PX3A2: Quantum Physics of Atoms

Warwick Physics Society

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0.1 Introduction, Credits and Notation

0.1.1 Credits

A big thank you to

- Chris, for producing the majority of the original content and equations in Chapters 1 - 8
- Chung, for adding in Two-level systems and elaborating/reorganising content on Chris's content and tidying up the document.

0.1.2 How to use the guide

Anything in a white box with a blue title frame like

> **Title here**
>
> Content placed in these contains information or principles that **must be remembered for the exams**. This applies information placed in the same colour box, but without a title!

Any equation which contains a regular, black box like $\boxed{this}$ is important information but you shouldn't need to memorise it.

This guide is very detailed, almost like its own set of lecture notes. It aims to answer as many questions as possible regarding both the maths and the physics in this module. Any parts non-examinable will be explicitly marked non-examinable. Beware that this can change over the years if this guide isn't updated and therefore check with the lecturer.

0.1.3 Tips

Past exams have generally been quite formulaic.

- It is almost guaranteed to be asked a perturbation theory question - you should ensure you memorise the algorithms rather than examples.
- Be familiar with formal quantum mechanics from second year. Stuff like quantum numbers, the spherical harmonics, raising and lowering operators are all assumed knowledge.
- There is a hefty set of problems alongside the past exams, so do all of them!

Another popular question is **integration**. We outline some general integral tricks here. Most importantly, **don't memorise any integrals or integral results**. They will always be given in the exam, and so if you find you don't use a standard integral, you may have an incorrect answer! This is true for anything perturbation theory related.

- The integral of an odd function $f(x)$, i.e. it satisfies $f(-x) = -f(x)$ over a **symmetric interval**, i.e. an interval of the form $[-L, L]$ or $(-\infty, \infty)$ is always 0. This applies to multiple integrals as well.

Chapter 1

Time-independent Non-Degenerate PT

1.1 Introduction

The vast majority of systems we consider in quantum mechanics don't have exact solutions and so need to be approximated. In fact there are only 2 known systems which have been solved exactly. These are the simple harmonic oscillator (SHO) and the potential well in 3D. However if the system we want to find the eigenvalues and eigenstates for is similar to one of these, then we can use perturbation theory (PT) as a way to approximate these eigenvalues and eigenstates. This involves taking a system which has been solved exactly and applying a small correction to make it resemble the system we wish to solve, and then consider perturbative expansions of the values that change.

1.2 Derivation

Generally speaking, there are only formulas and an algorithm that is needed to be remembered. The derivations following are, based on history, non-examinable.

We wish to find the corrections to our energy eigenvalues and corresponding eigenstates as a result of the perturbation we have applied. We begin by writing the Hamiltonian for our new perturbed system as:

$$\hat{H} = \hat{H}_0 + \beta\hat{V}, \tag{1.1}$$

where $\hat{H}_0$ is the Hamiltonian of our unperturbed solved system (like the SHO), $\hat{V}$ is the perturbation we apply and β is just a real number that controls the size of $\hat{V}$. Here we assume that $\hat{H}_0$ and $\hat{V}$ are both hermitian, so that $\hat{H}$ is also hermitian. We further assume that the eigenvalues of the unperturbed system are not degenerate, i.e there aren't any eigenstates with the same eigenvalue or an eigenstate with multiple eigenvalues. Therefore each unique eigenvalue has 1 eigenfunction. Note β is constrained by $0 \leq \beta < 1$ otherwise the expansions will not converge.

The *unperturbed* system solves its own Schrödinger equation:

$$\hat{H}_0 \left|\psi_n\right\rangle = E_n \left|\psi_n\right\rangle \tag{1.2}$$

We then consider our perturbed Hamiltonian eigenvalue equation:

$$\hat{H} \left|\psi_n\right\rangle = E_n \left|\psi_n\right\rangle, \tag{1.3}$$

where $|\psi_n\rangle$ is the eigenstate of the perturbed state in the n^{th} energy level, and E_n is the energy of the n^{th} energy level and $\hat{H}$ is given by Eq. (1.1).

The idea with PT is that since our system is the sum of the unperturbed system plus a 'little change' $\beta\hat{V}$, we are able to say that our perturbed energy is the sum of the original energies plus some 'little change'. If we want to be more accurate, we keep adding more 'little changes'. The perturbative expansions of E_n and $|\psi_n\rangle$ are:

$$E_n = E_n^0 + \beta E_n^1 + \beta^2 E_n^2 + \beta^3 E_n^3 ..., \tag{1.4}$$

$$|\psi_n\rangle = |\phi_n^0\rangle + \beta\,|\phi_n^1\rangle + \beta^2\,|\phi_n^2\rangle + \beta^3\,|\phi_n^3\rangle\,..., \tag{1.5}$$

where $|\phi_n^0\rangle$ and E_n^0 are the eigenstates and eigenvalues of the n^{th} energy level of the unperturbed system, $\hat{H}_0$.

The extra terms E_n^1, E_n^2 denote the correction energies to the unperturbed energy E_n^0 to the nth energy level. The notation is read as

E_n^i is the ith order correction to the unperturbed nth energy level.

The same concept is applied to the eigenstates, that is

$|\phi_n^i\rangle$ is the ith order wavefunction correction to the unperturbed nth wavefunction.

Since $\beta < 1$, the series in both energy and state converge. It might help to think of the perturbative expansions, Eq (1.4) and Eq (1.5), as Taylor series expansions (in terms of β) of the eigenvalues and eigenstates about the unperturbed eigenvalue and eigenstate.

Let us focus on the wavefunction expansion. The state $|\psi_n\rangle$ is written as the linear, infinite sum of other wavefunctions $|\phi_n^i\rangle$. Namely, we can think of all of the $|\phi_n^i\rangle$ as a **Hilbert space**, since the infinite sum converges (completeness) and we can still take inner products of wavefunctions with each other.

Now, a Hilbert space is a type of vector space. Can we form a basis of a vector space? Yes! Some linear algebra gladly tells us any vector space has a basis, and so our Hilbert space does have a basis of wavefunctions. What does this actually mean? This means we can, without question, say assume the $|\phi_n^i\rangle$ are **orthonormal**.

Remark. Some of you might wonder *why* can we assume them to be orthonormal? Well, suppose none of the $|\phi_n^i\rangle$ are orthonormal to each other. Since every vector space has a basis, we can write each $|\phi_n^i\rangle$ as a linear superposition of some basis wavefunctions, call them say $|\xi_n^i\rangle$. Then every term in the perturbative expansion can be written as

$$|\psi_n\rangle = \sum_i \gamma^i\,|\xi_n^i\rangle \tag{1.6}$$

so assuming we automatically have an orthonormal basis makes life easier.

For the following we assume that unperturbed eigenstates are orthonormal to one another and that corrections to the n^{th} unperturbed eigenstate are orthonormal to the unperturbed eigenstate, i.e:

$$\langle\phi_n^0|\phi_m^0\rangle = \delta_{nm} \tag{1.7}$$

$$\langle\phi_n^0|\phi_n^1\rangle = \langle\phi_n^0|\phi_n^2\rangle = \langle\phi_n^0|\phi_n^3\rangle = ... = 0. \tag{1.8}$$

Now combining Eq. (1.1) - Eq.(1.5), we find:

$$\hat{H}\left|\psi_n\right\rangle = (\hat{H}_0 + \beta\hat{V})(\left|\phi_n^0\right\rangle + \beta\left|\phi_n^1\right\rangle + \beta^2\left|\phi_n^2\right\rangle + \ldots) \tag{1.9}$$
$$= (E_n^0 + \beta E_n^1 + \beta^2 E_n^2 + ...)(\left|\phi_n^0\right\rangle + \beta\left|\phi_n^1\right\rangle + \beta^2\left|\phi_n^2\right\rangle + ...), \tag{1.10}$$

We then expand this and equate powers of β on the left and right hand side. So for **zero order terms**, i.e the terms which don't contain β, we find:

$$\hat{H}_0\left|\phi_n^0\right\rangle = E_n^0\left|\phi_n^0\right\rangle, \tag{1.11}$$

as we would expect, the unperturbed Hamiltonian operating on an unperturbed eigenstate returns that same eigenstate with the corresponding unperturbed eigenvalue. We now examine the series expansions up to different orders.

First order expansion :

$$\hat{H}_0\left|\phi_n^1\right\rangle + \hat{V}\left|\phi_n^0\right\rangle = E_n^0\left|\phi_n^1\right\rangle + E_n^1\left|\phi_n^0\right\rangle, \tag{1.12}$$

Proof. This is not clear to see but you must expand the brackets up to the and including the β terms. Thus we need to expand

$$(E_n^0 + \beta E_n^1)(\left|\phi_n^0\right\rangle + \beta\left|\phi_n^1\right\rangle) \tag{1.13}$$
$$= E_n^0\left|\phi_n^0\right\rangle + E_n^0\beta\left|\phi_n^1\right\rangle + \beta E_n^1\left|\phi_n^0\right\rangle + \beta^2 E_n^1\left|\phi_n^1\right\rangle \tag{1.14}$$

Now, the first term $E_n^0\left|\phi_n^0\right\rangle = \hat{H}_0\left|\phi_n^0\right\rangle$, the unperturbed wavefunction. We ignore any second order terms, so discard any β^2 and above terms. Now we are left with a term linear in β that is our first order perturbation. ☐

Note if we assume a sufficiently small perturbation $\hat{V}$ then we can just drop the βs, i.e. we just absorb it into the perturbation $\hat{V}$. Furthermore, the corrections $\left|\phi_n^i\right\rangle$ for $i > 0$ are generally *not eigenstates of* $\hat{H}_0$, but are rather linear combinations of other eigenstates themselves. This means if you were to act $\hat{H}_0$ on those eigenstates you would get a factor of E_n^0 out.

Second order expansion:

$$\hat{H}_0\left|\phi_n^2\right\rangle + \hat{V}\left|\phi_n^1\right\rangle = E_n^0\left|\phi_n^2\right\rangle + E_n^1\left|\phi_n^1\right\rangle + E_n^2\left|\phi_n^0\right\rangle. \tag{1.15}$$

We restrict ourselves to a first order perturbation for now. By pre-multiplying Eq. (1.12) by $\left\langle\phi_n^0\right|$:

$$E_n^0\left\langle\phi_n^0|\phi_n^1\right\rangle + \left\langle\phi_n^0|\hat{V}|\phi_n^0\right\rangle = E_n^0\left\langle\phi_n^0|\phi_n^1\right\rangle + E_n^1\left\langle\phi_n^0|\phi_n^0\right\rangle, \tag{1.16}$$

where we can remove the E_n^0 and E_n^1 terms from within the bra-ket notation as they are just scalars.

This then simplifies to give us:

First order energy correction

$$E_n^1 = \left\langle\phi_n^0|\hat{V}|\phi_n^0\right\rangle \tag{1.17}$$

thanks to the orthonormality condition, Eq. (1.7), we impose. This means that the first order correction to the n^{th} energy eigenvalue is given by the expectation value of the n^{th} energy level unperturbed eigenstates with the perturbation we have applied.

Now in order to find the first order corrections to the eigenstates, we assume it takes the form:

$$|\phi_n^1\rangle = \sum_{p,p\neq n} a_{np} |\phi_p^0\rangle \tag{1.18}$$

i.e it is a linear combination of all the unperturbed eigenstates of the system, other than the one we are trying to find the correction for, $|\phi_n^0\rangle$. Then pre-multiplying Eq. (1.12) by $\langle\phi_m^0|$, where $m \neq n$, using Eq. (1.18), Eq. (1.7) and Eq. (1.8) we find:

First order correction to the wavefunction

$$|\phi_n^1\rangle = -\sum_{p,p\neq n} \frac{\langle\phi_p^0| \hat{V} |\phi_n^0\rangle}{E_p^0 - E_n^0} |\phi_p^0\rangle \tag{1.19}$$

Following a similar process for the second order energy correction, we find:

Second order energy correction

$$E_n^2 = -\sum_{p,p\neq n} \frac{|\langle\phi_p^0| \hat{V} |\phi_n^0\rangle|^2}{E_p^0 - E_n^0} \tag{1.20}$$

Note how the numerator, $|\langle\phi_p^0| \hat{V} |\phi_n^0\rangle|^2$, is always positive. So if we further assume that $E_p^0 > E_n^0$ then its always true that $E_n^2 < 0$.

1.3 The TINDPT Algorithm

Figure out your favourite way of saying the acronym.

The Algorithm

Memorise this algorithm for the exam. It will apply to every non-degenerate PT question, ever. Please note if your system has particular properties - e.g. for a helium atom, there are 2 electrons - you must take into account the spin wavefunctions - you will need to ensure you include those in your calculations.

1. Determine what your perturbation $\hat{V}$ is. This is given in the question, so read it.
2. Find your unperturbed wavefunctions. Wavefunctions will always be given somewhere in the exam. However you may need to remember the formulae for energies of simple systems like the SHO or hydrogenic atom.
3. Identify what calculations you need and beware of the wording of the question. If it asks for the *corrections* you may calculate E_n^1, E_n^2 directly. If it asks you for the *final* energy don't forget to add E_n^0 to your corrections! Take note of whether it says to first or second order.
4. Calculate! Remember how to find expectation values with an integral. All necessary standard integrals will be given in the exam rubric.

Chapter 2

Time-independent Degenerate PT

2.1 Introduction

In the previous section we applied a perturbation to a known system and found the first and second order corrections to energy eigenvalues and the first order correction to eigenstates. However we assumed that there was no degeneracy involved. If our system we are considering does have degenerate energy levels, i.e distinct eigenstates with the same eigenvalue then problems arise. By considering Eq. (1.19) and Eq. (1.17) we can see that if there are degenerate energy levels, where $E_p^0 = E_n^0$, then these expressions diverge. Thankfully we can alter the process to account for this degeneracy and still find values for our system.

2.2 Derivation

As with the non-degenerate case, this derivation is **not examinable** so feel free to skip it.

Consider E_n^0, an eigenvalue of the unperturbed Hamiltonian $\hat{H}_0$. Suppose it is s-fold degenerate, so there are s linearly independent eigenstates which have energy E_n^0. We shall label these as $|u_{n\alpha}^0\rangle$ (so α indexes the *degenerate* states) and assume that they are orthornormal to each other[1]:

$$\langle u_{n\alpha}^0 | u_{n\beta}^0 \rangle = \delta_{\alpha\beta}, \tag{2.1}$$

where $\alpha, \beta = 1, 2, 3, \ldots s$ are labels for the s degenerate eigenstates of the n^{th} energy level.

Since any linear combination of $|u_{n\alpha}^0\rangle$ is an eigenstate of $\hat{H}_0$, then the unperturbed states we used previously in non-degenerate PT are not uniquely defined and so can't be used for PT. Therefore we need to find the correct normalised states which can be used in PT. Note there will be s of these states. We write these states in the following form:

$$|\phi_{ni}^0\rangle = \sum_{\alpha=1}^{s} c_{i\alpha} \, |u_{n\alpha}^0\rangle \,, \tag{2.2}$$

where the $c_{i\alpha}$ ensures we have the correct linear combination of unperturbed degenerate states to use in PT, and $i = 1, 2, 3, \ldots, s$.

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[1] This is again due to linear algebra, by the same reasoning presented in the previous chapter, though subtly different. If you took any linear algebra modules, these eigenfunctions span the eigenspace created by the degeneracy of E_0^n. Since they span and are linearly independent, they form a basis. We can always create an orthonormal basis because we work in a Hilbert space, so we are free to assume they can be orthonormal.

From Eq. (1.19) and Eq. (1.17), we can see the denominator tends to 0 as the system tends towards degeneracy. In order to ensure we have valid perturbative expansions, like Eq. (1.5) and Eq. (1.4), we make the numerator tend to 0 as well. This is ensured by the condition:

$$\langle\phi^0_{ni}|\hat{V}|\phi^0_{nj}\rangle = \langle\phi^0_{ni}|\hat{V}|\phi^0_{ni}\rangle\,\delta_{ij} \tag{2.3}$$

which can be represented as an $s \times s$ diagonal matrix[2] which ensures our perturbation expansions are valid. This means that we can now follow the same process as for the non-degenerate case, which results in a slightly modified Eq. (1.17):

First order energy correction to the i^{th} degenerate eigenfunction

$$E^1_{ni} = \langle\phi^0_{ni}|\hat{V}|\phi^0_{ni}\rangle\,. \tag{2.4}$$

Analogous to Eq. (1.17), the first order correction for the i^{th} degenerate state of the n^{th} energy level is given by the expectation value of the i^{th} degenerate eigenstate with the perturbation.

However you wouldn't normally use Eq. (2.4), since it doesn't tell you the correct linear combination of $|u^0_{n\alpha}\rangle$ which allows PT to work. There is an easier way to find the first order corrections for each of the degenerate eigenstates as well as the coefficients, $c_{i\alpha}$. We are going to go in for a hefty derivation, but it is non-examinable so you may skip straight to Eq. (2.10).

We begin with Eq. (1.12) but instead replace the subscripts $n \to ni$ so we have

$$\hat{H}_0\,|\phi^1_{ni}\rangle + \hat{V}\,|\phi^0_{ni}\rangle = E^0_n\,|\phi^1_{ni}\rangle + E^1_{ni}\,|\phi^0_{ni}\rangle\,, \tag{2.5}$$

We rearrange into a dodgy-looking form

$$-\left(\hat{V} - E^1_{ni}\right)|\phi^0_{ni}\rangle = \left(\hat{H}_0 \;\; - E^0_n\right) \tag{2.6}$$

Pre-multiply it by $\langle u^0_{n\beta}|$ and we get

$$-\left\langle u^0_{n\beta}\middle|\hat{V} - E^1_{ni}\middle|\phi^0_{ni}\right\rangle = \left\langle u^0_{n\beta}\middle|\hat{H}_0 - E^0_n\middle|\phi^1_{ni}\right\rangle \tag{2.7}$$

However note that from first-order expansion $\hat{H}_0\,|\phi^1_{ni}\rangle = E^0_n\,|\phi^1_{ni}\rangle$ so the RHS is just zero. Therefore we rearrange and get

$$\left\langle u^0_{n\beta}\middle|\hat{V}\middle|\phi^0_{ni}\right\rangle = E^1_{ni}\left\langle u^0_{n\beta}\middle|\phi^0_{ni}\right\rangle \tag{2.8}$$

We now substitute in our linear combination Eq. (2.2) - we want to find the coefficients $c_{i\alpha}$. We extract the sums to the outside because these operations are all linear (it's called linear algebra for a reason!)

$$\sum_{\alpha=1}^{s} c_{i\alpha}\left\langle u^0_{n\beta}\middle|\hat{V}\middle|u)n\alpha^0\right\rangle = \sum_{\alpha=1}^{s} E^1_{ni}c_{i\alpha}\left\langle u^0_{n\beta}\middle|u^0_{n\alpha}\right\rangle = E_{ni}\delta_{\alpha\beta} \tag{2.9}$$

by the orthonormality condition. Rearranging all to one side gives:

$$\boxed{\sum_{\alpha=1}^{s}\left(\langle u^0_{n\beta}|\hat{V}|u^0_{n\alpha}\rangle - E^1_{ni}\delta_{\alpha\beta}\right)c_{i\alpha} = 0\forall i = 1,\ldots,s} \tag{2.10}$$

This is most nicely represented by a matrix equation, where $\sum_{\alpha=1}^{s}\langle u^0_{n\beta}|\hat{V}|u^0_{n\alpha}\rangle$ is the matrix, the elements of which are determined by the expectation value of the degenerate eigenstates

---

[2] This is covered more in two-level systems, but it again comes from the idea that states can be *represented* as vectors, so operators can be represented as matrices.

with the perturbation. The term $-E^1_{ni}\delta_{\alpha\beta}$ can be seen as the form $-\lambda I$ where I is the identity matrix. Therefore, we can think of our system of s equations as solving for the *eigenvectors* of the matrix given by $\langle u^0_{n\beta}|\hat{V}|u^0_{n\alpha}\rangle$. Therefore we are solving the secular determinant

Secular determinant for degenerate PT

$$\det\left(\langle u^0_{n\beta}|\hat{V}|u^0_{n\alpha}\rangle - E^1_{ni}\delta_{\alpha\beta}\right) = 0 \tag{2.11}$$

So in order to find the first order corrections to the degenerate energy levels and their corresponding wave functions you simply solve Eq. (2.10) like any other eigenvalue equation.

Eigenvalues are the energy corrections

The eigenvalues of the matrix determine the first order corrections, E^1_{ni}, which are then re-inserted back into the equation to find $c_{i\alpha}$.

This then means you can determine $|\phi_{ni}\rangle$ for each E^1_{ni}, using Eq. (2.2).

Don't worry if none of this is making any sense it will hopefully make a lot more sense once you see an example and there aren't tons of greek letters and summation symbols all over the place.

2.3 Example: 2D SHO

In 1D the SHO is not a degenerate system, it has unique eigenstates for each of the energy levels given by $E_n = (n + \frac{1}{2})\hbar\omega$. However when we consider a 2D SHO, we are allowing oscillations in two directions, so the unperturbed Hamiltonian is just the sum of the 1D Hamiltonian in two directions:

$$\hat{H}_0 = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{1}{2}m\omega^2(x^2 + y^2), \tag{2.12}$$

where p_x, p_y are the momentum in the x and y directions respectively, and x, y the canonical coordinates. The unperturbed energy of this 2D system will now have contributions from the springs in both the x and y directions:

$$E^0_N = N\hbar\omega = (n_x + n_y + 1)\hbar\omega = \left[\left(n_x + \frac{1}{2}) + (n_y + \frac{1}{2}\right)\right]\hbar\omega, \tag{2.13}$$

with eigenstates given by:

$$u^0_N(x, y) = u^0_{n_x}(x)u^0_{n_y}(y), \tag{2.14}$$

where $u^0_{n_x}(x)$ are just the eigenstates for the 1D system. You again do not need to memorise the wavefunctions.

Now when $N = 1$, we can see there is no degeneracy present as in this case the only possibility is $n_x = n_y = 0$. So for E^0_1 the only possible eigenstate is $u^0_0(x, y) = u^0_0(x)u^0_0(y)$. However if we consider the first excited state $N = 2$, there is a 2-fold degeneracy, so $s = 2$. If $N = 2$, then there are 2 sets of possible values of n_x, n_y. These are $n_x = 0$ and $n_y = 1$, or $n_x = 1$ and $n_y = 0$. We can check this quickly: $E^0_2 = (n_x + n_y + 1)\,\hbar\omega$. Subtracting $\hbar\omega$ from either side gives $\hbar\omega = (n_x + n_y)\hbar\omega$. The only (integer) solutions that are valid are if one of n_x, n_y is 1 and the other is 0.

Remark. If it helps, write out a table or equation *explicitly* and count.

In the first set the spring in the x direction isn't oscillating it only has its zero point energy, whilst in the y direction the spring is oscillating in its first excited state.

