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# ▶ Quantum Mechanics

PH2210

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## Syllabus Information

### Quantum Mechanics - 60959 - PH 2210 - 0

**Associated Term:** 2012/13 Academic Session

Royal Holloway Campus  
Standard Schedule Type  
Traditional Instructional Method

**Learning Objectives:** Aims: To study in depth the use of Schrodinger's equation to solve problems involving the motion of a particle in a potential in one and three dimensions. To demonstrate how the solution predicts quantization of the energy of the particle and the need to introduce other quantum numbers to describe its behaviour. To demonstrate the solution to Schrodinger's equation for the hydrogen atom and to provide a simple understanding of the periodic table. To introduce the concept of mixed states. Learning Outcomes: By the end of the course students should be able to demonstrate a sound understanding of the use of Schrodinger's equation. They should be able to solve the equation for a number of simple potentials including the square well, the simple harmonic oscillator and the hydrogen atom. For each of these they should be able to sketch the potential, the energy level diagram and typical wave functions. They should be able to provide the definition of terms such as normalization and parity of wave functions, and degeneracy and to explain quantitatively the phenomenon of quantum mechanical tunnelling. Course Content: Review of the failure of classical physics and the introduction of quantum ideas; the uncertainty principle. Schrodinger's equation; the wave function and its interpretation. Operators, eigenvalues, eigenfunctions, expectation values; commutation relations, non-commutation. Applications of Schrodinger's equation in one-dimension: free particle, square well, harmonic oscillator; potential step, barrier and tunnelling (including alpha decay). Applications of Schrodinger's equation in three dimensions: particles in a rectilinear box, angular momentum, the hydrogen atom. The exclusion principle, atomic structure and the periodic table. Mixed states, Schrodinger's cat.

**Required Materials:** A P French & E F Taylor, An Introduction to Quantum Physics, van Nostrand Reinhold, 1978. (530.12.FRE) B H Bransden & C J Joachain, Introduction to Quantum Mechanics, Longman, 2nd edition 2000. (530.12.BRA)

**Technical Requirements:** Teaching & Learning Methods: 22 lectures and approximately 10 problem classes Approximately 118 hours private study time, to be used for learning the material in detail, answering coursework problems and revision. Assessment: Exam: - Two-hour examination - one compulsory question + two others to be answered out of four (90%) Coursework: Best five of six coursework assignments (10%). Deadlines: Stated with each problem sheet and normally about 10 days from the date issued.

## Problems with Classical physics

By the late nineteenth century the laws of physics were based on Mechanics and the law of Gravitation from Newton, Maxwell's equations describing Electricity and Magnetism, and on Statistical Mechanics describing the state of large collection of matter. These laws of physics described nature very well under most conditions, however, some measurements of the late 19th and early 20th century could not be understood (we discuss two of the problems below, the third one is black body radiation and the "Ultraviolet Catastrophe" which we discussed last year in PH1920 with Professor G.Blair).

### Photoelectric Effect

The Photoelectric effect was first famously explored by Albert Einstein in 1905. It is a *low energy interaction between matter and radiation*. The experiment conducted was simply shining some radiation at a conducting material (preferably one with excess electrons) and observing the electrons being emitted. The results were completely counter intuitive (from the point of view of the well-developed classical theory). The main questions it raised were:

- The electrons were emitted immediately - no time lag!
- Increasing the intensity of the light increased the number of photoelectrons, but not their maximum kinetic energy!
- Red light will not cause the ejection of electrons, no matter what the intensity!
- A weak violet light will eject only a few electrons, but their maximum kinetic energies are greater than those for intense light of longer wavelengths!<sup>[1]</sup>

The answers of course led us towards a completely new understanding of physical phenomena which was Quantum mechanics.

### Compton Scattering

The scattering of photons from charged particles is called Compton scattering after Arthur Compton who was the first to measure photon-electron scattering in 1922. The effect is usually observed by scattering X-rays or  $\gamma$ -rays on an electron. During the collision, some of the incident photon's energy is imparted to the electron, resulting in a decrease in the scattered photon's energy and therefore an increase in its wavelength. The energy lost by the photon is transferred to the electron in the form of recoil kinetic energy (imagine two snooker balls colliding). This is a maximum when the photon is scattered straight back ( $\theta=\pi$ ). By considering energy and momentum conservation before and after the collision, we find that the photon energies are related by a simple equation, the derivation of this was done by applying special relativity principles.<sup>[2]</sup>

*Compton Scattering equation*

$$\lambda' - \lambda = \frac{h(1 - \cos \theta)}{mc}$$

$\lambda'$  = Wavelength of photon after scattering

$\lambda$  = Wavelength of photon before scattering

$h$  = Planck constant ( $6.63 \times 10^{-34}$  Js)

$\theta$  = Scattering angle

$m$  = Mass of particle being scattered of (in our case the electron)

$c$  = Speed of electromagnetic radiation in a vacuum ( $3 \times 10^8$   $ms^{-1}$ )

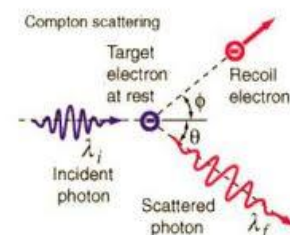


Figure 1

## Introduction of Quantum Physics

Quantum Mechanics incorporates a wave-particle duality and explains all of the above phenomena. In doing so, Quantum Mechanics changes our understanding of nature in fundamental ways. While the classical laws of physics are deterministic, *QM is probabilistic*. We can only predict the probability that a particle will be found in some region of space. Electromagnetic waves like light are made up of particles we call photons. The new idea of Quantum Mechanics is that every particle's *probability (as a function of position and time) is equal to the square of a probability amplitude function* and that these probability amplitudes obey a wave equation. This is much like the case in electromagnetism where the energy density goes like the square of the field and hence the photon probability density goes like the square of the field, yet the field is made up of waves. So probability amplitudes are like the fields we know from electromagnetism in many ways.

Einstein, based on Planck's formula, hypothesized that the particles of light had energy proportional to their frequency. The equation below solves the problem with the photoelectric effect as we see that the energy of the photon is independent of the intensity of the beam and depends only on its frequency. This is one of the two main pillars on which the theory of Quantum physics stands.

*Einstein's energy relation*

$$E = hf$$

*E = Energy of the particle*

*h = Planck constant ( $6.63 \times 10^{-34}$  Js)*

*f = Frequency (Hz)*

The other being the de Broglie relation in which de Broglie assumed that the laws of special relativity would hold in quantum phenomena and therefore would be invariant under the Lorentz transformations which led him to develop an equation in 1924 that showed that the momentum and wavelength were inversely related to each other (meaning every particle had a wavelength, even you and me!).

*de Broglie relation*

$$p = h/\lambda$$

*p = Momentum ( $\text{kgms}^{-1}$ )*

*h = Planck constant ( $6.63 \times 10^{-34}$  Js)*

*$\lambda$  = Wavelength (m)*

Three years after de Broglie came up with this theory, Davisson and Germer, who were two American physicists, designed an experiment to test the properties of Nickel by firing electrons at Nickel atoms in a vacuum (similar to Geiger and Marsden's experiment in 1909 which led Rutherford to put forward his theory of the atomic structure). However they accidentally led some air into the chamber and had to heat it and therefore deformed the structure of the Nickel (full details in the paper I have referenced)<sup>[3]</sup>. The observations they made showed the wave nature of electrons by the diffraction pattern (Bragg angle diffraction law applied to particle waves) given, therefore they had accidentally proven de Broglie's hypothesis which one him the Nobel prize in 1929!

## Postulates of Quantum Mechanics

This is where Quantum mechanics becomes very much like abstract mathematics. Based on a few improvable statements (just like axioms in mathematics) we can start doing the mathematics of Quantum mechanics which cannot be derived in any way from the principles of classical mechanics.

*Every state of a system at a given time is described by a normalisable wavefunction  $\Psi(x,t)$ .  $\Psi$  contains all the physical information about the system. Any (normalisable) wavefunction corresponds to a possible state of the system*

*Every physical observable is associated with a linear Hermitian operator; the result of a measurement is always one of the eigenvalues of the operator. If the operator  $\hat{A}$  has a discrete spectrum of eigenvalues and the corresponding eigenfunctions (in this case the  $\Psi$ 's), then using the *completeness theorem* (we have studied this in Mathematics, it comes from the Sturm-Louisville theory), the state function  $\Psi$  can be expanded in terms of the normalised eigenfunctions.*

*Wavefunction*

$$\Psi(x) = \sum_{n=1}^{\infty} c_n \Psi_n(x)$$

*Normalisation*

$$\sum_{n=1}^{\infty} |c_n|^2 = 1$$

If a measurement of A is carried out in this state of the system, the outcome is  $a_n$  with probability  $|c_n|^2$ .

*Immediately after such a measurement, the system is in the state with normalised wavefunction. This is known as collapse of the wavefunction (sounds a lot interesting then it really is!, however when we think about this, it leads to the so called 'Many Worlds' interpretation which opens the door to theories involving multiverses etc.<sup>[D]</sup>)*

*The average value of an observable  $\kappa$  is given by the expectation value. This is obtained by operating with the operator  $\langle K \rangle$  on the wavefunction  $\Psi(x)$  and then multiplying by its complex conjugate (we are exploiting the orthogonality of the functions here) and integrating with respect to  $x$  from  $-\infty$  to plus  $\infty$ .*

*Expectation Value*

$$\langle A \rangle = \sum_{n=1}^{\infty} |c_n|^2 \kappa_n$$

The Time Dependent Schrodinger Equation (TDSE) governs how the wavefunction changes with time.

## Wave mechanics and states of systems

The main difference between classical physics and quantum physics is the *logic* we use to solve classical problems does not work for quantum phenomena. This is not an easy concept to grasp as it is completely counter intuitive to what we see around us. However if you think about it, there *is no reason* for classical physical laws to hold be that in the classical world or on quantum scales. We simply develop laws that describe our observations, so maybe we should not be so surprised after all (or maybe it has something to do with weather our brain is 'Quantum' or 'Classical'.)<sup>[D]</sup> Classically a *state* of a system is deterministic, and can be described as a *point* in a *space of states* (this is studied by Set theory). However Quantum mechanically, a *state* is probabilistic and can in a way be seen as a vector in a vector space (this is how we expanded the state  $\Psi(x)$  in the postulates, the vector space is technically called a '*complex separable Hilbert space*'). This description of a state is radically different from classical mechanics as it *never tells us* exactly where a particle is or how it is moving, it just gives a *probability*.

One of the postulates given above says that the state of a system at any given time is given by a wavefunction and infact the time evolution can also be a wavefunction as we shall see. We will use the solutions of the wave equation as our starting point.

Wave equation

$$c^2 \hat{\nabla}^2 \Psi = \frac{\partial^2 \Psi}{\partial t^2}$$

$\nabla$  operator

$$\hat{\nabla} = \frac{\partial}{\partial x} \hat{i} + \frac{\partial}{\partial y} \hat{j} + \frac{\partial}{\partial z} \hat{k}$$

$c =$  Speed of electromagnetic radiation in a vacuum ( $3 \cdot 10^8 \text{ ms}^{-1}$ )  
 $\Psi =$  wavefunction we are trying to find the solution for

Solutions to this are of the form (in one dimension)<sup>[Derivation 1]</sup>:

Wavefunction

$$\Psi(x, t) = Ae^{i(\pm kx - \omega t)}$$

$k =$  Wave vector ( $1/\lambda$ ).

$\omega =$  Angular frequency  $2\pi f$

The solutions with a positive wave vector move to the right, the solutions with a negative wave vector move to the left. Substituting back into the wave equation we obtain a dispersion relation,  $\omega(k) = ck$ <sup>[Derivation 1]</sup>. As we can see, this is linear in  $k$ , however as we will see this is not the case for matter waves (the phase velocity  $(\frac{\omega}{k})$  and group velocity  $(\frac{\partial \omega}{\partial k})$  are not equal).

