8 Position and momentum

8.1 Introduction

Wave functions are commonly used to describe the quantum state of atoms and molecules, or more generally of systems characterized by the positions or the momenta of their constituents. These wave functions are vectors belonging to a Hilbert space of square-integrable functions. As noted previously in this course, such spaces are infinite dimensional, and the mathematics of infinite dimensional spaces is considerably more complicated than that of finite dimensional spaces.

In regards to Quantum Mechanics, the most important difference between finite and infinite dimensional Hilbert spaces concerns the eigenvalues and eigenvectors of the Hermitian operators representing dynamical variables. For example, spin states can be described by vectors belonging to a finite dimensional space, e.g., by N-component column vectors where N is a finite number ($N = 2$ for spin-1/2 particles). Spin observables can be represented by $N \times N$ Hermitian matrices acting on these column vectors. The eigenvectors of these matrices are themselves N-component column vectors and the corresponding eigenvalues are finite in number and form a discrete distribution (different eigenvalues are separated by a gap). Moreover, these sets of eigenvectors are complete and span the whole of the Hilbert space in which these matrices act, which is essential for the consistency of the probability calculations outlined in Part 4 of these notes.

Because they act on vectors belonging to an infinite-dimensional space, however, the operators representing such dynamical variables as the position, the momentum and the energy do not have, or do not always have, a complete set of eigenvectors. By eigenvectors, here, we mean square-integrable eigenfunctions f such that $Af = \lambda f$, where A is the operator and λ is a constant. Hence, it is often not possible to calculate probabilities for the corresponding measurements using the same method as for finite-dimensional Hilbert spaces. A mathematically rigorous way round this difficulty, based on projector operators, has been known since the early days of Quantum Mechanics. However, the probabilities of interest can often be calculated by following a different approach, in which the concept of eigenfunction is generalized to encompass non square-integrable functions. The possible results of a measurement are then taken to be the generalized eigenvalues associated with these generalized eigenfunctions. These "eigenvalues" are normally infinite in number and may form a continuous rather than a discrete distribution. This approach is illustrated in the next section by the example of the momentum operator (the operator corresponding to the momentum of a particle, $\mathbf{p} = m\mathbf{v}$ in Classical Mechanics).

8.2 Eigenfunctions of the momentum operator

As you have seen in Term 1, the x-component of the momentum of a particle is associated with the operator

$$P = -i\hbar\frac{\partial}{\partial x}, \tag{8.1}$$

in the formulation where the quantum state of the particle is described not by a ket vector but by a wave function [e.g., $\psi(x, y, z)$]. For simplicity, let us suppose that the particle is confined to the x-axis, so that the wave function has no dependence in y and z and Eq. (8.1) can be written as

$$P = -i\hbar\frac{\mathrm{d}}{\mathrm{d}x}. \tag{8.2}$$

This operator acts on wave functions $\psi(x)$ belonging to the Hilbert space of the functions square-integrable on $(-\infty, \infty)$.

According to the principles of Quantum Mechanics, the result of a measurement of the momentum of this particle should be an eigenvalue of P. However, here we hit the difficulty mentioned in the previous section: this operator has no eigenvalue within the normal definition of an eigenvalue. Indeed, for P to have an eigenvalue p, there should exist a square-integrable function $\psi_p(x)$ such that $P\psi_p(x) = p\,\psi_p(x)$ with $\psi_p(x)$ not identically zero. I.e., $\psi_p(x)$ must be a non-trivial solution of the equation

$$-i\hbar\frac{\mathrm{d}\psi_p}{\mathrm{d}x} = p\,\psi_p(x) \tag{8.3}$$

such that the integral

$$\int_{-\infty}^{\infty} |\psi_p(x)|^2\,\mathrm{d}x$$

exists and is finite. (By non-trivial solution one means a solution $\psi_p(x)$ which is not zero for all values of x.) We can deduce from Eq. (8.3) that

$$\psi_p(x) = C\exp(ipx/\hbar), \tag{8.4}$$

with C a constant.[1] Such solutions exist for any value of p, real or complex. However, they never belong to the Hilbert space of square-integrable functions on $(-\infty, \infty)$, and therefore they do not qualify as eigenvectors of the operator P in the mathematical sense of this term.

[1] Check: $-i\hbar\mathrm{d}\psi_p/\mathrm{d}x = (-i\hbar)(ip/\hbar)C\exp(ipx/\hbar) = p\,\psi_p(x)$. Eq. (8.3) is readily solved using the methods you have learned for dealing with separable equations or with linear differential equation with constant coefficients.

☞ As defined in Section 3.6, the eigenvectors of an operator are vectors belonging to the vector space in which this operator acts, here the space of functions square-integrable on $(-\infty, \infty)$. It is easy to see that there is no value of p for which $\psi_p(x)$ belongs to that space. Indeed, note that

$$\begin{aligned} |\psi_p(x)|^2 &= |\,(2\pi\hbar)^{-1/2} \exp[i(\mathrm{Re}\, p + i\mathrm{Im}\, p)x/\hbar]\,|^2 \\ &= |\,(2\pi\hbar)^{-1/2} \exp[i(\mathrm{Re}\, p)x/\hbar] \exp[i^2(\mathrm{Im}\, p)x/\hbar]\,|^2 \\ &= (2\pi\hbar)^{-1}\,|\exp[i(\mathrm{Re}\, p)x/\hbar]\,|^2\,|\exp[-(\mathrm{Im}\, p)x/\hbar]\,|^2, \end{aligned} \tag{8.5}$$

