Quantum Mechanics:
The Essentials

Rohul Hayat Adnan

B.Sc. Melbourne, Australia

Ph.D. Canterbury, New Zealand

rohuladnan@gmail.com
https://sites.google.com/view/nanoclusters

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Preface

Two pillars of modern physics are quantum mechanics and Einstein (special and general) theory of relativity. Quantum mechanics is undoubtedly one of the greatest contributions to human civilization. More than half of the world's gross domestic product (GDP) is from quantum mechanics particularly by the electronic industry. It seeks to explain the behaviour and properties of small objects in the microscopic realm. Nonetheless, it is not limited to the quantum realm, but the quantum effects are manifested in the macroscopic world such as superconductivity, superfluidity, quantum Hall effect and Higgs boson.

In this book, I present the essentials of quantum mechanics aimed at the undergraduate level. I am very fortunate that my training and education have equipped me with mathematical tools to understand quantum mechanics. While I was studying at Melbourne University, I took several mathematics courses including Applied Maths Advanced, Vector Analysis, Real & Complex Analysis, Mathematical Methods and Applied Partial Differential Equations. These courses help me to understand the mathematical formalism of quantum mechanics better. I realized however when I started teaching Quantum Chemistry, all students are not equipped with the essential mathematical tools due to the rigid structural program. In this book, I will try to present explicit and detailed mathematical formalism whenever possible (of course some equations cannot be derived such as time-dependent Schrodinger eqn.).

I do hope that you enjoy reading this book and make use of it for your quantum course or bed-time reading.

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Postulate 1

Quantum states

The behaviours of small objects at the atomic scale is completely different from everyday experience. The behaviour of large objects is predictable deterministically from the classical mechanics, particularly Newton laws of motion. However, this is not true for small objects where observable quantities can only be determined statistically. Our everyday intuition of matter at the atomic scale breaks down. Thus, it is imperative to build up intuition by embracing the essential ideas, postulates, toy models and real examples of quantum systems.

1.1   States

Quantum mechanics is based on two constructs: **wavefunction and operators** (*D.J. Griffiths, Introduction to Quantum Mechanics, Prentice Hall*). The physical observables of large objects are computed from the equation of motion (obtained by solving the Newton's 2nd law). In quantum mechanics, we have a similar expression; instead of equation of motion we have a wavefunction. A wavefunction characterizes the state of a quantum particle in a probabilistic way.[1] Everything (all information) we need to know about a system[2] is encoded by the wavefunction. Quantum physicists tend to call quantum theory as a theory of information since a wavefunction contain all information about the system of interest. Wavefunction is **generally complex** (involves imaginary number i), and it is a function of position and time.

$$\Psi(x, t) \sim \text{quantum state}$$

The above relation means: a **wavefunction describes the state of a particle**, or the state of a particle is characterized by a wavefunction. We know that states are characterized by wavefunctions but what are quantum states actually? Mathematically, a quantum state is a

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[1] From now on, I simply refer small/tiny objects to quantum particles.

[2] A system may be a particle like electron or a collection of particles like He atom with 2 electrons and 1 proton.

vector in the Hilbert space. Importantly, wavefunctions in Hilbert space are orthonormal (orthogonal and normalized).

$$\int \Psi_m{}^* \Psi_n \ dx = \begin{cases} 0, & m \neq n \\ 1, & m = n \end{cases} \tag{1.0}$$

It seems familiar from high school linear algebra *i.e.* inner product of two vectors where the inner product of perpendicular vectors is zero, and the same vectors is one. Now it is clear why wavefunctions are vectors in Hilbert space.[3] Sometimes, state vector is also used in place of state function or wavefunction; they are also used interchangeably. Chemists simply assume that states refer to energy levels since they are measurable by spectroscopy, but this is not always the case.

1.2 Born's rule

The modulus squared of wavefunction tells about the probability density of a particle. This is called **Born's rule**: the probability of finding a particle in a region (dx) is given by $|\Psi(x,t)|^2 \ dx$. In a sloppy language, the wavefunction is a probability amplitude for finding a particle. This is the odd of quantum mechanics where it predicts the probability of the outcome of an experiment instead of the exact outcome. This statistical interpretation introduces indeterminacy in quantum mechanics. For this reason, a wavefunction is sometimes called a probability amplitude. Brain Greene (string theorist) prefers to call it probability wave.