## Wave functions

The state of a system is represented by a complex wavefunction, as shown above, which has no physical meaning itself. The wavefunctions used must form a complete set of orthonormal basis vectors (discussed in mathematics course) for us to be able to use them. To get some physical information from it we take the intensity of the wavefunction (Amplitude squared) as being the probability density function for a particle's position or momentum. Mathematically given by:

*Probability Distribution*

$$P(x, t) = \Psi^*(x, t)\Psi(x, t) = |\Psi(x, t)|^2$$

Therefore by the rules that govern probability theory we can say that the probability of a particle being found in a given interval is given by:

*Probability of finding a particle in a given region*

$$P = \int_x^{x+\delta x} |\Psi(x, t)|^2 dx$$

The wavefunctions are restricted to a class of functions that are square integrable, that means they are finite when are squared and integrated because if they were not then they would have no physical meaning as the probability of the particle being found in a finite region of space being infinite would mean it has to be *everywhere* all the time.

*Normalisation integral*

$$\int_{-\infty}^{\infty} |\Psi(x, t)|^2 dx = 1$$

We also assume that the wavefunctions are continuous; particles cannot be created or destroyed (This assumption only holds in very basic potentials and does not allow for quantum fluctuations<sup>[10]</sup>).

Orthogonality is a very important property of the wavefunction we need as this means they can form a complete set of basis vectors.

*Orthogonality integral*

$$\int_{-\infty}^{\infty} \Psi_n^*(x)\Psi_m(x) dx = \delta_{nm}$$

$\delta_{nm}$  = Kronecker delta

A particle in a quantum state can be bound or unbound depending on the energy it has (kinetic) and the potential in which it is placed. If the particle has less energy than the potential it is confined in (such as a potential well) then it is to be in a bound state.

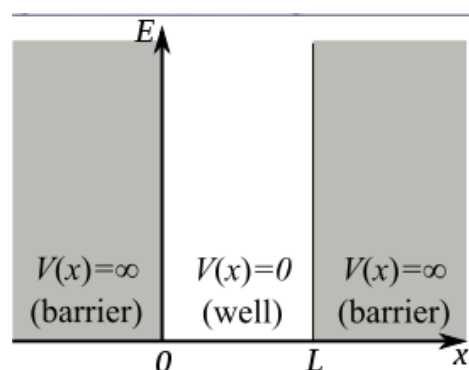


Figure 2

## Operators

Physics is an experimental science, after all the only way to test our theories are by experimenting them. In classical physics any observable in an experiment is in general a function of time, which we can observe with complete accuracy (however as we will see this is not the case in quantum mechanics, as to make an observation we have to interact with the system itself, usually by hitting it with a photon. Classically we can make this photon of negligible energy compared to the system we are observing, however on quantum scales, the energy of the photon itself will change the state of the system therefore we can never know the state of the system to complete accuracy, unless we find some *other method of 'observation'*<sup>[D1]</sup>). In quantum mechanics we cannot observe the state directly because as we stated above it is represented by a complex wavefunction, therefore has no physical meaning.

An operator  $\hat{A}$ , is a mathematical object that transforms one function into another (A mathematical transformer!). It always acts on the function or list of functions on the right of itself. The product of two operators is a third operator and the order of operators is important because in general they are not commutative. All the operators used in quantum mechanics are generally linear and the product of operators implies successive operations.

### Properties of Operators

<b>Linearity</b>	$\hat{A}(cf(x)) = c\hat{A}f(x)$
<b>Product of operators</b>	$\hat{B}\hat{A}f(x) = \hat{B}(\hat{A}f(x))$
<b>Product of two operators is a third operator</b>	$\hat{B}\hat{A}f(x) = \hat{C}f(x)$
<b>Non-commutative behaviour</b>	$\hat{B}\hat{A}f(x) \neq \hat{A}\hat{B}f(x)$
<b>Expectation value of operator</b>	$\langle \hat{A} \rangle = \int_{-\infty}^{\infty} \Psi^*(x, t) \hat{A} \Psi(x, t) dx$

As we postulated previously every observable quantity has a Hermitian operator associated with it. I will write down the two most important operators as they will be the ones used to derive the Schrodinger equation (the derivations will be given in the back).

*Momentum Operator* <sup>[Derivation 2]</sup>

$$\hat{p} = -i\hbar\hat{\nabla}$$

*Energy operator* ( $\hbar\omega$ ) <sup>[Derivation 3]</sup>

$$\hat{E} = i\hbar\frac{\partial}{\partial t}$$

$\hbar = \text{Planck's constant} \frac{1}{2\pi} (1.05 * 10^{-34} \text{ Js})$

$$\hat{\nabla} = \frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z}$$

*Hermitian Operator,  $\hat{A}$*

$$\int_{-\infty}^{\infty} \phi^*(x) \hat{A} \Psi(x) dx = \int_{-\infty}^{\infty} (\hat{A} \phi(x))^* \Psi(x) dx$$



## Schrodinger Equation (1 Dimension)

We will now use the classical concepts of energy and Hamilton's equations to derive the equation for quantum mechanical motion. For this we will assume that the wave solutions from the wave equation are also solutions on the quantum scale if the energy and momentum are given by the Einstein and de Broglie relation respectively.

$$\begin{aligned} & \text{Classical Hamiltonian} \\ & H = T + V \end{aligned}$$

T = Kinetic energy  $\left(\frac{p^2}{2m}\right)$

V = Potential energy

Quantum Mechanical Hamiltonian<sup>[Derivation 4]</sup>

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \hat{V}(x)$$

$\hbar$  = Planck's constant  $\frac{1}{2\pi}$  ( $1.05 * 10^{-34}$ )

m = Mass of particle (kg)

$\hat{V}$  = Potential energy operator

The total energy of a quantum mechanical particle is  $\hat{E} = \hbar\hat{\omega}$ . This is what we will use along with the Hamiltonian to derive the Schrodinger equation.

Schrodinger Equation<sup>[Derivation 5]</sup>

$$H(t) | \psi(t) \rangle = i\hbar \frac{d}{dt} | \psi(t) \rangle$$

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

Solutions of the wavefunctions that satisfy the Schrodinger equation determine everything that can be known about a given system. Therefore, the Schrodinger equation is a very powerful and elegant equation. This is the general Schrodinger equation and is equivalent to Newton's laws of motion for classical physics, as it describes the dynamical behaviour of systems over time.

This can be separated into a spatial part (Time Independent Schrodinger Equation, TISE) and a time evolution equation (by separation of variables, discussed in mathematics).

## Time Dependent Schrodinger Equation

*Time Dependent Schrodinger Equation*<sup>[Derivation 6]</sup>

$$i\hbar \frac{\partial \Psi(t)}{\partial t} = E\Psi(t)$$

The TDSE is a relatively straight forward 1<sup>st</sup> order linear differential equation. It does not depend on the potential energy function which means that the solution of  $\Psi(t)$  is independent of the system under consideration. Putting it another way, a wavefunction evolves with the same time dependence in any potential.

*TDSE solution*<sup>[Derivation 1]</sup>

$$\Psi(t) = Ae^{-i\omega t}$$

Where A is a constant set by the boundary conditions of the system and since  $\Psi(t)$  is a universal for all potentials, then to solve the general Schrodinger equation we solve the TISE and multiply the solution by  $e^{-i\omega t}$ .

*Normalisation Condition*

$$\int_{-\infty}^{\infty} |\Psi(t)|^2 dx = 1$$

In general any product solution of the TDSE is a stationary state as the energy will not change in time, however a superposition of states will have different energies, therefore the overall state is not going to be stationary (yes, that means that the particle will fluctuate by itself in time!).

## Time Independent Schrodinger Equation

*Time Independent Schrodinger Equation*<sup>[Derivation 6]</sup>

$$\left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \hat{V}(x) \right) \Psi(x) = E\Psi(x)$$

This is the equation we spend most of our time calculating and trying to understand, the derivations are long and mathematically challenging, therefore I will attach the derivations at the back. Here I will simply state and discuss the solutions for different potentials and their implications. To solve the TISE we need to find a set of boundary conditions to determine the constants obtained by the solving the equation.

- Firstly we insist that the wavefunction  $\Psi(x)$  is finite everywhere (we have discussed why this is necessary above).
- The energy and the potential must also be finite everywhere.
- From the TISE we can see that  $\Psi(x)''$  must also be finite (as the right hand side of the equation will be finite).
- We can compute all these conditions to find a general constraint on the possible solutions by integrating both sides of the TISE as the limits of integration become infinitesimally small. This leads to the following two conditions:
  - The wavefunction is continuous at any given potential boundary
  - The derivative of the wavefunction is also continuous at any given potential boundary

Before I start to discuss the Schrodinger equation for different potentials I will remind you that the force is the negative gradient of the potential.

$$\vec{F} = -\nabla V$$

$$\nabla = \frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z}$$

Therefore, a particle in a constant potential well experiences no *net* force. This is the case for finite and infinite potential wells; however the harmonic oscillator potential provides a restoring force (according to Hooke's Law).

*Harmonic Oscillator restoring force*

$$\vec{F} = -\frac{dV}{dx} = -k\vec{x}$$

$k$  = effective spring constant

This type of restoring force approximates the force on an atom in a solid that is displaced a small distance  $x$  from its equilibrium position. Therefore the wave functions that are solutions to Harmonic oscillator can represent the quantum states of atoms in a solid.