and since $|\exp[i(\mathrm{Re}\, p)x/\hbar]\,|^2 = 1$ (recall that $|\exp(iz)| = 1$ if z is real),

$$|\psi_p(x)|^2 = (2\pi\hbar)^{-1} \exp[-2(\mathrm{Im}\, p)x/\hbar].$$

Therefore $|\psi_p(x)|^2$ explodes exponentially when $x \to \infty$ if $\mathrm{Im}\, p < 0$ or when $x \to -\infty$ if $\mathrm{Im}\, p > 0$, and remains equal to $(2\pi\hbar)^{-1}$ at all values of x if $\mathrm{Im}\, p = 0$. Hence there is no value of p for which the integral

$$\int_{-\infty}^{\infty} |\psi_p(x)|^2\, \mathrm{d}x$$

exists and is finite.

☞ The mathematical definition of the spectrum of an operator was also mentioned in Section 3.6. In the Dirac notation, the spectrum of an operator $\hat{A}$ acting in a Hilbert space $\mathcal{H}$ is the set of the scalars λ such that the operator $\hat{A} - \lambda\hat{I}$ is not invertible, where $\hat{I}$ is the identity operator. This set always contains all the eigenvalues of this operator (i.e., all the scalars λ such that $\hat{A}|\psi\rangle = \lambda|\psi\rangle$ for some vector $|\psi\rangle$ belonging to $\mathcal{H}$). However, if $\mathcal{H}$ is infinite-dimensional, the spectrum may also contain values of λ for which there is no vector $|\psi\rangle$ such that $\hat{A}|\psi\rangle = \lambda|\psi\rangle$. This is the case for the momentum operator: mathematicians would say that the spectrum of P is $\mathbb{R}$, the set of all real numbers, even though this operator has no eigenvalues. The spectrum of P is thus a continuous distribution of numbers. That Eq. (8.3) has no square-integrable solutions is not an accident, as it can be shown that the continuous part of the spectrum of an operator is never associated with square-integrable eigenfunctions.

Following the approach usually adopted in elementary Quantum Mechanics, let us broaden the concept of eigenvalue and eigenfunction, consider that the functions $\psi_p(x)$ are eigenfunctions of P in a generalized sense, and use these functions to calculate probabilities as if they were square-integrable. We only consider real values of p to be eigenvalues, though, because the momentum of a particle is a real number (not a complex number).

☞ Mathematical notes:

1. The true mathematical reason for excluding complex values of p, however, is that they do not belong to the continuous spectrum of P in the mathematical definition of the continuous spectrum of an operator.

2. Wave functions are normally continuous and absolutely integrable, and can therefore be written as a Fourier transform (or inverse Fourier transform, see Appendix B of these course notes). In particular, if $\psi(x)$ is such a wave function, there exists a function $\phi(p)$ such that

$$\psi(x) = \frac{1}{(2\pi\hbar)^{1/2}} \int_{-\infty}^{\infty} \exp(ipx/\hbar)\phi(p)\,\mathrm{d}p. \tag{8.6}$$

In that sense, any wave function can be expanded on the set of the functions $\psi_p(x)$ defined by Eq. (8.4) with $C = (2\pi\hbar)^{-1/2}$ and p real, and there is no need to include functions $\psi_p(x)$ with complex values of p in this set to make it complete.

This result extends to the more general case of any square-integrable function, although the definition of the Fourier transform must then be suitably modified (the straightforward definition in terms of ordinary Riemann integrals you have probably seen in a maths course does not apply to functions that are square-integrable but not absolutely integrable).

8.3 Normalization to a delta function

In the case of a finite-dimensional Hilbert space, it is possible to construct an orthonormal basis for that space from amongst the eigenvectors of any Hermitian operator acting in that space. Denoting these basis vectors by $|\psi_n\rangle$, the orthonormality condition reads $\langle\psi_n|\psi\rangle_{n'} = \delta_{nn'}$. That is,

$$\int_{-\infty}^{\infty} \psi_n^*(x)\psi_{n'}(x)\,\mathrm{d}x = \delta_{nn'} \tag{8.7}$$

if each of the vectors $|\psi_n\rangle$ is represented by a square-integrable function $\psi_n(x)$ with $-\infty < x < \infty$.

Eq. (8.7) does not make sense for the generalized eigenfunctions of the momentum operators defined by Eq. (8.4), both because p varies continuously and because these functions are not square-integrable on $(-\infty, \infty)$. We note, however,

that

$$\int_{-\infty}^{\infty} \psi_p^*(x)\psi_{p'}(x)\,\mathrm{d}x = |C|^2 \int_{-\infty}^{\infty} \exp[i(p'-p)x/\hbar])\,\mathrm{d}x$$
$$= |C|^2\hbar \int_{-\infty}^{\infty} \exp[i(p'-p)\xi)\,\mathrm{d}\xi$$
$$= 2\pi|C|^2\hbar\,\delta(p'-p). \tag{8.8}$$

(We have passed from the first to the second equation by changing variable from x to $\xi = x/\hbar$, and from the second to the last by using Eq. (B4) of Appendix B of these notes with $x-x'$ replaced by $p'-p$ and k replaced by ξ.) It is convenient in the applications to choose the constant C such that this integral is exactly $\delta(p'-p)$. Setting $C = (2\pi\hbar)^{-1/2}$ and writing

$$\psi_p(x) = \frac{1}{(2\pi\hbar)^{1/2}} \exp(ipx/\hbar) \tag{8.9}$$

ensures that

$$\int_{-\infty}^{\infty} \psi_p^*(x)\psi_{p'}(x)\,\mathrm{d}x = \delta(p'-p). \tag{8.10}$$

Functions $\psi_p(x)$ satisfying this equation are said to be "normalized to a delta function in momentum space".