This means our degenerate eigenstates, using Eq. (2.14), are given by:

$$u^0_{21}(x,y) = u^0_1(x)u^0_0(y) \tag{2.15}$$
$$u^0_{22}(x,y) = u^0_0(x)u^0_1(y), \tag{2.16}$$

where the first equation corresponds to $n_x = 1$, $n_y = 0$ and the second corresponds to $n_x = 0$, $n_y = 1$. These equations correspond to our $|u^0_{n\alpha}\rangle$, defined by Eq. (2.1), where $N \equiv n = 2$ as we are in the first excited state of the system, and since there are 2 degenerate eigenstates $\alpha = 1, 2$. Now using Eq. (2.2), we define the correct linear combination of degenerate eigenstates that allows us to perform PT:

$$|\phi^0_{21}\rangle = c_{11}\,|u^0_{21}\rangle + c_{12}\,|u^0_{22}\rangle \tag{2.17}$$
$$|\phi^0_{22}\rangle = c_{21}\,|u^0_{21}\rangle + c_{22}\,|u^0_{22}\rangle\,, \tag{2.18}$$

these are our $|\phi^0_{ni}\rangle$ and $c_{i\alpha}$.

Now in order to find the first order corrections and correct linear combination, we need to solve Eq. (2.10). The matrix will be a 2×2 matrix since this a 2-fold degeneracy. The elements of the matrix are determined as:

$$V_{11} = \langle u^0_{21}|\hat{V}|u^0_{21}\rangle \tag{2.19}$$
$$V_{12} = \langle u^0_{21}|\hat{V}|u^0_{22}\rangle \tag{2.20}$$
$$V_{21} = \langle u^0_{22}|\hat{V}|u^0_{21}\rangle \tag{2.21}$$
$$V_{22} = \langle u^0_{22}|\hat{V}|u^0_{22}\rangle\,, \tag{2.22}$$

where V_{ij} is the matrix element of the i^{th} row and the j^{th} column. So the perturbation matrix looks like:

$$\hat{V} \doteq \begin{pmatrix} V_{11} & V_{12} \\ V_{21} & V_{22} \end{pmatrix} \tag{2.23}$$

Now assuming a perturbation of $\hat{V} = \lambda m\omega^2 xy$, and standard forms for the unperturbed eigenstates of the 1D SHO, we find by evaluating the matrix elements, that Eq. (2.23) is given by:

$$\hat{V} \doteq \begin{pmatrix} 0 & \frac{\lambda\hbar\omega}{2} \\ \frac{\lambda\hbar\omega}{2} & 0 \end{pmatrix} \tag{2.24}$$

Remark. Remember to evaluate the matrix elements using the integral definition, i.e.

$$\langle u^0_{2\alpha}|\hat{V}|u^0_{2\beta}\rangle = \int u^*_{2\alpha}\hat{V}u^0_{2\beta}d\mathbf{r} \tag{2.25}$$

where $d\mathbf{r}$ indicates to integrate over all degrees of freedom (e.g. x and y for the 2D SHO).

See the introduction for some extra tips on the integrals - in the exam they will save you time.

The first order corrections to the first excited energy level are then found from the eigenvalues of the above matrix to be $E_2^1 = \pm\frac{\lambda\hbar\omega}{2}$. Then our coefficients in Eq. (2.28) and Eq. (2.29) are determined from:

$$\begin{pmatrix} 0 & \frac{\lambda\hbar\omega}{2} \\ \frac{\lambda\hbar\omega}{2} & 0 \end{pmatrix} \begin{pmatrix} c_{11} \\ c_{12} \end{pmatrix} = +\frac{\lambda\hbar\omega}{2} \begin{pmatrix} c_{11} \\ c_{12} \end{pmatrix} \tag{2.26}$$

for Eq. (2.28), and:

$$\begin{pmatrix} 0 & \frac{\lambda\hbar\omega}{2} \\ \frac{\lambda\hbar\omega}{2} & 0 \end{pmatrix} \begin{pmatrix} c_{21} \\ c_{22} \end{pmatrix} = -\frac{\lambda\hbar\omega}{2} \begin{pmatrix} c_{21} \\ c_{22} \end{pmatrix} \tag{2.27}$$

for Eq. (2.29). Now we need to find the $c_{i\alpha}$. For the eigenvalue $+\lambda\hbar\omega/2$, we get $c_{11} = c_{12} = 1/\sqrt{2}$. For the eigenvalue $\lambda = -\lambda\hbar\omega/2, c_{21} = \frac{1}{\sqrt{2}}$ and $c_{22} = -\frac{1}{\sqrt{2}}$. Therefore the correct normalised eigenfunctions for perturbation theory are

$$|\phi_{21}^0\rangle = \frac{1}{\sqrt{2}}|u_{21}^0\rangle + \frac{1}{\sqrt{2}}|u_{22}^0\rangle \tag{2.28}$$

$$|\phi_{22}^0\rangle = \frac{1}{\sqrt{2}}|u_{21}^0\rangle - \frac{1}{\sqrt{2}}|u_{22}^0\rangle\,, \tag{2.29}$$

2.4 Key Results and The TIDPT Algorithm

Degenerate PT allows us to find approximate values for the energy eigenvalues and eigenstates of a degenerate system which resembles a system we can solve exactly. If you get asked to find the first order energy corrections for a degenerate system and/or the correct eigenstates that allow PT to work, then the process to follow is:

The Algorithm

1. Check what the degeneracy of the system is (s).
2. Find the forms of the s degenerate eigenstates, Eq. (2.1).
3. Form s linear combinations from the s degenerate eigenstates, Eq. (2.2).
4. Form the $s \times s$ perturbation matrix using the perturbation given and the degenerate eigenstates. Since the matrix is symmetric you won't have to calculate all the off diagonal elements individually, Eq. (2.10).
5. Calculate the eigenvalues of the matrix, these give you the first order energy corrections of the degenerate energy level you're considering. Note there will be s of them, but some may be repeated.
6. Then form an eigenvalue equation, with the perturbation matrix, the linear combinations of degenerate eigenstates and the eigenvalues to find the correct linear combinations.

Chapter 3

Variational Method

3.1 Introduction

The variational, or Rayleigh-Ritz, method is another approximation method we can use. We use this when dealing with a system where only the form of the Hamiltonian is known exactly. It involves making a prediction of what the ground state wave function of the system would look like and using this to calculate an upper bound for the energy of the ground state. This method can be applied to excited states as well, however it is slightly more complicated and you don't need to worry about this.

3.2 Derivation

From the third postulate of quantum mechanics, we know that any state of a particular system, $|\psi\rangle$, can be expressed as a linear combination of the eigenstates of an operator, such as the Hamiltonian, so long as they form a complete set:

$$|\psi\rangle = \sum_n c_n |\phi_n\rangle \, , \tag{3.1}$$

where $|\phi_n\rangle$ are the eigenstates of $\hat{H}$ and the sum is over the complete set of these eigenstates. Then considering the expectation value of $\hat{H}$:

Expectation of the Hamiltonian

$$\langle \hat{H} \rangle = I = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{\int \psi_T^* \hat{H} \psi_T d^3 r}{\int \psi_T^* \psi_T d^3 r} \tag{3.2}$$

If $|\psi\rangle$ is normalised the denominator is automatically one, so **always check before starting the calculation**. Assuming normalised wavefunctions, inserting Eq. (3.1) into Eq. (3.2), we find:

$$\langle \hat{H} \rangle = \sum_n |c_n|^2 E_n . \tag{3.3}$$

This means if we take $|\psi\rangle$ to be our **trial wave function** that we guess, which and we will denote as $|\psi_T\rangle$, then $\langle \hat{H} \rangle \geq E_1$ which is the ground state of the system.

This is because we assume that the energy eigenvalues, E_n, of $|\phi_n\rangle$ are ordered such that $E_1 < E_2 < E_3 < E_4$. So unless we accidentally pick the exact ground eigenstate of the Hamiltonian then our trial wave function will be a *combination of excited eigenstates* of the Hamiltonian, as we predict from Eq. (3.1). So our expectation value of the Hamiltonian will contain the sum of the corresponding energy eigenvalues for these eigenstates. For example if we let our trial wave function take the form:

$$|\psi_T\rangle = c_1 |\phi_1\rangle + c_5 |\phi_5\rangle + c_{23} |\phi_{22}\rangle , \tag{3.4}$$

where $c_1, c_5, c_{23} \neq 0$. Then Eq. (3.3) predicts:

$$\langle \hat{H} \rangle = |c_1|^2 E_1 + |c_5|^2 E_5 + |c_{23}|^2 E_{23}, \tag{3.5}$$

which must be larger than E_1. However if we say that:

$$|\psi_T\rangle = c_1 |\phi_1\rangle = |\phi_1\rangle , \tag{3.6}$$

where $c_1 = 1$ as $|\psi_T\rangle$ must be normalised. Then from Eq. (3.3):

$$\langle \hat{H} \rangle = |c_1|^2 E_1 = E_1. \tag{3.7}$$

We choose a form for $|\psi_T\rangle$ which is a function of some parameters, α_i, that we can tune, i.e $\psi_T = \psi_T(\alpha_1, \alpha_2, \alpha_3, \ldots)$. We then calculate the expectation value of the Hamiltonian with $|\psi_T\rangle$ using Eq. (3.2). The expectation value is then minimised with respect to $\alpha_1, \alpha_2, \alpha_3, \ldots$ with the final result representing the best estimate of the ground state energy of the system using $|\psi_T\rangle$ and **an upper bound for the actual ground state energy** of the system.

3.3 Key Results and the Algorithm

The variational method allows us to find an upper bound for the ground state energy of some system that we know the exact Hamiltonian for, but cannot solve exactly, by guessing a wave function. The general process for the variational method to always follow is:

The Algorithm

1. Guess the form of a trial wave function, $|\psi_T\rangle$, which depends on some parameters we can tune, so $\psi_T = \psi_T(\alpha_1, \alpha_2, \ldots)$.
2. Ensure that $|\psi_T\rangle$ is normalised.
3. Calculate $\langle \hat{H} \rangle = I = E(\alpha_1, \ldots)$ using the trial wave function.
4. Minimise $\langle \hat{H} \rangle$ with respect to any variational parameters, i.e. solve for when $\dfrac{\partial E(\alpha_1, \ldots)}{\partial \alpha_i} = 0 \forall i$.
5. Calculate the minimum value of $\langle \hat{H} \rangle$ using previously found value for variational parameter.

In an exam you will never have to guess a wave function yourself, it will always be given to you and there will always only be one parameter to minimise $\langle \hat{H} \rangle$ with respect to.

Note if we have 2 trial wave functions, and one of them gives a lower value for $\langle \hat{H} \rangle$ than the other, then this trial wave function gives a better estimate for the actual ground state energy of the system.

Chapter 4

SOC and the Zeeman effect

4.1 Introduction

This entire section is effectively a massive example of how useful degenerate PT is. Here we apply it to a hydrogenic system to quantify the magnitude of energy splittings when we apply an external magnetic field, allow spin-orbit coupling (SOC) or have a combination of both. This is done both using the brute force method, described in Section 2, and by figuring out what the correct eigenstates for PT are using symmetry, which I'll explain briefly in a minute.

Unfortunately the notation isn't great in places here, because in some cases V means the scalar potential of the nucleus and in others it means the potential energy of the electron in the scalar potential of the nucleus. I've tried to make it clear here using V_c meaning the potential energy. There's also some funny business going on with operator symbols.

4.2 Derivation

The Zeeman effect involves an external magnetic field coupling to the magnetic moments of an electron and SOC involves the coupling between these magnetic moments. In general the magnetic moment of a particle due to orbital motion is:

$$\boxed{\boldsymbol{\mu}_L = g_L \frac{q}{2m} \boldsymbol{L}} \tag{4.1}$$

where g_L is the orbital gyromagnetic ration, q is the charge of the particle, m the mass and $\boldsymbol{L}$ the orbital angular momentum vector. However all particles also have intrinisc angular momentum (spin), which also gives rise to a magnetic moment:

$$\boxed{\boldsymbol{\mu}_S = g_S \frac{q}{2m} \boldsymbol{S},} \tag{4.2}$$

where g_S is the **spin gyromagnetic ratio** and $\boldsymbol{S}$ the **spin angular momentum vector**.

Remark. For an electron $g_L = 1$, $g_S = 2$ and $q = -e$. Note that g_S doesn't exactly equal 2 there are some corrections to this value due to QED, which is also a perturbation theory but in the context of quantum field theory.

Now if we are going to apply degenerate PT to a hydrogenic system that experiences the Zeeman effect and SOC, we need to know the forms of the perturbation, $\hat{V}$, we apply. For the Zeeman effect, the operator is found from the interaction energy between $\boldsymbol{\mu}$ and $\boldsymbol{B}$:

Magnetic interaction energy

$$\hat{V}_{\text{mag}} = -\hat{\boldsymbol{\mu}} \cdot \hat{\boldsymbol{B}} = \frac{e}{2m}(\hat{L}_z + 2\hat{S}_z) \cdot B, \tag{4.3}$$

where we assume that $\boldsymbol{B} = (0, 0, B)$, i.e we align the magnetic field along the $\hat{z}$ direction, and $\hat{L}_z$ and $\hat{S}_z$ are the normal operators for returning the z-component of the orbital and spin angular momentum.

In the rest frame of the electron, the nucleus is orbiting it. This means the electron ”sees” a magnetic field due do the motion of the charged nucleus. It is given by:

$$\boldsymbol{B} = \frac{-\boldsymbol{v} \times \boldsymbol{E}(r)}{c^2}, \tag{4.4}$$

where $\boldsymbol{v}$ is the relative velocity of the nucleus, $\boldsymbol{E}(r)$ is the electric field due to the nucleus and c is the speed of light. Since the electric field of the nucleus is spherically symmetric we may write it as:

$$\boldsymbol{E}(r) = -\boldsymbol{\nabla} V = -\frac{\partial V}{\partial r}\hat{\mathbf{r}}, \tag{4.5}$$

where V is the scalar electric potential of the nucleus. The operator for SOC takes the form:

Potential due to spin-orbit coupling

$$\hat{V}_{\text{SOC}} = -\frac{1}{2}\hat{\boldsymbol{\mu}}_s \cdot \hat{\boldsymbol{B}}, \tag{4.6}$$

where the factor of $\frac{1}{2}$ arises from the Thomas precession which is a relativistic effect. So substituting in Eq. (4.2) and Eq. (4.4) into the above equation we find:

$$\hat{V}_{\text{SOC}} = \frac{e}{2m}\frac{\hat{\boldsymbol{S}} \cdot (\boldsymbol{v} \times \boldsymbol{r})}{c^2}\frac{1}{r}\frac{\partial V}{\partial r}, \tag{4.7}$$

where we have used that the radial unit vector, $\hat{\boldsymbol{r}} = \frac{\boldsymbol{r}}{r}$. Then using the relations $\boldsymbol{p} = m\boldsymbol{v}$, $\hat{\boldsymbol{L}} = \hat{\boldsymbol{r}} \times \boldsymbol{p} = -\boldsymbol{p} \times \hat{\boldsymbol{r}}$ and $\hat{\boldsymbol{S}} \cdot \hat{\boldsymbol{L}} = \hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}}$, we find:

$$\hat{V}_{\text{SOC}} = \frac{-e}{2m^2c^2}\frac{1}{r}\frac{\partial V}{\partial r}\hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}}. \tag{4.8}$$

There are a number of other forms that this operator can take, the most useful of which is found using:

$$\boxed{\hat{J}^2 = (\hat{L} + \hat{S})^2 = \hat{L}^2 + \hat{S}^2 + 2\hat{L} \cdot \hat{S}}, \tag{4.9}$$

in combination with Eq. (4.8):

$$\hat{V}_{\text{SOC}} = f(r)[j(j+1) - l(l+1) - s(s+1)], \tag{4.10}$$

where it should be noted that the square brackets here don’t mean commutator they are just brackets, and $f(r)$ is given by:

$$f(r) = \frac{\hbar^2}{4m^2c^2}\frac{1}{r}\frac{\partial V_c}{\partial r}, \tag{4.11}$$

where $V_c(r)$ is the potential energy of the electron in the nucleus' electric field, $\frac{-Ze^2}{4\pi\epsilon_0 r}$.

4.2.1 Correct eigenstates using symmetry

As I said at the end of Chapter 2, there is a more elegant way of doing degenerate PT. Instead of forming a matrix and finding its eigenvalues and corresponding eigenstates, we can figure out the correct eigenstates to use for degenerate PT using symmetry arguments.

The correct eigenstates for degenerate PT are ones that commute with the unperturbed hamiltonian, $\hat{H}_0$, the perturbation we apply, $\hat{V}$, and an arbitrary operator, $\hat{A}$, that we are free to choose. Once these eigenstates have been identified you can just use Eq. (2.4) to calculate the first order energy corrections for a degenerate system. Remember this expression is just the equivalent expression for Eq. (1.17) that accounts for degeneracy.

The reason this works is because any operators that commute with one another must share a set of common eigenstates. So if $[\hat{H}_0, \hat{A}] = [\hat{V}, \hat{A}] = 0$, then they all share a common set of eigenstates. Then so long as all the eigenvalues of $\hat{A}$ are unique, this automatically leads to the diagonalisation condition, Eq. (2.3), being satisfied. This in turn means that those eigenstates are the correct unperturbed states for degenerate PT.

Don't worry too much about trying to understand why this works, just know that the correct eigenstates for degenerate PT are ones that are eigenstates of $\hat{H}_0$, $\hat{V}$ and another operator, $\hat{A}$.

4.2.2 Spin-Orbit Coupling

We'll start off by considering the case of just SOC, so no external magnetic field has been applied. I'll start off with the symmetry argument method. Since we are considering a hydrogenic system, i.e a single electron orbiting a nucleus, the eigenstates of the unperturbed system only depend on the principal quantum number, n. We will use Eq. (4.10) as our perturbation, which requires eigenstates that depend on l, s and j. Now we choose our other operator, $\hat{A}$, to be $\hat{J}_z$. This is just the total angular momentum equivalent of $\hat{L}_z$ or $\hat{S}_z$, i.e $\hat{J}_z = \hat{L}_z + \hat{S}_z$. This means the correct eigenstates for degenerate PT look like $|n, l, s, j, m_j\rangle$. So now we can figure out the first order energy corrections using these eigenstates and Eq. (2.4):

Energy due to SOC

$$E^1_{\text{SOC}} = \langle n, l, s, j, m_j|\hat{V}_{\text{SOC}}|n, l, s, j, m_j\rangle\,, \tag{4.12}$$

then inserting Eq. (4.10) and Eq. (4.11), we find:

$$E^1_{\text{SOC}} = \frac{\hbar^2}{4m_e^2c^2}[j(j+1) - l(l+1) - s(s+1)]\left\langle \frac{1}{r}\frac{\partial V_c}{\partial r}\right\rangle, \tag{4.13}$$

where again the square brackets are just brackets and don't mean commutator, and the expectation value of $\frac{1}{r}\frac{\partial V_c}{\partial r}$ depends on which (n, l) orbital the electron occupies. You won't be asked to calculate what this expectation value is since its quite hellish to derive, but simplifying the above expression we find:

$$E^1_{\text{SOC}} = \frac{|E_n|\alpha^2}{n}\left(\frac{1}{l+\frac{1}{2}} - \frac{1}{j+\frac{1}{2}}\right) \tag{4.14}$$

where α is the fine structure constant which equals $\frac{1}{137}$ and E_n are the energy levels of a hydrogenic system, Eq. (6.2). Normally the factor in front is just written as λ.

From this equation we see that if we are in the s orbital of an energy level, i.e $l = 0$, then $E^1_{SOC} = 0$ since $j = s = \frac{1}{2}$, meaning the energy levels remain the same. However if $l \neq 0$ then each orbital is split into 2 levels, given by $j = l \pm \frac{1}{2}$, with each level being $2j + 1$ degenerate.

For the p orbital, $l = 1$, then j may either be $\frac{3}{2}$ or $\frac{1}{2}$, with the corresponding corrections being $E^1_{SOC} = \frac{\lambda}{6}$ and $E^1_{SOC} = \frac{-\lambda}{2}$.

This problem can also be solved using the brute force method, here the degenerate eigenstates are described by $|m_l, m_s\rangle$. This time we use a different form of the perturbation for SOC, we take Eq. (4.8) and expand out $\hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}}$ in terms of the raising and lowering operators, so that:

$$\boxed{\hat{V}_{\text{SOC}} = \delta \hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}} = \delta \left[\hat{L}_z \hat{S}_z + \frac{1}{2} \left(\hat{L}_+ \hat{S}_- + \hat{L}_- \hat{S}_+ \right) \right]}, \tag{4.15}$$

where again the square brackets don't mean commutator. As we described in Section 2, we form the perturbation matrix using our degenerate eigenstates $|m_l, m_s\rangle$ and the perturbation given by Eq. (4.15). At this point its very important to remember that the degenerate eigenstates are orthonormal to each other, Eq. (2.1), as well as the effect that the raising and lowering operators have on eigenstates. Note that the raising and lowering operators will be given to you in the exam. That being said, it is important to review how they act on quantum states

A quick tangent on raising and lowering operators

This should be familiar to you (you don't need to memorise per se, but doing these calculations in the exam should take minimal effort).

$$\hat{L}_\pm |n, l, m_l, s, m_s\rangle = \hbar \sqrt{l(l+1) - m_l(m_l \pm 1)}\, |n, l, m_l \pm 1, s, m_s\rangle \tag{4.16}$$

$$\hat{S}_\pm |n, l, m_l, s, m_s\rangle = \hbar \sqrt{s(s+1) - m_s(m_s \pm 1)}\, |n, l, m_l, s, m_s \pm 1\rangle \tag{4.17}$$

Then if you multiply one operator by another, treat it as composition of operators!

Forming the matrix

Remember for degenerate PT, you need to calculate the matrix elements which will be given in the form

$$E^1_{\text{SOC}} = \left\langle m_l, m_s \middle| \delta \hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}} \middle| m_l', m_s' \right\rangle \tag{4.18}$$

Let's take this step by step. You may need to do this in the exam after all

Algorithm to form the potential matrix

1. Create a table where each column is labelled with the m_l, m_s values. Label each row the same way. It actually doesn't matter how you sort the rows and column as long as the states are ordered identically. Mark the leading diagonal for yourself.
2. Apply $\delta \hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}}$ to each state. take your time doing this, it's easy to miscalculate. Keep track of all the *non-zero* terms, and make a note of the states on either side of the = sign.
3. When you're done, go to the row labelled with the state you *applied the operator to*, then go to the column labelled with the *final state*. Fill that slot in with the coefficient of that final state. By symmetry, you can also fill in the element directly opposite the leading diagonal with the same entry. Repeat until you have exhausted all your calculations
4. The final table is your matrix. It *will* be in block-diagonal form and if it isn't something is wrong. You then must **solve the secular determinant of that matrix**. There is a theorem in linear algebra which says the *determinant of a block-diagonal matrix is equal to the product of the determinant of all the individual blocks.* Note that the determinant of a 1 × 1 block is itself.
5. The eigenvalues will give you the energy shifts for each quantum state.

Note that repeated eigenvalues suggest that there are states which are shifted by the same amounts. This does not completely life (eliminate) the degeneracy of every state. However SOC along eliminates degeneracy in l, i.e. each l state is split into 2 m_l states.