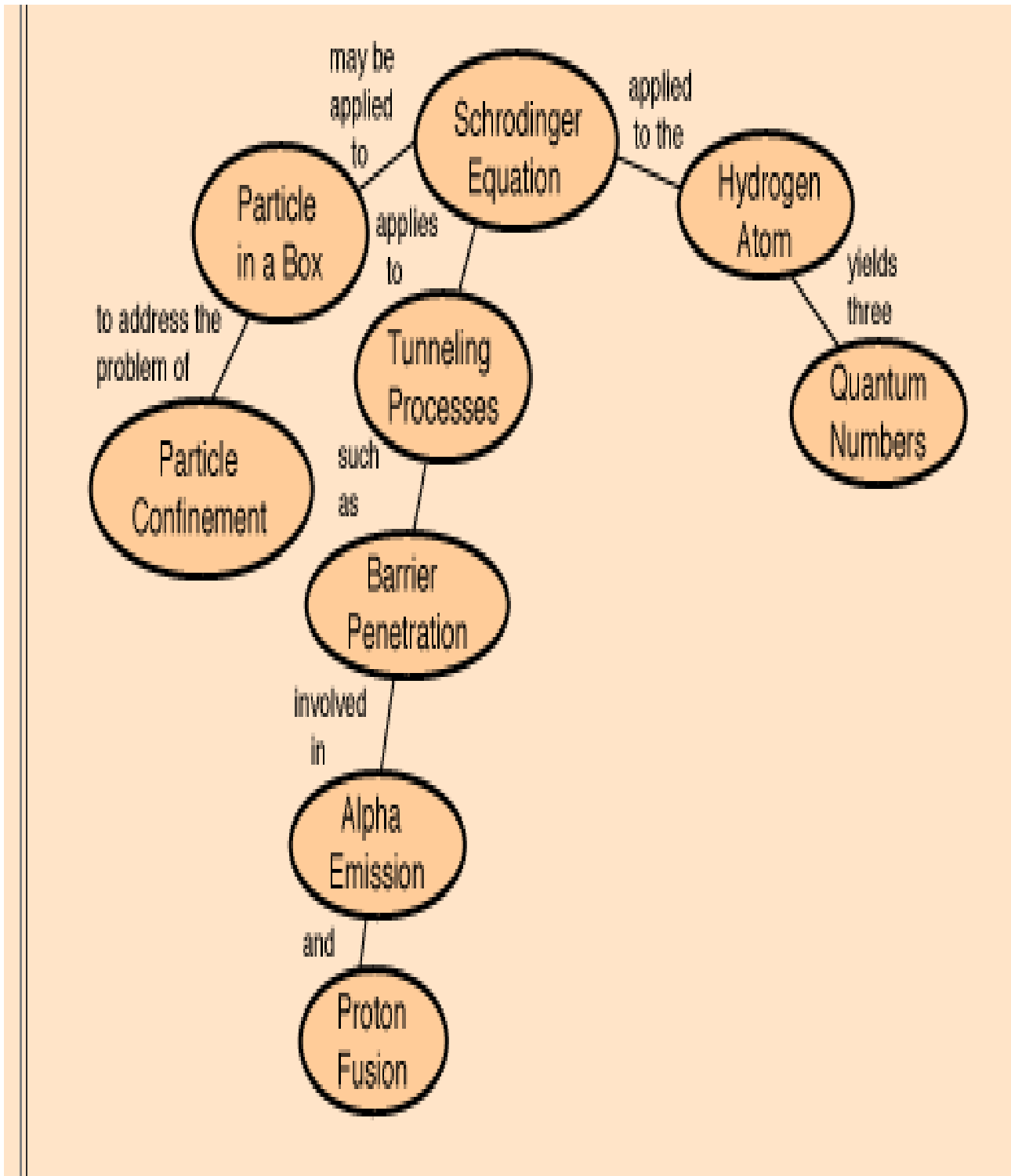


Figure 3<sup>(4)</sup>

**Free Particle** <sup>[Derivation 7]</sup>

A particle moving in space where the potential is zero,  $V=0$ .

The important thing to realise for the particle is that it does not experience any forces and also no boundaries, therefore the differential equation can be solved without any boundary conditions. The TISE in this case is a simple second order linear differential equation with solutions:

*Free particle solutions*

$$\Psi(x, t) = Ae^{i(kx - \omega t)} + Be^{i(-kx - \omega t)}$$

$$k = \sqrt{2mE/\hbar^2}$$

$$\omega = E/\hbar$$

We can interpret the plane wave solution as a beam of particles of uniform density. The number of particles everywhere is a constant ( $|\Psi|^2 = \text{constant}$ ).

To summarise we can say that for any given energy there are two possible solutions: a plane wave moving to the right with amplitude A and a plane wave moving to the left with amplitude B. The system is said to be doubly degenerate. Using the momentum operator, we can see that the solutions have momentum of  $\hbar k$  in the x-direction.

The wave solutions that we obtain do mean anything physical however can be seen as a flux of particles (probability current also means the same thing):

*Particle Flux ( $j(x)$ )* <sup>[Derivation 8]</sup>

$$j(x) = \frac{i\hbar}{2m} \left( \Psi(x) \frac{\partial \Psi^*(x)}{\partial x} - \Psi^*(x) \frac{\partial \Psi(x)}{\partial x} \right)$$

$\hbar$  = Planck constant ( $6.63 \times 10^{-34}$  Js)

$m$  = Mass of the particle (kg)

**Potential step** <sup>[Derivation 9]</sup>

A beam of particles with energy E moves into a space which has a potential  $V_0$ . We divide the regions into 1 and 2 (region 1 has no potential; region 2 has a potential  $V_0$ ).

*Potential Form*

$$\hat{V}(x) = \begin{cases} 0, & x < 0 \\ V, & x \geq 0 \end{cases}$$

The particles come from the left; some of them are reflected back into region 1 and some are transmitted into region 2.

The general boundary conditions apply to this situation. We can have two different scenarios here; either the energy of the particle is greater than the potential or it can be less. Classically if a particle has a greater kinetic energy than the potential it confronts, it will go through that space with probability one (Transmission coefficient is 1) and if it has less kinetic energy than the potential, then all of the particles would be reflected (Reflection coefficient is 1). The quantum mechanical solutions of this problem are:

$E > V_0$ :*Region 1 Wavefunctions*

$$\Psi_1(x, t) = Ae^{i(kx - \omega t)} + Be^{i(-kx - \omega t)}$$

*Region 2 Wavefunction*

$$\Psi_1(x, t) = Ce^{i(qx - \omega t)}$$

 $E < V_0$ :*Region 1 Wavefunctions*

$$\Psi_2(x, t) = Ae^{i(kx - \omega t)} + Be^{i(-kx - \omega t)}$$

*Region 2 Wavefunction*

$$\Psi_2(x, t) = Ce^{(-qx - \omega t)}$$

$$q = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$$

$$\omega = \frac{E}{\hbar}$$

$$k = \sqrt{\left(\frac{2mE}{\hbar^2}\right)}$$

**Infinite Square well** <sup>[Derivation 10]</sup>

The infinite square potential well is the simplest application of the TISE with a potential and it represents the crudest approximation of the potential energy of a particle confined in a region of space. In this model, a particle is located in region of zero potential between  $x = 0$  and  $x = a$ . At the boundaries, there is an infinite increase in the potential energy function.

*Potential form*

$$\hat{V}(x) = \begin{cases} 0, & 0 < x < a \\ \infty, & \text{otherwise} \end{cases}$$

Note here that we have started the potential well at the origin, we could change the starting point and get pretty much the same solutions and most importantly the energy corresponding to the quantum states remains the same (of course it would be something odd if the energy of the wavefunction depended on what part of space it was in as this would suggest that one part of space has different properties to another, which is not something we notice in nature. However it is interesting to consider that there is no law that we can state or derive that makes this condition necessary<sup>[D]</sup>). We solve the TISE for this potential:

*Wavefunction solutions*

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

*Energy*

$$E_n = \frac{\left(\frac{\hbar n \pi}{a}\right)^2}{2m}$$

Similarly we make more general examples of this potential in two and three dimensions and solve using separation of variables.

### Finite Square well <sup>[Derivation 11]</sup>

The finite square potential well is similar to the infinite potential well mode, with the difference being that the potential outside the well is constant instead of being infinite, where  $V_0$  is greater than  $E$ .

*Potential form*

$$\hat{V}(x) = \begin{cases} 0, & -a < x < a \\ V_0, & \text{otherwise} \end{cases}$$

From the potential step function above we would expect there to be a finite probability of a particle being found in the classical forbidden region of the potential being greater than kinetic energy of the particle. The penetration effects are visible in this region according to an equation.

*Penetration length*

$$L = \frac{1}{q} = -\frac{\hbar}{\sqrt{2m(V_0 - E)}}$$

Therefore we see that in the limit as  $V_0$  goes to  $\infty$ , the penetration length becomes zero, which is in agreement with the infinite potential well system. We can solve the TISE to gain the solutions of this system in the well region and the region of finite potential (greater than the kinetic energy). What will see (in the derivation) is that there are two types of solutions. There are solutions that are symmetric (even parity) and ones that are not symmetric (odd parity), this can be seen by defining a parity operator and commuting it with the Hamiltonian operator to see that they commute therefore they must have the same eigenfunctions (more to be discussed in the derivation).

Symmetric solutions	Asymmetric solutions
$Ae^{(qx-i\omega t)}, x < -a$	$De^{(qx-i\omega t)}, x < -a$
$B\cos(kx - \omega t), -a < x < a$	$C\sin(kx - \omega t), -a < x < a$
$Ae^{-(qx+i\omega t)}, x > a$	$-De^{-(qx+i\omega t)}, x > a$

$$k = \sqrt{\frac{2mE}{\hbar^2}}$$

$$q = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$$

The energies of the states cannot be calculated analytically therefore they have to be done numerically (which I will show in the derivation).

### Finite potential barrier <sup>[Derivation 12]</sup>

This is a similar problem to the potential step except that the step has a distance  $a$  instead of being infinite in length.

*Potential form*

$$\hat{V}(x) = \begin{cases} V_0, & 0 < x < a \\ 0, & \text{otherwise} \end{cases}$$

The potential energy is greater than the kinetic energy of the particle, therefore we get the tunnelling effect that we saw in the potential step, except that this time the particle will have a finite

probability of being transmitted (yes, that means it can come out of the other side!) and therefore can be observed. Solving the TISE with this potential and the usual boundary conditions we get the wavefunctions:

*Wavefunctions for the three different regions*

$$\Psi_1(x, t) = e^{i(kx - \omega t)} + re^{-i(kx - \omega t)} \text{ for } x < 0$$

$$\Psi_2(x, t) = Ae^{qx - i\omega t} + Be^{-qx - i\omega t} \text{ for } 0 < x < a$$

$$\Psi_3(x, t) = te^{i(kx - \omega t)} \text{ for } x > a$$

Probably the most important result we obtain here is the transmission coefficient:

*Transmission Coefficient*

$$t = \frac{2e^{-2ika}}{2 \cosh(qa) - i \left( \frac{k}{q} - \frac{q}{k} \right) \sinh(qa)}$$

The transmission coefficient squared gives the probability of the particle being found in that region. Applications of quantum tunnelling are alpha particle decay, scanning tunnelling microscopes and field emissions.

### Quantum Harmonic Oscillator <sup>[Derivation 13]</sup>

Here we will use Hooke's law and assume it holds on quantum scales to give us a potential that we can then solve for using the TISE.

$$H(t) | \psi(t) \rangle = i\hbar \frac{d}{dt} | \psi(t) \rangle$$

*Potential form*  
 $V(x) = \frac{1}{2} m \omega^2 x^2$

This can be approximated to many physical systems, in fact any system with an equilibrium position will have the form of a harmonic oscillator potential for relatively small displacements from its equilibrium position. Solving for this potential is not straight forward due to the  $x^2$  dependence. The solutions are Gaussian functions with a class a polynomials in front of them, known as Hermite polynomials.

*Wavefunctions*

$$\Psi_n(x) = \frac{H_n}{\sqrt{2^n n! \sqrt{\pi} a^2}} e^{-\frac{x^2}{2a^2}}$$

$H_n$  = Hermite polynomials <sup>[5]</sup>  
 n = principle quantum number

*Energies*

$$\left( n + \frac{1}{2} \right) \hbar \omega$$

It is important to note that all the solutions approach the classical results for very large quantum numbers; this is known as Bohr's correspondence principle.



## Commutators and conserved quantities

### Commutation

In Quantum mechanics we define commutation in a different way to the everyday use of the word. This is a very similar concept to the concept of Poisson brackets in classical mechanics (infact they are related simply by an  $\hbar^{[D]}$ ). It is easiest to show what commutation means mathematically:

*Commutation definition*

$$[\hat{A}, \hat{B}] = \hat{A} \hat{B} - \hat{B} \hat{A}$$

The method given above is denoted by the square brackets as shown above (simply called the commutators of A with B). It is important to note the order of the operations as I stated previously in general the order makes a difference. If a two operators commute then the order does not matter. The most important property of two operators commuting is that those operators share common eigenfunctions, which means they can be two observable quantities that can be known *simultaneously*.

### Ehrenfest's theorem

Another very important property that we can obtain using the commutators is to do with the rate of change of the expectation value of any given operator. The Ehrenfest theorem, named after Paul Ehrenfest, the Austrian physicist and mathematician, relates the time derivative of the expectation value for a quantum mechanical operator to the commutator of that operator with the Hamiltonian of the system, the result is closely related to Louisvillie's theorem in classical mechanics.

$$\frac{d\langle A \rangle}{dt} = \frac{1}{i\hbar} \langle [\hat{A}, \hat{H}] \rangle$$

*Ehrenfest's theorem* <sup>[Derivation 14]</sup>

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \hat{V}(x)$$

This results shows that any commuting operator with the Hamiltonian is infact a *conserved* quantity as it will not change with time.