Instead of the functions $\psi_p(x)$, it is often more convenient to introduce the wave number, k ($k = p/\hbar$ and $p = \hbar k$), and use the functions

$$\psi_k(x) = \frac{1}{(2\pi)^{1/2}} \exp(ikx). \tag{8.11}$$

These functions are such that

$$\int_{-\infty}^{\infty} \psi_k^*(x)\psi_{k'}(x)\,\mathrm{d}x = \frac{1}{(2\pi)} \int_{-\infty}^{\infty} \exp[i(k'-k)x)]\,\mathrm{d}x, \tag{8.12}$$

and therefore, in view of Eq. (B.4) of Appendix B,

$$\int_{-\infty}^{\infty} \psi_k^*(x)\psi_{k'}(x)\,\mathrm{d}x = \delta(k'-k). \tag{8.13}$$

Functions such as $\psi_k(x)$ satisfying this last equation are said to be "normalized to a delta function in k-space". Eqs. (8.10) and (8.13) replace Eq. (8.7) for non-square-integrable functions such as $\psi_p(x)$ and $\psi_k(x)$.

☞ Remember that here p is the x-component of the momentum of the particle and $k = p/\hbar$. Positive values of p and k correspond to a propagation in the positive x-direction and negative values to a propagation in the negative x-direction. The scalars p and k are the 1D analogues of the 3D momentum $\mathbf{p}$ and wave vector $\mathbf{k}$.

8.4 Probability densities

The fact that the possible values of p are continuously distributed also affects how probabilities are defined. In regards to predicting the result of a measurement of the x-component of the momentum, the quantity of interest is not the probability $\Pr(p)$ of obtaining a given value p, but rather the probability $\Pr([p_1, p_2])$ of obtaining a result between a certain value p_1 and a certain value p_2. There are two reasons for this: (1) The probability of obtaining a value specified to infinitely many digits in a measurement of a continuously distributed variable is zero, in the same way as the probability of drawing (at random) one particular ball from an urn containing infinitely many balls would be zero. (2) Since no detectors have an infinite resolution, an actual measurement of a variable distributed continuously can only determine a range of values for this variable.

The probability $\Pr([p_1, p_2])$ can be written as the integral of a certain density of probability (or probability density function) $\mathscr{P}(p)$:

$$\Pr([p_1, p_2]) = \int_{p_1}^{p_2} \mathscr{P}(p)\,\mathrm{d}p. \tag{8.14}$$

I.e., $\mathscr{P}(p)\,\mathrm{d}p$ is the probability of obtaining a value of the momentum between p and $p+\mathrm{d}p$ (or, which is equivalent because $\mathrm{d}p$ is an infinitesimal, the probability of obtaining a value of the momentum between $p - \mathrm{d}p/2$ and $p + \mathrm{d}p/2$). We stress that $\mathscr{P}(p)$ is a *density* of probability, not a probability. $\Pr([p_1, p_2])$ is a probability and has no physical dimensions. By contrast, $\mathscr{P}(p)$ has the physical dimensions of the inverse of a momentum.

Suppose that the particle is in a state described by a normalized wave function $\psi(x)$. According to the rules of Quantum Mechanics, and assuming that the eigenfunctions $\psi_p(x)$ are normalized as per Eq. (8.10),

$$\mathscr{P}(p) = \left| \int_{-\infty}^{\infty} \psi_p^*(x)\psi(x)\,\mathrm{d}x \right|^2 = \left| \frac{1}{(2\pi\hbar)^{1/2}} \int_{-\infty}^{\infty} \exp(-ipx/\hbar)\psi(x)\,\mathrm{d}x \right|^2. \tag{8.15}$$

Rather than working with the functions $\psi_p(x)$, it is often convenient to express the momentum p in terms of the wavenumber k and work with the $\psi_k(x)$ functions defined by Eq. (8.11). These two formulations are equivalent. In particular, the probability $\Pr([k_1, k_2])$ of obtaining a value between $k_1 = p_1/\hbar$ and $k_2 = p_2/\hbar$ in a measurement of the particle's wave number in the x-direction is

$$\int_{k_1}^{k_2} \mathscr{P}(k)\,\mathrm{d}k,$$

where $\mathscr{P}(k) = |\phi(k)|^2$ with $\phi(k)$ being the Fourier transform of $\psi(x)$:

$$\phi(k) = \int_{-\infty}^{\infty} \psi_k^*(x)\psi(x)\,\mathrm{d}x = \frac{1}{(2\pi)^{1/2}} \int_{-\infty}^{\infty} \exp(-ikx)\psi(x)\,\mathrm{d}x. \tag{8.16}$$