$$\Psi(x,t) \ \Rightarrow \ probability \ amplitude$$

$$|\Psi(x,t)|^2 \ \Rightarrow \ probability \ density$$

$$P = |\Psi(x,t)|^2 \ dx \ \Rightarrow \ probability$$

Since wavefunctions are generally complex, the probability density refers to

$$|\Psi(x,t)|^2 = \ \Psi(x,t)^* \Psi(x,t) \tag{1.1}$$

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[3] In fact, any vector spaces where inner products exist are Hilbert space.

where $\Psi(x, t)^*$ is known as complex conjugate.[4] For example, given that

$$\Psi(x,t) = (2 + i\sin\theta)e^{-\frac{r}{2a}}$$

$$\Psi(x,t)^* = (2 - i\sin\theta)e^{-\frac{r}{2a}}$$

$$|\Psi(x,t)|^2 = (4 + sin^2\theta)e^{-\frac{r}{a}}$$

When talking about probability, it makes sense to think the total probability is unity. It simply means the particle exist over the entire region. Such a statement leads to normalization condition: total probability is unity. While this statement is strong, it should bother you as how do we make sure the total probability is unity?

$$\int_{all\ space} |\Psi(x,t)|^2\ dx = 1 \tag{1.2}$$

If a wavefunction $\Psi(x,t)$ is a solution to the Schrodinger eqn., $N\Psi(x,t)$ is also a solution to the Schrodinger eqn. (the constant N has no effect since the Schrodinger eqn. is a linear, second order differential eqn.). We then pick a constant (N) and make sure it satisfies the normalization condition, eqn. 1.0; this process is called normalizing. Normalization condition sets stringent requirements for wavefunctions. The requirements for acceptable wavefunctions include:

1. Wavefunctions must be single-valued

2. Wavefunction cannot be zero. $\Psi(x,t) = 0$ simply means the particle does not exist.

3. Wavefunction must be square-integrable. The integral of probability density must be finite[5]

4. Continuity of wavefunction: wavefunctions and the first derivative of wavefunctions must be continuous[6]

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[4] Complex conjugate has the opposite sign before the imaginary number i.
[5] Normalization condition guarantees the total probability to be unity.
[6] This is not necessarily required for some systems. As we will see later, wavefunctions for s orbital in hydrogen atom has a singularity (discontinuity in the first derivative) at the origin.

Stationary states are states where the **probability density does not change over time**. The states, of courses, may change over time since the wavefunctions are a function of space and time. However, the time-dependent factor cancels out.

Proof:

$$\Psi(x,t) = \psi(x)e^{i\frac{Et}{\hbar}}$$

$$|\Psi(x,t)|^2 = \Psi(x,t)^*\Psi(x,t) = \psi(x)e^{-i\frac{Et}{\hbar}}\psi(x)e^{i\frac{Et}{\hbar}} = |\psi(x)|^2$$

1.3 Momentum space

Typically, we write wavefunctions in position space i.e. as a function of position (x). But there is nothing wrong to write wavefunctions in momentum space.[7] Given a wavefunction in position space Ψ(x, t), we can simply write it in momentum space Φ(p, t) by applying a Fourier transform to it.

$$\Phi(p,t) = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{+\infty} e^{-\frac{ipx}{\hbar}}\, \Psi(x,t)\, dx \tag{1.3}$$

Conversely, a momentum space wavefunction Φ(p, t) can be written as a position space wavefunction Ψ(x, t) by applying its inverse Fourier transform.

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{+\infty} e^{\frac{ipx}{\hbar}}\, \Phi(p,t)\, dp \tag{1.4}$$

Like position space wavefunctions, momentum space wavefunctions must also obey Born's rule. The probability of measuring momentum of a particle with a range of momentum (*dp*) is given by

$$|\Phi(p,t)|^2\, dp$$

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[7] Physicists sometimes write wavefunction in momentum space. Chemists do not bother at all.

It simply says that it is impossible to specify exactly the momentum of a particle in a measurement. What we will get upon measurement is a collection of different momenta. Now it is obvious that the wave character of particles introduces indeterminacy in quantum mechanics. Such indeterminacy leads to the famous Heisenberg uncertainty principle.[8] We will learn about it in the next chapter.