## Angular Momentum

Angular momentum is a quantity which we have been familiarised with in classical mechanics and we also use it often in Quantum mechanics to use the Schrodinger equation in spherical coordinates. As we know from classical mechanics there are two forms of angular momentum, orbital and rotational. However there is no reason for either of these to be quantities in the quantum world, but we know that orbital angular momentum does exist and has been observed. As we will come to see that in particles do have a kind of rotational angular momentum (however it is not like the classical momentum, as it may or may not have anything to do with actual rotation of the particle, like the earth spins on its axis) which is known as spin and it is simply an intrinsic property of certain particles.

### *Classical Orbital angular momentum*

$$\hat{L} = \hat{r} \times \hat{p}$$

### Orbital Angular momentum

We can calculate the operator for quantum mechanical orbital angular momentum in the three directions (Cartesian coordinates) <sup>[Derivation 15]</sup> from the classical definition of orbital angular momentum. We can also show that this is a conserved quantity by taking the commutator of the total angular momentum operator with the Hamiltonian and using Ehrenfest's theorem. It is important to note that the individual components of the angular momentum do *not* commute with each other therefore cannot be determined simultaneously; however the total angular momentum commutes with one of the components and hence can be determined simultaneously. The eigenfunctions of angular momentum are a class of functions called spherical harmonics (we have discussed them in detail in mathematics; therefore I will not spend time explaining them here). We do need to know much about them other than the eigenvalues given by them.

Operator	Eigenfunction equation	Commutator relations
Total Angular Momentum	$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$	$[\hat{L}^2, \hat{L}_z] = 0$ $\hat{L}^2 Y_{l,m}(\theta, \phi) = l(l+1)\hbar^2 Y_{l,m}(\theta, \phi)$
Angular momentum in z direction	$\hat{L}_z = -i\hbar(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x})$	$[\hat{L}_z, \hat{L}_y] = i\hbar \hat{L}_x$ $\hat{L}_z Y_{l,m}(\theta, \phi) = m\hbar Y_{l,m}(\theta, \phi)$

$Y_{l,m}$  = Spherical harmonics that depend on l and m quantum numbers

The spherical harmonics are symmetric for filled orbits (full set of quantum numbers) and therefore have no dependence on the angles. Hence we can see from these equations that in a vector model of the angular momentum it seems as if the angular momentum is precessing about the z axis much like the classical angular momentum, however this precession is fictitious and is not a physical phenomenon.

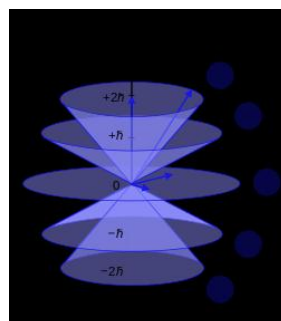


Figure 4

### Magnetic moment

The definition of a magnetic dipole moment  $\mu$  is:

$$\begin{aligned} & \text{Magnetic moment} \\ \mu &= \text{current} \times \text{area} = I \times \pi r^2 \end{aligned}$$

This can be rewritten if we take the current to be the charge per time and the time to be the circumference of the orbit divided by the velocity the particle is travelling at.

*Vectorial orbital magnetic moment*

$$\vec{\mu} = -\frac{e}{2m_e} \vec{L}$$

$e =$  the charge on an electron ( $1.6 \times 10^{-19}$  C)

### Spin

In 1921 two German physicists Stern and Gerlach conducted an experiment in which they fired neutral silver atoms through a non-uniform magnetic field to be collected on a glass plate. The ground state of a silver atom is spherically symmetric and therefore not expected to have any orbital angular momentum. At the time of the experiment the spin property was unknown; it was assumed that all of the magnetic moment came from the orbital angular momentum. If this were the case they would have expected the silver atom to not be deflected at all. As it turned out they noticed that the beam was split into two separate beams in opposite directions. The experiment showed that there must be another component to the overall angular momentum and has come to be known as the spin of a particle.

Since the beam was split into two separate beams, this new spin must have two orientations, either parallel or anti-parallel to the magnetic field. The two possible spin angular momentum states (also known as spin up or spin down) are consistent with the spin being  $s = \frac{1}{2}$ .

### Spin properties of an electron

- An electron possesses an internal degree of freedom which acts like spin. The complete understanding of why this is the case comes from combining quantum mechanics with special relativity and was first done by Dirac in 1928.
- The Hermitian operators corresponding to the x, y and z components and the magnitude of the spin are denoted by  $\hat{S}_x, \hat{S}_y, \hat{S}_z$  and  $\hat{S}^2$ . The commutator relations are the same as they are for the orbital angular momentum.
- Consistent with the two commutator relations given in the orbital angular momentum, are the eigenvalue equations as well
- A matrix representation of the angular momentum operator for a spin  $\frac{1}{2}$  particles is given by the Pauli spin matrices, with the eigenvalues as  $\frac{\hbar}{2}$ .
- The magnetic moment produced by spin angular momentum is almost the same as the orbital angular momentum except for the fact that it has a spin g-factor in front of it which has a value of approximately 2 (The precise value of g was predicted by relativistic quantum mechanics in the Dirac equation and was measured in the Lamb shift experiment. A natural constant which arises in the treatment of magnetic effects is called the Bohr magneton. The magnetic moment is usually expressed as a multiple of the Bohr magneton).

Spin wavefunctions for two electrons can form four possible states, three triplet states (In which the overall spin is 1 and a singlet state (In which the overall spin is 0). The triplet states are all symmetric under particle exchange; the singlet state is antisymmetric under particle exchange.

*Triplet states*

$$\phi_1 = U_1U_2$$

$$\phi_2 = D_1D_2$$

$$\phi_3 = (U_1D_2 + D_1U_2) \frac{1}{\sqrt{2}}$$

*Singlet state*

$$\phi_4 = (U_1D_2 - D_1U_2) \frac{1}{\sqrt{2}}$$

$U = \text{up state} = \text{spin } \frac{1}{2}$

$D = \text{down state} = \text{spin} - \frac{1}{2}$

### Quantum Numbers and Degeneracy

In an atom the total wavefunction is a product of the radial wavefunction, the orbital wavefunction and the spin wavefunction. Therefore there are four quantum numbers, three ( $n$ ,  $l$  and  $m_l$ ) that are spatial and one for spin ( $m_s$ ). The orbital angular momentum and the spin angular momentum numbers can be added to obtain the total angular momentum quantum number ( $m_j = m_l + m_s, \hat{J} = \hat{L} + \hat{S}$ ).

#### Quantum numbers

Name	Symbol	Orbital meaning	Range of values	Value examples
principal quantum number	$n$	shell	$1 \leq n$	$n = 1, 2, 3, \dots$
azimuthal quantum number (angular momentum)	$\ell$	Subshell (s orbital is listed as 0, p orbital as 1 etc.)	$0 \leq \ell \leq n - 1$	for $n = 3$ : $\ell = 0, 1, 2$ (s, p, d)
magnetic quantum number, (projection of angular momentum)	$m_\ell$	energy shift (orientation of the subshell's shape)	$-\ell \leq m_\ell \leq \ell$	for $\ell = 2$ : $m_\ell = -2, -1, 0, 1, 2$
spin projection quantum number	$m_s$	spin of the electron ( $-\frac{1}{2} = \text{"spin down"}$ , $\frac{1}{2} = \text{"spin up"}$ )	$-s \leq m_s \leq s$	for an electron $s = \frac{1}{2}$

**Degeneracy**

This is a term used when different states of a system correspond to the same energy. Most of the degeneracies occur when states have some quantum numbers in common that determine the energy and different other quantum number (for example the hydrogen atom, the same principle quantum number and different spin numbers give a degeneracy). There are also forms of accidental degeneracies when two states which are completely separate and not related in any way happen to have the same energy at a given point, these usually do not imply anything significant physically. Degeneracy can therefore be seen as a sign of symmetry in a system.

$$H(t) |\psi(t)\rangle = i\hbar \frac{d}{dt} |\psi(t)\rangle$$

## The Hydrogen Atom

The structure of the hydrogen atom is the best understood application of quantum mechanics, and predictions of quantum theory agree very well with experiment. A hydrogen atom consists of a single electron orbiting a single proton. The electron can occupy a set of discrete energy levels, which are each represented by specific wavefunction. We will apply the theory discussed previously to determine electron wavefunctions and what their corresponding energies are.

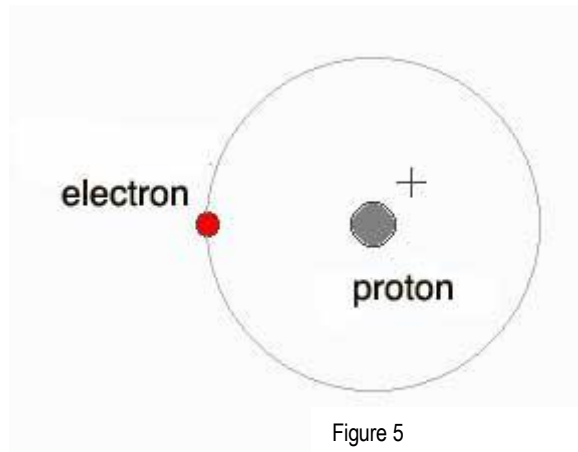


Figure 5

### Schrodinger equation

The electric potential energy of an electron in a hydrogen atom is proportional to the Coulomb potential of the nucleus. Therefore, the expression for the central potential of a hydrogen atom is:

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

$r$  = radial distance from the nucleus

$e$  = the charge on an electron ( $1.6 \times 10^{-19}$  C)

*Hamiltonian of hydrogen atom*

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{\hat{L}^2}{2mr^2} - \frac{e^2}{4\pi\epsilon_0 r}$$

As we see this is an equation in terms of the radial vector, which means in Cartesian coordinates it corresponds to a 3 dimensional equation. We can solve the 3 dimensional equations by the method of separation of variables. The natural coordinate system to work in is however the spherical polar's. The solutions in the spherical polar coordinates have solutions of the form:

*Spherical polar solutions*

$$\Psi(r, \phi, \theta) = R(r)P_l^m(\theta)\Phi(\phi)$$

$R(r)$  = Radial solution

$P_l^m$  = Legendre polynomials

$\Phi(\phi) = e^{im\phi}$

This shows that the solution we need to calculate is for the radial equation.

*Radial Time Independent Schrodinger Equation for Hydrogen atom*

$$\left( -\frac{\hbar^2}{2m_e r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \right) + \frac{l(l+1)\hbar^2}{2mr^2} - \frac{e^2}{4\pi\epsilon_0 r} \right) R(r) = ER(r)$$

Notice that we have substituted for the Angular momentum operator as we discussed above in the angular momentum section (The eigenvalues are substituted). We can see from the radial TISE that the angular momentum term and the Coulomb potential can add together to give an 'effective potential'.

$$\begin{aligned} & \text{Effective potential} \\ V_{eff} &= \frac{l(l+1)\hbar^2}{2mr^2} - \frac{e^2}{4\pi\epsilon_0 r} \end{aligned}$$

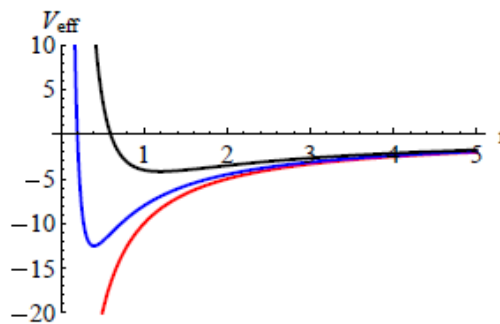


Figure 6

The radial Schrodinger equation for an electron in the hydrogen atom can be solved for small and large distances. <sup>[Derivation 16]</sup>

*Radial solutions for hydrogen atom*

$$R(r) = Ae^{-kr}, r \rightarrow \infty$$

$$R(r) = Br^l, r \rightarrow 0$$

$$k = \sqrt{2mE/\hbar^2}$$

*Normalisation of Radial function*

$$\int R(r)^2 r^2 dr = 1$$

Full solutions to the radial Schrodinger equation are the associated Laguerre polynomials (distantly related to the Hermite polynomials).