☞ The normalization to a delta function in p- or k-space ensures that the probability densities $\mathscr{P}(p)$ and $\mathscr{P}(k)$ can be calculated as stated above. To see that this is indeed the case, recall that

$$\mathscr{P}(k) = \left| \int_{-\infty}^{\infty} \psi_k^*(x)\psi(x)\,\mathrm{d}x \right|^2 \tag{8.17}$$

and note it is necessary that

$$\int_{-\infty}^{\infty} \mathscr{P}(k)\,\mathrm{d}k = 1 \tag{8.18}$$

in order for $\mathscr{P}(k)$ to be a probability density Now, suppose that we take $\psi_k(x)$ to be $C\exp(ikx)$, where C is a constant factor not necessarily equal to $(2\pi)^{-1/2}$. Then

$$\begin{aligned}\mathscr{P}(k) &= |C|^2 \left| \int_{-\infty}^{\infty} \exp(-ikx)\psi(x)\,\mathrm{d}x \right|^2 \\ &= |C|^2 \left[\int_{-\infty}^{\infty} \exp(-ikx)\psi(x)\,\mathrm{d}x \right]^* \left[\int_{-\infty}^{\infty} \exp(-ikx')\psi(x')\,\mathrm{d}x' \right].\end{aligned} \tag{8.19}$$

Therefore

$$\begin{aligned}\int_{-\infty}^{\infty} \mathscr{P}(k)\,\mathrm{d}k = |C|^2 \times \\ \int_{-\infty}^{\infty} \left[\int_{-\infty}^{\infty} \exp(-ikx)\psi(x)\,\mathrm{d}x \right]^* \left[\int_{-\infty}^{\infty} \exp(-ikx')\psi(x')\,\mathrm{d}x' \right] \mathrm{d}k.\end{aligned} \tag{8.20}$$

Let us now change the order in which these three integrals are done, so as to write this last equation as

$$\begin{aligned}\int_{-\infty}^{\infty} \mathscr{P}(k)\,\mathrm{d}k = |C|^2 \times \\ \int_{-\infty}^{\infty} \mathrm{d}x \int_{-\infty}^{\infty} \mathrm{d}x' \psi^*(x)\psi(x') \int_{-\infty}^{\infty} \mathrm{d}k \exp(ikx)\exp(-ikx').\end{aligned} \tag{8.21}$$

We can now do the integral over k easily, since

$$\int_{-\infty}^{\infty} \mathrm{d}k \exp(ikx)\exp(-ikx') = \int_{-\infty}^{\infty} \exp[ik(x-x')]\,\mathrm{d}k = 2\pi\delta(x-x'). \tag{8.22}$$

Therefore

$$\begin{aligned}\int_{-\infty}^{\infty} \mathscr{P}(k)\,\mathrm{d}k &= 2\pi|C|^2 \int_{-\infty}^{\infty} \mathrm{d}x \int_{-\infty}^{\infty} \mathrm{d}x'\, \psi^*(x)\psi(x')\delta(x-x') \\ &= 2\pi|C|^2 \int_{-\infty}^{\infty} \mathrm{d}x\, \psi^*(x)\psi(x) \\ &= 2\pi|C|^2.\end{aligned} \tag{8.23}$$

Requiring that $\mathscr{P}(k)$ integrates to 1 means that C should be such that $2\pi|C|^2 = 1$, hence that $|C| = (2\pi)^{-1/2}$. Therefore Eq. (8.17) would not be correct if $|C|$ was not equal to $(2\pi)^{-1/2}$. This relation does not define the sign of C; however, it is convenient to chose C to be positive and therefore define $\psi_k(x)$ as per Eq. (8.11).

8.5 Eigenfunctions of the position operator

In 1D, for a particle confined to the x-axis, the position operator, Q, is the operator which transforms any function $\psi(x)$ into the function $x\psi(x)$. Like the momentum operator, the position operator has no eigenfunction in the usual sense of the word. Indeed, an eigenfunction $\psi_q(x)$ of Q should be a function which is not everywhere zero and such that $Q\psi_q(x) = q\psi_q(x)$ where q is a constant. I.e., $\psi_q(x)$ should be such that $x\psi_q(x) = q\psi_q(x)$. Since q is a constant and x isn't, the only solution of this equation is $\psi_q(x) \equiv 0$, and this function does not qualify as an eigenfunction.

It is possible to go round this difficulty by broadening the definition of an eigenfunction even further than in the case of the momentum operator and take $\psi_q(x)$ to be the delta function $\delta(x-q)$. (Remember that despite its name, a delta function is not a function at all.) Doing so has the merit that the probability of finding the particle in a particular region of space can then be calculated in terms of these generalized eigenfunctions $\psi_q(x)$, in the same way as the probability of obtaining a value between p_1 and p_2 in a measurement of the particle's momentum can be calculated in terms of the generalized eigenfunctions $\psi_k(x)$. I.e., if the particle is in a state described by the wave function $\psi(x)$, the probability $\Pr([x_1, x_2])$ of finding it between x_1 and x_2 can be written as

$$\int_{x_1}^{x_2} \mathscr{P}(q)\,\mathrm{d}q,$$

where

$$\mathscr{P}(q) = \left| \int_{-\infty}^{\infty} \psi_q^*(x)\psi(x)\,\mathrm{d}x \right|^2 \tag{8.24}$$

with $\psi_q(x) = \delta(x-q)$. Indeed, replacing $\psi_q(x)$ by $\delta(x-q)$ in this last equation gives

$$\mathscr{P}(q) = \left| \int_{-\infty}^{\infty} \delta(x-q)\psi(x)\,\mathrm{d}x \right|^2 = |\psi(q)|^2, \tag{8.25}$$

in complete agreement with the probabilistic interpretation of the wave function.

