then, can have n^2 distinct states:

$$\sum_{l=0}^{n-1} (2l+1) = n^2 \tag{38}$$

referred to as the degeneracy of the nth energy level.

With hydrogen, as with just about everything else, this energy is measured indirectly via the emission or absorption of light, since $E = \frac{2\pi}{\lambda}$.