### Energy levels and degeneracy

The principle quantum number  $n$  determines the energy:

*Energy levels*

$$E = -\frac{E_R}{n^2}$$

$$E_R = \frac{e^2}{8\pi\epsilon_0 a_0}, \text{ Rydberg energy}$$

$a_0$  = Bohr radius (0.053 nm)

Remarkably the energy is the same as that found in the Bohr model, which correctly accounted for the spectral lines emitted by hot hydrogen atoms. There is however one important difference: the energy here is determined entirely by the principle quantum number, which is not the same as the angular momentum proposed by Bohr. Using quantum mechanics we find that the electrons are not in orbits of a certain radius, but are described by radial and angular probability distributions.

For each value of the principle quantum number there exist  $n-1$  states of different  $l$ . For each value of  $n$ ,  $l$  can take any integer value ranging between 0 and  $(n-1)$ . This means that each energy level  $n$  is degenerate in states of different total angular momentum,  $l$ . Furthermore, for each value of  $l$ , there are  $(2l+1)$  states of different angular momentum projections. Therefore, the total angular momentum degeneracy of the  $n^{\text{th}}$  energy level is  $n^2$ .

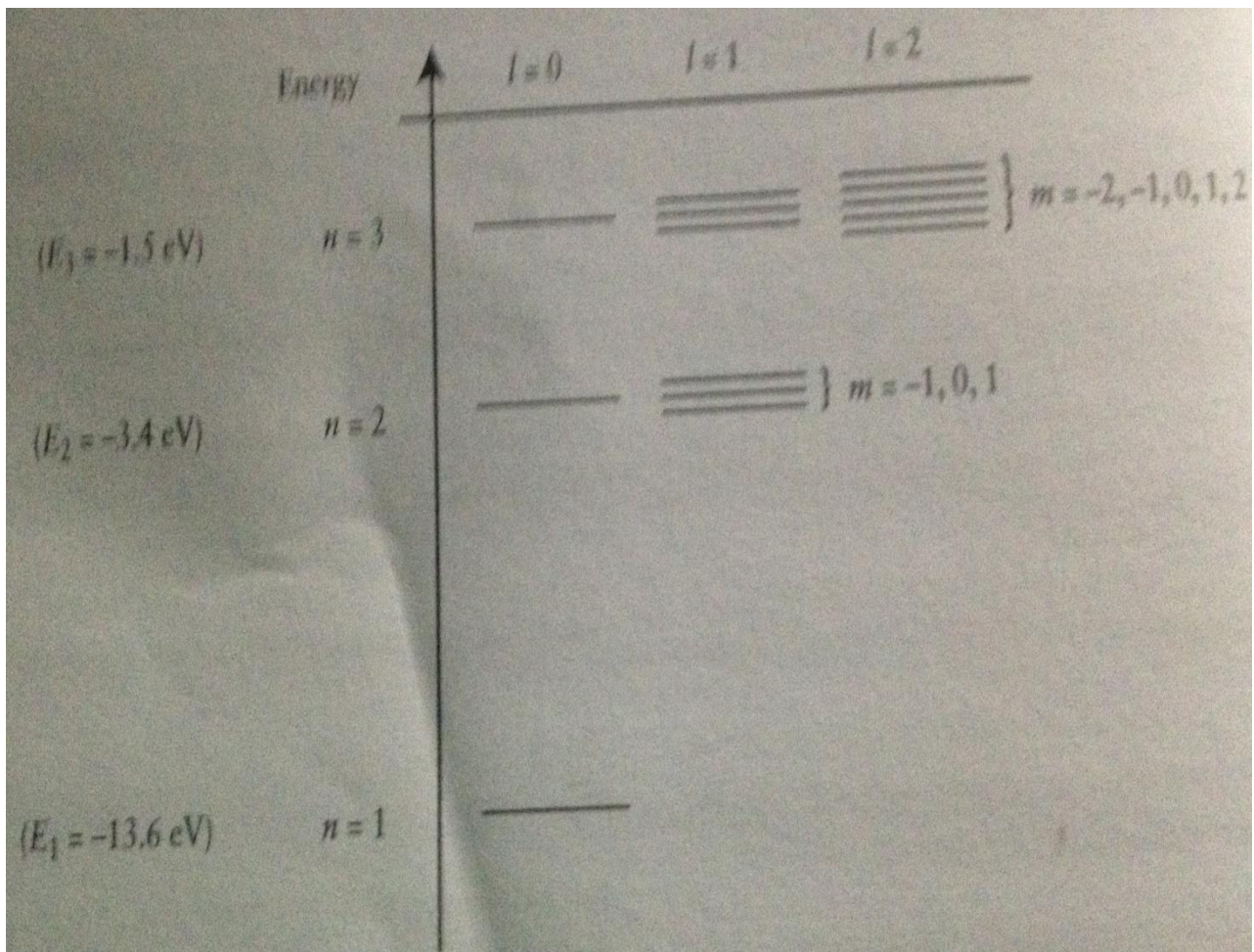


Figure 7



## Particles and multi electron atoms

Quantum mechanics only deals with the results of measurements, so there is no physical way of knowing whether two identical particles have been interchanged. In other words, under particle exchange the probability does not change.

*Wavefunction under particle exchange*

$$\Psi(x, y) = \pm\Psi(x, y)$$

If the negative sign holds, then the overall wavefunction is *antisymmetric*. Particles that have this property are called *fermions*; this includes protons, neutrons and electrons. *The Pauli Exclusion Principle* comes about from this; it states that two identical fermions cannot be in the same quantum state (as this would mean the wavefunction would be symmetric under particle exchange).

If the positive sign holds, then the overall wavefunction is *symmetric*. These particles are called *bosons*; this includes photons,  $\alpha$  particles, and Helium atoms.

The electron orbitals in multielectron atoms are filled up using two principles:

- The Aufbau principle: the electrons are put in orbitals of increasing energy.
- Pauli Exclusion Principle: no two electrons in a system can share an identical set of quantum numbers. In an atom this means that each electron must have different combinations of the quantum numbers.

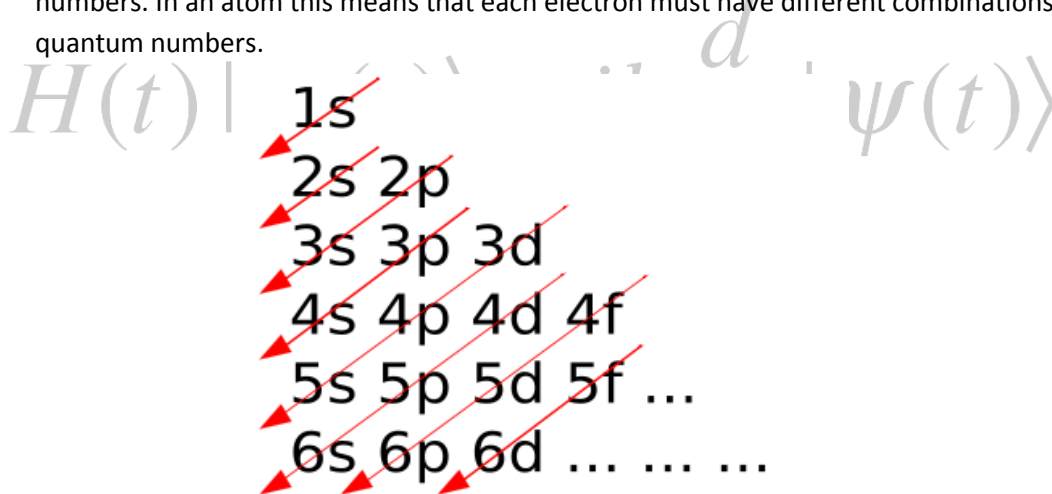


Figure 8

### Screening

The energy level structure of atoms with multiple electrons is modified from the hydrogen atom. This is because in heavier atoms the electrons will fill more and more shells and therefore will be further away from the nucleus. More importantly there will be the inner electrons between the outer electrons and the nucleus therefore for large distances the outer electrons will only 'see' part of the charge of the nucleus as the inner electrons will 'cancel' out some of the positive charge from the nucleus (we can use Gauss's law to see the mathematical model for it). This effect is known as 'Screening' and 'Shielding'. This effect will remove the degeneracy between the different orbital angular momentum,  $l$ , states in a given  $n$  level.

## First-order non-degenerate time-independent perturbation theory

There are only a few Quantum Mechanical problems that can be solved exactly; in real life problems numerical methods are used to solve the Time Independent Schrodinger Equation and find the energies and wave-functions. In this section we will consider one of the simplest techniques: first order, time-independent, non-degenerate perturbation theory. I will state the important equations here and leave the derivations for later.

*Perturbed energy*<sup>[Derivation17]</sup>

$$\epsilon = \int \Psi_0^* H_1 \Psi_0 dx$$

$\epsilon$  = change in the ground state energy

$H_1$  = addition to ground state Hamiltonian

*Coefficients of perturbed wavefunction*<sup>[Derivation 17]</sup>

$$c_n = \frac{\int \Psi_n^* H_1 \Psi_0 dx}{E_n - E_0}$$

It is important to see that even though the wavefunctions without the perturbations are normalised, the perturbed wavefunctions are not as they will have another term that needs to be added (the sum of the coefficients squared).

*Normalisation of perturbed wavefunctions*

$$\int \phi^* \phi dx = 1 + \sum_{n \neq 0} |c_n|^2 = 1 + \sum_{n \neq 0} \left| \frac{\int \Psi_n^* H_1 \Psi_0 dx}{E_n - E_0} \right|^2$$

## Wave packets and the Uncertainty Principle

A plane wave represents a solution that satisfies the wave equation and represents a wave propagating in the  $x$  direction with a given velocity. As we discussed previously they do not have any physical meaning, however their amplitude squared represents the probability density function. As we discussed right at the beginning the phase velocity and the group velocity are not the same for matter waves. The state function that represents the classical particle is a wavepacket which is constructed from a sum of the eigenstates that we find by solving the Schrodinger equation. The wavefunctions that describe the state (if you remember I discussed in the beginning that the state of quantum mechanical systems is like a vector in a vector space) can be transformed from  $x$ -space to  $k$ -space according to the Fourier transforms (we have discussed in our Mathematics course).

### Gaussian Wave packets

If we consider the width of the distribution as a measure of the uncertainty, it can be proven that the Gaussian wave packets provides the minimum uncertainty. This result shows that we cannot know the position of a particle and its momentum at the same time. If we try to localize a particle to a very small region of space, its momentum becomes uncertain. If we try to make a particle with a definite momentum, its probability distribution spreads out over space. Heisenberg's uncertainty principle states that it is impossible to determine with arbitrarily high accuracy both the position and momentum of a particle.

