1. Introduction

This chapter will serve as an introduction to the fundamental concepts that form the basis of Quantum Mechanics, including:

- Quantum States
- Operators and Observables
- The Position Representation
- The Momentum Representation

This material will assume familiarity with Dirac notation and the mathematics of operators found in Chapter 1 of the Mathematical Methods notes. It will form the mathematical and conceptual groundwork from which one can work to understand more interesting concepts.Many texts will make use of the hat symbol to denote an operator. That shall be the done here, as it turns out to be more trouble than it is worth; most thing those will write will be operators!

"Quantum Mechanics is a unique and special polyect to study as an undergraduate as it is the great intellectual accomplishment of the last centure IC, the piece of Physics the least understood...It is fundationally mysterious, and is explored inarily specific to Physics, and yet it underpine constraints." - Professor Comes Binney

1.1 Quantum States

Many readers may already be familiar with the general concept of a quantum state; the words like to get thrown around a lot in popular physics as a loose term used to refer to some configuration of a system. Here, we shall define it more rigorously.

The state of a quantum-mechanical system can be specified by giving the quantum amplitudes $(a_i, which may be complex)$ to possible outcomes of measurements, and we can completely specify the state of a system by giving a complete set of quantum amplitudes. We will see what exactly a quantum amplitude represents shortly. For example, consider the spin of a spin-1/2 particle, such as an electron, in the z-direction. This can take on two values; $\pm 1/2\hbar$. We can then assign the amplitudes as

$$a_+$$
: amplitude to measure $+\frac{1}{2}\hbar$
 a_- : amplitude to measure $-\frac{1}{2}\hbar$

This means that the set $\{a_+, a_-\}$ forms a complete set of amplitudes for the state of the system.

The knowledge of any quantum-mechanical system can be encoded in some quantum state that is written as $|\psi\rangle$. Evidently, the system may be in a linear combination of some possible basis states $|i\rangle$, and so it can be written as

where
$$a_i$$
 are the quantum emplorities of each state. We know begin to answer the question of what exactly 1 quantum amplitude is. Consider $\langle \psi | \psi \rangle$.

$$\langle \psi | \psi \rangle \stackrel{\textbf{a}}{=} \left(\sum_{i}^{j} a_i^* \langle i | \right) \left(\sum_{j} a_j | j \rangle \right)$$

$$= \sum_{ij} a_i^* a_j \langle i | j \rangle$$

$$= \sum_{ij} a_i^* a_j \delta_{ij}$$

$$= \sum_{ij} |a_i|^2 = 1$$

$$(1.1)$$

Let us assume that $|\psi\rangle$ is normalised such that this last sum is equal to one. Then we have the sum of the moduli of the quantum amplitudes are equal to one. The system must, by definition, be in some linear combination of the states $|i\rangle$; in other words, it has unit probability to be in said linear combination. Thus, we can think of the modulus-square of the quantum amplitudes a_i as being the probability of finding the system in the state $|i\rangle$. Thus, we indeed find that the expectation value of the operator Q is given by'

$$\langle Q \rangle = \langle \psi | Q | \psi \rangle = \sum_{i} P_{i} q_{i}$$
(1.3)

In general, the quantum analogue to the determination of an observable in classical physics is finding the expectation value of the operator that corresponds to that observable.

1.2.1 The Hamiltonian Operator

The most important operator in Quantum Mechanics is the Hamiltonian operator (we will see why it is so important later). It is defined as

$$H = \sum_{i} E_{i} |E_{i}\rangle \langle E_{i}|$$
(1.4)

It is a simple calculation to show that $\langle H \rangle$ will give the expectation value of the energy of a system.

1.2.2 Shared Eigenstates

Suppose that we have two operators A and B. Consider their commutator

$$[A, B] = AB - BA$$

$$= \left(\sum_{i} a_{i} |a_{i}\rangle \langle a_{i}|\right) \left(\sum_{j} b_{j} |b_{j}\rangle \langle b_{j}|\right) - \left(\sum_{i} b_{i} |b_{i}\rangle \langle b_{i}|\right) \left(\sum_{i} a_{i} |a_{j}\rangle \langle a_{i}|\right)$$

$$= \sum_{i} a_{i}b_{j} |a_{i}\rangle \langle a_{i}| |b_{j}\rangle \langle b_{j}| - \sum_{i} a_{i}b_{j} |b_{i}\rangle \langle b_{i}| |a_{i}\rangle \langle a_{j}\rangle$$

$$= \sum_{i} a_{i}b_{i} (|a_{i}\rangle \langle b_{i}| - |b_{i}\rangle \langle b_{i}|)$$

$$96$$

In order for this to be zero, we require the $|a_i\rangle = |b_i\rangle$. Thus, we obtain the condition that if [AO] = 0 then the operator A and B share a complete set of mutual eigenstates. The fact that it is complete means that we can write any state as a linear combination of these states. This is a very powerful statement.