Continuing with the example, our states we have available are

$$\left|+1,+\frac{1}{2}\right\rangle, \left|0,-\frac{1}{2}\right\rangle, \left|-1,-\frac{1}{2}\right\rangle, \left|0,+\frac{1}{2}\right\rangle, \left|+1,-\frac{1}{2}\right\rangle, \left|-1,+\frac{1}{2}\right\rangle,$$

Sorting this by order of m_l gives

$$\left|+1,+\frac{1}{2}\right\rangle, \left|+1,-\frac{1}{2}\right\rangle, \left|0,+\frac{1}{2}\right\rangle, \left|0,-\frac{1}{2}\right\rangle, \left|-1,+\frac{1}{2}\right\rangle, \left|-1,-\frac{1}{2}\right\rangle$$

Oh would you look at that, it automatically sorted itself out. We then form the matrix as so (using this order of states, rather than the order of states in the lectures)

$$\begin{bmatrix} \frac{\delta}{2} & 0 & 0 & 0 & 0 & 0 \\ 0 & -\frac{\delta}{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{\delta}{2}\sqrt{2} & 0 & 0 \\ 0 & 0 & \frac{\delta}{2}\sqrt{2} & 0 & \frac{\delta}{2}\sqrt{2} & 0 \\ 0 & 0 & 0 & \frac{\delta}{2}\sqrt{2} & -\frac{\delta}{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{\delta}{2} \end{bmatrix} \tag{4.19}$$

Then calculating the eigenvalues of this matrix, which correspond to the first order energy corrections. We do this by forming the secular determinant, that is solve

$$\det \begin{bmatrix} \frac{\delta}{2} - E^1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -\frac{\delta}{2} - E^1 & 0 & 0 & 0 & 0 \\ 0 & 0 & -E^1 & \frac{\delta}{2}\sqrt{2} & 0 & 0 \\ 0 & 0 & \frac{\delta}{2}\sqrt{2} & -E^1 & \frac{\delta}{2}\sqrt{2} & 0 \\ 0 & 0 & 0 & \frac{\delta}{2}\sqrt{2} & -\frac{\delta}{2} - E^1 & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{\delta}{2} - E^1 \end{bmatrix} = 0 \tag{4.20}$$

We find that we get $E^1_{\text{SOC}} = \frac{\delta}{2}$ four times and $E^1_{\text{SOC}} = -\delta$ two times. This result matches up with that found using the correct unperturbed eigenstates, as we would expect. It also shows that ordering of states doesn't matter as long as you're consistent about it.

4.2.3 Strong Field Zeeman Effect

If we apply an external magnetic field to a system, we will get the Zeeman effect. If this applied field is larger relative to the SOC field, i.e $\hat{V}_{mag} \gg \hat{V}_{SOC}$, then we are in the regime of the Strong field Zeeman effect. This means we can neglect any effects due to SOC and consider our unperturbed system as just the hydrogenic system again. In this case we use the neat method to find the first order energy corrections. The correct unperturbed eigenstates are given by $|n, l, m_l, m_s\rangle$, with our perturbation described by Eq. (4.3), so the first order energy corrections are found using Eq. (2.4) to be:

$$E^1_{\text{mag}} = \mu_B B_z (m_l + 2m_s), \tag{4.21}$$

where μ_B is the Bohr Magneton, given by $\frac{e\hbar}{2m_e}$. Note this is also known as the Paschen-Back effect.

4.2.4 Weak Field Zeeman Effect

Finally we consider what happens when we apply a small external magnetic field such that $\hat{V}_{\text{SOC}} \gg \hat{V}_{\text{mag}}$. This means that our unperturbed system includes SOC, i.e the unperturbed Hamiltonian is $\hat{H}_0 + \hat{V}_{\text{SOC}}$, with the external magnetic field $\hat{V}_{\text{mag}}$ acting as the perturbation. This problem again can be solved either with the brute force method or using the correct unperturbed eigenstates directly.

The correct unperturbed eigenstates are, as before, $|n, l, s, j, m_j\rangle$ with the perturbation given by Eq. (4.3), so using Eq. (2.4) and that $\hat{L}_z + 2\hat{S}_z = \hat{L}_z + \hat{S}_z + \hat{S}_z = \hat{J}_z + \hat{S}_z$, we find that the first order energy corrections take the form:

First order shifts to the magnetic energy

$$E^1_{\text{mag}} = m_j g_L \mu_B B, \tag{4.22}$$

where g_L is the Lande g factor:

$$\boxed{g_L = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}}. \tag{4.23}$$

You don't need to memorise the g_L-factor expression, but just note what the correction is and know g_L exists and you have to calculate it.

This means that each energy level is split into $2j + 1$ energy levels separated by $g_L \mu_B B$.

Alternatively we can solve this using the brute force method. Here the degenerate eigenstates are once again $|m_l, m_s\rangle$, and we use the unmodified version of Eq. (4.3) as our perturbation. Here we find all the corresponding perturbation matrix elements and add them to the original matrix we had when considering just SOC. Then as per usual we find the eigenvalues of this matrix, now knowing the matrix elements are

$$E^1_{\text{mag}} = \left\langle m_l, m_s \middle| \delta \hat{\boldsymbol{L}} + \cdot \hat{\boldsymbol{S}} + \hat{V}_{\text{mag}} \middle| m_l', m_s' \right\rangle \tag{4.24}$$

with the secular determinant being (using the order of states defined in these notes rather than the lectures)

$$\det\begin{bmatrix} \frac{\delta}{2}+2\mu_B B_z - E^1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -\frac{\delta}{2}-E^1 & 0 & 0 & 0 & 0 \\ 0 & 0 & \mu_B B_z - E^1 & \frac{\delta}{2}\sqrt{2} & 0 & 0 \\ 0 & 0 & \frac{\delta}{2}\sqrt{2} & -\mu_B B_z - E^1 & \frac{\delta}{2}\sqrt{2} & 0 \\ 0 & 0 & 0 & \frac{\delta}{2}\sqrt{2} & -\frac{\delta}{2}-E^1 & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{\delta}{2}-2\mu_B B_z - E^1 \end{bmatrix} = 0 \tag{4.25}$$

to find the first order energy corrections, which are found to be: $\frac{\delta}{2}+2\mu_B B_z$, $\frac{\delta}{2}-2\mu_B B_z$, $\frac{\delta}{2}+\frac{2}{3}\mu_B B_z$, $-\delta+\frac{1}{3}\mu_B B_z$, $\frac{\delta}{2}-\frac{2}{3}\mu_B B_z$ and $-\delta-\frac{1}{3}\mu_B B_z$ for an $l=1, s=\frac{1}{2}$ system.

Chapter 5

Identical Particles

5.1 Introduction

It is impossible to follow and identify one particular particle when dealing with a quantum system of identical particles. This is because any measurement we wish to make of the system will disturb it and all the particles are indistinguishable from one another.

The wave function, $|\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_k, \ldots, \mathbf{r}_N, t)\rangle$, is for a system which contains N indistinguishable particles, where $\mathbf{r}_k$ is the position vector for the k^{th} particle. This has the same normalisation condition as for a single particle state:

$$\langle\psi|\psi\rangle = 1 = \int |\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_k, \ldots, \mathbf{r}_N, t)|^2 d\mathbf{r}_1 d\mathbf{r}_2 \ldots d\mathbf{r}_k \ldots d\mathbf{r}_N. \tag{5.1}$$

where by $d\mathbf{r}_k$ we mean $dx_k dy_k dz_k$ This integral says that at some time t, there is a particle within a volume $d\mathbf{r}_1$ of $\mathbf{r}_1$ and another particle within $d^3\mathbf{r}_2$ of $\mathbf{r}_2$, etc. and not that there is a specific particle, since we can't distinguish between them.

Operators acting on multi-particle eigenstates must be symmetric under the permutation of particle labels, due to this indistinguishability.

An example of this is the Hamiltonian for the two electrons orbiting a Helium nucleus:

$$\hat{H}(1,2) = \sum_{i=1}^{2} \left(-\frac{\hbar^2}{2m} \nabla_i^2 - \frac{2e^2}{4\pi\epsilon_0 r_i} \right) + \frac{e^2}{4\pi\epsilon_0 r_{12}} \tag{5.2}$$

The indistinguishability of the electrons means that:

$$\hat{H}(1,2) = \hat{H}(2,1) \tag{5.3}$$

as no matter the order of the labels in the Hamiltonian we should get the same energy value.

Definition 5.1.1. The idea of eigenvalues of operators being degenerate under particle exchange is called **exchange degeneracy**.

5.2 Particle Exchange Operator

We can define an operator, $\hat{P}_{ij}$ that exchanges the i^{th} and j^{th} particles with each other, such that:

$$\hat{P}_{ij}(\hat{H}(i,j)\left|\psi(i,j)\right\rangle) = \hat{H}(j,i)\left|\psi(j,i)\right\rangle \tag{5.4}$$
$$= \hat{H}(i,j)\hat{P}_{ij}\left|\psi(i,j)\right\rangle, \tag{5.5}$$

where in between the lines we use a generalisation of Eq. (5.3) and that $\left|\psi(j,i)\right\rangle = \hat{P}_{ij}\left|\psi(i,j)\right\rangle$. From this we can see that:

Particle Exchange Operator

$$\hat{P}_{ij}\hat{H}(i,j)\left|\psi(i,j)\right\rangle = \hat{H}(i,j)\hat{P}_{ij}\left|\psi(i,j)\right\rangle, \tag{5.6}$$

which means that the commutator $[\hat{H}(i,j), \hat{P}_{ij}] = 0$, i.e the exchange operator commutes with the Hamiltonian operator. Crucially this means they **share a common set of eignenstates** (theorem from linear algebra). Also as particles are indistinguishable, $\hat{P}_{ij}$ must also commute with any operator that corresponds to an observable and so also share a common set of eigenstates. From your physics knowledge, this makes sense. Imagine 2 electrons whirling together, and suppose you know their initial states and the surrounding environment at all times. If you swapped the electron positions, then started them off in the exact same environment and positions, you would get the exact same physics!

Remark. It is *not* true that if an operator (even if it represents an observable) commutes with $\hat{P}_{ij}$ then it automatically commutes with the Hamiltonian - namely the commutator is not transitive, so don't fall into this trap.

Proposition 5.2.1. *The exchange operator is a self-inverse operator, i.e. applying it twice returns us to the same state, so it is an operator which is the inverse of itself.*

$$\hat{P}_{ij}\hat{P}_{ij} = I \implies \hat{P}_{ij} = \hat{P}_{ij}^{-1} \tag{5.7}$$

where I is the identity operator (matrix)

Proof.

$$\hat{P}_{ij}\hat{P}_{ij}\left|\psi(i,j)\right\rangle = \hat{P}_{ij}\left|\psi(j,i)\right\rangle = \left|\psi(i,j)\right\rangle, \tag{5.8}$$

□

This means that the eigenvalues of $\hat{P}_{ij}$ must be ± 1. The $+1$ eigenvalue indicates a symmetric eigenstate, whilst the -1 eigenvalue indicates a fully anti-symmetric eigenstate. This means any physically acceptable eigenstate that represents identical particles must be symmetric or fully anti-symmetric due to $\hat{P}_{ij}$ commutating with operators representing physical observables and hence share a common set of eigenstates.

Note that due to the TDSE, a symmetric eigenstate will remain symmetric and the same is true for an anti-symmetric eigenstate.

5.3 Fermions and Bosons

If our eigenstate describes a collection of identical particles with half integer spin, then it is anti-symmetric, for example:

$$\Psi(1,2) = \frac{1}{\sqrt{2}}(\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1)), \tag{5.9}$$

and so when the exchange operator is applied, we get an eigenvalue of -1. Note how if one of the particles (either particle 1 or 2) occupies the same quantum state as the other (a = b), then the eigenstate disappears:

$$\Psi(1,2) = \frac{1}{\sqrt{2}}(\psi_a(1)\psi_a(2) - \psi_a(2)\psi_a(1)) = 0. \tag{5.10}$$

This is the Pauli Exclusion Principle (PEP).

Pauli Exclusion Principle (PEP)

Any two half integer spin particles cannot occupy the exact same quantum state as each other

Definition 5.3.1. Half-integer spin particles are called **fermions**

They obey Fermi-Dirac statistics which is given by the Fermi-Dirac distribution:

Fermi-Dirac Distribution

$$f(E) = \frac{1}{e^{\beta(E-\mu)} + 1}, \tag{5.11}$$

where $f(E)$ gives the average occupation of a quantum state of energy E, $\beta = \frac{1}{k_B T}$ and μ is the chemical potential of the system.

However if our eigenstate describes a collection of identical particles with integer spin, then it is symmetric:

$$\Psi(1,2) = \frac{1}{\sqrt{2}}[\psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1)], \tag{5.12}$$

whereupon application of the exchange operator we obtain an eigenvalue of $+1$. These particles have no such restriction like the PEP.

Definition 5.3.2. Integer-spin particles are called **bosons**

They obey Bose-Einstein statistics which is described by the Bose-Einstein distribution:

Fermi-Dirac Distribution

$$f(E) = \frac{1}{e^{\beta(E-\mu)} - 1}, \tag{5.13}$$

Normally eigenstates, at least of simple systems, can be split into the product of a spatial component and a spin component. For a fermion, which needs an anti-symmetric eigenstate, the spatial and spin components must be of opposite parity. So when dealing with multiple fermions, this means the spin component may either by a spin singlet (symmetric) or a spin triplet (anti-symmetric).

In order to form an anti-symmetric eigenstate for N non-interacting fermions within a common potential, we calculate the **Slater determinant** of an $n \times N$ matrix, where n is the number of eigenstates available for each of the N fermions. The Slater determinant looks something like:

$$\Psi^{AS}(1,2,\ldots,N)=\frac{1}{\sqrt{N!}}\begin{vmatrix}\phi_{E_a\sigma_a}(1) & \phi_{E_a\sigma_a}(2) & \ldots & \phi_{E_a\sigma_a}(N)\\ \phi_{E_b\sigma_b}(1) & \phi_{E_b\sigma_b}(2) & \ldots & \phi_{E_b\sigma_b}(N)\\ & \ldots & & \\ \phi_{E_n\sigma_n}(1) & \phi_{E_n\sigma_n}(2) & \ldots & \phi_{E_n\sigma_n}(N)\end{vmatrix} \tag{5.14}$$

where $\frac{1}{\sqrt{N!}}$ is a normalisation constant and $\phi_{E_n\sigma_n}(N)$, is the eigenstate with energy E_n and spin σ_n that the N^{th} fermion occupies. It's important to note that if we interchange two columns, this is equivalent to applying the exchange operator, and the sign of the determinant changes. Also if we attempt to put two fermions into exactly the same quantum state (same energy level and same spin) then the determinant vanishes, as we would expect by the PEP.

Note that the Slater determinant is square, i.e. $n = N$. Trying to fit $N > 2$ particles into 2 quantum states is not going to go well.

5.4 Example: 2 electron system

Consider a system made up of two electrons, denoted by 1 and 2. Suppose they are constrained to a two-level system with energies E_a, E_b with positions r_a, r_b. We denote spin up by s_α and spin down by s_β.

We know the total wavefunction (which must be antisymmetric) describing the system is made up of **spatially dependent parts**, e.g. $u_{r_a}(1)$ and $u_{r_b}(2)$, and **spin dependent parts**, e.g. $s_\alpha(1), s_\beta(1)$. This gives us 4 possibilities for wavefunctions

$$\frac{1}{\sqrt{2}}[u_{r_a}(1)u_{r_b}(2)-u_{r_b}(1)u_{r_a}(2)]s_\alpha(1)s_\alpha(2) \tag{5.15}$$

$$\frac{1}{\sqrt{2}}[u_{r_a}(1)u_{r_b}(2)-u_{r_b}(1)u_{r_a}(2)]s_\beta(1)s_\beta(2) \tag{5.16}$$

$$\frac{1}{\sqrt{2}}[u_{r_a}(1)u_{r_b}(2)-u_{r_b}(1)u_{r_a}(2)]\frac{1}{\sqrt{2}}[s_\alpha(1)s_\beta(2)+s_\beta(1)s_\alpha(2)] \tag{5.17}$$

$$\frac{1}{\sqrt{2}}[u_{r_a}(1)u_{r_b}(2)+u_{r_b}(1)u_{r_a}(2)]\frac{1}{\sqrt{2}}[s_\alpha(1)s_\beta(2)-s_\beta(1)s_\alpha(2)] \tag{5.18}$$

Recall that $S = \sum_i m_{s,i}$ (the *system* spin angular momentum) and m_s (the z-component of individual fermion spin) has the range of $m_s = -s, -s+1, \ldots, s$ with $s = 1/2$ for fermions. Consequently $M_S = -S, \ldots, S$. Therefore we have a spin **triplet** when $S = 1$ because when $S = 1, M_S = -1, 0, +1$, i.e. we have 3 spin states. We also have a spin **singlet** at $S = 0$ since $M_S = 0$ only.

The consequence of these singlets and triplets will come into play in the next chapter.

The spin part of the functions are eigenfunctions of the operators representing the total spin S of the two particles and of their total z component M_S

- The first wavefunction has spin up for both particles, so both are spin up. This represents $S = 1, M_S = +1$
- Second wavefunction has s_β for both particles, so both are spin down. Then $S = 1, M_S = -1$
- Third wave function has sum of spin-up,spin-down states, so $S = 1, M_S = 0$
- Final wavefunction has difference of spin-up,spin-down states do $S = 0, M_S = 0$

The way you calculate the symmetric eigenstate for N non-interacting bosons within a common potential is found by calculating the **Slater permanent** from the same $n \times N$ matrix, as Eq. (5.14). The only difference between the permanent and determinant of a matrix is that you don't have to worry about the negative signs in the co-factors when calculating the permanent. You don't have to care about Slater permanents for the exam.

5.5 Key Results

In order for an eigenstate of an operator, which corresponds to a physical observable, to be physically acceptable it must also be an eigenstate of the particle exchange operator.

Changing the order of particle labels should have no measurable difference on the observable values that the operator return, this is exchange degeneracy.

Fermions are particles with half integer spin, they are described by Fermi-Dirac statistics, Eq. (5.11). Their overall eigenstate must be anti-symmetric. This is apparent when operated on by the particle exchange operator which returns an eigenvalue of -1. This eigenstate can be calculated using the Slater determinant, Eq. (5.14). Fermions must obey the PEP, which prevents two fermions from occupying the exact same quantum state.

Bosons are particles with integer spin, they are desribed by Bose-Einstein statistics, Eq. (5.13). Their overall eigenstate must symmetric. So when operated on by the particle exchange operator it returns an eigenvalue of $+1$. They have no such restriction like the PEP.

Chapter 6

Multi electron atoms and the periodic table

6.1 Multi-electron atoms

So far during this module, the focus has been on systems containing one electron. However we will now briefly look at some approximations of multi-electron systems. The first is essentially the hydrogenic atom, where each electron is treated as only seeing the Coulomb field due to the nucleus of charge Ze it orbits, in which case the Hamiltonian of the system looks like:

$$\hat{H}(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_Z) = \frac{-\hbar^2}{2m}\sum_{i=1}^{Z}\nabla_i^2 + \sum_{i=1}^{Z}\frac{-Ze^2}{4\pi\epsilon_0 r_i}, \tag{6.1}$$

where the eigenstates and energy levels are just those of a hydrogen like atom, i.e they only depend on the principal quantum number, n:

$$\boxed{E_n = \frac{-Z^2 \times 13.6eV}{n^2} \qquad (6.2)}$$

Note each energy level is $\boxed{2n^2}$ degenerate, where the factor of 2 arises to account for spin. Each n level is known as an **energy level shell**.

This approximation can be improved drastically by taking into account the effect electrons have on one another. This is done by assuming the electrons move in a field due to the nucleus that has been screened by the presence of the other $Z-1$ electrons, in which case the Hamiltonian takes the form:

$$\hat{H}(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_Z) = \frac{-\hbar^2}{2m}\sum_{i=1}^{Z}\nabla_i^2 + \sum_{i=1}^{Z}-V_{\text{eff}}(r_i), \tag{6.3}$$

where:

$$V_{\text{eff}}(r_i) = \frac{-Z_{\text{eff}}e^2}{4\pi\epsilon_0 r_i} + \frac{\hbar^2 l(l+1)}{2mr_i^2}, \tag{6.4}$$

where Z_{eff} is the effective charge on the nucleus that the electron sees due to the other electrons shielding the nucleus. This means that in this approximation, the energy levels of electrons depend on the value of n and l and each shell has a degeneracy of $\square(2s+1)(2l+1)$. The eigenstates of this system are now labelled according to the values n, l, m_l and m_s.

The second term is known as the potential barrier and accounts for the difference in energy between electrons which reside in the same shell. This is because for each shell there are a number of orbitals that the electrons can occupy, and these orbitals vary in distance from the nucleus. Using this potential barrier term and the energy levels for a hydrogenic atom, Eq. (6.2), we can begin to order the atomic orbits of atoms.

The ordering of these atomic orbits, according to their energy is: 1s, 2s, 2p, 3s, 3p, [4s, 3d], 4p, [5s, 4d], ..., where they are written in the form (nl), with $l = 0 \equiv s$, $l = 1 \equiv p$, $l = 2 \equiv d$, $l = 3 \equiv f$, etc. Note that the terms in square brackets are of similar energy, as the coulombic attraction and potential barrier compete.

The most accurate Hamiltonian, with no approximations involved, also includes the interactions between the electrons directly and not just through the coulombic field attraction of the nucleus. It is given by:

$$\hat{H}(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_Z) = \frac{-\hbar^2}{2m} \sum_{i=1}^{Z} \nabla_i^2 + \sum_{i=1}^{Z} -V_{\text{eff}}(r_i) + \sum_{i,j=1}^{i \neq j} \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} \tag{6.5}$$

The periodic table is formed by considering the energies of the atomic orbitals and by obeying the PEP when filling up these orbitals. This orders elements into periods and groups of the periodic table, which determine which elements have similar physical and chemical properties respectively.

6.2 The Periodic Table

You should know the properties of notable groups/blocks of the periodic table. You should also be able to know how to state the ground state electronic configuration of atoms, you do not need to memorise any.

Definition 6.2.1. The (Pauling) electronegativity scale from 0.0 - 4.0 measures a tendency of an atom's ability to attract electrons to its outer shell, with 0.0 being the weakest and 4.0 being the strongest

Remark. Fun fact: (non-examinable). Caesium holds the weakest electronegativity at 0.659 whilst fluorine holds the strongest at 4.0.

- Hydrogen: a single electron $1s^+$ where + means spin up
- Noble gases (He, Ne, Ar, etc.): Full valence shell in the ground state, so they are generally chemically inert.
- Alkali metals (Li, Na, K, Rb, Cs, Fr): single electron in the valence shell. Low electronegativity.
- Alkali Earth metals (Be, Mg, Ca, Sr): 2 electrons in outer shell. Slightly higher electronegativity than alkali metals but still low.
- Halogens (F, Cl, Br, I): 7 electrons in valence shell, 5 in its outermost p-subshell. High electronegativity, wish to accept one electron to form a stable closed shell.
- Transition metals: Here the (4s) shell fills before the (3d). As a result, the series of elements in which the 3d states are being filled all have similar chemical properties. This is the same for the (4d) and (5d) states.