1.4 Expansion of wavefunctions

Because wavefunctions live in Hilbert space, any other function *f(x)* can be written as an expansion (linear combination) of wavefunctions.

$$f(x) = \sum_{n=1}^{\infty} c_n \psi_n(x)$$

Mathematically, this is known as completeness.[9] A complete set of function is where other function can be written as a linear combination of functions. The coefficient c_n can be found by using Fourier's trick (as it is called by D.J. Griffiths). Multiply both sides of eqn. 1.4 by a dummy wavefunction ψ_m(x) and integrate with respect to *dx*, we get

$$\int \psi_m(x)^* f(x)\, dx \ = \ \sum_{n=1}^{\infty} c_n \int \psi_m(x)^* \psi_n(x)\, dx = \ \sum_{n=1}^{\infty} c_n \delta_{mn} = \ c_m \qquad (1.5)$$

Orthonormality (right angleness) of wavefunctions allows us to exploit the integral in term of Kronecker delta function. The subscript *m* is just a dummy letter which we can always change to any letter we like. Thus, thus coefficient can be expressed as

$$c_n = \int \psi_n(x)^* f(x)\, dx \qquad (1.6)$$

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[8] There is a generalized uncertainty principle that states the commutation relation for any two incompatible observables is not zero.

[9] I am not going to prove completeness here. Any textbooks on advanced calculus provides it.

The Kronecker delta function is defined as

$$\delta_{mn} = \begin{cases} 0, & m \neq n \\ 1, & m = n \end{cases}$$

As such, the Kronecker delta function is useful in writing the inner product of wavefunctions.

$$\int \Psi_m{}^* \Psi_n \ dx = \delta_{mn} = \begin{cases} 0, & m \neq n \\ 1, & m = n \end{cases}$$

Postulate 2

Operators and Observables

Observables quantities[10] in quantum mechanics are associated with (linear, Hermitian) operators. Operators are mathematical operations that transform a vector into another vector. Observables are values that can be measured in the lab using some instruments: spectrophotometer, Geiger counter, ruler etc. Each observable has its own operator.[11] Operators relate mathematical framework (theory) and experiment (something that can be measured). An operator is labelled by a letter with hat on it. Some operators are shown below. For simplicity, I only show the operator in 1D, but it can be generalized for 3D.

Observable	Label	Operator
Position	$\hat{x}$	x
Momentum	$\hat{p}$	$-i\hbar \dfrac{d}{dx}$
Kinetic energy	$\hat{T}$	$-\dfrac{\hbar^2}{2m}\dfrac{d^2}{dx^2}$
Potential energy	$\hat{V}$	V
Hamiltonian	$\hat{\mathcal{H}}$	$-\dfrac{\hbar^2}{2m}\dfrac{d^2}{dx^2} + V$

2.1 Hermitian operators

Quantum mechanical operators must be Hermitian. Hermitian operator is defined[12]

$$\int f^*\left(\hat{Q}g\right)\,d\tau = \int \left(\hat{Q}f\right)^* g\,d\tau \tag{2.1}$$

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[10] Physicists simply refer observables quantities as observables.

[11] In quantum mechanics, it almost always returns to the same vector.

[12] Some books use the definition of Hermitian operators as $\int f^*\hat{S}g\,d\epsilon = \left\{\int g^*\hat{S}f\,d\epsilon\right\}^*$ which is very messy and confusing.

There are two critical features of Hermitian operators: the eigenvalues are real, and the eigenfunctions are orthogonal.

Proof of Hermitian:

i. position operator is Hermitian

$$\int f^*(\hat{x}g)\ dx = \int f^* x g\ dx = \int x f^* g\ dx = \int (x^* f^*)g\ dx = \int (\hat{x}f)^* g\ dx$$

ii. momentum operator is Hermitian

Mathematical aside

Recall integration by parts

$$uv = \int u\,\frac{dv}{dx}\ dx + \int v\,\frac{du}{dx}\ dx$$

$$\int u\,\frac{dv}{dx}\ dx = uv - \int v\,\frac{du}{dx}\ dx$$

End of mathematical

2.2 Commutation relation

The definition of commutator for operator A and B is [A, B] = AB − BA. [13] Here, the order is very important since AB is not necessarily equal to BA. For two operators associated with their corresponding observables whose commutator is zero, we refer those operators commute with each other. When the commuter is non-zero, those operators do not commute. Some books refer the observables whose operators commute as compatible, and whose operators do not commute as incompatible.

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[13] Here, I just drop the hat on top of the operator.

Given the operators in Chapter 2, we can construct the commutation relation. For example, position and momentum operators.

$$[\hat{x}, \hat{p}] = \hat{x}\hat{p} - \hat{p}\hat{x}$$

We put a dummy function, f(x) at the end of both sides and using the operators

$$
\begin{aligned}
[\hat{x}, \hat{p}]f &= x\left(-i\hbar\frac{d}{dx}\right)f - \left(-i\hbar\frac{d}{dx}\right)xf \\
&= -i\hbar\, x\frac{df}{dx} + i\hbar\left[x\frac{df}{dx} + f\frac{dx}{dx}\right] \\
&= -i\hbar\, x\frac{df}{dx} + i\hbar x\frac{df}{dx} + i\hbar f \\
&= i\hbar f
\end{aligned}
$$

∴ $[\hat{x}, \hat{p}] = i\hbar$. This shows that position and momentum operators in quantum mechanics do not commute.[14] Or position and momentum are incompatible observables. We can use this commutation relation to derive the Heisenberg uncertainty principle.

