# Further Quantum Mechanics

## University of Cambridge Part II Natural Sciences Tripos

---

**Yue Wu**

*Yusuf Hamied Department of Chemistry*
*Lensfield Road,*
*Cambridge, CB2 1EW*

*yw628@cam.ac.uk*

## Acknowledgements

Nothing in these lecture notes is original. They are largely based on the notes by Dr. John Morgan, who lectured this course in 2025. Moreover, they are nowhere near accurate representations of what was actually lectured, and in particular, all errors are almost surely mine.

## Preface

This course focuses on quantum mechanics, and it is slightly more advanced than what you have learned in Part IB Chemistry A: *Introduction to Quantum Mechanics*. It will mostly focus on perturbation theory, including both the time independent and the time dependent cases, and it also covers topics that are removed from the A4 *Theoretical Techniques* course this year, namely normal modes. This course will avoid the rigorous mathematical formulation of quantum mechanics, and especially, it will not introduce concepts like projective Hilbert space or functional analysis. If you want a more mathematical approach to quantum mechanics, you can find my notes on Mathematical Tripos Part II: *Principles of Quantum Mechanics*.

# Contents

**1 Foundational Principles** **4**

1.1 Wavefunctions and Operators . . . . . 4

1.2 Hermitian Operators . . . . . 5

1.3 Unitary Operators . . . . . 7

# 1 Foundational Principles

We will start from a revision of the foundational principles of quantum mechanics that should be familiar from part IB Chemistry A.

## 1.1 Wavefunctions and Operators

In quantum mechanics, all physical information about a system is embodied in its wavefunction, denoted $\Psi$. The wavefunction is complex-valued, and we will use the *position representation* of the wavefunction, so it a function of the spatial coordinates. In the Born's interpretation, the probability density of finding a particle at $\mathbf{r}$ is

$$P(\mathbf{r}) \propto |\Psi(\mathbf{r})|^2 \,. \tag{1.1}$$

Wavefunctions should be single-valued and (at least) twice differentiable. Under such interpretation, we would often choose to normalise the wavefunction such that

$$\int \mathrm{d}\tau \, \Psi^* \Psi = 1 \,, \tag{1.2}$$

where $\mathrm{d}\tau$ is a shorthand notation for integrating over all spatial coordinates. This integral should converge for a proper wavefunction, so that it can be normalised.

A quantum mechanical system is defined by its Hamiltonian, $H$, the total energy operator. The Hamiltonian usually includes the kinetic and potential energies of the particles. A quantum mechanical system evolve according to the time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \Psi = H\Psi \,. \tag{1.3}$$

Often, the Hamiltonian operator is independent of time. For such time-independent system, the wavefunction satisfies the time-independent Schrödinger equation (which we often directly refers to as the Schrödinger equation)[1]

$$H\psi = E\psi \,, \tag{1.5}$$

where the constant $E$ is the energy of the system[2] and $\psi(\mathbf{r})$ is now a wavefunction independent of time. This is a (partial) differential equation, so it is only analytically solvable in a few limited cases, most of which you have seen already. Approximations are generally needed to solve for more complex systems, and one of the most important approximation techniques, the perturbation theory, is exactly the main theme of this course.

In general, the Schrödinger equation will have multiple (usually a countably infinite number of) solutions, which can be indexed by a quantum number $n$ such that

$$H\psi_n = E_n \psi_n \,. \tag{1.6}$$

The $\psi_n$ are different states available to the system, and the state with the lowest energy $E_n$ is known as the ground state. We usually arrange the states in sequence so that the ground state is labelled $\psi_0$ (or $\psi_1$ if you find it more convenient to start numbering from $n = 1$). We say two or more states are degenerate if they have the same energy. Any linear combination of degenerate wavefunctions is also a solution to the Schrödinger equation with the same energy.

[1] This is because if $H$ is independent of $t$, then a special class of solutions of the time-dependent Schrödinger equation exists

$$\Psi(\mathbf{r}, t) = \psi(\mathbf{r}) e^{-iEt/h} \,, \tag{1.4}$$

where $\psi(\mathbf{x})$ is independent of time and satisfied the time-independent Schrödinger equation.