- Rare Earths: Here the (4f) shell fills after the (6s) shell is filled so the rare earths have similar chemical properties. Many of the rare earths are magnetic due to unpaired electrons in the f shel

6.3 Spectroscopic Notation

Instead of writing orbital states as (nl), we can describe them by assigning total angular momentum quantum numbers. This means we describe states using multiplets which take the form ${}^{2S+1}L$, where L is the total orbital angular momentum of the (nl) orbital, S is the total spin momentum of the (nl) orbital and $2S+1$ is known as the **multiplicity**. As before with the single particle state orbital angular momentum quantum number l, we write letters instead of numbers, so

$$\begin{aligned} L =& 0 \to S && (6.6)\\ & 1 \to P && (6.7)\\ & 2 \to D && (6.8)\\ & 3 \to F && (6.9)\\ & 4 \to G && (6.10)\\ & \vdots && (6.11) \end{aligned}$$

and then for higher L we follow alphabetical order skipping letters L, P, Q.

We may also combine the values L and S to give $J = L + S$, the **total angular momentum** of the system. This is used in the spectroscopic term which we write as ${}^{2S+1}L_J$ which describes the multiplet of the atom.

6.4 Hund's Rules

Hund's rules are a way of determining the correct spectroscopic term for the ground state of an atom. They generally only work for the lighter elements. The process is:

Hund's rules

1. First we maximise $S = \sum_i m_{si}$
2. Next we maximise $L = \sum_i m_{li}$
3. For a shell that is less than half full $J = |L - S|$. However if the shell is more than half full $J = |L + S|$ and if the shell is exactly half full then $L = 0$, so $J = S$.

The physical reasoning behind the first rule is that there is large coulombic repulsion between electrons that occupy the same space but with opposite spins, so is not favourable in terms of energy. For the second rule, the reasoning is similar in that repulsion between electrons is minimised for larger L as the electrons spend more time further apart, meaning the overall energy of the system is lower.

6.5 Spin-orbit and Zeeman interactions

Finally we consider the effects of spin-orbit coupling and the application of a magnetic field. Instead of specifying $(2L+1)(2S+1)$ states for ${}^{2S+1}L$ multiplet by the quantum numbers L, S, M_L and M_S we can use L, S, J, M_J instead where again $J = L+S, L+S-1, \ldots, |L-S|$ and $M_J = M_L + M_S = -J, -J+1, \ldots, J$.

In Chapter 4, spin-orbit coupling perturbation splits the ${}^{2S+1}L$ multiplet into several levels characterised by L, S, and J and denoted by ${}^{2S+1}L_J$.

However, SOC did not completely lift the degeneracy in J, as each level was $2J+1$-fold degenerate corresponding to the values of M_J. The Zeeman effect lifts any remaining degeneracy (because the magnetic field interacts with spin) which means every M_J level is a **singlet**.

6.6 Key Results

You should make sure that you know what each of the quantum numbers n, l, m_l and m_s mean in regards to atomic orbitals, as well as be able to calculate L and S for multi-electron atoms. However the most important thing to take from this section is how to find the ground state multiplet for the electronic structure of some atom, using Hund's rules, and then being able to write it in spectroscopic notation. You will never have to find an excited state multiplet it will always be the ground state multiplet.

Chapter 7

Time dependent PT

7.1 Introduction

Up to this point all the systems we have solved are time independent, i.e the Hamiltonian has no time dependence $\hat{H} \neq \hat{H}(t)$, such that the potential energy operator, $\hat{V}$, is only a function of position and not time: $\hat{V} = \hat{V}(\mathbf{r})$. This is known as quantum statics. This means that the Time Dependent Schrodinger Equation (TDSE):

$$i\hbar \frac{\partial}{\partial t} |\Psi(\mathbf{r}, t)\rangle = \hat{H}(\mathbf{r}) |\Psi(\mathbf{r}, t)\rangle , \tag{7.1}$$

can be solved using separation of variables, such that we can write $\Psi(\mathbf{r}, t) = \psi(\mathbf{r})\phi(t)$, where $\psi(\mathbf{r})$ satisfies the Time Independent Schrodinger Equation (TISE):

$$\hat{H}(\mathbf{r}) |\Psi(\mathbf{r})\rangle = E |\Psi(\mathbf{r})\rangle \tag{7.2}$$

and $\phi(t) = e^{\frac{-iEt}{\hbar}}$, with E the energy eigenvalue corresponding to the eigenstate $|\Psi(\mathbf{r})\rangle$. However in this section we consider some basic quantum dynamics, i.e $\hat{V} = \hat{V}(\mathbf{r}, t)$.

7.2 Derivation

7.2.1 Non-Stationary States

Recall that for a quantum static system, if the system occupies an eigenstate of the time independent Hamiltonian, $\hat{H}_0$, then it is said to be in a stationary state of the system. This just means that no matter what time you measure the system it is always in the same eigenstate with the same eigenvalue, i.e initially it's in the state $|\psi_m\rangle$ and then at some later time t in state $|\psi_m\rangle e^{\frac{-iE_m t}{\hbar}}$ which are equivalent once a measurement is applied.

However now consider what happens when the same quantum static system is not in a stationary state of the system, $|\Psi(\mathbf{r}, t)\rangle$. Suppose at $t = 0$, the state of the system may be written as a linear combination of the complete set of eigenstates that the system can occupy:

$$|\Psi(\mathbf{r}, t = 0)\rangle = \sum_n = c_n |\psi_n\rangle , \tag{7.3}$$

such that:

$$|\Psi(\mathbf{r}, t)\rangle = \sum_n = c_n |\psi_n\rangle e^{\frac{-iE_n t}{\hbar}} . \tag{7.4}$$

This linear combination of stationary states means that we have a system, described by a Hamiltonian which is inherently time independent, that can undergo transitions (or quantum jumps) between different states assuming the system doesn't start in a stationary state.

This should become more clear after the following 2-level system example. Consider a system with Hamiltonian, $\hat{H}_0$, which is initially in the state:

$$|\Psi(\mathbf{r}, t=0)\rangle = c_m |\psi_m\rangle + c_n |\psi_n\rangle, \tag{7.5}$$

where $|\psi_m\rangle$ and $|\psi_n\rangle$ are the orthonormal eigenstates of the system, with eigenvalues E_m and E_n respectively. This means that in the absence of any perturbation we have:

$$|\Psi(\mathbf{r}, t)\rangle = c_m |\psi_m\rangle e^{\frac{-iE_m t}{\hbar}} + c_n |\psi_n\rangle e^{\frac{-iE_n t}{\hbar}}, \tag{7.6}$$

where we note that normalisation requires $|c_m|^2 + |c_n|^2 = 1$. Consider the expectation value of this system with respect to some arbitrary time independent operator $\hat{A}$:

$$\langle\psi| \hat{A} |\psi\rangle = \langle a\rangle_t = |c_m|^2 A_{mm} + |c_n|^2 A_{nn} + 2\,\mathrm{Re}[c_m^* c_n A_{mn} e^{i\omega t}], \tag{7.7}$$

where $|\psi\rangle$ is given by Eq. (7.6), $\omega = \frac{E_m - E_n}{\hbar}$, $A_{mn} = \langle\psi_m| \hat{A} |\psi_n\rangle$ and we have used the hermiticity of $\hat{A}$. Note the subscript t on $\langle a\rangle$ denotes that the expectation value varies with time. From Eq. (7.7) we can see that $\langle a\rangle_t$ oscillates with a period $T = \frac{2\pi}{\omega}$ between:

$$|c_m|^2 A_{mm} + |c_n|^2 A_{nn} \pm 2c_m^* c_n A_{mn}, \tag{7.8}$$

since $\mathrm{Re}[e^{i\omega t}] = \cos(\omega t)$. This oscillation represents the $\boxed{\text{transitions or quantum jumps between eigenstates}}$.

7.2.2 Time Dependent Perturbation Theory

In general, to allow the quantum jumps between energy eigenstates we saw in the previous section we can allow $\hat{H} = \hat{H}(\mathbf{r}, t)$. This is normally done by introducing a time dependent potential, $\hat{V}(t)$, which we can treat as a perturbation if $\hat{V}(t) \ll \hat{H}_0$. This is known as time dependent perturbation theory. This means that the Hamiltonian of the system will now take the form:

$$\hat{H} = \hat{H}_0 + \hat{V}(t) \tag{7.9}$$

If we introduce a time dependent perturbation, $\hat{V}(t)$, to our 2 level system, Eq. (7.6) becomes:

$$|\Psi(\mathbf{r}, t)\rangle = c_m(t) |\psi_m\rangle e^{\frac{-iE_m t}{\hbar}} + c_n(t) |\psi_n\rangle e^{\frac{-iE_n t}{\hbar}}, \tag{7.10}$$

where the coefficients $c_m(t), c_n(t)$ are now functions of time. This is the main difference compared to time-independent PT. We wish to determine the form of these coefficients. We can generalise this argument easily to an n-level system with n eigenstates. We can solve for each $c_n(t)$ by demanding that our linear superposition of states, analogous to Eq. (7.10):

$$|\Psi(\mathbf{r}, t)\rangle = \sum_n c_n(t) |\psi_n\rangle e^{\frac{-iE_n t}{\hbar}} \tag{7.11}$$

obeys the TDSE, Eq. (7.1), which results in:

$$i\hbar \sum_n \dot{c}_n(t) \left|\psi_n\right\rangle e^{\frac{-iE_n t}{\hbar}} = \sum_n \hat{V}(t) \left|\psi_n\right\rangle e^{\frac{-iE_n t}{\hbar}} c_n(t). \tag{7.12}$$

where $\dot{c}_n(t) = \dfrac{\mathrm{d}c_n}{\mathrm{d}t}$.

By pre-multiplying the above equation by $\left\langle\psi_p\right|$, i.e take the inner product, we find:

$$\begin{aligned} i\hbar \sum_n \dot{c}_n(t) \left\langle\psi_p|\psi_n\right\rangle e^{\frac{-iE_n t}{\hbar}} &= \sum_n \left\langle\psi_p\middle|\hat{V}(t)\middle|\psi_n\right\rangle e^{\frac{-iE_n t}{\hbar}} c_n(t) & (7.13)\\ i\hbar \dot{c}_p(t) e^{\frac{-iE_p t}{\hbar}} &= \sum_n \left\langle\psi_p\middle|\hat{V}(t)\middle|\psi_n\right\rangle e^{\frac{-iE_n t}{\hbar}} c_n(t) & (7.14)\\ i\hbar \dot{c}_p(t) &= \sum_n V_{pn}(t) e^{i\omega_{pn}t} c_n(t) & (7.15)\end{aligned}$$

Also, $V_{pn} = \left\langle\psi_p\right| \hat{V} \left|\psi_n\right\rangle$ and $\omega_{pn} = \frac{E_p - E_n}{\hbar}$, which is known as the **Bohr frequency**. Note in the second line, on the LHS of the equation we have used the orthonormality condition $\left\langle\psi_p|\psi_n\right\rangle = \delta_{np}$ which sets $n = p$ and removes the summation. We then move the exponential on the LHS to the RHS. Up to this point we haven't actually applied any perturbative expansions, all of this is exact. However we now assume $\hat{V}(t)$ is small and that the system begins in an eigenstate of the system, i.e $c_p(0) = \delta_{pn}$. What we are doing is treating $c_p(t)$ as the sum of perturbations

$$c_p(t) = c_p^{(0)} + c_p^{(1)}(t) + c_p^{(2)}(t) + \dots \tag{7.16}$$

By our initial condition, we require $c_p^{(0)} = \delta_{pn}$, so that to first order we find from Eq. (7.15):

$$i\hbar \dot{c}_p^{(1)}(t) = V_{pn}(t) e^{i\omega_{pn}t}, \tag{7.17}$$

where the *superscript on the coefficient $c_p(t)$ represents to first order.* We find this equation from substituting the zeroth order values onto the RHS of Eq. (7.15). Now, take it slow. Equation. (7.17) is the linear ODE (in time t). Therefore, we can directly integrate it such that

$$c_n^{(1)}(\tau) = \frac{1}{i\hbar} \int_0^\tau V_{pn}(t) e^{i\omega_{pn}t} dt \tag{7.18}$$

subject to the initial condition Eq. (7.17). Now, bringing it all together, we have the *total* amplitude to first order is given by (for $p = n$) is the sum $c_n^1(\tau) = c_n^{(0)}(\tau) + c_n^{(1)}(\tau)$ is given by

$$\boxed{c_n^1(\tau) = 1 + \frac{1}{i\hbar} \int_0^\tau V_{nn}(t) dt}, \tag{7.19}$$

and:

$$\boxed{c_p^1(\tau) = \frac{1}{i\hbar} \int_0^\tau V_{pn}(t) e^{i\omega_{pn}t} dt. \qquad (7.20)}$$

Remark. It is in the lecture notes that he suddenly removes the brackets from the superscripts of c. We've gone with the convention that $c_n^{(1)}$ represents the *first-order correction* itself and then c_n^1 is the first order correction *plus* $c_n^{(0)}$, i.e.the total amplitude to first order. Note then Eq. (7.20) doesn't have brackets in the superscript, but that's because we interpret it as the total probability of a transition between non-equal states happening! In the exam this distinction won't matter.

The terms $c_p^1(\tau)$ is the **amplitude** of the transition from state $n \to p$ if $p \neq n$, i.e. the weight given to the transition happening.

Similarly,

We interpret $|c_p^1(\tau)|^2$ as the probability to first order that after some time τ the system has performed a transition from state $|\psi_n\rangle$ to $|\psi_p\rangle$.

Note that for first order PT to be valid we require:

$$P^{(1)}_{n\to p}(\tau) = |c_p^1(\tau)|^2 \ll 1, \tag{7.21}$$

i.e that the probability of such a transition occurring is much smaller compared to the probability of the system remaining in its initial state.

7.2.3 Example: Sinusoidal perturbation

We now consider a specific example where the perturbation is sinusoidal in time:

$$\hat{V}(\mathbf{r},t) = \hat{V}(\mathbf{r})\cos(\omega t). \tag{7.22}$$

Using this form of the perturbation in Eq. (7.20) and considering only driving frequencies, ω, that are close to the resonant Bohr frequency, ω_{pn}. Set $V_{pn} = \langle\psi_p|\hat{H}(\mathbf{r})|\psi_n\rangle$ which is independent of t, and remember $\cos(\omega t) = \frac{1}{2}(e^{i\omega t} + e^{-i\omega t})$ we find:

$$\begin{aligned} c_p^1(\tau) &= \frac{V_{pn}}{2i\hbar}\int_0^\tau \left\{ e^{i(\omega_{pn}-\omega)t} + e^{i(\omega_{pn}+\omega)t} \right\} dt \\ &= -\frac{V_{pn}}{2\hbar}\left\{ \frac{e^{i(\omega_{pn}-\omega)\tau}-1}{\omega_{pn}-\omega} + \frac{e^{i(\omega_{pn}+\omega)\tau}-1}{\omega_{pn}+\omega} \right\} \\ &= -i\frac{V_{pn}}{\hbar}\frac{\sin[(\omega_{pn}-\omega)\frac{\tau}{2}]}{\omega_{pn}-\omega}e^{i(\omega_{pn}-\omega)\frac{\tau}{2}}, \end{aligned} \tag{7.23}$$

therefore the resulting probability transitioning from $n \to p$ (to first order) is:

$$P^{(1)}_{n\to p}(\tau) = \frac{{V_{pn}}^2}{\hbar^2}\frac{\sin^2[(\omega_{pn}-\omega)\frac{\tau}{2}]}{(\omega_{pn}-\omega)^2}. \tag{7.24}$$

Note how this probability oscillates with time. Further note, for future reference, that the approximation of considering only $\omega \simeq \omega_{pn}$ is known as the **rotating wave approximation** (See Chapter 9).

- The perturbation is valid when the maximum probability at

$$\frac{|V_{pn}|^2}{\hbar^2(\omega_{pn}-\omega)^2} \ll 1$$

- At times $t_s = \frac{2s\pi}{|\omega_{pn}\omega|}$, where $s \in \mathbb{N}$ the particle is **certain** to be back in the **lower energy** state.
- the probability of a transition is **greatest** when the driving frequency is close to the natural frequency, ω_{pn}

We now consider the case where the system isn't in a stationary state and our perturbation is time independent, $\hat{V} \neq \hat{V}(t)$. So transitions will occur which means we can use time dependent PT. Then from Eq. (7.20) we find that:

$$c_p^{(1)}(\tau) = \frac{V_{pn}}{\hbar\omega_{pn}}(1 - e^{i\omega_{pn}\tau}), \tag{7.25}$$

and the resulting probability:

$$P_{n\to p}^{(1)}(\tau) = \frac{4|V_{pn}|^2}{\hbar^2}\frac{\sin^2(\frac{\omega_{pn}\tau}{2})}{\omega_{pn}^2}. \tag{7.26}$$

7.2.4 Fermi's Golden Rule

Time dependent PT can also be used for when the final states are not discrete and well separated - i.e they form a continuum. The number of states within some interval is given by $\rho(E_p)dE_p$, then we find:

$$P_{n\to G}^{(1)}(\tau) = \tau\frac{2\pi}{\hbar}[|V_{pn}|^2\rho(E_p)]_{E_p=E_n}. \tag{7.27}$$

It's important to note that this is proportional to τ, so the transition probability per unit time is given by:

$$\boxed{R_{n\to G}^{(1)}(\tau) = \frac{2\pi}{\hbar}\left[|V_{pn}|^2\rho(E_p)\right]_{E_p=E_n}}. \tag{7.28}$$

This is an example of Fermi's Golden Rule. In general,

Fermi's Golden Rule

$$R_{n\to G}^{(1)} = \frac{\mathrm{d}P_{n\to G}^{(1)}(\tau)}{\mathrm{d}\tau} \tag{7.29}$$

The equivalent Fermi's Golden Rule for transitions between 2 discrete states is:

$$\boxed{R_{n\to G}^{(1)}(\tau) = \frac{2\pi}{\hbar}|V_{pn}|^2\delta(E_p - E_n)}. \tag{7.30}$$

Going back to the sinusoidal perturbation, instead of saying we are transitioning at 2 discrete energy states, we are instead transitioning from n to a *group of states* G, then we must consider the density of states $\rho(E_p)$ which is constant within G, and so is $|V_{pn}|^2$. We therefore must integrate and set $E_p = E_n$, which means integrating in an interval $[E_n - \Delta E, E_n + \Delta E]$

$$P_{n\to G}^{1}(\tau) = \left[\frac{4|V_{pn}|^2}{\hbar^2}\rho(E_p)\right]_{E_p=E_n} \times I$$

where

$$I = \int_{E_n-\Delta E}^{E_n+\Delta E}\frac{\sin^2\left(\frac{1}{2}\omega_{pn}\tau\right)}{\omega_{pn}^2}dE_p = \frac{1}{2}\tau\hbar\int_{-\tau\Delta E/2\hbar}^{\tau\Delta E/2\hbar}\frac{\sin^2\xi}{\xi^2}d\xi \tag{7.31}$$

and $\xi = \frac{1}{2}\omega_{pn}\tau$. If $\Delta E \gg 2\pi\hbar/\tau$, the integrals can be evaluated at $\pm\infty$, so the integral evaluates to π and $I = \frac{1}{2}\tau\hbar\pi$ and we recover Eq. (7.27).

7.2.5 Emission and Absorption of EM radiation

We are now going to use time dependent PT for the emission and absorption of EM radiation by an atom. The atom primarily interacts with the electric component of the EM field:

$$\mathbf{E}(\mathbf{r},t) = E_0 \hat{\mathbf{n}} \cos(\mathbf{k}\cdot\mathbf{r} - \omega t), \tag{7.32}$$

where assuming the wavelength of EM radiation is much larger compared to the size of the atom we can neglect the spatial variation of the field, this is known as the dipole approximation, and results in the electric field taking the form:

$$\mathbf{E}(\mathbf{r},t) = E_0 \hat{\mathbf{n}} \cos(\omega t). \tag{7.33}$$

This means that our perturbation takes the form:

$$\hat{V}(t) = \hat{\mathbf{D}} \cdot \mathbf{E}(t) = \frac{1}{2} \hat{D}_n E_0 (e^{i\omega t} + e^{-i\omega t}), \tag{7.34}$$

where $\hat{\mathbf{D}}$ is the electric dipole operator of the atom:

$$\hat{\mathbf{D}} = -q \sum_{j=1}^{Z} \hat{\mathbf{r}}_j \tag{7.35}$$

This is effectively a sum over all the positions of the electrons that surround an atom with atomic number, Z. Then following the same procedure as before we find:

$$c_p^{(1)}(\tau) = \frac{E_0}{2i\hbar} \langle\psi_p| \hat{D}_n |\psi_n\rangle \left[\frac{e^{i(\omega_{pn}-\omega)\tau} - 1}{i(\omega_{pn}-\omega)} + \frac{e^{i(\omega_{pn}+\omega)\tau} - 1}{i(\omega_{pn}+\omega)} \right]. \tag{7.36}$$

We now have 2 cases to consider. The first is $\omega = \omega_{pn}$ which corresponds to stimulated absorption. So the probability of an incoming photon causing an electron to move from a lower energy state to a higher energy state is:

$$P_{n\to p}^{(1)}(\tau) = \frac{E_0^2}{\hbar^2} |\langle\psi_p| \hat{D}_n |\psi_n\rangle|^2 \frac{\sin^2[(\omega_{pn}-\omega)\frac{\tau}{2}]}{(\omega_{pn}-\omega)^2}. \tag{7.37}$$

The second case is that of $\omega = -\omega_{pn}$ which corresponds to stimulated emission. So the probability of an incoming photon causing an electron to move from a higher energy state to a lower energy state by emitting another photon is given by:

$$P_{p\to n}^{(1)}(\tau) = \frac{E_0^2}{\hbar^2} |\langle\psi_n| \hat{D}_n |\psi_p\rangle|^2 \frac{\sin^2[(\omega_{pn}-\omega)\frac{\tau}{2}]}{(\omega_{pn}-\omega)^2}. \tag{7.38}$$

7.2.6 Spontaneous Emission of Radiation

There is a third mechanism for radiation interacting with matter, known as spontaneous emission.

Definition 7.2.1. Spontaneous emission: an atom in an excited state makes a transition towards a lower energy state, with the release of a photon, but *without any applied electromagnetic field* to initiate the process

Here even if an atom is in an excited state and there are no incident photons, the electron can still move to a lower energy state. This is because due to QED there are still fields present that the atom can interact with which can cause this photon emission even in a vacuum state.

The transition probability per unit time is

$$R_{n\to p} = \frac{4\alpha}{3q^2c^2}\omega_{ip}^3 \left|\left\langle \psi_p|\hat{\mathbf{D}}|\psi_n\right\rangle\right|^2 . \tag{7.39}$$

7.3 Key Results and the Algorithm

You should know how to carry out a generic perturbation theory question for both discrete states and for continuous states using Fermi's Golden Rule. Previous exam questions include finding the probability of transitions, therefore understanding the example is a necessity.

The Algorithm

1. Identify your time-dependent perturbation $\hat{V}(t)$.
2. Calculate the matrix element $V_{pn} = \langle \psi_p|\hat{V}(t)|\psi_n\rangle$.
3. Find the perturbation coefficients, e.g. in Eq. (7.20).
4. Find the orthonormal wavefunctions using those coefficients as in Eq.@(7.11).
5. Find any desired quantities the question asks for, e.g. the transition probability by $|c_p^1(\tau)|^2$, or the transition probability per unit time as in Eq. (7.27).