Most texts, at this point, will state that if two operators share a set of mutual eigenstates, then they can be simultaneously determined. This is in fact too weak of a condition. This can be illustrated by considering a particle that moves in a potential $V(\underline{x})$ and is known to have energy E_k . Can it have well defined momentum for a particular $V(\underline{x})$? If we consider the energy to be the sum of the kinetic $(p^2/2m)$ and potential $(V(\underline{x}))$ energies, then energy is only well defined given that the kinetic energy (and thus momentum) is well defined. However, this is only valid provided that $V(\underline{x}) = \text{constant}$. This means that under certain conditions, the particle can have well-defined momentum. If we had blindly worked out the commutator, we would have concluded that it could not have well defined momentum.

Another trap that students can fall into is assuming that if [A, B] = 0, and the system is in an eigenstate of A, then it is also in an eigenstate of B. This is not the case, mainly as a result of degeneracy. Essentially, just because there is a complete set of eigenstates which spans both operators, this does not mean that both operators contain all of said eigenstates. For example, if we have $A |u\rangle = a |u\rangle$ and $A |v\rangle = a |v\rangle$, then $|\theta\rangle = \cos \theta |u\rangle + \sin \theta |v\rangle$ also satisfies $A |\theta\rangle = a |\theta\rangle$. But we might also have $B |u\rangle = b_1 |u\rangle$ and $B |v\rangle = b_2 |v\rangle$. So we can use $|u\rangle$ and $|v\rangle$ as a complete set of mutual eigenstates, but $|\pi/4\rangle$ and $|-\pi/4\rangle$ are orthogonal states of A that are not eigenstates of B. Then,

$$0=2i\hbar\left\langle E\right|\frac{p^{2}}{2m}\left|E\right\rangle -i\hbar\left\langle E\right|\underline{x}\cdot\nabla V\left|E\right\rangle$$

Re-arranging, this becomes

$$2\left\langle T\right\rangle = \left\langle E\right|\underline{x}\cdot\nabla V\left|E\right\rangle$$

Suppose that the potential is of the form

$$V(\underline{x}) = A|\underline{x}|^{\alpha}$$

This could be, for example, a Coulomb potential with a = -1. Then:

$$\underline{x} \cdot \nabla V = A |\underline{x}|^{\alpha - 1} \underline{x} \cdot \nabla |\underline{x}| \alpha$$
$$= \alpha A |\underline{x}|^{\alpha - 1} \underline{x} \cdot \frac{\underline{x}}{|\underline{x}|}$$
$$= \alpha V$$

Substituting this back in, we obtain the expression

$$2\langle T \rangle = \alpha \langle V \rangle \tag{2.11}$$

A3

This is known as the *Virial Theorem*. As it has been derived in a Quantum 41 chanical setting, it must also be true on a Classical level; this means we were apply it to a lot of other scenarios. Astute students will have notice the relationship cropping up a lot when dealing with gravitational force that clots.

Only the last of these is a particular winteresting result big confirms our expectation that Quantum Mechanics in some way agree with Classical Mechanics.

Thus,

$$\Delta \phi = \phi' - \phi = \frac{r\pi}{2}$$
$$P_r = \cos^2\left(\frac{r\pi}{2}\right)$$
$$= 0$$

Thus, we were able to obtain the same result through much simpler algebra, though we do not have explicit forms for the reflection and transmission coefficients.

3.3.2 The Infinite Well

This is a limiting case of the square well. As $V_o \to \infty$ with a fixed, $W \to \infty$, meaning that the values of k that solve the defining equations for the odd and even solutions tend to $k = n\pi/2a$ and $k = (2n+1)\pi/2a$ respectively. This means we obtain the wave-function

$$\psi(x) = \begin{cases} \frac{1}{\sqrt{a}} \cos\left(\frac{(2n+1)\pi x}{2a}\right) & \text{for even parity} \\ \frac{1}{\sqrt{a}} \sin\left(\frac{n\pi x}{2a}\right) & \text{for odd parity} \end{cases}$$
(3.6)

for n = 0, 1, 2, 3, ..., and the pre-factor has come from simply normalising the wave-function. We can infer from this that wave-functions vanish at the edges of a region with infinite potential energy.



for $n = 1, 2, 3, \ldots$ Know that we know these values, it is simple to find the time evolution of the system using (2.4).