The ==general uncertainty relation== between two operators is given by

$$\sigma_A \sigma_B \geq \frac{1}{2i}\langle[A, B]\rangle$$

For position-momentum commutator,

$$\sigma_x \sigma_p \geq \frac{1}{2i}\langle[\hat{x}, \hat{p}]\rangle = \frac{1}{2i}\langle i\hbar\rangle = \frac{\hbar}{2}$$

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[14] This surprising commutation relation prompted mathematician and physicist John von Neumann to emphasize that the difference between classical and quantum mechanics is that operators in quantum mechanics usually do not commute.

Postulate 3

Eigenvalue Equation

In the last chapter we talk about operators relate theory and experiment. Well, a natural question arises: what can be measured in experiment and how? Observable quantities that are measurable in the lab are eigenvalues. An eigenvalue equation is a mathematical statement that bridge theory and experiment in such a way that an operator acts on a function to give a real number multiplied by the same function.[15]

$$(\text{operator})(\text{function}) = (\text{real number})(\text{function})$$

$$\hat{Q}f(x) = qf(x) \tag{3.1}$$

Or in terms of operator and observable language:

$$(\text{operator})(\text{function}) = (\text{observable})(\text{function})$$

$$\hat{A}\psi_n(x) = a_n\psi_n(x)$$

The subscript n appears because each eigenfunction gives a corresponding eigenvalue. And different states (characterized by n) have different eigenfunctions. In other words, different eigenfunctions yield different eigenvalues. For example, the ground state ψ_0 and first excited state ψ_1 of a quantum harmonic oscillator are

$$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} e^{-\frac{\alpha}{2}x^2} \qquad \psi_1(x) = \left(\frac{4\alpha^3}{\pi}\right)^{\frac{1}{4}} x\, e^{-\frac{\alpha}{2}x^2}$$

But what happens if different eigenfunctions give the same eigenvalue? Is it possible at all? Answer: Yes, it is possible to have a set of eigenfunctions with the same eigenvalue, and such

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[15] Because operators act on a function, you cannot simply cancel the function on both sides.

states are called degenerate. For example, a set of 2p (p_x, p_y and p_z) orbitals in hydrogen atom are degenerate.

3.1   Schrodinger equation

The Schrodinger equation is an eigenvalue equation whose operator is Hamiltonian (sum of kinetic and potential energy) and eigenfunction is a wavefunction and eigenvalue is the total energy. It is conveniently written as

$$\widehat{\mathcal{H}}\Psi(x,t) = E\Psi(x,t) \quad or \quad \widehat{\mathcal{H}}\psi(x) = E\psi(x) \tag{3.2}$$

where the first eqn. involves time-dependent wavefunction and the second eqn. time-independent one. The Hamiltonian operator is

$$\widehat{\mathcal{H}} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$$

Here I am dealing with 1D coordinate for simplicity. Of course, in a 3D world, the Schrodinger eqn. should read

$$\widehat{\mathcal{H}}\Psi(x,y,z,t) = E\Psi(x,y,z,t) \tag{3.3}$$

It is worth to have a glimpse how the (time-independent) Schrodinger eqn. was derived. A wavefunction for classical wave is

$$\Psi(x,t) = \psi(x)\cos\omega t \tag{3.4}$$

The classical non-dispersive wave equation

$$\frac{\partial^2\Psi(x,t)}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2\Psi(x,t)}{\partial t^2} \tag{3.5}$$

Substituting the wavefunction into the wave eqn. and use $\omega = 2\pi f$ and $v = f\lambda$, we get

$$\frac{d^2\psi(x)}{dx^2} + \frac{\omega^2}{v^2}\psi(x) = 0$$

$$\frac{d^2\psi(x)}{dx^2} + \frac{4\pi^2}{\lambda^2}\psi(x) = 0 \tag{3.6}$$

Up to this point, everything is classical. Using the **de Broglie's relationship λ = h/p** to introduce quantum condition. From the Hamiltonian, total energy of the system $E = p^2/2m + V \rightarrow p^2/2m = E - V$

$$\frac{d^2\psi(x)}{dx^2} + \frac{8\pi^2 m}{h^2}[E - V(x)]\psi(x) = 0 \tag{3.7}$$