Note you will either be given the density of states, or in more simple systems, be asked to calculate the density of states (but the latter has never come up so far). Recall from statistical mechanics that the density of states is the number of states available per wavevector volume.

Chapter 8

Lasers

8.1 Introduction

This chapter aims to explain the basic operating principles of how a laser actually works. This is done using the Einstein coefficients and briefly motivates the use of time dependent PT which was described in the previous chapter. It finishes by exploring how a He-Ne laser using metastable states operates.

8.2 Derivation

A laser produces coherent, highly directional and near monochromatic light by using Light Amplification by Stimulated Emission of Radiation (LASER). This process involves exciting electrons to higher energy levels of an atom and then using an external source of photons to cause stimulated emission in order to produce more photons.

8.2.1 Einstein Coefficients

An easy way to model how a laser fundamentally works is by using Einstein coefficients. This is done by considering an atom contained within a cavity which possesses two energy levels, E_j and E_i, which are separated by $h\nu$ and where E_j is the ground state energy level.

The Holy Trinity

We assume there are 3 processes that an electron within this system can undergo in the presence of light and that each of these processes had some constant associated with them which contains the dynamics and likelihood of the process. They are **stimulated absorption**, **stimulated emission** and **spontaneous emission**, with Einstein coefficients B_{ji}, B_{ij} and A_{ij} respectively.

We further assume that the photons are quantised with energy $h\nu$ and that the spectral energy density of photons within the cavity is given by:

$$U(\nu, T) = \frac{8\pi h\nu^3}{c^3\left(e^{\frac{h\nu}{k_B T}} - 1\right)}, \tag{8.1}$$

where ν is the frequency of the photons and T is the temperature of the cavity.

So if we consider an ensemble of identical atoms in thermal equilibrium within the cavity, then the rate of atoms which have electrons moving to the excited state is given by:

$$R_{j\to i} = N_j B_{ji} U(\nu, T), \tag{8.2}$$

where N_j is the number of atoms with an electron in the ground state. This is because there is only one process that can take the electron from the ground state, E_j, to the excited state, E_i, which is stimulated absorption. However, the rate of atoms with electrons moving from the excited state to the ground state is given by:

$$R_{i\to j} = N_i[A_{ij} + B_{ij} U(\nu, T)], \tag{8.3}$$

where N_i is the number of atoms with the electron in E_i. Contained in this are the other two processes: stimulated emission and spontaneous emission, which cause electrons to move to the ground state. If we assume that the rate of atoms with electrons moving between E_j and E_i are equal, i.e $R_{j\to i} = R_{i\to j}$, we find that:

$$U(\nu, T) = \frac{A_{ij}}{B_{ji} e^{\frac{h\nu}{k_B T}} - B_{ij}}, \tag{8.4}$$

where we have assumed that, since the atoms are in thermal equilibrium, the population of atoms with an electron in the excited state follows the Boltzmann distribution:

$$N_i = N_j e^{\frac{-h\nu}{k_B T}}. \tag{8.5}$$

If we compare Eq. (8.4) to Eq. (8.1), we find that when in thermal equilibrium:

$$B_{ij} = B_{ji} \tag{8.6}$$

$$\frac{A_{ij}}{B_{ji}} = \frac{8\pi h \nu^3}{c^2}. \tag{8.7}$$

As a result, if we can experimentally determine one of the coefficients then we can determine the other two coefficients as well.

Instead of the rate of change of atoms with electrons in some particular energy level, we can consider the rate of change of the number of photons within some cavity simply by modifying Eq. (8.2) and Eq. (8.3) to include the number of photons with a particular frequency, $N(\nu)$, instead of $U(\nu, T)$, such that:

$$\frac{dN^+}{dt} = N_i A_{ij} + N_i B_{ij} N(\nu), \tag{8.8}$$

is the rate of increase of photons within the cavity and:

$$\frac{dN^-}{dt} = N_j B_{ji} N(\nu), \tag{8.9}$$

is the rate of decrease of photons within the cavity. There will also be a loss of photons due to leakage from the cavity. So the overall rate of change of photons within the cavity is given by:

$$\frac{dN}{dt} = \frac{dN^+}{dt} - \frac{dN^-}{dt} = N_i A_{ij} + N_i B_{ij} N(\nu) - N_j B_{ji} N(\nu) - \frac{N(\nu)}{\tau_0}, \tag{8.10}$$

where the final term accounts for the leakage of photons using some characteristic timescale, τ_0. If we assume that $B_{ji} = B_{ij}$, as suggested by Eq. (8.6), then we can rearrange the above expression into the following form:

$$\frac{dN}{dt} = N_i A_{ij} + N(\nu)\left[(N_i - N_j)B_{ij} - \frac{1}{\tau_0}\right]. \tag{8.11}$$

This shows that unless $N_i > N_j$ then $\frac{dN}{dt} < 0$, meaning the number of photons present in the cavity will decrease with time. However according to Eq. (8.5) this won't be the case at thermal equilibrium. This means that through some non-thermal method we need to create a

> **population inversion** where there are more atoms with their electrons occupying the excited state than there are occupying the ground state.

There are a number of ways of creating this population inversion.

One of the more common methods is to use **metastable** states.

Definition 8.2.1. A **metastable state** is an (excited) electronic state with (unusually) long lifetimes when occupied, and the system may spontaneously leave the metastable state at any time.

A typical lasing medium that involves metastable states is a combination of Helium and Neon:

> Don't memorise word-for-word but know this is a way of population inversion to produce light.
> 1. First, one of the ground state He atoms is excited into an excited metastable state using an electrical discharge
> 2. This He atom will then collide with a Ne atom causing the energy the excited electron in the He atom gained to be transferred to the Ne atom, meaning one of its electrons moves into an excited state
> 3. At this point the external photon causes stimulated emission of the Ne atom, causing the excited electron to move to a lower energy excited state, where the energy difference in energy levels corresponds to the energy of the initial incoming photon.
> 4. This means two photons of the same frequency are produced. The electron will then de-excite further to the ground state

Other combinations of different elements which contain metastable states can be chosen in order to change the wavelength of light that the laser produces.

8.2.2 Time Dependent PT

In order to determine the form of the Einstein coefficients we can use time dependent PT. In this case, much like in the previous chapter, the perturbation arises due to a time varying electric field. The operator for the electric field (DO NOT MEMORISE), within a cavity, has the form:

$$\hat{\mathbf{E}}(\mathbf{r}, t) = \frac{1}{\sqrt{V}} \sum_{\mathbf{k},\lambda} \sqrt{\frac{\hbar\omega}{2\epsilon_0}} \boldsymbol{\epsilon}_\lambda(\mathbf{k}) \left[-i\hat{A}^+_\lambda(\mathbf{k})e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega t} + i\hat{A}^-_\lambda(\mathbf{k})e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}\right], \tag{8.12}$$

where

- $\boldsymbol{\epsilon}_\lambda(\mathbf{k})$ is the polarization vector (perpendicular to the direction of propagation) of the electromagnetic radiation that is enclosed in a volume V.

- $\hat{A}^+_\lambda(\mathbf{k})$ and $\hat{A}^-_\lambda(\mathbf{k})$ are the **creation** and **annihilation** operators for a single photon with wave vector $\mathbf{k}$ and polarization λ which act to increase and decrease the number of photons in the system:

$$\hat{A}^+_\lambda \left|N_\lambda(\mathbf{k})\right\rangle = \sqrt{N(\mathbf{k})+1}\left|N_\lambda(\mathbf{k})+1\right\rangle$$
$$\hat{A}^-_\lambda \left|N_\lambda(\mathbf{k})\right\rangle = \sqrt{N(\mathbf{k})}\left|N_\lambda(\mathbf{k})-1\right\rangle$$

The transition rates (Eq. (7.26)) (which are the quantum mechanical analogues of the Einstein coefficients) are proportional to product of the square of the matrix elements

$$\langle i|\hat{V}|j\rangle$$

connecting the atomic states $|i\rangle$ and $|j\rangle$ and the density of states $\rho(\nu)$ which is the number of pairs of levels i, j, that have an energy difference between $h\nu_{ij}$ and $h(\nu_{ij}+d\nu_{ij})$.

8.3 Key Results

You basically just need to know how to make a laser, unfortunately actually building one is non-examinable do you'll just have to pretend

Your epic laser

1. A lasing medium in which two of the energy levels, E_i and E_j, are separated by an energy gap ($E_i - E_j = +h\nu$ and $h\nu > kT$). The atoms in the upper level can make transitions that are stimulated by the presence of photons of the correct frequency.
2. Some mechanism for repopulating the upper level for repeated operation.
3. A cavity in which the stimulated photons and the lasing medium can be contained. The cavity contains the lasing medium and is connected to the pumping mechanism required to generate the population inversion. Mirrors keep the photons inside the cavity to build up the number of photons that stimulate emission but allow a proportion of the light to escape as the laser beam.

You will also need to know what populaton inversion is, how to create population inversion and the 3 modes of interaction: stimulated absorption/emission and spontaneous emission.

Chapter 9

Two level systems

9.1 Introduction

The rest of this module studies **two-level systems** - quantum systems whose entire space of states can be determined by a unique combination of two **orthonormal basis states**. From a more mathematical point of view, we say that the space of states H (a Hilbert space because it is QM) has a span given by 2 orthonormal states (denote them by, $|0\rangle, |1\rangle$) such that $H = \text{span}(|0\rangle, |1\rangle)$.

Examples of two-level systems (which we will study later) include the ammonia molecule and qubits - the quantum information analogue to the classical bit.

9.2 Matrix mechanics

If you didn't enjoy rushing Dirac notation last year, you'll hate it this year because we do truly invoke some hidden functional analysis (which you don't need to know unless you take MA3G7) to make them maths, and thus physics, make sense.

9.2.1 A review of Hilbert spaces and Dirac Notation

Definition 9.2.1. A **Hilbert space** is a vector space with the following properties:

- Completeness
- Inner product $(\cdot, \cdot) : H \times H \to \mathbb{C}$

Vector spaces have to be over some scalar field, namely the **complex numbers** $\mathbb{C}$. For physicists, this is because wavefunctions can be complex (e.g. complex coefficients or complex phase factors $e^{i\phi}$). It is non-examinable, but important as to why we do this because everyone has questions about this. We will come back to the definition in a bit, let's define everyone's favourite thing: notation.

Dirac notation

Traditionally, a vector in a vector space is denoted with a boldfont, e.g. **E** for the electric field. In QM, we use Dirac notation, where the ket $|\psi\rangle$ is the vector of Hilbert space and physically represents the state of some system. It is important to note that anything can go inside the brakets as long as it describes a state.

Its dual is the bra: $\langle f|$. Here, $f : H \to \mathbb{C}$ is the linear functional acting on the space H. Therefore doing $\langle f|\psi\rangle$ gives you a complex number - f acts on the vector $|\psi\rangle$. Using something called the Riesz representation theorem (non-examinable!) means that our inner product of 2 states $(f, g) = (|f\rangle, |g\rangle) = \langle f| (|g\rangle)$ is exactly $\langle f|g\rangle$.

Definition 9.2.2. The **conjugate transpose** of a state $|\psi\rangle$ is denoted $|\psi\rangle^\dagger = \langle\psi|$

It is important to note that this is well-defined on finite-dimensional spaces (with a corresponding definition for infinite-dimensional Hilbert spaces). So that is what physicists take for granted - luckily in this part of the module we only have a two-dimensional vector space.

We now return to our definition of Hilbert spaces.

Why completeness? Consider the general form of a wavefunction

$$|\psi(t)\rangle = e^{i\hat{H}t/\hbar} |\psi(0)\rangle \tag{9.1}$$

where $\hat{H}$ is the Hamiltonian (which produces the energy). Now, $\hat{H}$ is an operator, so $e^{\hat{H}}$ is an operator acting on $|\psi(0)\rangle$. Using spectral theory (non-examinable), we define the exponential of an operator $\hat{H}$ with a "Taylor expansion"

$$e^{\hat{H}} = \sum_{\alpha=1}^{\infty} \frac{\hat{H}^\alpha}{\alpha!} \tag{9.2}$$

In order for this to converge (using said spectral theory and Riesz representation) is the same as requiring completeness. Moreover, a physical observable **may not have a complete set of eigenstates**, which would basically break down the entirety of QM. So, let's not do that and continue soldiering (suffering) onwards!

9.2.2 Outer products and the Projection operator

Why an inner product? If you didn't realise, inner products allow us to extract physical information about our system, by letting us find states which can describe the entirety of the space of states. Let's see this in terms of vectors in $\mathbb{R}^2$ which we will denote by boldface: $\mathbf{x}_1, \mathbf{y}_1$. Now, $\mathbb{R}^2$ has 2 different bases:

$$\mathbf{x}_1 = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad \mathbf{y}_1 = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{9.3}$$

$$\mathbf{x}_2 = \begin{pmatrix} -\frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix} \qquad \mathbf{y}_2 = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix} \tag{9.4}$$

You can construct any vector in $\mathbb{R}^2$ by a linear combination of either $\mathbf{x}_1$ and $\mathbf{y}_1$ or $\mathbf{x}_2$ and $\mathbf{y}_2$, i.e. given $\mathbf{v} \in \mathbb{R}^2$:

$$\mathbf{v} = \alpha_x \mathbf{x}_1 + \alpha_y \mathbf{y}_1 = \beta_x \mathbf{x}_2 + \beta_y \mathbf{y}_2 \tag{9.5}$$

for some $\alpha_{x,y}, \beta_{x,y} \in \mathbb{R}$. The question is how do we convert between the two bases? Notice what happens if we decide to draw out these bases, see Figure 9.1. In order to write $\mathbf{v}$ in terms of one of the bases, we must 'project' it onto each of $\mathbf{x}_1, \mathbf{y}_1$ and $\mathbf{x}_2, \mathbf{y}_2$. A projection here is just the geometrical meaning of the dot product! So for any orthonormal basis $\{\mathbf{e}_i\}_{i=1}^{\infty}$

$$\mathbf{v} = \sum_i (\mathbf{e}_i \cdot \mathbf{v}) \mathbf{e}_i \tag{9.6}$$

However the dot product is an inner product over $\mathbb{R}$ but we want one over $\mathbb{C}$ for our Hilbert space. Moreover we are operating on the vector $\mathbf{e}_i$. Associating $\mathbf{e}_i \to |i\rangle, \mathbf{v} \to |\psi\rangle$ this beautiful equation becomes

$$|\psi\rangle = \sum_i (\langle i|\psi\rangle) |i\rangle = \sum_i |i\rangle (\langle i|\psi\rangle) = \sum_i (|i\rangle\langle i|) |\psi\rangle = \sum_i c_i |\psi\rangle \tag{9.7}$$

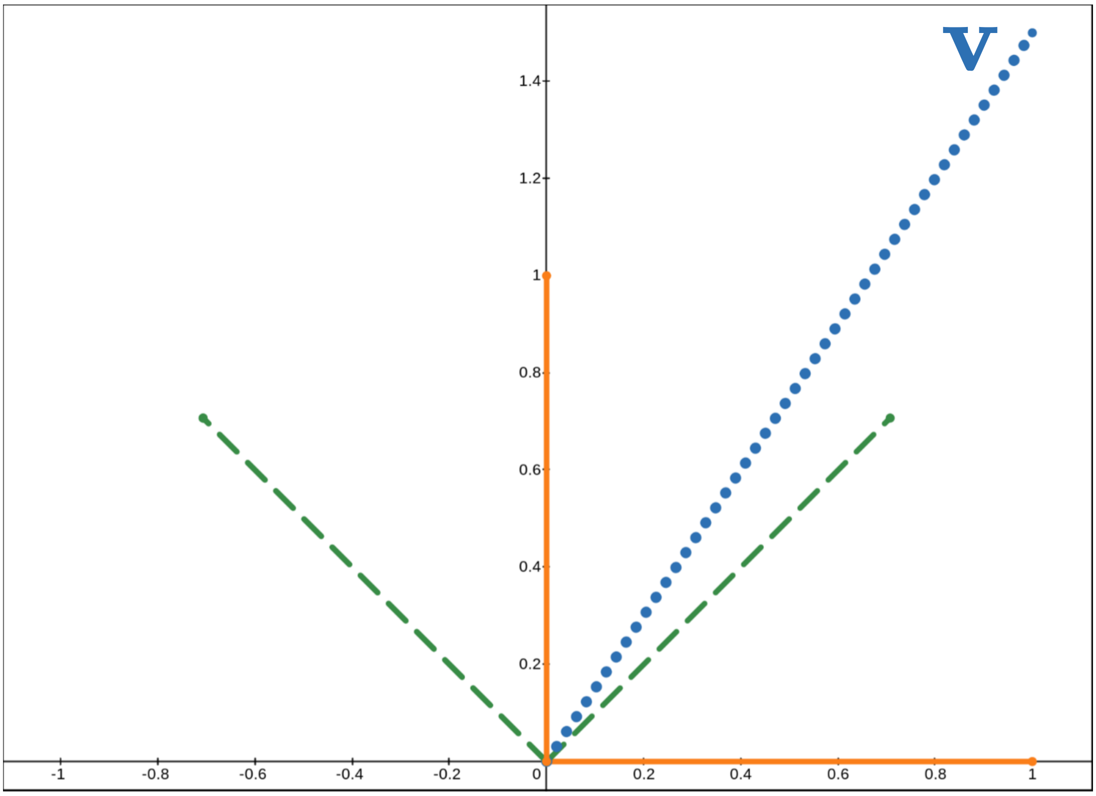

Figure 9.1: 2 bases of $\mathbb{R}^2$ along side the vector $\mathbf{v}$.The green, dashed lines denote the basis $\mathbf{x}_2, \mathbf{y}_2$ and the orange, solid lines denote the basis $\mathbf{x}_1, \mathbf{x}_2$

Definition 9.2.3. The **outer product** of 2 states $|i\rangle, |j\rangle$ is denoted $|i\rangle\langle j|$. It produces a matrix and is thus a linear operator on a vector.

Note, if kets are column vectors, then bras are row vectors, so the outer product written in this way does produce a matrix. The question to ask yourself is now: what does an outer product *mean* geometrically? Well we saw earlier what an outer product does to a vector. The dot product projects the amount of $\mathbf{v}$ in the direction of $\mathbf{e}_i$. This then multiplies $\mathbf{e}_i$, so in effect the outer product gives us a vector whose magnitude is how much of $\mathbf{v}$ is in the direction of $\mathbf{e}_i$. This is exactly the same notion in the Dirac notation! If we write our wavefunction $|\Psi\rangle$ in terms of orthonormal wavefunctions $|\psi_i\rangle$

$$|\psi\rangle = \sum_i c_i |i\rangle \tag{9.8}$$

then c_i gives us the amplitude of state $|i\rangle$, i.e. how much of state $|i\rangle$ contributes to $|\psi\rangle$. We therefore define

Definition 9.2.4. The **projection operator** is the outer product $|i\rangle\langle i|$, i.e. it projects the component of $|\psi\rangle$ onto $|i\rangle$

We now move onto some important properties of the projection . We now solidify our notation and say $|\psi_i\rangle = |i\rangle$. Recall

Theorem 9.2.1. *The eigenfunctions of a Hermitian operator form a complete basis set. Furthermore, if the eigenfunctions are not normalised, we can do so to form an complete orthornormal basis.*

This gives us the following proposition

Proposition 9.2.1. *The sum of the projection operator over an orthonormal basis gives the* *identity matrix (operator) I*

$$\sum_i |i\rangle\langle i| = I \tag{9.9}$$

Proof. This is a bit hard to see. Remember that $|i\rangle$ is an orthonormal state to all other states $|j\rangle$ when $j \neq i$. Since each state is orthonormal, we can 'represent'[1] each state $|i\rangle$ by

$$|1\rangle = \begin{pmatrix} 1 \\ 0 \\ \vdots \end{pmatrix}, |2\rangle = \begin{pmatrix} 0 \\ 1 \\ \vdots \end{pmatrix} \tag{9.10}$$

Then our sum becomes

$$\sum_i |i\rangle\langle i| = |1\rangle\langle 1| + |2\rangle\langle 2| + \dots \tag{9.11}$$

$$= \begin{bmatrix} 1 & 0 & \dots & \\ 0 & 0 & \dots & \\ 0 & 0 & \dots & \\ \vdots & \vdots & \dots & \ddots \end{bmatrix} + \begin{bmatrix} 0 & 0 & \dots & \\ 0 & 1 & \dots & \\ 0 & 0 & \dots & \\ \vdots & \vdots & \dots & \ddots \end{bmatrix} + \dots \tag{9.12}$$

$$= \begin{bmatrix} 1 & 0 & \dots & 0 \\ 0 & 1 & \dots & 0 \\ 0 & 0 & 1 & \\ \vdots & \vdots & \dots & \ddots \end{bmatrix} = I \tag{9.13}$$

□

Definition 9.2.5. Let $\hat{Q}$ be an operator[2] on a Hilbert space H. Then it is **idempotent** if and only if $\hat{Q}^2 = \hat{Q}\hat{Q} = \hat{Q}$

Why is this useful? It gives us another property of the projection operator, namely

Lemma 9.2.1. *The projection operator is idempotent*

Proof. We apply $|i\rangle\langle i|$ twice:

$$((|i\rangle\langle i|))^2 = (|i\rangle\langle i|)(|i\rangle\langle i|) = |i\rangle \langle i|i\rangle \langle i| = |i\rangle (\langle i|i\rangle) \langle i| = |i\rangle\langle i| \tag{9.14}$$

where we used the orthonormality of states which gives that $\langle i|i\rangle = 1$. □

Generally speaking, if we have states $|i\rangle, |j\rangle$ then applying the projection operator for state j onto i satisfies

$$|j\rangle \langle j|i\rangle \langle i| = \delta_{ij} |j\rangle\langle i| \tag{9.15}$$

Geometrically, this says once you have projected some arbitrary state in one basis state, you can't re-project it onto a different basis state. Instead, if you re-project onto the same basis state, you'll just return the original projection.

Physically, this allows us to use the projection operator to **find energy eigenvalues**. consider an arbitrary state which is a superposition of basis states

$$|\psi\rangle = \sum_k c_k |k\rangle \tag{9.16}$$

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[1] Note: this is not the same as '=' although we will write an equals sign. What we are saying is that having an orthonormal basis set is like having the orthonormal basis of $\mathbb{C}^n$. More specifically, we have an *isomorphism* of Hilbert spaces.

[2] Necessarily this operator should be *bounded*, but in physics they generally are so we will shove this under the rug.