*Probability function for the Gaussian wavepacket*

$$|\Psi(x, t)|^2 = \frac{\pi^2}{\alpha^2 + \beta^2 t^2} e^{-\frac{\alpha(x - v_g t)^2}{2(\alpha^2 + \beta^2 t^2)}}$$

*Heisenberg's Uncertainty Principle*

$$\Delta x \Delta p = \frac{\hbar}{2}$$

# Derivations

## Derivation 1

### Solutions of the one dimensional wave equation using method of separation of variables

We start with the one dimensional wave equation:

$$c^2 \frac{\partial^2 \Psi(x, t)}{\partial x^2} = \frac{\partial^2 \Psi(x, t)}{\partial t^2}$$

Now we seek product solutions for the function  $\Psi$ , such that:

$$\Psi(x, t) = \phi(x)\tau(t)$$

Note here that we assume that the wavefunction is separable (this is not always case, this means that the product solutions are independent of each other, which in classical probability theory means that their solutions have independent probability distributions, we see this is an important aspect when it comes to entangled as product solutions cannot be entangled<sup>[1]</sup>).

Substitute for the product solutions in the wave equation:

$$c^2 \tau(t) \frac{\partial^2 \phi(x)}{\partial x^2} = \frac{\partial^2 \tau(t)}{\partial t^2} \phi(x)$$

Divide both sides of the equation by the product solution to get each side only depending on a single variable:

$$\frac{1}{\phi(x)} \frac{\partial^2 \phi(x)}{\partial x^2} = \frac{\frac{\partial^2 \tau(t)}{\partial t^2} c^2}{\tau(t)}$$

Now we see that both sides of the equation that are only depending on two separate independent variables are equal to each other. The only way this would be possible is if they are both equal to a constant (that may be zero, however this would lead to trivial solutions of the equation which we are not interested in). We call the separation constant  $-k^2$ , this leads us to obtaining two linearly ordinary homogenous differential equations which we can solve easily (find the complementary function, particular integral etc.):

$$\text{Space dependent: } \frac{\partial^2 \phi(x)}{\partial x^2} = -\phi(x)k^2$$

$$\text{Time dependent: } \frac{\partial^2 \tau(t)}{\partial t^2} = -\tau(t)k^2 c^2$$

Solve the linear homogenous ordinary differential equations:

$$\text{Spatial solution : } Ae^{ikx} + Be^{-ikx}$$

$$\text{Time solution: } Ce^{i\omega t} + De^{-i\omega t}, \quad \omega = kc$$

These solutions can now be combined by summing over the product solutions to give the overall wavefunction solution to the wave equation:

$$\Psi(x, t) = \sum \phi(x)\tau(t)$$

Which, for a special case of a wave moving to the right is given by the solution stated in the notes:

$$\Psi(x, t) = Ae^{i(\pm kx - \omega t)}$$

$$H(t) |\psi(t)\rangle = i\hbar \frac{d}{dt} |\psi(t)\rangle$$

**Derivation 2**Momentum operator in one dimension

Consider a wavefunction that has the form of a plane wave as stated in derivation 1 and differentiate it with respect to position (in one dimension we call it  $x$ ):

$$\begin{aligned}\frac{\partial \Psi(x, t)}{\partial x} &= \frac{\partial}{\partial x} A e^{i(kx - \omega t)} \\ \frac{\partial \Psi(x, t)}{\partial x} &= ik A e^{i(kx - \omega t)} \\ \frac{\partial \Psi(x, t)}{\partial x} &= ik \Psi(x, t)\end{aligned}$$

Since this equation holds for any 'well behaved' function, we can divide through by the function and  $i$  to obtain the Wavevector operator:

$$\hat{k} = -i \frac{\partial}{\partial x}$$

From the de Broglie relation we know:

$$p = \hbar k$$

Now we *postulate* that this equation holds for operator's aswell to obtain the momentum operator:

$$H(t) | \psi(t) \rangle \stackrel{\hat{p} = \hbar \hat{k}}{\hat{p} = -i\hbar \frac{\partial}{\partial x}} = i\hbar \frac{d}{dt} | \psi(t) \rangle$$

**Derivation 3**Energy operator in one dimension

Consider a wavefunction that has the form of a plane wave as stated in derivation 1 and differentiate it with respect to time:

$$\begin{aligned}\frac{\partial \Psi(x, t)}{\partial t} &= \frac{\partial}{\partial t} A e^{i(kx - \omega t)} \\ \frac{\partial \Psi(x, t)}{\partial t} &= -i\omega A e^{i(kx - \omega t)} \\ \frac{\partial \Psi(x, t)}{\partial t} &= -i\omega \Psi(x, t)\end{aligned}$$

Since this equation holds for any 'well behaved' function, we can divide through by the function and  $i$  to obtain the frequency operator:

$$\hat{\omega} = i \frac{\partial}{\partial t}$$

From the Einstein relation we know:

$$E = \hbar \omega$$

Now we *postulate* that this equation holds for operator's aswell to obtain the energy operator:

$$\hat{E} = \hbar \hat{\omega}$$

$$\hat{E} = i\hbar \frac{\partial}{\partial t}$$

This definition can also be used to derive the Hamiltonians in classical and quantum mechanics.

**Derivation 4**Quantum mechanical Hamiltonian operator

We start with the classical definition of the Hamiltonian:

$$H = T + V, T = \text{kinetic energy}, V = \text{potential energy}$$

Now we assume as we have done before that this equation also holds for operators:

$$\hat{H} = \hat{T} + \hat{V}$$

Now we need to obtain the kinetic energy and potential energy operators. Starting with the kinetic energy operator, we take the classical definition for kinetic energy and use the operators to find the quantum mechanical version:

$$\text{Classical: } T = \frac{p^2}{2m}$$

Substitute the momentum operator into the classical definition:

$$\text{Quantum Mechanical: } \hat{T} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$$

The potential energy varies from system to system, as it depends on the environment of the system, therefore generally we assume the potential to be dependent on the distance and generally write it as:

$$\hat{H}(t) |\psi(t)\rangle = i\hbar \frac{d}{dt} |\psi(t)\rangle$$

$$\hat{V} = V(x)$$

Combining the equations of the potential energy operator and the kinetic energy operator to give the Hamiltonian operator:

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)$$



**Derivation 5**  
Schrodinger equation

The TDSE can be derived by combining all the derivations we have discussed above.

The total energy of system will be given by the energy operator, operating on the wavefunction:

$$\hat{E}\Psi(x, t) = i\hbar \frac{\partial \Psi(x, t)}{\partial t}$$

We can equate this to the Hamiltonian acting on the wavefunction which yields the TDSE:

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

This equation describes the behaviour of a particle of mass  $m$ , moving under the influence of a potential energy function. Solutions of the wavefunctions that satisfy the Schrodinger equation determine everything that can be known about the system. Therefore, the Schrodinger equation is very powerful and elegant equation.

$$H(t) | \psi(t) \rangle = i\hbar \frac{d}{dt} | \psi(t) \rangle$$

**Derivation 6**Separation of variables for TDSE

We use the same sort of method as we did to solve for the wave equation (as they are both partial differential equations with two variables). Start with the TDSE:

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

Separate the spatial part from the temporal part by looking for product solutions of the form:

$$\Psi(x, t) = \phi(x)\tau(t)$$

Substituting the product solution into the TDSE:

$$-\frac{\tau(t)\hbar^2}{2m} \frac{\partial^2 \phi(x)}{\partial x^2} + V(x)\phi(x)\tau(t) = \phi(x)i\hbar \frac{\partial \tau(t)}{\partial t}$$

Divide through by the product solution to get two independent linear homogenous ordinary equations:

$$\frac{1}{\phi(x)} \left( -\frac{\hbar^2}{2m} \frac{d^2 \phi(x)}{dx^2} + V(x) \right) = \frac{1}{\tau(t)} i\hbar \frac{d\tau(t)}{dt}$$

Equating both sides of the equation to a constant which we call energy; E (This is in analogy of the classical system):

*Time independent Schrodinger equation*

$$\left( -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right) \phi(x) = E\phi(x)$$

*Time evolution*

$$i\hbar \frac{d\tau(t)}{dt} = E\tau(t)$$

**Derivation 7**Free Particle wavefunctions

This is a particle with no potential energy term, therefore the Hamiltonian only consists of the kinetic energy, and therefore the TISE is:

$$-\frac{\hbar^2}{2m} \frac{d^2 \phi(x)}{dx^2} = E\phi(x)$$

This is a linear homogenous ordinary differential equation which we can solve using normal methods of finding the auxiliary equation etc.:

$$\phi(x) = Ae^{ikx} + Be^{-ikx}$$

This can now be combined with the temporal part of the solution to give the full solution of the wavefunction of a free particle:

*Free particle solutions*

$$\Psi(x, t) = Ae^{i(kx - \omega t)} + Be^{i(-kx - \omega t)}$$

$$H(t) | \psi(t) \rangle = i\hbar \frac{d}{dt} | \psi(t) \rangle$$

**Derivation 8**Particle Flux

Consider two fluxes of particles coming in at two points,  $x_1$  and  $x_2$ . They add to give rate of increase of  $\int \Psi^* \Psi dx$  in the limit that  $x_1 - x_2 \rightarrow 0$ . We need to find  $\frac{\partial}{\partial t} \int_{x_1}^{x_2} \Psi^* \Psi dx$ , so we let the Schrodinger equation and its complex conjugate equal:

$$S: -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V\Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

$$S^*: -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi^*}{\partial x^2} + V\Psi^* = -i\hbar \frac{\partial \Psi^*}{\partial t}$$

The following derivation is complex and we are not expected to know it, just be able to interpret the result (which is best done by understanding the derivation!):

$$\int_{x_1}^{x_2} (\Psi^* S - S^* \Psi) dx = \frac{\hbar^2}{2m} \int_{x_1}^{x_2} \left( \Psi \frac{\partial^2 \Psi^*}{\partial x^2} - \Psi^* \frac{\partial^2 \Psi}{\partial x^2} \right) dx$$

First term on R.H.S:

$$\int_{x_1}^{x_2} \left( \Psi \frac{\partial^2 \Psi^*}{\partial x^2} \right) dx = \left[ \Psi \frac{\partial \Psi^*}{\partial x} \right]_{x_1}^{x_2} - \int_{x_1}^{x_2} \frac{\partial \Psi}{\partial x} \frac{\partial \Psi^*}{\partial x} dx$$

We can find a similar equation for the second term (simply swap the complex conjugate with the non-conjugated wavefunctions. This can then be substituted into the equation above to give:

$$j(x_2) - j(x_1) + \frac{d}{dt} \int_{x_1}^{x_2} \Psi^* \Psi dx = 0$$

Where  $j(x)$  represents the flux at any given position and is calculated by:

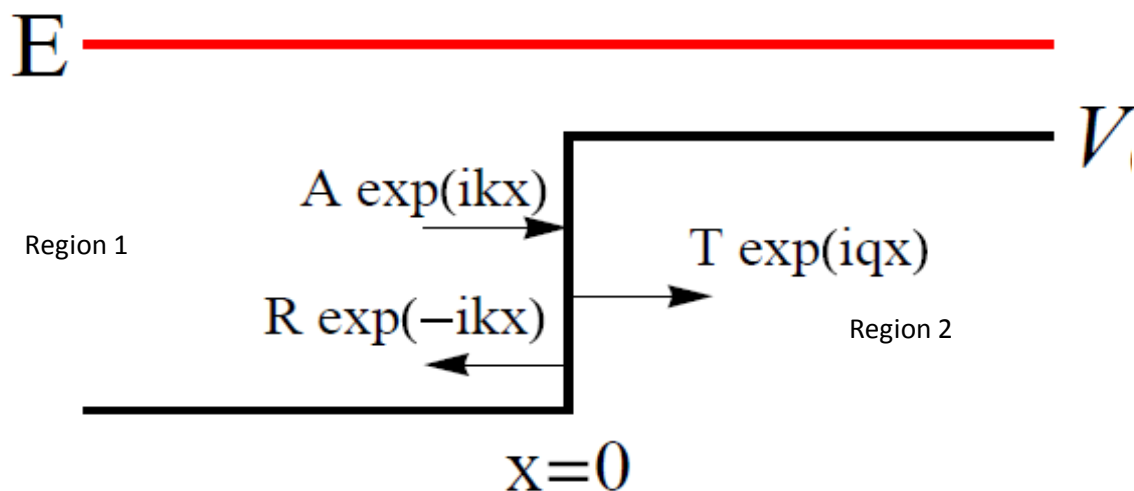
$$j(x) = \frac{i\hbar}{2m} \left( \Psi \frac{\partial \Psi^*}{\partial x} - \Psi^* \frac{\partial \Psi}{\partial x} \right)$$

**Derivation 9**Potential Step TISE solutions*Potential form*

$$\hat{V}(x) = \begin{cases} 0, & -a < x < a \\ V_0, & \text{otherwise} \end{cases}$$

Consider a beam of particles is incident on a potential step of height  $V$ . The particles are incident from the left, some of them are reflected back and some are transmitted into the region with the potential. The boundary between the two regions of different potential occurs at  $x = 0$ . In this derivation the electron is unbound, classically we expect that the probability for reflection is 1 if  $E < V$ , and is 0 otherwise.