We note, also, that the generalized eigenfunctions $\psi_q(x)$ can be said to be normalized to a delta-function since, as will be shown in a workshop,

$$\int_{-\infty}^{\infty} \psi_q^*(x)\psi_{q'}(x)\,\mathrm{d}x = \int_{-\infty}^{\infty} \delta(x-q)\delta(x-q')\,\mathrm{d}x = \delta(q'-q). \tag{8.26}$$

8.6 The position representation and the momentum representation

We have seen that any state vector can be written as the expansion

$$|\psi\rangle = \sum_n c_n |\psi_n\rangle \tag{8.27}$$

with $c_n = \langle\psi_n|\psi\rangle$ if $\{|\psi_n\rangle, n = 1, 2, \ldots\}$ is an orthonormal basis. Taking together as a single set, the coefficients c_n represent the state $|\psi\rangle$ in the basis $\{|\psi_n\rangle\}$. Moreover, probability that the system is found to be in a state $|\psi_n\rangle$ in a measurement made on the state $|\psi\rangle$ is $|\langle\psi_n|\psi\rangle|^2$.

The position operator Q and the momentum operator P we have considered so far have been defined as operators acting on functions of x, not on ket vectors. However, one can also define a position operator $\hat{Q}$ and a momentum operator $\hat{P}$ acting on ket vectors. The eigenvalue equations $Q\psi_q(x) = q\psi_q(x)$ and $P\psi_p(x) = \psi_p(x)$ then correspond to the equations $\hat{Q}|q\rangle = q|q\rangle$ and $\hat{P}|p\rangle = p|p\rangle$, where q and p are constants distributed continuously. These two equations have no solutions in the Hilbert space of the ket vectors $|\psi\rangle$, in the same way as the equations $Q\psi_q(x) = q\psi_q(x)$ and $P\psi_p(x) = \psi_p(x)$ have no solutions in the Hilbert space of the square-integrable functions on $(-\infty, \infty)$. However, let us proceed as if the vectors $|q\rangle$ and $|p\rangle$ existed, formed a complete set, and were orthonormal in the sense that

$$\langle q|q'\rangle = \delta(q' - q) \qquad \text{and} \qquad \langle p|p'\rangle = \delta(p' - p).$$

Then any vector $|\psi\rangle$ could be written both as

$$|\psi\rangle = \int_{-\infty}^{\infty} \psi(q)|q\rangle \, \mathrm{d}q \tag{8.28}$$

and as

$$|\psi\rangle = \int_{-\infty}^{\infty} \phi(p)|p\rangle \, \mathrm{d}p, \tag{8.29}$$

with, respectively,

$$\psi(q) = \langle q|\psi\rangle \qquad \text{and} \qquad \phi(p) = \langle p|\psi\rangle. \tag{8.30}$$

Eqs. (8.28) and (8.29) are formally equivalent to Eq. (8.27), apart that their right-hand sides are integrals rather than discrete sums. The coefficients $\psi(q)$ and $\phi(p)$ of these two expansions are wave functions. The functions $\psi(q)$ (or $\psi(x)$ if instead of q we use the letter x to denote the position) are "wave functions in position space", and the functions $\phi(p)$ are "wave functions in momentum space". The former are nothing else than the wave functions you have already

encountered in Year 1. We have already mentioned their probabilistic interpretation: the *density* of probability that the particle is found to be at a position q is $|\psi(q)|^2$ (i.e, $|\langle q|\psi\rangle|^2$). Likewise, the *density* of probability that the particle is found to have a momentum p is $|\phi(p)|^2$ (i.e., $|\langle p|\psi\rangle|^2$).

Both $\psi(q)$ and $\phi(p)$ are sets of numbers representing the ket $|\psi\rangle$ in the bases of the "eigenvectors" of $\hat{Q}$ and of those of $\hat{P}$, in the same way as $\{c_n\}$ is a set of numbers representing $|\psi\rangle$ in the $\{|\psi_n\rangle\}$ basis used to write Eq. (8.27). Working in the $\{|q\rangle\}$ basis is working in the "position representation", and working in the $\{|p\rangle\}$ basis is working in the "momentum representation".

Let us call the position co-ordinate x now, rather than q. In the position representation, ket vectors are represented by functions of x, $\hat{Q}$ by the operator multiplying any function $\psi(x)$ by x, and $\hat{P}$ by the operator $-i\hbar\mathrm{d}/\mathrm{d}x$. Conversely, in the momentum representation ket vectors are represented by functions of p, the momentum operator $\hat{P}$ by the operator multiplying any function $\phi(p)$ by p, and the position operator $\hat{Q}$ by the operator $i\hbar\mathrm{d}/\mathrm{d}p$ (this last equation will be obtained in a workshop). Moreover, the wave function in momentum space is the Fourier transform of the wave function in position space, and conversely the wave function in position space is the inverse Fourier transform of the wave function in momentum space (see Eqs. (B.1) and (B.2) of Appendix B):

$$\phi(p) = (2\pi\hbar)^{-1/2} \int_{-\infty}^{\infty} \exp(-ipx/\hbar)\psi(x)\,\mathrm{d}x, \tag{8.31}$$

$$\psi(x) = (2\pi\hbar)^{-1/2} \int_{-\infty}^{\infty} \exp(ipx/\hbar)\phi(p)\,\mathrm{d}p. \tag{8.32}$$

☞ Let us justify these last two equations. We have seen that the functions $\psi_p(x)$ defined by Eq. (8.9) are normalized "eigenfunctions" of this last operator. Hence we can write $\psi_p(x)$ as $\langle x|p\rangle$ and $\psi_p^*(x)$ as $\langle p|x\rangle$:

$$\langle x|p\rangle = \frac{1}{(2\pi\hbar)^{1/2}}\exp(ipx/\hbar), \qquad \langle p|x\rangle = \frac{1}{(2\pi\hbar)^{1/2}}\exp(-ipx/\hbar). \tag{8.33}$$