Then the probability of the state $|\psi\rangle$ collapsing into the *ith* state can be calculated as

$$|\langle i|\psi\rangle|^2 = \left|\sum_k c_k \langle i|k\rangle\right|^2 = \delta_{ik} c_i^2 \langle i|k\rangle \tag{9.17}$$

which gives us the corresponding energy E_i. In particular, making a measurement *changes* the system so that it arrives in state $|i\rangle$. Therefore determining the energy is given by the *expectation value* of the Hamiltonian:

$$\begin{aligned} \langle\psi|\hat{H}|\psi\rangle &= \langle\psi|E_k|\psi\rangle \qquad (9.18)\\ &= \left\langle \sum_k |k\rangle \langle k|\psi\rangle \middle| E_k \middle| \psi \right\rangle \\ &= \sum_k \langle\psi|k\rangle E_k \langle k|\psi\rangle \\ &= \sum_k |\langle k|\psi\rangle|^2 E_k \end{aligned}$$

If you are unsure how we got from the 2nd line to the third line, remember that the left side of the braket must be replaced with the **Hermitian conjugate** (conjugate transpose) before you can remove the braket notation entirely, so $\langle k|\psi\rangle = (\langle\psi|k\rangle)^\dagger$ and $|k\rangle^\dagger = \langle k|$. Now focus on the third line. If we remove the ψ from either side we get

$$\boxed{\hat{H} = \sum_k E_k |k\rangle\langle k|} \tag{9.19}$$

This is true for **any Hermitian operator** where the scalar coefficient is just its eigenvalues instead of energies specifically (note, the energies are themselves eigenvalues of the Hamiltonian, which is hermitian!).[3]

9.2.3 Matrix representations

Notice our expression for the Hamiltonian, Eq. (9.19), the terms in the sums can be represented as **matrices** like we discussed earlier in this chapter. This is because of the outer product. We can generalise this.

Suppose we have a finite orthonormal basis of size n, i.e. we have n basis states. Let $\hat{O}$ be an operator. We can represent $\hat{O}$ as a matrix, which then will act on vectors (which *represent* states). Then

$$\hat{O} = \sum_j \sum_i |j\rangle \langle j|\hat{O}|i\rangle \langle i| \tag{9.20}$$

This takes advantage of Proposition 9.2.1 by applying the projection operator and $\hat{O}$ to both sides.

Note then that the term $\langle j|\hat{O}|i\rangle$ is a **matrix element** since it is sandwiched between the outer product $|j\rangle\langle i|$. This corresponds to the jith matrix element $\hat{O}_{ji}$ so

$$\boxed{\hat{O} \doteq \begin{pmatrix} \langle 1|\hat{O}|1\rangle & \langle 1|\hat{O}|2\rangle & \dots \\ \langle 2|\hat{O}|1\rangle & \langle 2|\hat{O}|2\rangle & \dots \\ \vdots & \vdots & \ddots \end{pmatrix} \qquad (9.21)}$$

where we introduce the notation $\doteq$ to mean ‘is represented by’ rather than confusingly write it as an equals sign.

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[3] For those takinh MA3G7, this is an application of the Hilbert-Schmidt theorem.

9.2.4 Outer product as a matrix representation

Given two arbitrary states $|\alpha\rangle$ and $|\beta\rangle$ in a finite-dimensional space with basis kets $|i\rangle$, the states can be represented as column vectors by expanding the state across the basis kets,

$$|\alpha\rangle \doteq \begin{pmatrix} \langle i \mid \alpha\rangle \\ \langle j \mid \alpha\rangle \\ \langle k \mid \alpha\rangle \\ \vdots \end{pmatrix} \quad |\beta\rangle \doteq \begin{pmatrix} \langle i \mid \beta\rangle \\ \langle j \mid \beta\rangle \\ \langle k \mid \beta\rangle \\ \vdots \end{pmatrix}$$

The outer product $|\beta\rangle\langle\alpha|$ is given by

$$|\beta\rangle\langle\alpha| \doteq \begin{pmatrix} \langle i \mid \beta\rangle\langle i \mid \alpha\rangle^* & \langle i \mid \beta\rangle\langle j \mid \alpha\rangle^* & \dots \\ \langle j \mid \beta\rangle\langle i \mid \alpha\rangle^* & \langle j \mid \beta\rangle\langle j \mid \alpha\rangle^* & \dots \\ \vdots & \vdots & \ddots \end{pmatrix}$$

Don't forget to take the conjugate transpose when converting a bra to a ket and vice versa!

9.3 Ammonia Molecule

The ammonia molecule NH_3 has 2 classically stable configurations

- One with the nitrogen above the hydrogen ions with its lone pair pointing up. Denote this as $|1\rangle$.
- One with the nitrogen below the hydrogen ions with its lone pair pointing down. Denote this as $|2\rangle$.

We will use these as 2 distinct states and model it using two-level theory, ignoring other degrees of freedom of the molecule e.g., electronic, nuclear, vibrational, and rotational excitations. We will also ignore any relativistic effects. We consider the two configurations in terms of some coordinate and define an energy (Hamiltonian) in terms of this coordinate.

As this is a very basic model, we can attribute any experimental deviations to the fact that our model is incomplete.

For the ammonia to flip between the 2 states, there has to be some *potential barrier*. We will consider 2 cases: the infinite and finite potential barriers.

9.3.1 Infinite potential barrier

We would be considering two configurations which are identical by symmetry but disconnected from one another, so there is no coupling terms like $|1\rangle\langle 2|$ in our Hamiltonian. Therefore, the energies of each state will be the same (denote this by ϵ_0) and our Hamiltonian is

$$\hat{H} = |1\rangle\langle 1| \, \epsilon_0 + |2\rangle\langle 2| \, \epsilon_0 \tag{9.22}$$

Now we can use our knowledge from matrix representations, noting that off-diagonal terms are 0 due to the lack of coupling and

$$\hat{H} \doteq \begin{bmatrix} \epsilon_0 & 0 \\ 0 & \epsilon_0 \end{bmatrix} \qquad |1\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \qquad |2\rangle = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \tag{9.23}$$

Suppose we kick the ammonia molecule to start purely in one of $|1\rangle$ or $|2\rangle$. Then the general evolution will be something like $\exp(i\epsilon_0 t/\hbar)\,|1\rangle$ - a **stationary state**. We would never oscillate into $|2\rangle$. Same thing if we started in $|2\rangle$ instead.

9.3.2 Finite potential barrier

For a finite potential barrier, e.g. 0.25eV, the expected frequency of inversion of 1.3 GHz. However due to **quantum tunnelling** it is 24 GHz. This suggests there is coupling between the 2 states, so any off-diagonal terms may be non-zero! This means that $\langle 1|\hat{H}|2\rangle = \hat{H}_{12} = \hat{H}^*_{21} = -V, V > 0$. Note that the minus sign is a convention. Then

$$\hat{H}_0 = |1\rangle\langle 1|\, \epsilon_0 + |2\rangle\langle 2|\, \epsilon_0 - V\, |1\rangle\langle 2| - V^*\, |2\rangle\langle 1| \tag{9.24}$$

so the Hamiltonian is represented by

$$\hat{H} \doteq \begin{bmatrix} \epsilon_0 & -V \\ -V^* & \epsilon_0 \end{bmatrix} \tag{9.25}$$

The eigenstates of this system are linear combinations of $|1\rangle$ and $|2\rangle$. Before moving on, we recall a theorem from linear algebra

Theorem 9.3.1. *Hermitian operators have real eigenvalues*

Therefore we will assume $V = V^*$ is real. We get 2 pairs of eigenvalues-eigenvectors. They are

$$\epsilon_g = \epsilon_0 - V \qquad |g\rangle = \frac{|1\rangle + |2\rangle}{\sqrt{2}} \tag{9.26}$$

$$\epsilon_e = \epsilon_0 + V \qquad |e\rangle = \frac{|1\rangle - |2\rangle}{\sqrt{2}} \tag{9.27}$$

The coupling between the states results in the lifting of their degeneracy (because both states had the same energy ϵ_0). 'e' stands for excited and 'g' stands for ground (because it is the lowest energy). Again, the fact the signs may appear a bit backwards is because of our convention to choose $-V$. Also note that the new states $|g\rangle, |e\rangle$ form an orthonormal basis.

The 2 states $|g\rangle, |e\rangle$ represent symmetric and anti-symmetric combinations of $|1\rangle, |2\rangle$.

We now want to study time evolution. Denote the initial state at $t = 0$, by $|\psi(0)\rangle$. Then at any time t, the state is

$$|\psi(t)\rangle = c_g(t)\, |g\rangle + c_e\, |e\rangle \tag{9.28}$$

Substitute this into the Schrödinger equation (which we can because we are ignoring relativity), which remember is given by

$$i\hbar \frac{\mathrm{d}|\psi(t)\rangle}{\mathrm{d}t} = \hat{H}\, |\psi(t)\rangle \tag{9.29}$$

Therefore

$$\begin{aligned} i\hbar\frac{dc_g}{dt}\, |g\rangle\, \hbar\frac{dc_e}{dt}\, |e\rangle = \hat{H}|\psi(t)\rangle &= c_g\hat{H}\, |g\rangle + c_e\hat{H}\, |e\rangle \\ &= c_g\epsilon_g\, |g\rangle + c_e\epsilon_e\, |e\rangle \end{aligned} \tag{9.30}$$

The time-dependent coefficients $c_g(t), c_e(t)$ are directly

$$c_g(t) = c_g(0)e^{-i\epsilon_g t/\hbar} \qquad c_e(t) = c_e(0)e^{-i\epsilon_e t/\hbar} \tag{9.31}$$

As before, if $c_g(0) = 1$ or $c_e(0) = 1$, the system is in an eigenstate of the coupled Hamiltonian and we recover stationary states of definite energy $\epsilon_0 \pm V$.

However, suppose our initial starting state is a **superposition** of $|g\rangle, |e\rangle$, e.g. suppose our initial wavefunction is $|\psi(0)\rangle = |1\rangle = \frac{1}{\sqrt{2}}(|g\rangle + |e\rangle)$, so that $c_g(0) = c_e(0) = \frac{1}{\sqrt{2}}$. Then we have **sinusoidal oscillation** since

$$|\psi(t)\rangle = \exp\left(\frac{-i\epsilon_0 t}{\hbar}\right)\left(\cos\left(\frac{Vt}{\hbar}\right)|1\rangle + i\sin\left(\frac{Vt}{\hbar}\right)|2\rangle\right) \tag{9.32}$$

which you can derive by substituting in for $|g\rangle, |e\rangle, \epsilon_g, \epsilon_e$ and using a particularly famous relation between complex exponentials and trig functions.

Therefore, we have sinusoidal oscillation between the states $|1\rangle, |2\rangle$ with angular frequency $\omega = V/\hbar$. The **probabilities** of finding the nitrogen lone pair pointing up or down is

$$P_1(t) = |\langle 1|\psi\rangle|^2 = \cos^2\left(\frac{Vt}{\hbar}\right) \tag{9.33}$$

$$P_2(t) = |\langle 2|\psi\rangle|^2 = \sin^2\left(\frac{Vt}{\hbar}\right) \tag{9.34}$$

We have derived the time-dependence using only pure quantum mechanics - this analysis can be generalised to any two-level system.

9.4 General Undriven 2-level system

We will again choose $|1\rangle, |2\rangle$ to be our orthonormal basis. Therefore any state can be represented as a linear superposition

$$|\psi\rangle = \alpha\,|1\rangle + \beta\,|2\rangle \tag{9.35}$$

Again we choose to represent the kets by some orthonormal vectors and choose

$$|1\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \qquad\qquad |2\rangle = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \tag{9.36}$$

once again, so that we can write our arbitrary state as a vector

$$|\psi\rangle = \begin{bmatrix} \alpha \\ \beta \end{bmatrix} \tag{9.37}$$

Since we have a two-level system, our Hamiltonian (and the rest of our operators) can be represented as a 2×2 matrix

$$\hat{H} = \begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix} \tag{9.38}$$

and therefore its expectation value reduces to matrix multiplication

$$\langle\psi|\hat{H}|\psi\rangle = \begin{bmatrix} \alpha & \beta \end{bmatrix} \begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix} \begin{bmatrix} \alpha \\ \beta \end{bmatrix} \tag{9.39}$$

The off-diagonal terms H_{12}, H_{21} are referred to as **mixing matrix elements** or **coupling terms**.

Lemma 9.4.1. *If we set $H_{21} = H_{12} = 0$ then the basis states we have chosen $|1\rangle, |2\rangle$ and eigenstates of the Hamiltonian coincide*

Proof.

$$\begin{aligned} \begin{pmatrix} H_{11} & 0 \\ 0 & H_{22} \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} &= H_{11} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = H_{11}|1\rangle \quad (= \epsilon_1|1\rangle) \\ \begin{pmatrix} H_{11} & 0 \\ 0 & H_{22} \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} &= H_{22} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = H_{22}|2\rangle \quad (= \epsilon_2|2\rangle)\,. \end{aligned} \tag{9.40}$$

Hence we see that $|1\rangle, |2\rangle$ are indeed eigenstates ☐

Proposition 9.4.1. *The Hamiltonian is invariant under a global phase change.*

This means if we were to shift all states by the same phase $\exp(i\phi)$ then the system would remain exactly the same. Alternatively, if we did something like $\hat{H} \to \hat{H} + I\epsilon_0$ (i.e. shift the Hamiltonian by the energy), then this would also leave the system unchanged. All it does is offset the values. However, this is not true for **phase differences between states in superposition**, also called relative phase.

Since global change is invariant, it will be useful to rewrite the Hamiltonian in a different way which shifts the Hamiltonian to the mean energy $(\epsilon_1 + \epsilon_2)/2$. We first note the most general Hamiltonian has complex entries

$$\hat{H} \doteq \begin{bmatrix} \xi - \delta & \Delta e^{i\phi} \\ -\Delta e^{-i\phi} & \xi + \delta \end{bmatrix} \tag{9.41}$$

In order to go from $(\epsilon_1 + \epsilon_2)/2 \to \epsilon_1$ we must *add* the **energy difference** $(\epsilon_1 - \epsilon_2)/2$ which we will set to $-\epsilon$. Similarly to get to ϵ_2 we must subtract the energy difference which is ϵ. Our Hamiltonian is therefore

$$\hat{H} \doteq \begin{bmatrix} -\epsilon & \Delta e^{i\phi} \\ -\Delta e^{-i\phi} & \epsilon \end{bmatrix} \tag{9.42}$$

Δ in this case is a **coupling term**.

We therefore consider the Schrödinger equation again by substituting in $|\psi\rangle$ and $\hat{H}$ so

$$i\hbar \frac{d}{dt} \begin{bmatrix} \alpha \\ \beta \end{bmatrix} = \begin{bmatrix} -\epsilon & -\Delta \exp(i\phi) \\ -\Delta \exp(-i\phi) & \epsilon \end{bmatrix} \begin{bmatrix} \alpha \\ \beta \end{bmatrix} \tag{9.43}$$

To solve it, we attempt to use something like Eqs. (9.30). To do that, we need an orthonormal basis. We can do this by solving the secular/characteristic equation $\det\left(\hat{H} - \lambda I\right) = 0$:

$$\begin{vmatrix} -\epsilon - \lambda & -\Delta \exp(i\phi) \\ -\Delta \exp(-i\phi) & \epsilon - \lambda \end{vmatrix} = 0 \implies \lambda^2 - \epsilon^2 - \Delta^2 = 0 \tag{9.44}$$

We get 2 eigenvalues

$$\lambda_\pm = \pm\eta \qquad \eta = \sqrt{\epsilon^2 + \Delta^2} \tag{9.45}$$

We denote the corresponding eigenvectors by $|-\rangle = \begin{bmatrix} \alpha_- \\ \beta_- \end{bmatrix}, |+\rangle = \begin{bmatrix} \alpha_+ \\ \beta_+ \end{bmatrix}$. To find them, we substitute back into the secular equation (like how you would find eigenvectors normally) and we get

$$\alpha_- = \frac{\Delta}{\eta - \epsilon} e^{i\phi} \beta_- \qquad \alpha_+ = -\frac{\Delta}{\eta + \epsilon} e^{i\phi} \beta_+ \tag{9.46}$$

So we have 2 equations but 4 unknowns - that's not good. However, we can directly deduce 2 other equations from a physical principle: wavefunctions should be normalised. Remember the alphas and beta correspond to the superposition in Eq. (9.35). Therefore we require

$$|\alpha_\pm|^2 + |\beta_\pm|^2 = 1 \tag{9.47}$$

(1 equation for each sign) to satisfy the normalisation condition. So now we have a consistent system of equations. You can solve by substituting the alphas into Eq (9.47). We get

$$|-\rangle = \begin{pmatrix} \alpha_- \\ \beta_- \end{pmatrix} = \begin{pmatrix} \cos\frac{\theta}{2} \\ e^{-i\phi} \sin\frac{\theta}{2} \end{pmatrix} \qquad |+\rangle = \begin{pmatrix} \alpha_+ \\ \beta_+ \end{pmatrix} = \begin{pmatrix} -\sin\frac{\theta}{2} \\ e^{-i\phi} \cos\frac{\theta}{2} \end{pmatrix} \tag{9.48}$$

with

$$\sin\theta = \frac{\Delta}{\eta} \qquad \cos\theta = \frac{\epsilon}{\eta} \qquad \tan\theta = \frac{\Delta}{\epsilon} \tag{9.49}$$

Definition 9.4.1. The angle θ is called the **mixing angle** which describes the relationship between the uncoupled basis states and those states of the coupled Hamiltonian in terms of ϵ, Δ.

We have 2 regimes now

- **Weak coupling**: $\epsilon \gg \Delta$, θ small. The energy separation between the bare (uncoupled) states dominates over the coupling rates between the two states. In this case, the eigenbasis of the coupled Hamiltonian approaches the bare basis states.
- **Strong coupling**: $\epsilon \ll \Delta$. Eigenbasis from coupled Hamiltonian deviates further from the uncoupled states. Maximal mixing occurs in the limit $\epsilon \to 0, \tan\theta \to \infty, \theta \to \pi/2$. Then the coupled states are equal combinations of the uncoupled states.

Remark. In the ammonia example, we found that our states $|g\rangle, |e\rangle$ were equal combinations of $|1\rangle, |2\rangle$, so it was an example of strong coupling.

Let us now drop the phase factor $e^{-i\phi}$ temporarily. Recall from linear algebra that to transform between 2 orthonormal bases, you have a change-of-basis matrix U. In our case, U satisfies

$$\begin{bmatrix} |-\rangle \\ |+\rangle \end{bmatrix} = U \begin{bmatrix} |1\rangle \\ |2\rangle \end{bmatrix} = \begin{bmatrix} \cos\theta/2 & \sin\theta/2 \\ -\sin\theta/2 & \cos\theta/2 \end{bmatrix} \begin{bmatrix} |1\rangle \\ |2\rangle \end{bmatrix} \tag{9.50}$$

We can also do the inverse:

$$\begin{bmatrix} |1\rangle \\ |2\rangle \end{bmatrix} = U^{-1} \begin{bmatrix} |-\rangle \\ |+\rangle \end{bmatrix} = \begin{bmatrix} \cos\theta/2 & \sin\theta/2 \\ -\sin\theta/2 & \cos\theta/2 \end{bmatrix}^{-1} \begin{bmatrix} |-\rangle \\ |+\rangle \end{bmatrix} \tag{9.51}$$

Definition 9.4.2. A matrix is **unitary** if its Hermitian adjoint is also its inverse:

$$U^\dagger U = UU^\dagger = I \tag{9.52}$$

Unitary operators (and hence unitary matrices) preserve the inner product i.e., they preserve the length and angles between two vectors. This reinforces the parameterisation of the basis change as a rotation from the uncoupled basis set to the coupled basis set. Unitary operators have an important place in quantum mechanics, for example in the time evolution operator $e^{-i\hat{H}t/\hbar}$ we saw earlier. In quantum computing, quantum logic gates are unitary operators.

9.5 General Driven 2-level system

We now consider a system where we can control the transitions between states. Consider a laser interacting with an atomic transition. We can split the Hamiltonian for this total system into a time-independent Hamiltonian $\hat{H}_0$ (the atomic transition) plus a time-dependent *perturbation* $\hat{V}(t)$ (the laser). You will need to know Time-Dependent Perturbation theory to understand the rest of this section.

We write $\hat{H} = \hat{H}_0 + \hat{V}(t)$. Now, ignore the potential for now. We model the atom much like our ammonia molecule with a ground state and excited state well-separated in energy so

$$\hat{H}_0 = \frac{-\epsilon}{2} |g\rangle\langle g| + \frac{\epsilon}{2} |e\rangle\langle e| \tag{9.53}$$

Since $|g\rangle, |e\rangle$ form a complete orthonormal basis we have the matrix representation be

$$\hat{H}_0 \doteq \begin{bmatrix} -\epsilon/2 & 0 \\ 0 & \epsilon/2 \end{bmatrix} \tag{9.54}$$

where the two states $|g\rangle$ and $|e\rangle$ are (energy) eigenstates of this Hamiltonian and are characterized by the **transition frequency** $\omega_0 = \epsilon/\hbar$

9.5.1 Applying a perturbation

We now excite the atom with an oscillating electric field $\hat{V}(t) = \hat{V}_0 \cos\omega t$ with $\hat{V}_0 = -\mathbf{d}\cdot\mathbf{E}_0$ where $\mathbf{d}$ is the dipole moment and $\mathbf{E}_0$ the electric field polarisation of the laser field. In this section, we make use of the **dipole approximation**, where wavelength of radiation is much larger than atom size so we can treat the atom as a point. This is valid for UV light and longer.

First, we show an important state of the dipole moment

Lemma 9.5.1. *The dipole moment is odd under parity exchange, i.e.* $\mathbf{d}(x) = -\mathbf{d}(-x)$

This should be clear because reversing the direction of the dipole moment is the same as mirroring the entire space it is in. A dipole pointing 'backwards' is the opposite of a dipole pointing 'forwards'.

Consequently, we need to find the matrix representing $\hat{V}$. We use our formalism in Eq. (9.21) setting $\hat{O} = \hat{V}(t)$. Observe that the expectation values $\langle e|\hat{V}|e\rangle = \langle g|\hat{V}|g\rangle = 0$ because the integral of an odd function over all space is 0 (use the integral definition of an expectation value if you aren't convinced). Therefore the only terms that remain are the off-diagonal terms. The full Hamiltonian is then

$$\hat{H} = \begin{bmatrix} -\epsilon/2 & 0 \\ 0 & \epsilon/2 \end{bmatrix} + \begin{bmatrix} 0 & V_0\cos\omega t \\ V_0^*\cos\omega t & 0 \end{bmatrix} \tag{9.55}$$

with $V_0 = \langle e|\hat{V}_0|g\rangle = \langle g|\hat{V}_0^*|e\rangle^*$

9.5.2 Rotating wave approximation

We now require the Schrödinger equation. Recall any 2 level state can be written as $|\psi(t)\rangle = c_g(t)\,|g\rangle + c_e(t)\,|e\rangle$

$$i\hbar\frac{d}{dt}\begin{bmatrix} c_g(t) \\ c_e(t) \end{bmatrix} = \begin{bmatrix} -\epsilon/2 & V_0\cos\omega t \\ V_0^*\cos\omega t\exp(-i\phi) & \epsilon/2 \end{bmatrix}\begin{bmatrix} c_g(t) \\ c_e(t) \end{bmatrix} \tag{9.56}$$

Now, in the final solution, we will have 2 contributions to the time-dependence: the phase factor $e^{-i\hat{H}_0 t/\hbar}$ from the atom and unperturbed Hamiltonian, as well as time-dependence from the perturbation itself. The traditional method to solving the TDSE in this case is to eliminate the exponential phase factors by a transform into the so-called **interaction picture**.

Therefore for a state $|\psi\rangle$:

In the Schrödinger picture

$$|\psi(t)\rangle = \sum_n c_n(t)\,|n\rangle \tag{9.57}$$

so c_n is the amplitude in the Schrödinger picture.