The infinite well is one of these problems for which there is a clear classical analogue of a ball bouncing completely elastically between two walls at $x = \pm a$. The Correspondence Principle dictates that for high energies, and thus high n, that the quantum and classical results must agree. In this case, let us shift the well to the right such that the zero point is located at the left-hand edge of the well; otherwise, we would get trivial results for the expectation values, making it uninteresting. For this, the odd parity solutions will remain the same.

$$\langle x \rangle = \int_0^{2a} dx \ x \left(\frac{1}{\sqrt{a}} \sin\left(\frac{n\pi x}{2a}\right)\right)^2$$
$$= a$$

Interestingly, this is independent of the energy of the state; the expectation value is being

What about the commutator of these two operators?

$$[A^{\dagger}, A] = \frac{1}{2m\hbar\omega} [m\omega x - ip, m\omega x + ip]$$

= $\frac{1}{2m\hbar\omega} (im\omega[x, p] - im\omega[p, x])$
= $\frac{i}{\hbar} [x, p]$
= -1

Thus,

$$[A^{\dagger}, A] = -1 \tag{4.5}$$

This is all just groundwork for the derivations in the next sections, so do not worry if it feels a little disjointed.

Preview from Notesale.co.uk Page 35 of 96

4.3 Wave-functions of Stationary States

We want the find the position representation of these energy eigenstates. Using the definition of the ground-state:

$$0 = A |0\rangle$$

= $\langle x | A |0 \rangle$
= $\langle x | (m\omega x + ip) |0 \rangle$
= $m\omega \langle x | x |0 \rangle + i \langle x | p |0 \rangle$
= $\left(\frac{m\omega}{\hbar}x + \frac{\partial}{\partial x}\right) \langle x |0 \rangle$

Using the integrating factor method,

$$\frac{\partial}{\partial x} \left(\langle x | 0 \rangle \, e^{x^2/4\ell^2} \right) = 0$$
$$\langle x | 0 \rangle = A \cdot e^{-x^2/4\ell^2}$$

for some constant A. Now, remark that $\langle x|0\rangle$ is of the form of a Gaussian. We require it's modulus-square to be properly normalised to one:

$$P_0(x) = |\langle x|0\rangle|^2$$
$$= A^2 e^{-x^2/2\ell^2}$$

Comparing this to the normal form of the Gaussian, it follows that the ground state wavefunction is $\langle x|0\rangle = -\frac{1}{100} \frac{100}{100} \frac{$

It follows quite quickly that we can obtain success vertable functions by repeatedly applying the creation operates X to this. That is $\langle x|n \rangle = (A^{\dagger})^n \langle x|0 \rangle$

In order to do this, it is helpful to write A^{\dagger} in a more useful form.

$$A^{\dagger} = \frac{m\omega x - ip}{\sqrt{2m\hbar\omega}}$$

= $\frac{\ell m\omega}{\hbar} x - \frac{i\ell}{\hbar} p$
= $\frac{2\ell}{4\ell^2} x - \frac{i\ell}{\hbar} \left(-i\hbar \frac{\partial}{\partial x} \right)$

Simplifying, this becomes

 $A^{\dagger} = \frac{x}{2\ell} - \ell \frac{\partial}{\partial x}$ (4.10)

As an example, let us apply this to the ground-state to obtain the wave-function of the first excited state.

$$\begin{aligned} \langle x|1\rangle &= A^{\dagger} \langle x|0\rangle \\ &= \left(\frac{x}{2\ell} - \ell \frac{\partial}{\partial x}\right) \frac{1}{(2\pi\ell^2)^{1/4}} e^{-x^2/4\ell^2} \\ &= \frac{1}{(2\pi\ell^2)^{1/4}} \frac{x}{\ell} e^{-x^2/4\ell^2} \end{aligned}$$

The Uncertainty Principle

As we did with the Harmonic Oscillator, we are now going to consider the uncertainty relation that is associated with the angular momentum \underline{J} . We know from (1.5) that

$$\sigma_{J_x}\sigma_{J_y} \ge \frac{\hbar}{2} \left| \langle J_z \rangle \right| = \frac{m\hbar^2}{2}$$

The states $|j,m\rangle$ are symmetric with respect to x and y as z is the only direction that we know about, meaning that $\sigma_{J_x}\sigma_{J_y} = (\sigma_{J_x})^2$. As $\langle J_x \rangle = 0$, $\sigma_{J_x}^2 = \langle J_x^2 \rangle$. By symmetry,

$$\langle J_x^2 \rangle = \frac{1}{2} \langle J^2 - J_z^2 \rangle = \frac{1}{2} (j(j+1) - m^2)\hbar^2$$

Substituting these results into the uncertainty relation above, we find that

$$j(j+1) \ge m(m+1)$$

which we know to be true as $m \leq j$. This means that angular momentum does in fact satisfy the uncertainty relation.