[2] This is essentially the conservation of energy — if a system has time-translational symmetry, then the energy of the system is conversed. This is an example of the Noether's theorem.

The Schrödinger equation is a specific example of the more general eigenvalue equation. In quantum mechanics, all physical observables $A$ has a corresponding operator $\hat{A}$, if the wavefunction satisfies

$$\hat{A}\psi = a\psi\,, \tag{1.7}$$

then the value of $A$ will always be measured to be $a$. If this equation is not satisfied, then measured values of $A$ will be drawn from a probability distribution. The expectation and the uncertainty of $A$ is

$$\langle A\rangle = \frac{\int \mathrm{d}\tau\, \psi^* \hat{A}\psi}{\int \mathrm{d}\tau\, \psi^*\psi} \tag{1.8}$$

$$\Delta A = \sqrt{\langle A^2\rangle - \langle A\rangle^2}\,. \tag{1.9}$$

To avoid writing integrations over and over again, we introduce the Dirac bra-ket notation, in which a bra is $\langle\psi| \equiv \psi^*$ and a ket is $|\psi\rangle \equiv \psi$, and a pair of a bra and a ket forms a bra-ket (or just bracket), which implies integrations[3]

$$\langle\psi|\psi\rangle \coloneqq \int \mathrm{d}\tau\, \psi^*\psi\,. \tag{1.10}$$

An operator can be placed in middle of a bra-ket, so

$$\left\langle\psi\middle|\hat{A}\middle|\psi\right\rangle \coloneqq \int \mathrm{d}\tau\, \psi^*\hat{A}\psi\,. \tag{1.11}$$

To know what the quantum operator $\hat{A}$ corresponding to a physical observable $A$ is, we write the classical expression of $A$ in terms of position and momentum, and we replace the position and momentum with their quantum operators[4]

$$\hat{x} \longrightarrow x \tag{1.12}$$

$$\hat{p}_x \longrightarrow -i\hbar\frac{\partial}{\partial x}\,. \tag{1.13}$$

In general, a wavefunction cannot simultaneously be an eigenfunction of two (or more) operators. However, this will happen if and only if the commutator of the two operators, defined as

$$[\hat{A},\hat{B}] \coloneqq \hat{A}\hat{B} - \hat{B}\hat{A} \tag{1.14}$$

is zero. If this is the case, then we say the two operators commute. If the condition is not met, then the commutator places a lower bound on the product of the uncertainties

$$\Delta A \Delta B \geq \frac{1}{2}\left|\langle[A,B]\rangle\right|\,. \tag{1.15}$$

## 1.2 Hermitian Operators

Not all operators can correspond to physical observables. First of all, it has to be linear, so that

$$\hat{A}(a\,|\phi\rangle + b\,|\psi\rangle) = a\hat{A}\,|\phi\rangle + b\hat{A}\,|\psi\rangle\,, \tag{1.16}$$

[3]Actually more formally, $|\psi\rangle$ what truly fundamental, and is the quantum state of a system living in an abstract vector space called a (projective) Hilbert space $\mathcal{H}$. The wavefunction $\psi(\mathbf{x})$ is just the position-space representation of the vector $|\psi\rangle$. If a quantum state is a vector in the Hilbert space, $|\psi\rangle \in \mathcal{H}$, then an operator is an operator in $\mathcal{H}$, $\hat{A} : \mathcal{H} \to \mathcal{H}$, and a bra will be a dual vector living in the dual space of $\mathcal{H}$, $\langle\psi| \in \mathcal{H}^*$. What allows us to do this is the Risez representation theorem, which shows for any $|\psi\rangle \in \mathcal{H}$, there is always a corresponding $\langle\psi| \in \mathcal{H}^*$ and *vice versa*.