Boundary conditions are that the wavefunction and its derivative must be equal in both the regions, which means that the wavefunction and its derivative are continuous at  $x = 0$ .

 $E > V$ 

Region 1:

The Hamiltonian in this region has no potential (same as the free particle, as the electron is unbound), therefore only has the kinetic energy term:

$$-\frac{\hbar^2}{2m} \frac{d^2 \phi(x)}{dx^2} = E \phi(x)$$

The solutions are therefore the same as the ones found for the motion of a free particle in this region:

$$\phi(x) = A e^{ikx} + B e^{-ikx}, k = \sqrt{\frac{2mE}{\hbar^2}}$$

Region 2:

The Hamiltonian in this region has a potential  $V$ :

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

The solutions are found using the same method as before except this time we have a potential energy:

$$\phi(x) = Ce^{iqx} + De^{-iqx}, q = \sqrt{\frac{2m(E - V)}{\hbar^2}}$$

We can set  $D = 0$ , as left moving wave is not physical.

Applying the boundary condition we get:

$$\begin{aligned} A + B &= C \\ ik(A - B) &= iqC \end{aligned}$$

Solving these equations:

$$\begin{aligned} \frac{B}{A} &= \frac{k - q}{k + q} \\ \frac{C}{A} &= \frac{2k}{k + q} \end{aligned}$$

We should note here that  $C$  is essentially the transmission coefficient and  $B$  is the reflection coefficient (this can be seen from the form of the solutions), therefore we can relabel  $C = T$  and  $B = R$  and  $A$  can always be set to 1. For  $E > V$ ,  $k$  and  $q$  are real.

Reflection and Transmission probabilities are given by the amplitude squares of the respective coefficients.

$E < V$

Region 1:

Same as before

Region 2:

The solutions are similar to what we found in region one, except that  $q$  is imaginary therefore we have a  $\pm i$  in front of the power, which means the function is an exponential instead of an oscillation.

$$\phi(x) = Ce^{-qx}$$

This function is exponentially decaying, therefore there is a finite probability of finding the particle in the classically inaccessible region  $x > 0$ . This barrier penetration is a quantum mechanical phenomenon, the exponentially decaying wavefunction is called an evanescent wave.

Once again we can apply the boundary conditions to the solutions:

$$\begin{aligned} A + B &= C \\ ik(A - B) &= -qC \end{aligned}$$

Solve the two equations:

$$\frac{B}{A} = \frac{k - iq}{k + iq}$$
$$\frac{C}{A} = \frac{2k}{k + iq}$$

$$H(t) |\psi(t)\rangle = i\hbar \frac{d}{dt} |\psi(t)\rangle$$

**Derivation 10**  
Infinite Square Well

*Potential form*

$$\hat{V}(x) = \begin{cases} 0, & 0 < x < a \\ \infty, & \text{otherwise} \end{cases}$$

A particle is confined in space between  $0 < x < a$  as it would require an infinite amount of energy to be outside this region. Therefore the wavefunction must be zero in the regions of infinite potential and hence we only have to solve for the region with zero potential.

The Hamiltonian is the same as it was for a free particle:

$$-\frac{\hbar^2}{2m} \frac{d^2 \phi(x)}{dx^2} = E \phi(x)$$

With the same solutions:

$$\phi(x) = A e^{ikx} + B e^{-ikx}, k = \sqrt{\frac{2mE}{\hbar^2}}$$

The interesting part is the boundary conditions are slightly different.  $\phi(x)$  is continuous; therefore, the wavefunctions must vanish at the boundaries with complex exponential solutions like the ones we have.

The first boundary condition is that the wavefunction at  $x = 0$  must be zero:

$$\phi(0) = 0$$

Therefore:

$$A = -B$$

$$\phi(x) = C \sin(kx)$$

The second boundary condition is that the wavefunction at  $x = a$  must be zero:

$$\phi(a) = C \sin(ka) = 0$$

Therefore:

$$k_n = \sum_{n=1}^{\infty} \frac{n\pi}{a}$$

Now that we have the wavefunctions we can normalise them because we know that the probability of finding the particle in the interval from 0 to  $a$  must be 1:

$$\int_0^a |\phi(x)|^2 dx = 1$$

Substitute for  $\phi$  the solution we have obtained:

$$C^2 \int_0^a \sin^2(kx) dx = \frac{C^2 a}{2}$$



Therefore we get the normalised wavefunction to be:

$$\phi(x) = \sqrt{\frac{2}{a}} \sin(k_n x)$$

We can also obtain values for the energy now that we know that  $k$  is quantised:

$$E_n = \frac{(\hbar k_n)^2}{2m}$$

$$E_n = \frac{\hbar^2}{2m} \left(\frac{n\pi}{a}\right)^2$$

$$H(t) | \psi(t) \rangle = i\hbar \frac{d}{dt} | \psi(t) \rangle$$

**Derivation 11**  
Finite Square Well

$$\hat{V}(x) = \begin{cases} 0, & -a < x < a \\ V_0, & \text{otherwise} \end{cases}$$

There are two regions that we need to solve for. The well, in which the potential is zero has the same solutions as the infinite square well with the same region so I will just state them from the derivation above.

Well Hamiltonian:

$$-\frac{\hbar^2}{2m} \frac{d^2 \phi(x)}{dx^2} = E\phi(x)$$

Solutions:

$$\phi(x) = Ae^{ikx} + Be^{-ikx}, k = \sqrt{\frac{2mE}{\hbar^2}}$$

Hamiltonian for the region with potential energy:

$$-\frac{\hbar^2}{2m} \frac{d^2 \phi(x)}{dx^2} + V_0\phi(x) = E\phi(x)$$

The solutions for this are the same as the solutions for the potential step function; therefore I will simply quote the result:

$$\phi(x) = Ce^{qx} + De^{-qx}, q = \sqrt{\frac{2m(E - V_0)}{\hbar^2}}$$

We can see that for the region  $x < -a$  the solution must be the part which is moving to the left and the opposite for the region of  $x > a$ . Therefore we can summarise the solutions as:

$$\phi_{1,2,3}(x) = \begin{cases} Ae^{qx}, & \text{for } x < -a \\ B\cos(kx) + C\sin(kx), & \text{for } -a < x < a \\ De^{-qx}, & \text{for } x > a \end{cases}$$

Now we have to determine the boundary conditions. In this case they are the usual ones that we state in the beginning (the function and its derivative are continuous at the two boundaries):

At  $x = -a$ :

$$\begin{aligned} \phi_1(-a) &= \phi_2(-a) \\ \left(\frac{d\phi_1(x)}{dx}\right)_{(x=-a)} &= \left(\frac{d\phi_2(x)}{dx}\right)_{(x=-a)} \end{aligned}$$

At  $x = a$ :

$$\phi_2(a) = \phi_3(a)$$

$$\left(\frac{d\phi_2(x)}{dx}\right)_{(x=a)} = \left(\frac{d\phi_3(x)}{dx}\right)_{(x=a)}$$

These boundary conditions give us four simultaneous equations, which can be solved to determine values for the integration constants A, B, C and D, as well as place restrictions to k and q. When written as a matrix, the four simultaneous equations are:

$$\begin{pmatrix} e^{-qa} & -\cos(ka) & \sin(ka) & 0 \\ qe^{-qa} & -k\sin(ka) & -k\cos(ka) & 0 \\ 0 & -\cos(ka) & -\sin(ka) & e^{-qa} \\ 0 & k\sin(ka) & -\cos(ka) & -qe^{-qa} \end{pmatrix} \begin{pmatrix} A \\ B \\ C \\ D \end{pmatrix} = 0$$

Solutions for these equations are of two sorts:

Symmetric solutions: A = D and C = 0

$$\phi(x) = \begin{cases} Ae^{qx}, & \text{for } x < -a \\ B\cos(kx), & \text{for } -a < x < a \\ Ae^{-qx}, & \text{for } x > a \end{cases}$$

The values of A and B are set by the system in the question. This wavefunction is symmetric about the origin; therefore, this wavefunction is said to have even parity. Under these coefficient restraints, if we expand lines 1 and 2 of the matrix and take their ratio, we see that k and q are related by:

$$\text{Asymmetric solutions: } A = -D \text{ and } B = 0 \quad k\tan(ka) = q$$

$$\phi(x) = \begin{cases} De^{qx}, & \text{for } x < -a \\ C\cos(kx), & \text{for } -a < x < a \\ -De^{-qx}, & \text{for } x > a \end{cases}$$

The values of C and D are set by the system in question. This wavefunction is asymmetric about the origin; therefore, this wavefunction is said to have odd parity. Under these coefficient restraints, if we expand the lines 3 and 4 of the matrix and take their ratio, we see that k and q are now related by:

$$k\cot(ka) = -q$$

The boundary conditions are only satisfied if the equations for k and q are solved. However both these equations are transcendental therefore they cannot be solved analytically and have to be obtained numerically.

**Derivation 12**Finite potential barrier

The potential energy is a step function given by:

$$\hat{V}(x) = \begin{cases} V_0, & 0 < x < a \\ 0, & \text{otherwise} \end{cases}$$

Note that  $V_0 > E$

In the classical case we know that the particle traveling towards the potential barrier has no probability of going through it, however in the quantum mechanical case there is a probability of a particle going through the barrier and coming out the other side (examples are radioactivity of nuclei).

From the potential we can see that the TISE can be split into three different regions, we have solved all of the TISE's in previous derivations therefore I simply quote the results here for the three regions:

$$\phi_{1,2,3}(x) = \begin{cases} e^{ikx} + re^{-kx}, & x < 0 \\ Ae^{qx} + Be^{-qx}, & 0 < x < a \\ te^{ikx}, & x > a \end{cases}$$

We have three solutions here for the three separate regions (k and q have their usual definition from previous derivations), I have labelled the coefficients r and t as what they are (transmission and reflection coefficients). It is also important to note that I have set the coefficient of the incoming wave equal to one as that is what we can control.