Decomposing \underline{J}

Suppose that we can decompose our angular momentum operator \underline{J} into two components, namely

$$\underbrace{\underline{J}}_{\text{Total}} = \underbrace{\underline{L}}_{\text{Orbital}} + \underbrace{\underline{S}}_{\text{spin}}$$

It is completely within our rights to do this as we are simply writing \underline{J} as the sum of two other operators. As we shall section to ving sections, L corresponds to orbital angular momentum (that is analogous to the classical angular momentum that we are used to), while \underline{S} corresponds to the orbital quantum encodernical effect that is spin angular momentum.

What effect does this have on our rotational transform U?

$$U(\underline{J}) = \exp\left(-\frac{i}{\hbar}\underline{\alpha} \cdot \underline{J}\right) = \exp\left(-\frac{i}{\hbar}\underline{\alpha} \cdot (\underline{L} + \underline{S})\right) = \exp\left(-\frac{i}{\hbar}\underline{\alpha} \cdot \underline{L}\right) \exp\left(-\frac{i}{\hbar}\underline{\alpha} \cdot \underline{S}\right)$$

This means that we can simply write that

$$U(\underline{J}) = U(\underline{L}) U(\underline{S})$$
(5.12)

This means that our rotation can be decomposed into a rotation associated with the orbital angular momentum, and a rotation associated with the spin angular momentum. The order is unimportant.

The last important thing to note about this decomposition is that due to linearity, both \underline{L} and \underline{S} obey the same commutation relations, and thus eigenvalue equations as \underline{J} . This means that the results derived in Section (5.1.4) hold for both \underline{L} and \underline{S} . We will make the changes $j \to \ell$ and $j \to s$ respectively.

49

the θ dependant cosine functions always remains equal to ℓ . It can be shown that the eigenfunctions of L^2 are given by the spherical harmonics

$$\langle \theta, \phi | \ell, m \rangle = Y_{\ell}^{m}(\theta, \phi) \propto P_{\ell}^{m}(\cos(\theta)) e^{im\phi}$$
(5.17)

where $P_{\ell}^{m}(\cos \theta)$ are the associated Legendre polynomials. By the definition of m, we have $2\ell + 1$ possible eigenfunctions for a given value of ℓ , and so we have to specify both ℓ and m when denoting a particular eigenfunction. Some of the results for lower values of ℓ are worth remembering, and are as follows:

$$Y_0^0 = \frac{1}{\sqrt{4\pi}} \qquad Y_1^0 = \sqrt{\frac{3}{4\pi}} \cos \theta \qquad Y_1^{\pm 1} = \mp \sqrt{\frac{3}{8\pi}} \sin \theta e^{\pm i\theta}$$

The normalisation constants come from integrating these eigenfunctions over both θ and ϕ ; this is obvious, but not worth forgetting. However, we often find that normalisation is irrelevant, as we are more interested in determining the values of ℓ and m based on the form of the eigenfunctions.

A system's wavefunction is proportional to $\sin^2 \theta$. What are the possible measurements of L_z and L^2 ? Give the probabilities of each outcome.

We need to write the angular dependence as the sum of the spherical harmonics, because then it becomes very easy to to read off the possibilities. This can be done by oble ving that

This means that

Thus, clearly a measurement of L_z will always yield zero, though we could have read this off immediately from the fact that the angular part of the wavefunction is independent of ϕ . L^2 has possibilities 0 and 6 ($\ell = 2$) with probabilities $\frac{5}{6}$ and $\frac{1}{6}$ respectively.