Combining Eq. (8.28) with the identity $\phi(p) = \langle p|\psi\rangle$ yields

$$\phi(p) = \int_{-\infty}^{\infty} \psi(x)\langle p|x\rangle\,\mathrm{d}x, \tag{8.34}$$

which in view of Eq. (8.33) is nothing else than Eq. (8.31). Similarly, Eq. (8.32) follows from the equation

$$\psi(x) = \int_{-\infty}^{\infty} \phi(p)\langle x|p\rangle\,\mathrm{d}p, \tag{8.35}$$

which is obtained by combining Eq. (8.9) with the identity $\psi(x) = \langle x|\psi\rangle$.

☞ The approach followed in these last paragraphs may appear to be purely formal since the eigenvalue equations $\hat{Q}|q\rangle = q|q\rangle$ and $\hat{P}|p\rangle = p|p\rangle$ have no solutions in the Hilbert space. However, it can be given a precise mathematical meaning, even though the symbols $\langle q|\psi\rangle$ and $\langle p|\psi\rangle$ do not represent inner products of vectors in the usual sense of that term.

8.7 The commutator of Q and P

Recall that in the position representation the position operator Q and the momentum operator P transform any wave function $\psi(x)$ into, respectively, $x\psi(x)$ and $-i\mathrm{d}\psi/\mathrm{d}x$. As you have seen in the Term 1 course, these two operators do not commute; instead,

$$[Q, P] = i\hbar. \tag{8.36}$$

It follows from Eq. (6.20) that measurements of the corresponding dynamical variables (x and p) are subject to the uncertainty relation $\Delta x \Delta p \geq \hbar/2$.

8.8 Position and momentum operators in 3D space

A position operator and a momentum operator can be defined for each direction of space. In particular, the operators $\hat{x}$ and $\hat{p}_x$ for the x-direction, the operators $\hat{y}$ and $\hat{p}_y$ for the y-direction and the operators $\hat{z}$ and $\hat{p}_z$ for the z-direction ($\hat{x}$ and $\hat{p}_x$ are the same operators as those we denoted by $\hat{Q}$ and $\hat{P}$ in the previous sections). In the position representation, $\hat{p}_x$, $\hat{p}_y$ and $\hat{p}_z$ are represented by the operators

$$-i\hbar\frac{\partial}{\partial x}, \quad -i\hbar\frac{\partial}{\partial y}, \quad \text{and} \quad -i\hbar\frac{\partial}{\partial z}.$$

These operators obey the commutation relations

$$[\hat{x}, \hat{p}_x] = [\hat{y}, \hat{p}_y] = [\hat{z}, \hat{p}_z] = i\hbar. \tag{8.37}$$

By contrast, operators pertaining to *orthogonal* directions always commute with each other (we stress the word *orthogonal* here):

$$[\hat{x}, \hat{p}_y] = [\hat{x}, \hat{p}_z] = 0, \qquad [\hat{y}, \hat{p}_x] = [\hat{y}, \hat{p}_z] = 0, \qquad [\hat{z}, \hat{p}_x] = [\hat{z}, \hat{p}_y] = 0. \tag{8.38}$$

Moreover, position operators commute with position operators and momentum operators with momentum operators:

$$[\hat{x}, \hat{y}] = [\hat{x}, \hat{z}] = [\hat{y}, \hat{z}] = [\hat{p}_x, \hat{p}_y] = [\hat{p}_x, \hat{p}_z] = [\hat{p}_y, \hat{p}_z] = 0. \tag{8.39}$$

☞ Why a position operator always commutes with a momentum operator for an orthogonal direction is easily understood. For example,

$$\begin{aligned}[x, p_y]\psi(x,y,z) &= -i\hbar\left[x\frac{\partial}{\partial y}\psi(x,y,z) - \frac{\partial}{\partial y}x\psi(x,y,z)\right] \\ &= -i\hbar\left[x\frac{\partial}{\partial y}\psi(x,y,z) - x\frac{\partial}{\partial y}\psi(x,y,z)\right] = 0. \end{aligned} \tag{8.40}$$

All what we have seen for the 1D case generalizes to the 3D case. For example, in position representation, the 1D momentum operator $-i\hbar\mathrm{d}/\mathrm{d}x$ becomes the 3D momentum operator $-i\hbar\nabla$, where

$$\nabla = \hat{\mathbf{x}}\frac{\partial}{\partial x} + \hat{\mathbf{y}}\frac{\partial}{\partial y} + \hat{\mathbf{z}}\frac{\partial}{\partial z}, \tag{8.41}$$

with $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$ and $\hat{\mathbf{z}}$ the unit vectors in the x-, y- and z-directions (the hats here indicate that these vectors have unit norm, not that they are operators). Likewise, the functions $\psi_k(x)$ of Eq. (8.11) become the "plane waves"

$$\psi_{\mathbf{k}}(\mathbf{r}) = (2\pi)^{-3/2}\exp(i\,\mathbf{k}\cdot\mathbf{r}), \tag{8.42}$$

where $\mathbf{r} = x\,\hat{\mathbf{x}} + y\,\hat{\mathbf{y}} + z\,\hat{\mathbf{z}}$ and $\mathbf{k} = k_x\,\hat{\mathbf{x}} + k_y\,\hat{\mathbf{y}} + k_z\,\hat{\mathbf{z}}$. (Note that $\mathbf{k}$ is a wave vector.)