[4]This is the position-space representations of these operators, which we can act on wavefunctions that are written as a function of spatial coordinates. These operators have different representations in different basis.

where $a, b \in \mathbb{C}$ are constants. Moreover, operators that correspond to physical observable must be Hermitian. For any linear operator $\hat{A}$, we define its adjoint $\hat{A}^\dagger$ to be the operator such that

$$\left\langle \phi \middle| \hat{A} \middle| \psi \right\rangle = \left\langle \hat{A}^\dagger \phi \middle| \psi \right\rangle . \tag{1.17}$$

A operator is Hermitian if it is self-adjoint,[5] meaning $\hat{A} = \hat{A}^\dagger$, so that

$$\left\langle \phi \middle| \hat{A} \middle| \psi \right\rangle = \left\langle \hat{A}\phi \middle| \psi \right\rangle = \left\langle \psi \middle| \hat{A} \middle| \phi \right\rangle^* . \tag{1.18}$$

It is not difficult to show that taking the adjoint has the following properties:

$$(a\hat{A})^\dagger = a^* \hat{A}^\dagger \tag{1.19}$$
$$(\hat{A} + \hat{B})^\dagger = \hat{A}^\dagger + \hat{B}^\dagger \tag{1.20}$$
$$(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger \hat{A}^\dagger \tag{1.21}$$
$$(\hat{A} \left|\psi\right\rangle)^\dagger = \left\langle \psi \right| \hat{A}^\dagger . \tag{1.22}$$

A Hermitian operator has the following nice properties:

(i) The eigenvalues are all real.

(ii) Eigenfunctions with different eigenvalue are orthogonal. Even if some eigenfunctions are degenerate, orthogonal eigenfunctions can always be constructed.

(iii) The eigenfunction form a complete basis set.

Two functions are orthogonal means that their inner product, defined as $\langle \phi | \psi \rangle$, is zero. Moreover, the completeness of the basis set means that any wavefunction $\psi$ satisfying the boundary conditions can be expressed as a linear combination of the eigenfunctions,

$$\psi = \sum_i c_i \phi_i . \tag{1.23}$$

We can always make this basis set, which we denote as $\{\phi_i\}$, orthonormal by normalising the orthogonal eigenfunctions, so that $\langle \phi_i | \phi_j \rangle = \delta_{ij}$. Then taking the inner product of the above eigenfunction expansion with $\phi_j$, we have

$$\begin{aligned} \langle \phi_j | \psi \rangle &= \left\langle \phi_j \middle| \sum_i c_i \phi_i \right\rangle \\ &= \sum_i c_i \langle \phi_j | \phi_i \rangle \\ &= \sum_i c_i \delta_{ij} = c_j , \end{aligned} \tag{1.24}$$

and so

$$\psi = \sum_i \langle \phi_i | \psi \rangle \left| \phi_i \right\rangle . \tag{1.25}$$

From now on, we will denote the eigenstates just by its quantum number in the bra-ket notation: $|i\rangle \equiv |\phi_i\rangle$, so that for example, we have

$$\left|\psi\right\rangle = \sum_i \langle i | \psi \rangle \left| i \right\rangle . \tag{1.26}$$

[5]There is actually some extremely subtle differences between self-adjoint and Hermitian operators in functional analysis, but they would only bother pure mathematicians.

## 1.3 Unitary Operators

Apart from position space representations, there are many other basis we can represent the wavefunctions, such as the momentum space, or the basis spanned by eigenstates. An important class of linear operators is the *unitary operators* that are used for transformations of basis. To define unitary operators, we first need to define the identity operator. We define the identity operator to be an operator $\hat{I}$ such that

$$\hat{I}\,|\psi\rangle = |\psi\rangle \tag{1.27}$$

for any $|\psi\rangle$. An useful way of constructing the identity operator is the *resolution of identity*. For any complete orthonormal basis set $\{\phi_i\}$, we have

$$\hat{I} = \sum_i |i\rangle\,\langle i|\ . \tag{1.28}$$

This is because if we act this operator on any $|\psi\rangle$, we get its eigenfunction expansion is that basis

$$\hat{I}\,|\psi\rangle = \sum_i |i\rangle\,\langle i|\psi\rangle = \sum_i \langle i|\psi\rangle\,|i\rangle = |\psi\rangle\ , \tag{1.29}$$

where we moved $\langle i|\psi\rangle$ to the front to make the expression more obvious — we are allowed to do this because $\langle i|\psi\rangle$ is just a number.