Using the reduced Planck's constant $\hbar = h/2\pi$, we arrived at **time-independent Schrodinger equation (TISE)**.[16]

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \tag{3.8}$$

This is only valid when the potential energy is a function of x only (independent of time, t). The wavefunctions generally take the form

$$\Psi(x,t) = \psi(x)e^{-i\frac{Et}{\hbar}} \tag{3.9}$$

with constant energy E. That is to say, once you find a wavefunction $\psi(x)$ by solving the time-independent Schrodinger equation (TISE), it is just a matter of tacking the phase factor (or time-dependent function) exp(- $iEt/\hbar$) to $\psi(x)$ to find the general wavefunction $\Psi(x,t)$. Easy!

Time-dependent Schrodinger equation is

$$i\hbar\frac{\partial\Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} + V(x,t)\Psi(x,t) \tag{3.10}$$

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[16] Historically, Schrodinger actually developed the TISE before the TDSE.

$$ i\hbar \frac{\partial \Psi(\mathrm{x,t})}{\partial t} = \hat{\mathcal{H}} \Psi(x,t) \tag{3.11} $$

3.2   Schrodinger-like eqns.

The Schrodinger eqn.[17] is impossible to solve for many-body systems even for the next simplest atom, Helium, which consists of 2 electrons. Approximations have been developed to approximate the Schrodinger eqn. which takes the general form of an eigenvalue eqn. One of them is the Hartree-Fock eqn.

$$ \hat{F}\varphi(x) = \varepsilon\varphi(x) \tag{3.12} $$

where *F* is the Fock operator, φ is Fock orbital and ε is the orbital energy. The Hartree-Fock method is based on the assumption based one-electron orbitals and its energy because it allows the use of quantum numbers *n, l, m$_l$* to calculate the energy eigenvalues for a quantum system. The Fock operator is given by

$$ \hat{F} = \sum_{i}^{n} \mathcal{H} + \sum_{i}^{n/2} \sum_{j}^{n/2} (2J_{ij} - K_{ij}) $$

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[17] Now onwards, when I use Schrodinger eqn., it always almost refers to the TISE since many cases in quantum mechanics deal with it.

Postulate 4

Expectation value

Expectation value is also known as the average value. The formal definition of expectation value is the average value of **repeated measurements** in an ensemble of **identically prepared system**s.[18] Expectation value of any observable is defined as

$$\langle Q \rangle = \int \psi^* \hat{Q} \psi \ d\tau$$

Expectation value is nothing new in physics. In fact, **Ehrenfest's theorem** states: expectation values in quantum mechanics follow those of classical mechanics. For example, the expectation value of momentum is

$$\langle p \rangle = m \frac{d\langle x \rangle}{dt}$$

The relation between expectation value of any quantum mechanical operator A with the expectation of the commutator of that operator and the Hamiltonian of a system is

$$\frac{d\langle A \rangle}{dt} = \frac{1}{i\hbar} \langle [A, \mathcal{H}] \rangle + \langle \frac{\partial A}{\partial t} \rangle$$

4.1 Standard deviation

The standard deviation of an operator is defined as

$$\sigma_A \cong \Delta A = \sqrt{\langle A^2 \rangle - \langle A \rangle^2}$$

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[18] Many students confuse that expectation value is the average of, say, 100 measurements on a system. This is wrong. It is the average measurement on 100 identically prepared systems. Once you perform a measurement, a wavefunction collapse hence the state of a system changes.

Chemists usually assume that $\sigma_Q \cong \Delta Q$. The generalized uncertainty principle for two incompatible observables is given by

4.2 Average energy

The expectation value of energy is simply referred to as average energy. For many states, the total wavefunction is a sum of all eigenfunctions. This is referred to as a linear combination of states.

$$\psi(x) = \sum_{n=1} c_n f_n(x)$$

The coefficient c_n (also known as probability coefficient) tells how much a state f_n is contained in a wavefunction $\psi(x)$. can be found using Fourier's trick.

$$c_n = \langle f_n | \psi \rangle = \int f_n(x)^* \psi(x) \, dx$$

Again, total probability must be unity $\sum_n |c_n|^2 = 1$. Moreover, the average energy can be written as

$$E = \langle \mathcal{H} \rangle = \sum_{n=1} |c_n|^2 E_n$$

where $|c_n|^2$ can be interpreted as the probability of getting energy E_n.

Postulate 5

16

Time-dependent Schrodinger equation

The time-dependent Schrodinger equation (TDSE) is used for a potential that varies as a function of position, x and time, t.