Since $\mathbf{k}\cdot\mathbf{r} = k_x x + k_y y + k_z z$, each of these functions factorizes into a product of three exponentials:

$$\psi_{\mathbf{k}}(\mathbf{r}) = (2\pi)^{-3/2}\exp(ik_x x)\exp(ik_y y)\exp(ik_z z). \tag{8.43}$$

Therefore

$$\begin{aligned}\int \psi^*_{\mathbf{k}}(\mathbf{r})\psi_{\mathbf{k}'}(\mathbf{r})\,\mathrm{d}^3r = &\frac{1}{(2\pi)}\int_{-\infty}^{\infty}\exp[i(k'_x - k_x)x]\,\mathrm{d}x \times \\ &\frac{1}{(2\pi)}\int_{-\infty}^{\infty}\exp[i(k'_y - k_y)y]\,\mathrm{d}y \times \\ &\frac{1}{(2\pi)}\int_{-\infty}^{\infty}\exp[i(k'_z - k_z)z]\,\mathrm{d}z. \end{aligned} \tag{8.44}$$

Hence,

$$\int \psi^*_{\mathbf{k}}(\mathbf{r})\psi_{\mathbf{k}'}(\mathbf{r})\,\mathrm{d}^3r = \delta(k'_x - k_x)\delta(k'_y - k_y)\delta(k'_z - k_z). \tag{8.45}$$

More succinctly,

$$\int \psi^*_{\mathbf{k}}(\mathbf{r})\psi_{\mathbf{k}'}(\mathbf{r})\,\mathrm{d}^3r = \delta(\mathbf{k}' - \mathbf{k}), \tag{8.46}$$

with the "3D delta function" $\delta(\mathbf{k}' - \mathbf{k})$ defined by the equation

$$\delta(\mathbf{k}' - \mathbf{k}) = \delta(k'_x - k_x)\delta(k'_y - k_y)\delta(k'_z - k_z). \tag{8.47}$$

8.9 Continua of energy levels

For systems described by state vectors belonging to a finite dimensional space, the eigenvalues of the Hamiltonian (the eigenenergies of the system) are finite in numbers and form a discrete distribution (i.e., each energy level is separated from the adjacent levels by an energy gap). This may or may not be the case in infinite dimensional spaces. For example, harmonic oscillators and infinite square wells only have discrete energy levels. However, there are also systems for which the Hamiltonian has no eigenvalue in the mathematical definition of the term but has generalized eigenvalues forming a continuous distribution, and systems which have both discrete eigenvalues and a continuous distribution of generalized eigenvalues.

A free particle in 3D is an example of system with a continuous distribution of generalized eigenvalues. That a particle of mass m is free means that its Hamiltonian can be written as $-(\hbar^2/2m)\nabla^2$, without a potential energy term. The functions $\psi_{\mathbf{k}}(\mathbf{r})$ of Eq. (8.42) are generalized eigenfunctions of this Hamiltonian and the corresponding generalized eigenenenergies are $\hbar^2 k^2/(2m)$ with $k = |\mathbf{k}|$: To see this, note that $\nabla \exp(i\,\mathbf{k}\cdot\mathbf{r}) = i\mathbf{k}\exp(i\,\mathbf{k}\cdot\mathbf{r})$ and therefore $\nabla\cdot\nabla\exp(i\,\mathbf{k}\cdot\mathbf{r}) = (i)^2\mathbf{k}\cdot\mathbf{k}\exp(i\,\mathbf{k}\cdot\mathbf{r})$, whence

$$-\frac{\hbar^2}{2m}\,\nabla^2\psi_{\mathbf{k}}(\mathbf{r}) = \frac{\hbar^2 k^2}{2m}. \tag{8.48}$$

Since the wave number k varies continuously, these generalized eigenenergies are continuously distributed and form a continuum of energy levels.

Typically systems such as finite square wells, atoms, molecules and nuclei have *both* discrete energy levels and a continuum of energy levels. Atomic hydrogen is a good example of such systems. You have studied the bound states of that atom in Term 1. The corresponding energy levels are discrete and correspond to wave functions which go to zero for $r \to \infty$, where r is the distance between the electron and the nucleus. This means that the electron has a vanishingly small probability to be arbitrarily far away from the nucleus (which is why we can say that in such states the electron is bound to the nucleus).

The energy of these bound states is negative, which can be understood from the following argument: Suppose for an instant that the electron is a classical particle with a well defined trajectory obeying the rules of Classical Mechanics. Its energy, E, would then be the sum of its potential energy,

$$V(r) = -\frac{e^2}{4\pi\epsilon_0}\,\frac{1}{r}, \tag{8.49}$$

which is negative for all values of r, and its kinetic energy, T, which cannot be negative ($mv^2/2 \geq 0$ since $m > 0$ and $v^2 \geq 0$). Classically, an electron with a

total energy $E = T + V(r)$ can be located at any distance r from the nucleus at which $T = E - V(r) \geq 0$. I.e., when $E < 0$ the electron cannot go beyond the distance r_E at which $V(r_E) = E$, according to the rules of Classical Mechanics.

According to the rules of Quantum Mechanics, however, the electron may go beyond r_E by "tunnelling" through the potential barrier, but the probability of finding it at a distance r must then go to zero for $r \to \infty$. Mathematically, the Schrödinger equation has a solution finite everywhere and going to zero for $r \to \infty$ only for certain values of the energy; these values are the bound state eigenenergies you have found in Term 1.