We are now going to consider the parity of the spherical harmonics, as this can often become very useful in order to simplify integrals, and in other such calculations. In polar coordinates, an application of the parity operator P gives rise to the transformation $[\theta, \phi] \mapsto$ $[\pi - \theta, \phi + \pi]$. Recalling Equation (5.16):

$$P\langle\theta,\phi|\ell,\ell\rangle \propto P\sin^{\ell}\theta e^{i\ell\phi} = \sin^{\ell}(\pi-\theta)e^{i\ell(\phi+\pi)} = (-1)^{\ell}\sin^{\ell}\theta e^{i\ell\phi} = (-1)^{\ell}\langle\theta,\phi|\ell,\ell\rangle$$

As the lowering and raising operators L_{\pm} are parity symmetric, applying them to the above state will not change it's parity. This means that the parity of a general state is given by

$$P |\ell, m\rangle = (-1)^{\ell} |\ell, m\rangle$$
(5.18)

5.2.2 Angular Momentum and Orbits

In a similar way to our treatment of orbits in Classical Mechanics, we want to decompose the momentum into a radial and angular part, such that we can reduce it to a



5.4.3 Combining Angular Momentum

As we are now working with composite systems, we want to examine how to combine angular momenta. Suppose that we have two angular momenta denoted by quantum numbers j_1 and j_2 that lead to a combined angular momenta denoted by the quantum number J with z-component M. J_1^2 and J_2^2 will commute with all components of \underline{J} , but components of \underline{J}_1 and \underline{J}_2 do not individually commute with J^2 . This means that we can know

- j_1, m_1, j_2, m_2 and M but not J **OR**
- j_1, j_2, M and J but not m_1 or m_2

We know that $M = m_1 + m_2 \leq j_1 + j_2$. When $M = j_1 + j_2$, we have one state of the system, $M = j_1 + j_2 - 1$, we have two states...the number of states will increase until we reach $M = |j_1 - j_2|$. This means that J can take values

$$J = |j_1 - j_2|, |j_1 - j_2| + 1, \dots, j_1 + j_2$$
(5.27)

We have already seen that the multiplicity of the individual angular momenta are

$$g(j_1) = 2j_1 + 1$$
$$q(j_2) = 2j_2 + 1$$

Using (5.27), we multiplicity of the combined angular momentum is then given by

$$g(J) = \sum_{J=|j_1-j_2|}^{j_1+j_2} \sum_{M=-J}^{J} M = \sum_{J=|j_1+j_2}^{j_1+j_2} 2J + 10 \sum_{n=0}^{2j_2} (j_1 - j_2 + n) + 1$$

= $(2j_2+1)(1j_1 - 2j_2 + 1) + 2\sum_{h=0}^{2j_2} n (2j_1 + 1)(2j_2 + 1)$
We rence find that
$$g(J) = g(j_1 + j_2) = g(j_1)g(j_2)$$
(5.28)

This is equal to the number of states of the two angular momenta as the system is a product state of the two original states, giving rise to this degeneracy.

Clebsh-Gordan Coefficients

We can write the total state of the system as

$$|J,M\rangle = \sum_{m_1=-j_1}^{j_1} \sum_{m_2=-j_2}^{j_2} C_{JM} |j_1,m_1,j_2,m_2\rangle$$

where $C_{JM} = \langle j_1, m_1, j_2, m_2 | J, M \rangle$ are known as the *Clebsch-Gordan coefficients*. The evaluation of these is quite a lengthy, and annoying process, so they are generally looked up in a set of reference tables, such as those overleaf.

A box containing two spin-1 objects A and B is found to have angular momentum quantum numbers J = 2 and M = 1. Determine the the probabilities for the various eigenvalues when J_z is measured for A.

Putting all of these results together, we finally find that the eigenfunctions for the states of a hydrogenic atom are given by

$$\langle r, \theta, \phi | n, \ell, m \rangle \propto r^{\ell} e^{-\frac{Zr}{na_{\mu}}} L_{n-\ell-1}^{2\ell+1} \left(\frac{2Zr}{na_{\mu}}\right) Y_{\ell}^{m}(\theta, \phi)$$

These eigenfunctions give the same value for energy as predicted by the Bohr model if we calculate the expectation values of the kinetic and potential energy. When normalising these functions, remember to integrate over r, θ and ϕ . It is often easier to separately normalise the radial and the angular parts separately.

Let us quickly consider an interesting property of the spherical harmonics in the context of an 'orbiting' electron. What is the probability of finding an electron at (r, θ, ϕ) given that it is in a state of well defined angular momentum? Suppose that we do not know anything else about the angular dependence of the wave-functions. This means that the only fair assumption we can make is that the electron as an equal probability of being in any of the states for a given ℓ, θ and ϕ . It in fact turns out that

$$P(\text{electron at } \theta, \phi) = \frac{1}{2\ell + 1} \sum_{m=-\ell}^{\ell} |Y_{\ell}^m|^2 = \frac{1}{4\pi}$$

Note how the last term is essentially the inverse of the solid angle for a sphere, essentially telling us that there is equal probability at being at each (θ, ϕ) in the absence of ψ_{α} there tesale.co.u information.