In the Interaction picture

$$|\psi(t)\rangle = \sum_n a_n(t)e^{-i\hat{H}_0 t/\hbar}\,|n\rangle = \sum_n a_n(t)e^{-iE_n t/\hbar}\,|n\rangle \tag{9.58}$$

So a_n is the amplitude in the interaction picture.

Remark. If $\hat{V} = 0$ then $a_n(t)$ becomes constant as $\hat{H} = \hat{H}_0$ so each state evolves at its characteristic frequency $E_n/\hbar$. By rewriting the amplitudes in the interaction picture, it is clear $a_n(t) \neq 0 \iff \hat{V} \neq 0$, i.e. an interaction has to exist for this to make sense.

Writing our amplitudes in the interaction picture we get

$$c_g = a_g(t)e^{-i\hat{H}_0 t/\hbar}\left|g\right\rangle = a_g(t)e^{i\epsilon t/2\hbar}\left|g\right\rangle \tag{9.59}$$

$$c_e = a_e(t)e^{-i\hat{H}_0 t/\hbar}\left|e\right\rangle = a_e(t)e^{-i\epsilon t/2\hbar}\left|e\right\rangle \tag{9.60}$$

(identical to Eq. (7.10)) therefore to convert between the 2 amplitudes we use a matrix

$$\begin{bmatrix} c_g(t) \\ c_e(t) \end{bmatrix} = \begin{bmatrix} \exp(i\epsilon t/2\hbar) & 0 \\ 0 & \exp(-i\epsilon t/2\hbar) \end{bmatrix} \begin{bmatrix} a_g(t) \\ a_e(t) \end{bmatrix} \tag{9.61}$$

A lot of things are gonna happen

1. Set $\omega_0 = \epsilon/\hbar = (E_g - E_e)/\hbar$
2. Write $V_0 \cos\omega t = \frac{V_0}{2}(e^{-i\omega t} + e^{-i\omega t})$
3. Substitute Eq. (9.61) into Eq. (9.56)

This gives us the definitely long matrix equation

$$i\hbar\frac{d}{dt}\begin{bmatrix} a_g(t)e^{i\omega_0 t/2} \\ a_e(t)e^{-i\omega_0 t/2} \end{bmatrix} = \begin{bmatrix} -\hbar\omega_0/2 & \frac{V_0}{2}\left(e^{-i\omega t} + e^{-i\omega t}\right) \\ \frac{V_0^*}{2}\left(e^{-i\omega t} + e^{-i\omega t}\right) & \hbar\omega_0/2 \end{bmatrix} \begin{bmatrix} a_g(t)e^{i\omega_0 t/2} \\ a_e(t)e^{-i\omega_0 t/2} \end{bmatrix} \tag{9.62}$$

We can diagonalise the matrix so that the leading diagonal is just full of zeros. This is a fairly long process which will be detailed shortly. In summary, it is product rule, multiplication of exponentials and collecting terms. You can skip to Eq. (9.64).

Product rule on the LHS of the above yields

$$i\hbar\left[\frac{d}{dt}\begin{bmatrix} a_g(t) \\ a_e(t) \end{bmatrix}\begin{pmatrix} \exp\left(i\omega_0 t/2\right) \\ \exp\left(-i\omega_0 t/2\right) \end{pmatrix} + \frac{i\omega_0}{2}\begin{pmatrix} a_g(t)\exp\left(i\omega_0 t/2\right) \\ -a_e(t)\exp\left(-i\omega_0 t/2\right) \end{pmatrix}\right]$$

Explicitly multiplying out the exponentials on the RHS yields

$$\begin{bmatrix} -\frac{\hbar\omega_0}{2}\exp\left(i\omega_0 t/2\right) & \frac{\hat{V}_0}{2}\exp\left(-i\omega_0 t/2\right)\left[\exp(i\omega t) + \exp(-i\omega t)\right] \\ \frac{\hat{V}_0^*}{2}\left[\exp(i\omega t) + \exp(-i\omega t)\right]\exp\left(i\omega_0 t/2\right) & \frac{\hbar\omega_0}{2}\exp\left(-i\omega_0 t/2\right) \end{bmatrix} \tag{9.63}$$

Considering the top row only, we now have

$$i\hbar\tfrac{da_g(t)}{dt}\exp\left(i\omega_0 t/2\right) - \tfrac{\hbar\omega_0}{2}a_g(t)\exp\left(i\omega_0 t/2\right) = \\ -\tfrac{\hbar\omega_0}{2}a_g(t)\exp\left(i\omega_0 t/2\right) + \tfrac{\hat{V}_0}{2}\cos(\omega t)\exp\left(-i\omega_0 t/2\right)a_e(t)$$

The second and third terms cancel. Dividing through by $\exp\left(i\omega_0 t/2\right)$ yields

$$i\hbar\frac{da_g(t)}{dt} = +\frac{\hat{V}_0}{2}\left[\exp(i\omega t) + \exp(-i\omega t)\right]\exp\left(-i\omega_0 t\right)a_e(t)$$

Considering the bottom row only, we have

$$i\hbar\tfrac{da_e(t)}{dt}\exp\left(-i\omega_0 t/2\right) + \tfrac{\hbar\omega_0}{2}a_e(t)\exp\left(-i\omega_0 t/2\right) = \\ \tfrac{\hat{V}_0^*}{2}\cos(\omega t)a_g(t)\exp\left(i\omega_0 t/2\right) + \tfrac{\hbar\omega_0}{2}\exp\left(-i\omega_0 t/2\right)a_e(t)$$

The second and third terms cancel. Dividing through by $\exp\left(-i\omega_0 t/2\right)$ yields

$$i\hbar\frac{da_e(t)}{dt} = +\frac{\hat{V}_0^*}{2}\left[\exp(i\omega t) + \exp(-i\omega t)\right]\exp\left(i\omega_0 t\right)a_g(t)$$

We arrive at the system of equations

$$i\hbar\frac{d}{dt}\begin{bmatrix}a_g(t)\\a_e(t)\end{bmatrix}=\begin{bmatrix}0 & \begin{array}{c}\frac{V_0}{2}\left[\exp\left(-i\left(\omega+\omega_0\right)t\right)\right.\\ \left.+\exp\left(i\left(\omega-\omega_0\right)t\right)\right]\end{array}\\ \begin{array}{l}\frac{V_0^*}{2}\left[\exp\left(i\left(\omega+\omega_0\right)t\right)\right.\\ \left.+\exp\left(-i\left(\omega-\omega_0\right)t\right)\right]\end{array} & 0\end{bmatrix}\begin{bmatrix}a_g(t)\\a_e(t)\end{bmatrix} \tag{9.64}$$

Taking $V_0\in\mathbb{R}\implies V_0=V_o^*$ assume $V_0\ll\omega_0$, i.e. interaction is weak compared to transition frequency, and we are interested on the timescales of response which scale $\sim 1/V_0$. On these timescales we may neglect those terms which oscillate at frequency $\omega+\omega_0$, since they will average to zero: dropping these terms constitutes the **Rotating Wave Approximation**.

Writing $\Delta=\omega-\omega_0$ and applying the rotating wave approximation gives

$$i\hbar\frac{d}{dt}\begin{bmatrix}a_g(t)\\a_e(t)\end{bmatrix}=\frac{V_0}{2}\begin{bmatrix}0 & \exp\left(-i\Delta t\right)\\ \exp\left(i\Delta t\right) & 0\end{bmatrix}\begin{bmatrix}a_g(t)\\a_e(t)\end{bmatrix} \tag{9.65}$$

9.5.3 Dynamics of a driven two-level system

On-resonance driving

This is when the driving frequency matches the transition frequency, i.e. $\Delta=0$. Then our system of equations greatly simplifies to

$$i\hbar\frac{d}{dt}\begin{bmatrix}a_g(t)\\a_e(t)\end{bmatrix}=\frac{V_0}{2}\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix}\begin{bmatrix}a_g(t)\\a_e(t)\end{bmatrix} \tag{9.66}$$

Dividing by $i\hbar$ on both sides we now have 2 coupled ODEs. Using theory from ODEs, we must first solve for the eigenvectors and then form the general solution. Set $V_0/\hbar=\Omega/2$. Then the eigenvalues are obtained from the secular equation which is

$$\det\begin{bmatrix}-\lambda & -\frac{i\Omega}{4}\\ -\frac{i\Omega}{4} & -\lambda\end{bmatrix}=0\implies\lambda_\pm=\mp\Omega/2 \tag{9.67}$$

the normalised eigenvectors are then

$$\mathbf{c}_+=\frac{1}{\sqrt{2}}\begin{bmatrix}1\\1\end{bmatrix}\qquad\qquad \mathbf{c}_-=\frac{1}{\sqrt{2}}\begin{bmatrix}1\\-1\end{bmatrix} \tag{9.68}$$

The general solution is therefore

$$|\phi(t)\rangle=c_0^0e^{-i\Omega t/2}\begin{bmatrix}1\\1\end{bmatrix}+c_1^0e^{i\Omega t/2}\begin{bmatrix}1\\-1\end{bmatrix} \tag{9.69}$$

with c_0^0,c_1^0 constants determined from initial conditions (we absorb $1/\sqrt{2}$ into those constants). Assuming the initial state is the ground state $|g\rangle$ with $c_0^0=c_1^0=1/2$ then

$$|\phi(t)\rangle=\frac{1}{2}\begin{bmatrix}e^{-i\Omega t/2}+e^{i\Omega t/2}\\ e^{-i\Omega t/2}-e^{i\Omega t/2}\end{bmatrix}=\begin{bmatrix}\cos(\Omega t/2)\\-i\sin(\Omega t/2)\end{bmatrix} \tag{9.70}$$

However we are still in the *interaction picture*, we solved everything in terms of the amplitudes a. We now need to return to the Schrödinger picture (the lab frame if you will) by multiplying $|\phi\rangle$ by the matrix in Eq. (9.61) and we get

$$|\psi(t)\rangle=\begin{bmatrix}e^{i\epsilon t/2\hbar}\cos(\Omega t/2)\\-ie^{-i\epsilon t/2\hbar}\sin(\Omega t/2)\end{bmatrix} \tag{9.71}$$

The system therefore oscillates between $|g\rangle$ and $|e\rangle$ at a frequency Ω which is proportional to the amplitude of the laser's electric field (*not* its intensity). By turning the laser irradiation on and off, we can choose particular linear combinations of the two states involved. The relative populations of $|g\rangle$ and $|e\rangle$ are given by

$$P_g(t)-P_e(t)=\cos^2(\Omega t/2)-\sin^2(\Omega t/2)=\cos(\Omega t) \tag{9.72}$$

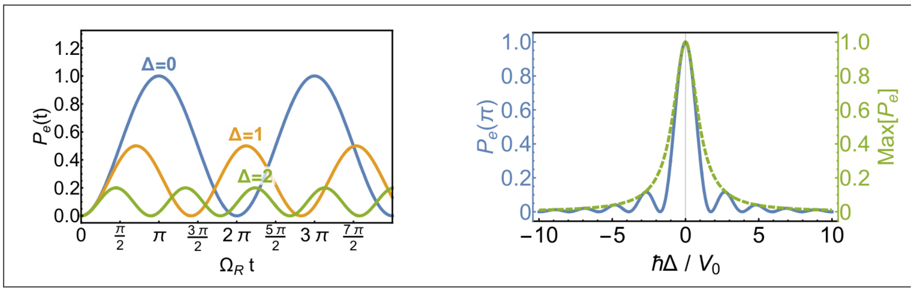

Figure 9.2: Probability of finding the system in state $|e\rangle$ for different Δ as a function of time (left) and different detunings at fixed time (right) for $V_0 = \hbar = 1$

Definition 9.5.1. A pulse of length $t = \pi/\Omega$ which transfers the ground state population into the excited state (i.e., population inversion), is called a π-**pulse**.

Therefore a π pulse will transform the population $|g\rangle \leftrightarrow |e\rangle$. If we however have a pulse exactly half as long, so $t = \pi/(2\Omega)$ then the wavefunction lies exactly halfway between $|g\rangle, |e\rangle$, which means a **coherent** superposition of $|g\rangle, |e\rangle$ and

$$\left|\psi\left(t = \frac{\pi}{2\Omega}\right)\right\rangle = \frac{|g\rangle - i\,|e\rangle}{\sqrt{2}} \tag{9.73}$$

General case

We now assume $\Delta \neq 0$. This is **off-resonance driving**. We take our linear ODEs in Eq. (9.66) and choose to eliminate $a_g(t)$, i.e. we rearrange one of the ODEs and sub it into the other:

$$\frac{d^2 a_e(t)}{dt^2} - i\Delta \frac{da_e(t)}{dt} + \frac{|V_0|^2}{4\hbar^2} a_e(t) = 0 \tag{9.74}$$

We now have a second-order linear ODE purely in terms of $a_e(t)$ and known constants which suspiciously looks like the ODE for a damped harmonic oscillator - in fact it is! We can therefore skip straight to the general solution (if it was necessary you would be given this in the exam because the timings are too short) which is

$$a_e(t) = e^{i\Delta t/2} \left(A\cos(\Omega_R t) + B\sin(\Omega_R t)\right) \tag{9.75}$$

where we define the **Rabi frequency** as

$$\boxed{\Omega_R = \frac{1}{2}\sqrt{\Delta^2 + \frac{V_0^2}{\hbar^2}}} \tag{9.76}$$

Using the initial condition $P_e(0) = 0, P_g(0) = 1$ - which is the initial condition of starting entirely at the ground state $|g\rangle$ the probability of measuring the atom in its ground and excited states are

$$P_e(t) = |a_e(t)|^2 = \frac{V_0^2}{V_0^2 + \Delta^2\hbar^2} \sin^2\left(\Omega_R t\right) \tag{9.77}$$

$$P_g(t) = 1 - P_e(t). \tag{9.78}$$

As in the $\Delta = 0$ (on resonance) case, the amplitude oscillates between $|g\rangle$ and $|e\rangle$ at a frequency related to the amplitude of the driving field. However, the (Rabi) frequency of oscillation and the peak inversion probability are now affected by the detuning Δ, i.e. as Δ increases, the resulting oscillations get more out of phase and more frequent. See left of Figure 9.2.

Transfer of population from $|g\rangle \rightarrow |e\rangle$ is maximised when $\Delta = 0$, i.e. when the system is on resonance, i.e. when the frequency of the input field matches the energy splitting of the two states). When on-resonance, the population is transferred **coherently** from $|g\rangle$ to $|e\rangle$ with a frequency $\boxed{V_0/\hbar}$.

Off-resonance, the efficiency of the drive between the two states *decreases*, see right of Figure 9.2. Additionally, the frequency of the oscillations increases as the detuning increases.

Comparison to perturbation theory results

Refer to Eq. (7.26) which is the time-dependent perturbation theory calculation for the transition probability between states $n \to p$.

$$P^{(1)}_{n\to p}(\tau) = \frac{|V_{pn}|^2}{\hbar^2}\frac{\sin^2(\frac{\omega_{pn}\tau}{2})}{\omega_{pn}^2}.$$

The probability for $|g\rangle \to |e\rangle$ as we derived is

$$P_e(t) = |a_e(t)|^2 = \frac{V_0^2}{V_0^2+\Delta^2\hbar^2}\sin^2\left(\frac{1}{2}t\sqrt{\Delta^2+\frac{V_0^2}{\hbar^2}}\right) \tag{9.79}$$

The perturbation theory result can be recovered from the Rabi model in 2 ways

- If $V_0/\hbar \ll \Delta$.
- Or if the timescale is really small such that we can Taylor expand Ω_R to its first term which is about $\Omega_R \approx \Delta$.

For large V_0 or small Δ, the perturbation approach is no longer valid.

9.6 Bloch Sphere Visualisation

We study the spin-1/2 particle in a magnetic field. The unit normal in spherical coordinates

$$\mathbf{n} = (n_x, n_y, n_z) = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta) \tag{9.80}$$

where θ is the angle to the z-axis and ϕ is the azimuth.

9.6.1 Spin and Pauli matrices

The Pauli matrices are

$$\hat{\sigma}_1 = \hat{\sigma}_x = \begin{bmatrix}0 & 1\\1 & 0\end{bmatrix} \tag{9.81}$$

$$\hat{\sigma}_2 = \hat{\sigma}_y = \begin{bmatrix}0 & -i\\i & 0\end{bmatrix} \tag{9.82}$$

$$\hat{\sigma}_3 = \hat{\sigma}_z = \begin{bmatrix}1 & 0\\0 & -1\end{bmatrix} \tag{9.83}$$

Remark. These 3 matrices (along with the identity matrix if you really want to) span the space of observables of the complex two-dimensional Hilbert space.

Some other properties of Pauli matrices are

- $\hat{\sigma}_i^2 = 1$
- The commutator $[\hat{\sigma}_i, \hat{\sigma}_j] = 2i\epsilon_{ijk}\hat{\sigma}_k$
- $\mathrm{tr}(\hat{\sigma}_i) = 0$

We can write the **spin operator** as

$$\mathbf{S} = (\hat{S}_x, \hat{S}_y, \hat{S}_z) = \frac{\hbar}{2}\boldsymbol{\sigma} \qquad\qquad \boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z) \tag{9.84}$$

(Yes, we have a vector of matrices). The spin in direction of **n** is calculated by dot product:

$$\widehat{S}_{\mathbf{n}} = \mathbf{n}\cdot\mathbf{S} = n_x\hat{S}_x + n_y\hat{S}_y + n_z\hat{S}_z = \frac{\hbar}{2}\mathbf{n}\cdot\boldsymbol{\sigma} \tag{9.85}$$

9.6.2 Eigenvectors and Eigenvalues

Lemma 9.6.1. *The spin operator in direction* **n** *is Hermitian*

Lemma 9.6.2. *If* **n** *is one of the cardinal directions* x, y, z, *then the eigenvalues are* $\pm\hbar/2$. *In fact, the eigenvalues are* $\pm\hbar/2$ *for any unit vector* **n**

This lemma corresponds to an important physical principle

For a free particle in space, there are no preferred directions

Proof. If you substitute in the Pauli matrices, an explicit matrix representation of $\hat{S}_{\mathbf{n}}$ is

$$\hat{S}_{\mathbf{n}} = \frac{\hbar}{2}\begin{bmatrix}\cos\theta & e^{-i\phi}\sin\phi\\ e^{i\phi}\sin\theta & -\cos\theta\end{bmatrix} \tag{9.86}$$

Finding the eigenvalues is again by way of solving the secular determinant:

$$\begin{vmatrix}\frac{\hbar}{2}\cos\theta-\lambda & \frac{\hbar}{2}\sin\theta\exp(-i\phi)\\ \frac{\hbar}{2}\sin\theta\exp(i\phi) & -\frac{\hbar}{2}\cos\theta-\lambda\end{vmatrix} = -\frac{\hbar^2}{4}\left(\cos^2\theta+\sin^2\theta\right)+\lambda^2 = 0 \tag{9.87}$$

which proves the lemma ☐

So, we obtain eigenvalues for 2 directions $\lambda_\pm = \pm\hbar/2$. From now on, we define

Definition 9.6.1. The state $|\pm_{\mathbf{n}}\rangle$ as the eigenvectors for $\lambda_\pm$ in the direction of **n**.

By convention, spin states are described in the z basis so $|\pm_{\mathbf{z}}\rangle := |\pm\rangle$ so for an arbitrary direction **n** we may write

$$|+_{\mathbf{n}}\rangle = \alpha_+|+\rangle + \beta_+|-\rangle = \begin{bmatrix}\alpha_+\\ \beta_+\end{bmatrix} \tag{9.88}$$

$$|-_{\mathbf{n}}\rangle = \alpha_-|+\rangle + \beta_-|-\rangle = \begin{bmatrix}\alpha_-\\ \beta_-\end{bmatrix} \tag{9.89}$$

Therefore we have

$$\frac{\hbar}{2}\begin{bmatrix}\cos\theta & e^{-i\phi}\sin\theta\\ e^{i\phi}\sin\theta & -\cos\theta\end{bmatrix}\begin{bmatrix}\alpha_\pm\\ \beta_\pm\end{bmatrix} = \pm\frac{\hbar}{2}\begin{bmatrix}\alpha_\pm\\ \beta_\pm\end{bmatrix} \tag{9.90}$$

We only need one of the signs, lets take the +. Multiplying out the first row gives

$$\alpha_+(1-\cos\theta) = \beta_+e^{-i\phi}\sin\theta \tag{9.91}$$

Using the trig identities $1-\cos\theta = 2\sin^2(\theta/2)$ and $\sin\theta = 2\sin(\theta/2)\cos(\theta/2)$ we obtain the coefficients

$$\alpha_+ = \cos(\theta/2) \qquad\qquad \beta_+ = e^{i\phi}\sin(\theta/2) \tag{9.92}$$

which tells us

$$|+_{\mathbf{n}}\rangle = \cos\frac{\theta}{2}|+\rangle + e^{i\phi}\sin\frac{\theta}{2}|-\rangle \tag{9.93}$$

$$|-_{\mathbf{n}}\rangle = -e^{i\phi}\sin\frac{\theta}{2}|+\rangle + \cos\frac{\theta}{2}|-\rangle \tag{9.94}$$

Lemma 9.6.3. *The eigenvectors* $|\pm_{\mathbf{n}}\rangle$ *are orthogonal*

Proof. It is a one-liner:

$$\langle +_{\mathbf{n}} \mid -_{\mathbf{n}} \rangle = -\sin\frac{\theta}{2}\exp(-i\phi)\cos\frac{\theta}{2} + \cos\frac{\theta}{2}\exp(-i\phi)\sin\frac{\theta}{2} = 0 \tag{9.95}$$

□

Lemma 9.6.4. *For any eigenstate* $|+_{\mathbf{n}}\rangle$, *then*

$$|+_{\mathbf{n}}\rangle = |-_{-\mathbf{n}}\rangle \tag{9.96}$$

Proof. Begin with the eigenstate $|+_{\mathbf{n}}\rangle$ which you could say is projected in the 'forwards' direction, i.e. in the direction of $\mathbf{n}$. The eigenvector $|+_{-\mathbf{n}}\rangle$ is the eigenvector which is projected in the $-\mathbf{n}$ direction. Therefore $|-_{-\mathbf{n}}\rangle$ is the eigenvector in the $\mathbf{n}$ direction which is exactly $|+_{\mathbf{n}}\rangle$. □

Combining these 2 lemmas produces the important principle

Orthogonal spin states do not correspond to orthogonal directions.

9.6.3 The Bloch Sphere

Definition 9.6.2. A **qubit** is the basic unit of processing in quantum computing and has 2 quantum states.