There is no classical potential barrier for $E > 0$, though: Since $V(r) < 0$, the kinetic energy, $E - V(r)$, is positive at all values of r when $E > 0$. Therefore a classical electron can go arbitrarily far from the nucleus if its total energy is positive. Correspondingly, in Quantum Mechanics, the atom can be in an unboud state of positive energy. As the electron can be arbitrarily far in such states, its wave function does not need to go to zero for $r \to \infty$. Therefore the boundary condition which restricts the energy of bound states to discrete values does not apply for unbound states, with the consequence that such states exist for any positive values of E. The corresponding eigenenergies (in the sense of generalized eigenvalues of the Hamiltonian) form a continuous distribution. The corresponding wave functions can be obtained analytically, but they are considerably more complicated than the bound state wave functions you have studied in Term 1.

More generally, the energy eigenfunctions of a Hamiltonian H can correspond to bound states or to continuum states. The eigenenergies of bound states form a discrete distribution of energy levels and the corresponding eigenfunctions ($\psi_i(\mathbf{r})$, say) are square-integrable:

$$H\psi_i(\mathbf{r}) = E_i\psi_i(\mathbf{r}), \qquad \text{with} \qquad \int \psi_i^*(\mathbf{r})\psi_j(\mathbf{r})\,\mathrm{d}^3r = \delta_{ij}. \tag{8.50}$$

(The index used here to label these eigenfunctions stands for the set of all the quantum numbers necessary to identify each of the functions unambiguously. E.g., for atomic hydrogen, $i \equiv \{n, l, m\}$ where n is the principal quantum number, l the orbital angular momentum quantum number and m the magnetic quantum number.)

The eigenenergies of continuum states are distributed continuously. The corresponding eigenfunctions ($\psi_{\mathbf{k}}(\mathbf{r})$, say) are not square-integrable but can be normalized to a delta function:

$$H\psi_{\mathbf{k}}(\mathbf{r}) = E_{\mathbf{k}}\psi_{\mathbf{k}}(\mathbf{r}), \qquad \text{with} \qquad \int \psi_{\mathbf{k}}^*(\mathbf{r})\psi_{\mathbf{k}'}(\mathbf{r})\,\mathrm{d}^3r = \delta(\mathbf{k} - \mathbf{k}'). \tag{8.51}$$

(For simplicity, we label these continuum wave functions by a wave vector $\mathbf{k}$; in

some applications of this formalism one may need additional quantum numbers or several wave numbers to uniquely identify each of these eigenfunctions.)

Bound states wave functions are always orthogonal to continuum state wave functions since these states correspond to different eigenenergies:

$$\int \psi_n^*(\mathbf{r})\psi_{\mathbf{k}}(\mathbf{r})\,\mathrm{d}^3r = 0. \tag{8.52}$$

Depending on the Hamiltonian, its eigenenergy spectrum may be entirely discrete, or entirely continuous, or include both discrete energy levels and a continuum of energy levels. In the latter case, a complete set of energy eigenstates always includes both bound eigenstates and continuum eigenstates. Expanding a wave function $\psi(\mathbf{r})$ on a basis of energy eigenfunctions then involves both a summation on the former and an integral on the latter:

$$\psi(\mathbf{r}) = \sum_n c_n\,\psi_n(\mathbf{r}) + \int c_{\mathbf{k}}\,\psi_{\mathbf{k}}(\mathbf{r})\,\mathrm{d}^3k \tag{8.53}$$

Since the eigenfunctions $\psi_n(\mathbf{r})$ and $\psi_{\mathbf{k}}(\mathbf{r})$ are orthonormal,

$$c_n = \int \psi_n^*(\mathbf{r}')\psi(\mathbf{r}')\,\mathrm{d}^3r', \qquad c_{\mathbf{k}} = \int \psi_{\mathbf{k}}^*(\mathbf{r}')\psi(\mathbf{r}')\,\mathrm{d}^3r'. \tag{8.54}$$

Replacing c_n and $c_{\mathbf{k}}$ by these integrals in Eq. (8.53) yields

$$\psi(\mathbf{r}) = \int \left[\sum_n \psi_n(\mathbf{r})\psi_n^*(\mathbf{r}') + \int \psi_{\mathbf{k}}(\mathbf{r})\psi_{\mathbf{k}}^*(\mathbf{r}')\,\mathrm{d}^3k\right]\psi(\mathbf{r}')\,\mathrm{d}^3r'. \tag{8.55}$$

Since this relation must hold for any wave function $\psi(\mathbf{r})$ and at any position vector $\mathbf{r}$, we see that

$$\sum_n \psi_n(\mathbf{r})\psi_n^*(\mathbf{r}') + \int \psi_{\mathbf{k}}(\mathbf{r})\psi_{\mathbf{k}}^*(\mathbf{r}')\,\mathrm{d}^3k = \delta(\mathbf{r}-\mathbf{r}'). \tag{8.56}$$

This equation generalizes the completeness relation we have derived for the case of a finite-dimensional Hilbert space in Section 5.2 of these notes. Here we work in an infinite-dimensional Hilbert space, with the consequences that the summation over n may encompass an infinite number of terms and that continuum eigenstates may need to be included. Clearly, Eq. (8.56) includes an integral over $\mathbf{k}$ only if H has a continuous spectrum and a sum over n only if H has a discrete spectrum.

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