Radial Wavefunctions

Evidently, one does not have to be able to wave-functions, but the one worth remembering is that of the ground-state

$$Preview \qquad preview \qquad preview \qquad (5.33)$$

where again $a_{\mu} = \frac{m_e}{\mu} a_0$. Note that this had been normalised over all space. A notable point about the groundstate (as well as all other $\ell = 0$ states) is that it has a non-vanishing probability of being near r = 0, as the Coulomb potential is unbounded near the origin, only held in check by the Strong Force. Some graphs of the lower order radial wavefunctions are shown in the figure overleaf.

The plots in the left-hand column simply show the wavefunction, while those in the righthand column show the probability of finding the electron in the range [r, r+dr]. There are n-1 nodes for each value of n, and so as you increase n, you will obtain more frequent, and sharper peaks. This means that for higher n, the electrons tend to be found in more and more discrete bands further away from the origin.

Size of Orbit

Let us finish by calculating the expectation value of $\langle r \rangle$ to give us an idea of the typical size of a 'circular' orbit. To get this, we take $\ell = \ell_{\max} = n - 1$. This means that $L_0^{2\ell+1} = 1$, and we have a much simpler radial wavefunction of the form

$$R(r) \propto r^{n-1} e^{-Zr/(na_{\mu})}$$

where the last equality follows from evaluating the second term in the integrand, assuming that the wave-function is well defined in space. This means that, with normalisation, we obtain the required result.

Now for $\psi = e^{-br}$. As an exercise for the reader, it is trivial integration to show that $\langle H \rangle$ becomes:

$$\langle H\rangle = \frac{\hbar^2 b^2}{2m} - \frac{e^2 b}{4\pi\epsilon_0}$$

This is a function of the free parameter b. By Rayleigh's Theorem, we want to minimise this expression:

$$\frac{\partial \langle H \rangle}{\partial b}: \quad \frac{\hbar^2}{m}b - \frac{e^2}{4\pi\epsilon_0} = 0 \implies b = \frac{me^2}{4\pi\hbar^2\epsilon_0} = a_0^{-1}$$

We thus re-obtain the un-normalised form of the ground-state wave-function with the Bohr radius. Substituting this value for b back into $\langle H \rangle$, we obtain:

$$\langle H \rangle = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2} = -\frac{1}{2}m(\alpha c)^2 = -\mathcal{R}$$

We thus also obtain the expression for the Rydberg constant, assuming that we know that the energy takes the form given in Equation (5.32).

Equation (6.7) can also be used to prove the useful result that any potential well has at least one bound state. Suppose that a potential well is described by V_w , and consequently the Hamiltonian H_w . Let $V_{sq} > V_w$ be the potential describing a square well that 'fits' inside the potential V_w . For some state $|\psi\rangle$:



 $\langle \psi | H | \psi \rangle < \langle \psi | H_{sq} | \psi \rangle < 0$

As we know that the square well as at least one bound state, this means that our potential V_w must also have a bound state by the variational principle.

6.3 Time-Dependent Perturbation Theory

The result for time evolution in Equation (2.4) only holds for the case where the Hamiltonian in time-independent, meaning that we need another method to find the time evolution of states if H = H(t). In essence, we need to solve

$$i\hbar\frac{\partial\left|\psi\right\rangle}{\partial t}=H(t)\left|\psi\right\rangle$$

The method we use depends on how 'quickly' the Hamiltonian changes, measured with respect to the time-scale

$$\tau_H = \frac{\hbar}{E_n - E_m} \tag{6.8}$$

where E_n and E_m are the energy eigenvalues of two energy levels n and m respectively. τ_H corresponds to the evolution of a state under a time-independent Hamiltonian. We shall detail the main methods used in the following sections.

6.3.1 The Sudden Approximation

In this case, we assume that the change occurs over a time $t \ll \tau_H$ such that the system does not have enough time to modify it's wave-function to 'adjust' to the change. Suppose that the system is initially in a state that satisfies some time-independent Hamiltonian H_i which is suddenly (almost instantaneously) changed to another time-independent Hamiltonian H_f . In this case, we write the Hamiltonian as

 $H(t) = \begin{cases} H \text{ of e Sale COntrol for all of the state of } H \\ H \text{ of e Sale COntrol for all of } H \text{ of e Sale COntrol for all of } H \text{ of e Sale COntrol for all of } H \text{ of e Sale COntrol for a state of } H \text{ of e Sale COntrol for all of } H \text{ of e Sale COntrol for a state of$

The only question that remains is what are the coefficients a_n ? Are the TDSE is first order in time, it is pretty evident that these should be given by

$$a_n = \left\langle n \left| \psi(t = 0^-) \right\rangle \right] \tag{6.9}$$

This means that calculations using the sudden approximation are typically very easy, as they simply involve calculating matrix elements.