As with the finite square well the boundary conditions are that the wavefunction and its derivative must be continuous at the boundaries of the potential:

$x=0$

$$\begin{aligned} \phi_1(0) &= \phi_2(0) \\ \left(\frac{d\phi_1}{dx}\right)_{x=0} &= \left(\frac{d\phi_2}{dx}\right)_{x=0} \end{aligned}$$

These lead to two equations:

$$\begin{aligned} 1 + r &= A + B \\ ik - irk &= Aq - Bq \end{aligned}$$

These equations can be used to eliminate r and obtain an equation equal to A:

$$A = \frac{B(q-1) - ik + 1}{q+1}$$

$x = a$

$$\begin{aligned} \phi_2(a) &= \phi_3(a) \\ \left(\frac{d\phi_2}{dx}\right)_{x=a} &= \left(\frac{d\phi_3}{dx}\right)_{x=a} \end{aligned}$$

These lead to two equations:

$$\begin{aligned} Ae^{qa} + Be^{-qa} &= te^{ika} \\ qAe^{qa} - qBe^{-qa} &= ikte^{ika} \end{aligned}$$

These two equations can be used to eliminate B and to obtain an equation equal to A:

$$A = \frac{te^{ika}(q + ik)}{2qe^{qa}}$$

We know use the fact that  $r + t = 1$  and substitute it in we obtain the equation for the transmission coefficient:

$$t = \frac{2e^{-2ika}}{2 \cosh(qa) - i\left(\frac{k}{q} - \frac{q}{k}\right) \sinh(qa)}$$

We can square this expression and use the trig identity:

$$\cosh^2 x - \sinh^2 x = 1$$

to obtain the probability of transmission:

$$|t|^2 = \left(1 + \left(\frac{k^2 + q^2}{2kq}\right) \sinh^2(qa)\right)^{-1}$$

We can now substitute for the values of k and q to get:

$$|t|^2 = \left(1 + \frac{\sinh^2\left(\sqrt{v^2\left(1 - \frac{E}{V_0}\right)}\right)}{4\left(\frac{E}{V_0}\right)\left(1 - E/V_0\right)}\right)^{-1}$$

Where  $v$  is a dimensionless quantity defined as:

$$v^2 = \frac{2mV_0a^2}{\hbar^2}$$

**Derivation 13**  
Harmonic oscillator

The potential of an harmonic oscillator comes from Hooke's law and is of the form:

$$V(x) = \frac{1}{2}m\omega^2 x^2$$

Therefore the TISE becomes:

$$\left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2\right) \phi(x) = E\phi(x)$$

First we change the variables to obtain a dimensionless equation. Therefore we let:

$$x = ay, \text{ where } a = \sqrt{\frac{\hbar}{m\omega}}$$

This gives the differential equation:

$$\frac{\hbar\omega}{2} \left(-\frac{d^2}{dy^2} + y^2\right) \phi(y) = E\phi(y)$$

We know that a Gaussian solution satisfies the TISE above (this can be shown by substitution):

$$\phi(y) = Ae^{-\frac{x^2}{2a^2}}$$

Applying the normalisation condition, we can find an expression for the constant A, thus giving us the normalised ground state wavefunction:

$$\int_{-\infty}^{\infty} |\phi|^2 dx = 1$$

$$A^2 \int_{-\infty}^{\infty} e^{-\frac{x^2}{a^2}} dx = A^2 a \sqrt{\pi}$$

Therefore we get a condition on the normalisation:

$$A = \left(\frac{1}{a^2\pi}\right)^{\frac{1}{4}}$$

For the ground state wavefunction we have:

$$\phi_0(x) = \left(\frac{1}{a^2\pi}\right)^{\frac{1}{4}} e^{-\frac{x^2}{2a^2}}$$

The ground state energy is given by substituting the wavefunction back into the TISE:

$$\frac{\hbar\omega}{2} (1 - y^2 + y^2) Ae^{-\frac{y^2}{2}} = E_0 Ae^{-\frac{y^2}{2}}$$

Therefore:

$$E_0 = \frac{\hbar\omega}{2}$$

For higher energy solutions, we try a Gaussian solution multiplied by a polynomial in y, H(y):

$$\phi(y) = H(y)e^{-\frac{y^2}{2}}$$

Doing this and defining  $\epsilon = \frac{2E}{\hbar\omega}$ , we find that the TISE obeys a special ordinary differential equation called Hermite's equation:

$$H''(y) - 2yH'(y) + H(y)(\epsilon - 1) = 0$$

The functions that satisfy this equation are called Hermite polynomials,  $H(y)$ .

It turns out that the solutions are only normalisable when  $\epsilon = 2n + 1$  where  $n$  is an integer starting at 0. (This is found using a power series method of solution, which we have covered in our mathematics course.)

$$E_n = \left(n + \frac{1}{2}\right) \hbar\omega$$

$$H(t) | \psi(t) \rangle = i\hbar \frac{d}{dt} | \psi(t) \rangle$$

**Derivation 14**  
Ehrenfest Theorem

Consider the wavefunction of the form:

$$\Psi(x, t) = e^{i(kx - \omega t)}$$

We start with the expectation value of an arbitrary operator  $\hat{A}$ :

$$\langle A \rangle = \int_{-\infty}^{\infty} \Psi^*(x, t) \hat{A} \Psi(x, t)$$

To find the change in time of a quantity we differentiate both sides of the equation with respect to time:

$$\frac{d\langle A \rangle}{dt} = \frac{d}{dt} \int_{-\infty}^{\infty} \Psi^*(x, t) \hat{A} \Psi(x, t)$$

Differentiate each term on the R.H.S with respect to x using the chain rule:

$$\frac{d\langle A \rangle}{dt} = \left( \int_{-\infty}^{\infty} \frac{d\Psi^*(x, t)}{dt} \hat{A} \Psi(x, t) \right) + \left( \int_{-\infty}^{\infty} \Psi^*(x, t) \frac{d\hat{A}}{dt} \Psi(x, t) \right) + \left( \int_{-\infty}^{\infty} \Psi^*(x, t) \hat{A} \frac{d\Psi(x, t)}{dt} \right)$$

It can be seen that the first term on the R.H.S brings down a factor of  $i\omega$ , the 2 term is just the expectation value of the quantity  $\langle \frac{d\hat{A}}{dt} \rangle$ , the third term brings down a factor of  $-i\omega$ :

$$\frac{d\langle A \rangle}{dt} = \frac{i}{\hbar} \left( \int_{-\infty}^{\infty} \Psi^*(x, t) \hat{H} \hat{A} \Psi(x, t) \right) - \frac{i}{\hbar} \left( \int_{-\infty}^{\infty} \Psi^*(x, t) \hat{A} \hat{H} \Psi(x, t) \right) + \left\langle \frac{d\hat{A}}{dt} \right\rangle$$

The first two terms on the R.H.S can be rewritten as:

$$\frac{d\langle A \rangle}{dt} = \frac{i}{\hbar} \left( \int_{-\infty}^{\infty} \Psi^*(x, t) \hat{H} \hat{A} - \hat{A} \hat{H} \Psi(x, t) \right)$$

Using the definition of commutators this can be simply written as:

$$\frac{d\langle A \rangle}{dt} = \frac{i}{\hbar} \langle [\hat{H}, \hat{A}] \rangle + \left\langle \frac{d\hat{A}}{dt} \right\rangle$$

This is Ehrenfest's Theorem and is very powerful as it can be seen that if a quantity has no time dependence and it commutes with the Hamiltonian then it must be a conserved quantity.



**Derivation 15**  
Orbital angular momentum

We use the classical definition of Angular momentum:

$$\mathbf{L} = \mathbf{r} \times \mathbf{p}$$

Define the position and momentum operators:

$$\begin{aligned}\mathbf{r} &= x\hat{\mathbf{i}} + y\hat{\mathbf{j}} + z\hat{\mathbf{k}} \\ \mathbf{p} &= \hat{p}_x\hat{\mathbf{i}} + \hat{p}_y\hat{\mathbf{j}} + \hat{p}_z\hat{\mathbf{k}}\end{aligned}$$

Now we assume that the values of linear momentum can be equated to the quantum mechanical operators in this equation aswell and take the cross product:

$$\begin{vmatrix} \hat{\mathbf{i}} & \hat{\mathbf{j}} & \hat{\mathbf{k}} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$

This gives values of the orbital angular momentum in Cartesian components:

$$\begin{aligned}\hat{L}_x &= -i\hbar \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \\ \hat{L}_y &= -i\hbar \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \\ \hat{L}_z &= -i\hbar \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)\end{aligned}$$

$$H(t) | \psi(t) \rangle = i\hbar \frac{d}{dt} | \psi(t) \rangle$$

**Derivation 16**TISE of hydrogen atom for small and large distances

We start with the TISE for the hydrogen atom:

$$\left( -\frac{\hbar^2}{2m_e r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \right) + \frac{l(l+1)\hbar^2}{2mr^2} - \frac{e^2}{4\pi\epsilon_0 r} \right) R(r) = ER(r)$$

Let  $R(r) = \frac{f(r)}{r}$ :

$$\frac{\hbar^2}{2m_e} \frac{d^2 f(r)}{dr^2} = \left( E + \frac{l(l+1)\hbar^2}{2m_e r^2} - \frac{e^2}{4\pi\epsilon_0 r} \right) f(r)$$

As  $r \rightarrow \infty$ :

$$\frac{\hbar^2}{2m_e} \frac{d^2 f(r)}{dr^2} = E f(r)$$

This is a second order linear homogenous equation that we have solved many times, the solutions are:

$$f(r) = A e^{-kr} + B e^{kr}$$

The term that is exponentially increasing is not physical and  $k$  has its usual meaning, therefore:

$$R(r \rightarrow \infty) \rightarrow A e^{-kr}$$

As  $r \rightarrow 0$ :

$$\frac{\hbar^2}{2m_e} \frac{d^2 f(r)}{dr^2} = \left( \frac{l(l+1)\hbar^2}{2m_e r^2} \right) f(r)$$

Now we try  $f(r) = Cr^x$  as a solution:

$$x(x-1)r^{x-2} = l(l+1)r^{x-2}$$

$$x^2 - x - l(l+1) = 0$$

$$x = -l \text{ or } (l+1)$$

Substitute the value of  $x$  into the equation for  $f(r)$ :

$$f(r) = Cr^{-l} + Dr^{(l+1)}$$

The solution with the negative power of  $r$  is unphysical for small values of  $r$  (also the value of  $+1$  in the positive power is irrelevant), therefore:

$$R(r \rightarrow 0) \rightarrow D e^l$$

**Derivation 17**  
Perturbation theory

Start with unperturbed system:

$$H_0 \Psi_0(x, t) = E_0 \Psi_0(x, t)$$

Introduce a perturbation in the energy:

$$\begin{aligned} H_0 &= H_0 + H_1 \\ E_0 &= \epsilon + E_0 \\ \Psi_0(x, t) &= \Psi_0(x, t) + \sum_{n=1}^{\infty} C_n \Psi_n(x, t) \end{aligned}$$

Substitute these relations into the top equation:

$$(H_0 + H_1)(\Psi_0(x, t) + \sum_{n=1}^{\infty} C_n \Psi_n(x, t)) = (\epsilon + E_0)(\Psi_0(x, t) + \sum_{n=1}^{\infty} C_n \Psi_n(x, t))$$

Multiplying through and ignoring the second order terms (as they will be extremely small for small perturbations) we get:

$$H_0 \sum_{n=1}^{\infty} C_n \Psi_n(x, t) + H_1 \Psi_0(x, t) = E_0 \sum_{n=1}^{\infty} C_n \Psi_n(x, t) + \epsilon H_0(x, t)$$

Multiply through by  $\Psi_0^*(x, t)$  and integrate over all space we get:

$$\epsilon = \frac{\int_{-\infty}^{\infty} \Psi_0^*(x, t) H_1 \Psi_0(x, t) dx}{\int_{-\infty}^{\infty} \Psi_0^*(x, t) \Psi_0(x, t) dx}$$

Multiply through by  $\Psi_n^*(x, t)$  and integrate to get an equation to calculate the coefficients:

$$C_n = - \frac{\int_{-\infty}^{\infty} \Psi_n^*(x, t) H_1 \Psi_0(x, t) dx}{E_n - E_0}$$

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- [D] *DDK*

$$H(t) | \psi(t) \rangle = i\hbar \frac{d}{dt} | \psi(t) \rangle$$