Having defined the identity operator, we can define the inverse of an operator $\hat{A}$, denoted $\hat{A}^{-1}$, to be the operator such that

$$\hat{A}\hat{A}^{-1} = \hat{A}^{-1}\hat{A} = \hat{I}\,. \tag{1.30}$$

A unitary operator $\hat{U}$ is one for which the adjoint is equal to the inverse,

$$\hat{U}^{-1} = \hat{U}^\dagger\,, \tag{1.31}$$

so that

$$\hat{U}\hat{U}^\dagger = \hat{U}^\dagger\hat{U} = \hat{I}\,. \tag{1.32}$$

As we claimed before, unitary operators are used to define transformations between different representations.[6] Therefore, if we have an operator $\hat{A}$, we would like to know what its representation has transformed into after the transformation. Suppose the operator $\hat{A}$ acts on a general wavefunction $\psi$ to get

$$\hat{A}\psi = \phi\,, \tag{1.33}$$

and after the transformation, we have

$$\psi' = \hat{U}\psi\ , \qquad \phi' = \hat{U}\phi\,. \tag{1.34}$$

Then we would like to find $\hat{A}'$, which is the representation of $\hat{A}$ after the transformation, such that

$$\hat{A}'\psi' = \phi'\,. \tag{1.35}$$

We have

$$\hat{A}'\hat{U}\psi = \hat{U}\phi = \hat{U}\hat{A}\psi \implies \hat{A}'\hat{U} = \hat{U}\hat{A}\,. \tag{1.36}$$

Therefore,

$$\hat{A}' = \hat{U}\hat{A}\hat{U}^\dagger \quad \text{or} \quad \hat{A} = \hat{U}^\dagger\hat{A}'\hat{U}\,. \tag{1.37}$$

By taking the adjoint of the above equation, we can see that a Hermitian operator after unitary transformation is still an Hermitian operator.

[6] Unitary operators are linked to basis transformations, just like unitary matrices are linked to basis transformations in vector spaces. We will show this later, when we transform a wavefunction from the position basis (wavefunction) to the momentum basis (the momentum representation of the wavefunction), and transform an orbital from the AO basis in to the SO basis.

Moreover, a transformed eigenfunction of an operator is still an eigenfunction of the transformed operator with the same eigenvalue. This means that if

$$\hat{A}\psi_n = a_n\psi_n \,, \tag{1.38}$$

then since we can insert an identity operator anywhere,

$$\hat{A}\hat{U}^\dagger\hat{U}\psi_n = a_n\hat{U}^\dagger\hat{U}\psi_n \,, \tag{1.39}$$

and so

$$\hat{U}\hat{A}\hat{U}^\dagger\hat{U}\psi_n = a_n\hat{U}\psi_n \,, \tag{1.40}$$

which implies

$$\hat{A}'\psi'_n = a_n\psi'_n \,. \tag{1.41}$$

We can also show that the expectation values are the same:

$$\begin{aligned}\int \mathrm{d}\tau\, \psi_n^*\hat{A}\psi_n &= \int \mathrm{d}\tau\, \psi_n^*\hat{U}^\dagger\hat{U}\hat{A}\hat{U}^\dagger\hat{U}\psi_n \\ &= \int \mathrm{d}\tau\, (\hat{U}\psi_n)^*\hat{U}\hat{A}\hat{U}^\dagger\hat{U}\psi_n \\ &= \int \mathrm{d}\tau'\, \psi'^*_n\hat{A}'\psi'_n \,. \end{aligned} \tag{1.42}$$

If we let $\hat{A} = \hat{I}$, then

$$\int \mathrm{d}\tau'\, \psi'^*_n\psi_n = \int \mathrm{d}\tau\, \psi_n^*\psi_n \,, \tag{1.43}$$

so a normalised state remains normalised after transformation.[7]

[7] We are deliberately not using the bra-ket notation here because technically, $\psi_n$ and $\psi'_n$ corresponds to the same $|n\rangle$, just being represented in different basis. For example, if $\psi_n$ is represented in the position ($x$) basis and $\psi'_n$ is represented in the momentum ($p$) basis, then $\psi_n(x) = \langle x|n\rangle$ and $\psi'_n(p) = \langle p|n\rangle$, where $|x\rangle$ and $|p\rangle$ are the position and momentum eigenstates.