A tritium atom, ${}^{3}H$ is in its ground state when the nucleus undergoes a beta decay and becomes ${}^{3}He$. Assuming that the decay occurs over a short time interval, calculate the probability that this helium ion is in the 1s state.

The only difference between the initial and final states in the nucleic charge:

Initial State : $|1, 0, 0, Z = 1\rangle$ Final State : $|1, 0, 0, Z = 2\rangle$

6.4 Transitions and Selection Rules

We are now going to consider the case of a sinusoidal perturbation on the system, as we know from Fourier analysis that we can represent a large number of functions to a high degree of accuracy as a sum of sinusoidal components. Let

$$\delta H(t) = V_0 e^{-i\omega t}$$

Let $\omega_{nm} = (E_m - E_n)/\hbar$, meaning that our amplitude for the transition can be written as

$$a_{m} = -\frac{i}{\hbar} \int dt \ e^{i\omega_{nm}t} \langle m | \, \delta H \, | n \rangle = -\frac{1}{\hbar} \langle m | \, V_{0} \, | n \rangle \ \frac{e^{i(\omega_{nm}-\omega)t} - 1}{\omega_{nm} - \omega}$$

with associated probability

$$P_{nm} = \frac{|\langle m | V_0 | n \rangle|^2}{\hbar^2} \underbrace{\frac{\sin^2\left(\frac{\omega_{nm}-\omega}{2}t\right)}{\left(\frac{\omega_{nm}-\omega}{2}\right)^2}}_{\text{transition cross section } \sigma(t)}$$

For a given t, $\sigma(t)$ is dominated by a bump around the origin that is of height t^2 and width $2\pi/t$. Hence, the area under the bump is proportional to t, and in the limit of large t we can write

$$\sigma(t) \propto t \,\delta(\omega_{nm} - \omega)$$

The constant of proportionality turns out to be 2π , which can be found by integrating the area under $\sigma(t)$. Thus, the rate at which the transition $n \mapsto m$ have reacting the by

 $\nu_{mn} = \frac{2\pi}{\hbar^2} |\langle m| \ W_{N} \rangle^{(2)} (\omega_{nm} - \omega)$ (6.12) This expression gives right what is known to *lemnic Valden rule* of perturbation theory: Appintervation $V_0 e^{-i\omega t}$ causes system to transition to a new state higher in energy by $\hbar\omega$ at a real perportional to the mod-square of the matrix element of V_0 between the initial and final states.

It is very easy to see that for $\delta H = V_0 e^{i\omega t}$, there will be a transition to a new state that is lower in energy by $\hbar \omega$. To find the 'total' transition rate, we must integrate over all possible rates of transitioning from a given state *n* to all other possible states *m*. There are two possible cases:

1. We can have discrete E_n and E_m that are being considered, meaning that ω_{nm} remains fixed. However, there may be a range of ω in the incoming energy, with associated density of states $g(\omega)$.

$$\sum \nu_{nm} = \int d\omega \ g(\omega)\nu_{nm} = \frac{2\pi}{\hbar^2} |\langle m| V_0 |n\rangle|^2 g(\omega_{nm})$$

2. The energies may vary continuously (meaning a continuous range in E_m), but ω of the incoming energy remains constant. Let the number of final states in $[E_m, E_m + dE_m]$ be $g(E_m)dE_m$.

$$\sum \nu_{nm} = \int dE_m g(E_m) \nu_{nm} = \frac{2\pi}{\hbar} |\langle m | V_0 | n \rangle|^2 g(E_m + \hbar\omega)$$

Note that in this last expression, a factor of \hbar has disappeared when integrating over energy.

79

Now, define the operators $x_{\pm} = x \pm iy$. It follows quickly from the commutation relations of angular momentum with vector operators that $[L_z, x_{\pm}] = \pm \hbar x_{\pm}$. Then:

$$L_z(x_{\pm} | n, \ell, m \rangle) = x_{\pm}(L_z \pm 1) | n, \ell, m \rangle = (m+1)(x_{\pm} | n, \ell, m \rangle)$$

So $x_{\pm} | n, \ell, m \rangle$ is an eigenket of L_z with eigenvalue $m \pm 1$. Given that x and y can both be written in terms of x_{\pm} , we conclude that the matrix elements for x and y are zero unless

$$|m - m'| = 1$$

for orthogonality reasons. Note that x_{\pm} do not commute with L^2 ; this means that we cannot use them in the place of L_{\pm} to derive the eigenvalue relations as in Section (5.1.4). In any case, as summary of the important results is shown in the box below. We are assuming that the electric field is orientated along z.

$$\Delta \ell = \pm 1 \tag{6.13}$$

$$\Delta m = 0 \quad \text{for } z \tag{6.14}$$

$$\Delta m = \pm 1 \quad \text{for } x, y \tag{6.15}$$

How can we interpret these selection rules physically? This can be thought about in terms of the polarisation of the photon that is emitted as a result of these radiative transitions. Suppose that the photon is emitted in the same direction as the imposed electric field. If we observe the system along z, then the electric field vector of the radiation will be in the x-y plane, giving rise to circular polarisation. In fact, $\Delta m = 1$ corresponds to the field direction of observation is perpendicular to the imposed field, the electric vector of the radiation can be either perpendicular to the field, in which case $\Delta m = \pm 1$, or parallel to the field, and then $\Delta m = 0$. This unals that linear polarisation can only be observed in the x-y plane, as linear polarisation requires no angular momentum.

On an symplex the distribution of the emitted radiation may be circularly polarised even in the absence of the electric field. This argument is bogus. The introduction of the electric field splits the energy levels, meaning that the frequencies of the radiation observed along z depends on the polarisation state (eg. left-handed has higher energy). Without the field, the circular polarisations will have the same energy, meaning that one cannot distinguish between them; the superposition thus creates linearly polarised light.

7.1Exchange Symmetry

Let $|a,b\rangle$ be the ket representing the state of two particles; the first particle on the left (in state 1) and the second particle on the right (in state 2). Let us now 'swap' the two particles. Assuming that they are indistinguishable, this should not change the modulus of the state vector; this is analogous to not changing the value of any physical observables.

$$\begin{split} | \left| a, b \right\rangle |^2 &= | \left| b, a \right\rangle |^2 \\ | b, a \rangle &= e^{i\phi} \left| a, b \right\rangle \end{split}$$

If we now swap the particles in the second ket, we obtain

$$|b,a\rangle = \underbrace{e^{2i\phi}}_{e^{i\phi}=\pm 1} |b,a\rangle$$

This means that there are two possible *exchange symmetries*:

- 1. $|a,b\rangle = |b,a\rangle$ for bosons that have integer spin
- 2. $|a,b\rangle = -|b,a\rangle$ for fermions that have half odd-integer spin

Suppose now that that the states "a" and "b" are in fact the same state. This means that for fermions $|a,a\rangle = -|a,a\rangle = 0$; that is, no two fermions can occupy the same quantum co.uk state. This is known, quite famously, as the Pauli Exclusion Principle.

Wave-Functions and Exchange Symmetry 7.1.1

These exchange symmetries restrict the behaviour of particles in a multiple particle system, and thus restrict the way that we form our care-functions as we have to preserve said A preserve said symmetries. In general, for identical icles the Hamiltonian will be of the form



If $H_{\rm int.} = 0$ (the particles are non-interacting), then the TISE can simply be solved via separation of variables, as the states are uncorrelated. However, this does not apply in the general case. When solving a partial differential equation like the above, the general solution is usually a superposition of factored solutions. Let us consider a system of two identical bosons or fermions, with wave-functions ϕ_i . Then we can write the spatial wavefunction as

$$\psi(\underline{r}_1, \underline{r}_2) = \frac{1}{\sqrt{2}} \left[\phi_1(\underline{r}_1) \phi_2(\underline{r}_2) \pm \phi_1(\underline{r}_2) \phi_2(\underline{r}_1) \right]$$
(7.1)

where the positive sign corresponds to bosons, and the negative sign to fermions. Notice how the wave-function disappears in the case where $\phi_1 = \phi_2$; this is the Pauli Exclusion Principle in action.

Suppose that we have p indistinguishable particles, and n single-particle states available to the system. How many distinct states of the system are possible? The best way to answer this equation is combinatorially. Following the lead of Statistical Mechanics, let Ω_p denote the number of distinct states that the system may occupy. Then for fermions, we have to