No matter how you make a qubit, all of them follow the same maths which we have been doing. It is important to understand what these states look like in an abstract sense. We can parameterise a general two-level state in a given orthonormal basis (e.g. $|0\rangle, |1\rangle$ as is used in quantum computing) by

$$|\phi\rangle = \alpha|0\rangle + \beta|1\rangle \tag{9.97}$$

with $\alpha, \beta \in \mathbb{C}$. Since the coefficients are complex, we need 4 real parameters such that $\alpha = a + ib, \beta = c + id$ with $a, b, c, d \in \mathbb{R}$. However any complex number can be written in exponential form so we write

$$\begin{aligned} |\psi\rangle &= r_0 e^{i\phi_0}|0\rangle + r_1 e^{i\phi_1}|1\rangle && (9.98) \\ &= e^{i\phi_0}\left[r_0|0\rangle + r_1 e^{-i(\phi_1 - \phi_0)}|1\rangle\right] && (9.99) \end{aligned}$$

As before, we see $e^{-i\phi_0}$ is a global phase factor multiplying a state, so we can get rid of it since global phase is unobservable. Consequently we just absorb $\phi = \phi_1 - \phi_0$. Similarly, note $r_0^2 + r_1^2 = 1$ and we can parameterise by $r_0 = \cos(\theta/2)$ and $r_1 = \sin(\theta/2)$ so

$$|\psi\rangle = \cos\frac{\theta}{2}|0\rangle + e^{i\phi}\sin\frac{\theta}{2}|1\rangle \tag{9.100}$$

What we have effectively done is turn our two-level system into something that can be visualised like a 3D sphere! We take ϕ to be the azimuth, θ the angle from the z-axis, and we know that the norm of $|\psi\rangle$ is 1 (because of the normalisation condition on the coefficients), so all our states lie on the **unit sphere**! We call this unit sphere the **Bloch sphere**, shown in Figure 9.3.

We see that the 2 basis states are diametrically opposite each other, aligned along the z-axis (by convention), showing that orthogonal states do not correspond to orthogonal directions. In 2D, the states are in orthogonal directions. Any normalised superposition is a point on this sphere, with coordinates given by the wavefunction coefficients.

By convention, the lower energy state (if it exists) is assigned to $|0\rangle$ and the higher energy to $|1\rangle$. Just make sure to check the exam question if they specify this.

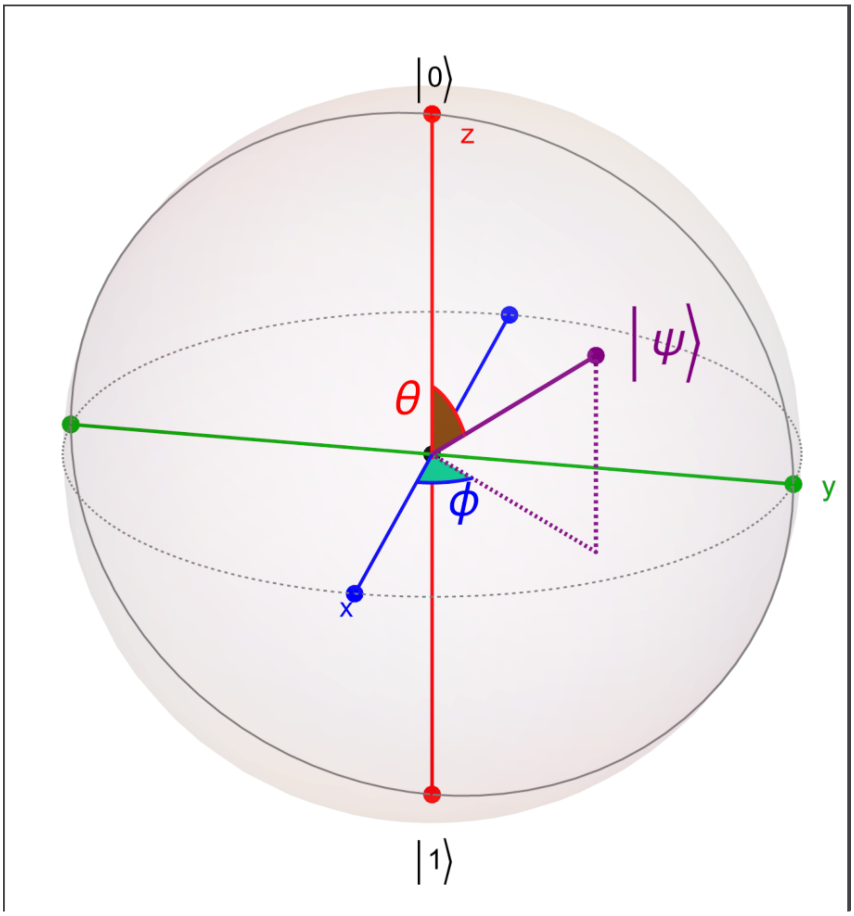

Figure 9.3: The Bloch sphere (reproduced from lecture notes)

In an electron system, the lower energy state is spin-down, whilst the higher energy is spin up.

Another thing to remember is that bases of Hilbert space are not unique! Work in the basis state that makes the maths the easiest - you can always convert between them. Don't make life hard for yourselves!

9.6.4 Decomposition of 2×2 Hermitian matrices

Earlier, we said in a remark that the Pauli matrices plus identity span the 2D Hilbert space. Indeed this is equivalent to saying any 2×2 Hermitian matrix can be written as

$$\hat{A} = n_0 I + \mathbf{n} \cdot \boldsymbol{\sigma} \tag{9.101}$$

which we got from deriving the spin operator.

The eigenvalues are

$$n_0 \pm |\mathbf{n}| = n_0 \pm \sqrt{n_1^2 + n_2^2 + n_3^2} \tag{9.102}$$

We derived earlier the parameterisation of $\hat{S}_{\mathbf{n}}$ into θ, ϕ. Comparing it to the matrix directly above, we see the exponentials $e^{\pm i\phi}$ in the off-diagonal elements acts as a phase. This corresponds to **rotations in the $x - y$ plane**.

9.6.5 Rotation matrices

Rotation matrices are a type of unitary matrix. We can construct them directly from the Pauli matrices. This is also a problem on the problem sheet.

Proposition 9.6.1. *The rotation by angle θ around each axis x, y, z is given by*

$$R_x(\theta) = \exp\left(-\frac{i\sigma_x\theta}{2}\right) = \begin{bmatrix} \cos\theta/2 & -i\sin\theta/2 \\ -i\sin\theta/2 & \cos\theta/2 \end{bmatrix} \tag{9.103}$$

$$R_y(\theta) = \exp\left(-\frac{i\sigma_y\theta}{2}\right) = \begin{bmatrix} \cos\theta/2 & \sin\theta/2 \\ -\sin\theta/2 & \cos\theta/2 \end{bmatrix} \tag{9.104}$$

$$R_z(\theta) = \exp\left(-\frac{i\sigma_z\theta}{2}\right) = \begin{bmatrix} \cos\theta/2 - i\sin\theta/2 & 0 \\ 0 & i\sin\theta/2 + \cos\theta/2 \end{bmatrix} \tag{9.105}$$

For an arbitrary direction $\mathbf{n} = (n_x, n_y, n_z)$ *we have*

$$R_{\mathbf{n}}(\theta) = \begin{bmatrix} \cos\left(\frac{\theta}{2}\right) - in_z\sin\left(\frac{\theta}{2}\right) & (-in_x - n_y)\sin\left(\frac{\theta}{2}\right) \\ (-in_x + n_y)\sin\left(\frac{\theta}{2}\right) & \cos\left(\frac{\theta}{2}\right) + in_z\sin\left(\frac{\theta}{2}\right) \end{bmatrix} \tag{9.106}$$

9.7 Magnetic Resonance

Spectroscopy is a fundamental area of physics which has allowed us to understand swathes of quantum and condensed matter etc. What we have shown is that our formalism maps beautifully onto any $S = 1/2$ or $I = 1/2$ (I is the nuclear spin). When we look at magnetic resonance, we consider what happens to an electron in a magnetic field. Indeed, it is time to bring back the Zeeman effect.

We know that the Hamiltonian for an electron placed in a static magnetic field is described by the coupling between its magnetic diopole moment and the magnetic field so

$$\hat{H}_{\text{Zeeman}} = -\boldsymbol{\mu} \cdot \mathbf{B} \tag{9.107}$$

For a particle of charge q, rest mass m, the magnetic dipole moment is given by

$$\boldsymbol{\mu} = g\frac{q\hbar}{2m}\mathbf{S} \tag{9.108}$$

For an electron, this reduces to

$$\boldsymbol{\mu} = g\mu_B\mathbf{S} = -\gamma\mathbf{S} \tag{9.109}$$

with μ_B the **Bohr magneton** and γ the **gyromagnetic ratio**. All constants will be given in the exam so you don't need to memorise the actual values. Maybe remember what they are in terms of other constants if you feel fancy.

The full free electron Hamiltonian is

$$\hat{H}_{\text{Zeeman}} = \gamma\mathbf{B}^T \cdot \hat{S} \tag{9.110}$$

where we have written it like this because remember, $\hat{S}$ is the **vector of Pauli matrices** and $\hat{H}$ will be a matrix. Remember that $\mathbf{B} = \begin{bmatrix} B_x \\ B_y \\ B_z \end{bmatrix}$ so $\mathbf{B}^T = (B_x, B_y, B_z)$. Hence:

$$\hat{H}_{\text{Zeeman}} = \gamma(B_x\hat{S}_x + B_y\hat{S}_y + B_z\hat{S}_z) \tag{9.111}$$

We now place the electron into a *static* magnetic field $\mathbf{B}_0 = B_0\mathbf{z}$ and then *apply* a circularly-polarised magnetic field of strength B_1 perpendicular to the static field (so it covers x, y) and our overall magnetic field is

$$\mathbf{B}(t) = B_0\mathbf{z} + B_1(\mathbf{x}\cos(\omega t + \phi) - \mathbf{y}\sin(\omega t + \phi)) \tag{9.112}$$

Note this field oscillates clockwise (when looking down towards positive z). Substituting this field into the electron Hamiltonian yields

$$\hat{H}_{\text{Zeeman}} = \gamma \left(B_0 \hat{S}_z + B_1 \left(\cos(\omega t + \phi)\hat{S}_x - \sin(\omega t + \phi)\hat{S}_y \right) \right) \tag{9.113}$$

We will use this Hamiltonian for the rest of the chapter

9.7.1 Into the rotating frame

Last time we transformed from the Schrödinger picture into the so-called interaction picture, which let us separate the Hamiltonian into some $\hat{H}_0$ (due to the bare atom) plus $\hat{V}(t)$ (due to the time-dependent magnetic field). We did this by applying a unitary transformation

$$\hat{U}_I = e^{-i\hat{H}_0 t/\hbar} \qquad\qquad |\psi_I\rangle = \hat{U}_I^\dagger |\psi_S\rangle \tag{9.114}$$

i.e., we did a unitary transformation into a frame which rotates at the same frequency as the bare atom. However, we still had remaining explicit time dependency due to the driving field.

We can get rid of this issue by instead transforming the *entire Hamiltonian* into a frame which rotates with the driving field at frequency ωt. We therefore need to go from $\hat{H}_S \to \hat{H}_{\text{RF}}$ and so $|\psi_S\rangle \to |\psi_{\text{RF}}\rangle$. This eliminates the Larmor precession.

In particular, we will make the unitary transformation

$$\hat{U}_{\text{RF}} = \exp\left(+i\frac{i\omega t}{2}\hat{\sigma}_z \right) \tag{9.115}$$

Note that the Hermitian conjugate is the complex-conjugate transpose, hence put a negative in the exponential and note that the Pauli matrix $\hat{\sigma}_z$ is symmetric and

$$\hat{U}_{\text{RF}}^\dagger = \exp\left(-i\frac{i\omega t}{2}\hat{\sigma}_z \right) \tag{9.116}$$

Theorem 9.7.1. *Prove*

$$\hat{H}_{\text{RF}} = \hat{U}_{\text{RF}}^\dagger \hat{H}_S \hat{U}_{\text{RF}} + i\hbar \frac{\partial \hat{U}_{\text{RF}}^\dagger}{\partial t}\hat{U}_{\text{RF}} = \hat{U}_{\text{RF}}^\dagger \hat{H}_S \hat{U}_{\text{RF}} - \frac{\hbar\omega}{2}\hat{\sigma}_z. \tag{9.117}$$

(Also a question in problem sheet)

Proof. Start with the TDSE in the RF and substitute it for $|\psi_S\rangle$ and expand using the product rule:

$$i\hbar\frac{\partial}{\partial t}|\psi_{\text{RF}}\rangle = i\hbar\frac{\partial}{\partial t}\left(\hat{U}_{\text{RF}}^\dagger(t)|\psi_S(t)\rangle \right) \tag{9.118}$$

$$= \hat{U}_{\text{RF}}^\dagger(t)\left(i\hbar\frac{\partial}{\partial t}|\psi_S(t)\rangle \right) + \left(i\hbar\frac{\partial}{\partial t}\hat{U}_{\text{RF}}^\dagger(t) \right)|\psi_S(t)\rangle \tag{9.119}$$

However notice that

$$\left(i\hbar\frac{\partial}{\partial t}|\psi_S(t)\rangle \right) = \hat{H}_S|\psi_S(t)\rangle \tag{9.120}$$

so that simplifies the expression down to

$$i\hbar\frac{\partial}{\partial t}|\psi_{\text{RF}}\rangle = \left(\hat{U}_{\text{RF}}^\dagger(t)\hat{H}_S + i\hbar\frac{\partial}{\partial t}\hat{U}_{\text{RF}}^\dagger(t) \right)|\psi_S(t)\rangle \tag{9.121}$$

However earlier we stated that $|\psi_{\text{RF}}\rangle = \hat{U}_{\text{RF}}^\dagger|\psi_S\rangle$ so since the operator is unitary we have $|\psi_S\rangle = \hat{U}_{\text{RF}}|\psi_{\text{RF}}\rangle$. We substitute this latter expression in by expanding the brackets:

$$i\hbar\frac{\partial}{\partial t}|\psi_{\text{RF}}\rangle = \left(\hat{U}_{\text{RF}}^\dagger(t)\hat{H}_S\hat{U}_{\text{RF}} + i\hbar\frac{\partial}{\partial t}\hat{U}_{\text{RF}}^\dagger(t)\hat{U}_{\text{RF}} \right)|\psi_{\text{RF}}(t)\rangle \tag{9.122}$$

The Hamiltonian is the thing in brackets and we are done. □

It is at this point some of you may wonder what does all of this maths mean. It encapsulates the idea that for a general unitary transform (of which transformation into a rotating frame is a special case), the evolution of the system depends on the evolution of the operator *and* the quantum state in question, so we must operate with both $\hat{U}_{\mathrm{RF}}$ and $\hat{U}_{\mathrm{RF}}^{\dagger}$.

Returning to our problem at hand, we use $\hat{H}_{\mathrm{Zeeman}}$ in place of $\hat{H}_S$ and we get

$$\begin{aligned}\hat{H}_{\mathrm{RF}} &= \exp\left(-i\frac{\omega t}{2}\hat{\sigma}_z\right)\left[\gamma\left(B_0\hat{S}_z + B_1\left(\cos(\omega t+\phi)\hat{S}_x - \sin(\omega t+\phi)\hat{S}_y\right)\right)\right]\exp\left(+i\frac{\omega t}{2}\hat{\sigma}_z\right) - \frac{\hbar\omega}{2}\hat{\sigma}_z \\ &= \exp\left(-i\frac{\omega t}{2}\hat{\sigma}_z\right)\left[\frac{\hbar\omega_0}{2}\hat{\sigma}_z + \frac{\hbar\Omega}{2}\left(\cos(\omega t+\phi)\hat{\sigma}_x - \sin(\omega t+\phi)\hat{\sigma}_y\right)\right]\exp\left(+i\frac{\omega t}{2}\hat{\sigma}_z\right) - \frac{\hbar\omega}{2}\hat{\sigma}_z\end{aligned} \tag{9.123}$$

where $\Omega = \gamma B_1$ and $\omega_0 = \gamma B_0$. We can simplify this expression greatly. Notice the exponentials cancel out, and we have 2 $\hat{\sigma}_z$ terms which we can absorb together:

$$\hat{H}_{\mathrm{RF}} = -\frac{\hbar\Delta}{2}\hat{\sigma}_z + \frac{\hbar\Omega}{2}\left(\cos(\omega t+\phi)\hat{\sigma}_x - \sin(\omega t+\phi)\hat{\sigma}_y\right) \tag{9.124}$$

Notice $\Delta = \omega - \omega_0$ as we saw last time. This Δ is the **detuning** of the driving field (magnetic field) from the Larmor precession of the spin. ϕ is the phase factor which rotates the field around the xy plane.

Remark. The lecture notes remove the ωt somehow from the trig inputs. No idea what maths led to that, but perhaps expanding in terms of the matrices or doing some special trick resolves it. Nonetheless the exact derivations are non-examinable as far as we can tell.

$$\hat{H}_{\mathrm{RF}} = -\frac{\hbar\Delta}{2}\hat{\sigma}_z + \frac{\hbar\Omega}{2}\left(\cos(\phi)\hat{\sigma}_x - \sin(\phi)\hat{\sigma}_y\right) \tag{9.125}$$

Now, factor out a $\hbar/2$ and remember that $\hat{\sigma}_{\mathbf{n}} = \mathbf{n}\cdot\boldsymbol{\sigma}$, i.e. $\hat{\sigma}_x = \mathbf{x}\cdot\boldsymbol{\sigma}$ and so on. Therefore we can replace all the sigmas with dot products and define a new vector $\boldsymbol{\Omega}_t$ satisfying

$$\hat{H}_{\mathrm{RF}} = \frac{\hbar}{2}\boldsymbol{\Omega}_t\cdot\boldsymbol{\sigma} \qquad\qquad \boldsymbol{\Omega}_t = -\Delta\mathbf{z} + \Omega\left(\cos(\phi)\mathbf{x} - \sin(\phi)\mathbf{y}\right) \tag{9.126}$$

We have removed all time-dependence from the Hamiltonian! Therefore our wavefunction *in the rotating frame* evolves as

$$|\psi_{\mathrm{RF}}(t)\rangle = \exp\left[-\frac{i\boldsymbol{\Omega}_t\cdot\boldsymbol{\sigma}t}{2}\right]|\psi_{\mathrm{RF}}(0)\rangle \tag{9.127}$$

Now, recall the wavefunction in Eq. (9.100). It had a phase factor $e^{i\phi}$ where ϕ caused a rotation around its Bloch sphere. Here, we have the same thing - a phase factor $\exp\left[-\frac{i\boldsymbol{\Omega}_t\cdot\boldsymbol{\sigma}t}{2}\right]$, a function of the azimuth ϕ, which causes rotations in its own Bloch sphere! The question is what axis does it rotate about? It rotates around the $\boldsymbol{\Omega}_t$ axis! We can find the unit vector characterising this axis:

$$\hat{\Omega}_{\mathrm{t}} = \frac{\boldsymbol{\Omega}_t}{|\boldsymbol{\Omega}_t|} = \frac{-\Delta\mathbf{z} + \Omega(\cos(\phi)\mathbf{x} + \sin(\phi)\mathbf{y})}{\sqrt{\Delta^2+\Omega^2}}. \tag{9.128}$$

Now, we want to solve for the evolution of our charged particle. To do this, we use the same analysis we did for the ammonia and qubit: form a matrix equation and solve. We can get the Hamiltonian directly from Eq. (9.125) and substitute in the Pauli matrices:

$$\hat{H}_{\mathrm{RF}} = \frac{\hbar}{2}\left[-\Delta\begin{bmatrix}1 & 0\\ 0 & -1\end{bmatrix} + \Omega\left(\cos(\phi)\begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix} - \sin(\phi)\begin{bmatrix}0 & -i\\ i & 0\end{bmatrix}\right)\right] \tag{9.129}$$

$$= \frac{\hbar}{2}\left[\begin{bmatrix}-\Delta & 0\\ 0 & \Delta+\end{bmatrix} + \begin{bmatrix}0 & \Omega(\cos\phi - i\sin\phi)\\ \Omega(\cos\phi + i\sin\phi) & 0\end{bmatrix}\right] \tag{9.130}$$

$$= \frac{\hbar}{2}\begin{bmatrix}-\Delta & \Omega e^{-i\phi}\\ \Omega e^{i\phi} & \Delta\end{bmatrix} \tag{9.131}$$

So now we can form our Schrödinger equation in the *rotating frame* as

$$i\hbar\frac{d}{dt}\left|\psi_{\mathrm{RF}}(t)\right\rangle = \frac{\hbar}{2}\begin{bmatrix}-\Delta & \Omega e^{-i\phi} \\ \Omega e^{i\phi} & \Delta\end{bmatrix}\left|\psi_{\mathrm{RF}}(t)\right\rangle \tag{9.132}$$

Remark. Some of you might question the fact we have 3 coordinates $\mathbf{x}, \mathbf{y}, \mathbf{z}$ but only a 2×2 Hamiltonian. The reason is because we have casted the problem in terms of 2 axes, that is the $\mathbf{z}$ axis and "stuff perpendicular to $\mathbf{z}$".

9.7.2 Visualisation of Rabi oscillations

It is time to solve the Schrödinger equation in the rotating frame in different cases, and then see what the spin vector does. Since we can choose any orthonormal bases no matter what our frame of reference is, we choose the standard $|0\rangle, |1\rangle$ bases *in the rotating frame.*

Rotating frame, on resonance

If something is *on resonance*, the driving frequency matches the natural frequency so $\Delta = 0$. The Hamiltonian is now

$$\hat{H}_{\mathrm{RF}} = \frac{\hbar}{2}\begin{bmatrix}0 & e^{-i\phi} \\ e^{i\phi} & 0\end{bmatrix} \tag{9.133}$$

Therefore the axes of precession can be chosen to be about the $\mathbf{z}$ axis since the $\Delta\mathbf{z} = 0$ in the expression for $\hat{\Omega}_t$.

We form the secular determinant

$$\begin{vmatrix}-\lambda & \frac{\hbar\Omega}{2}\exp(-i\phi) \\ \frac{\hbar\Omega}{2}\exp(i\phi) & -\lambda\end{vmatrix} = 0 \quad\Longrightarrow\quad \lambda^2 - \frac{\hbar^2\Omega^2}{4} = 0 \tag{9.134}$$

so the eigenvalues are $\lambda_\pm = \pm\frac{\hbar\Omega}{2}$. The eigenvectors are found by solving:

$$\frac{\hbar}{2}\begin{bmatrix}0 & e^{-i\phi} \\ e^{i\phi} & 0\end{bmatrix}\begin{bmatrix}\alpha_\pm \\ \beta_\pm\end{bmatrix} = \pm\frac{\hbar\Omega}{2}\begin{bmatrix}\alpha_\pm \\ \beta_\pm\end{bmatrix} \tag{9.135}$$

This produces the system of equations (cancelling out $\hbar/2$ from both sides)

$$\beta_\pm e^{-i\phi} = \pm\Omega\alpha_\pm \qquad\qquad \alpha_\pm e^{i\phi} = \pm\Omega\beta_\pm \tag{9.136}$$

We cannot forget our lovely normalisation condition

$$|\alpha_\pm|^2 + |\beta_\pm|^2 = 1$$

Taking the first system of equations and the normalisation condition leads us to

$$\alpha_\pm = \frac{1}{1+|\Omega|^2} \qquad\qquad \beta_\pm = \pm\frac{\Omega e^{i\phi}}{1+|\Omega|^2} \tag{9.137}$$

So what does this mean? It means we have rotations in the azimuth plane (due to the $e^{i\phi}$ term) about the $\hat{\Omega}_t$ axis of constant radius! Suppose $\phi = 0$. Then our axis of rotation given by Eq. (9.128) tells us we are rotating about $\mathbf{x}$ with constant radius. Now suppose that $\phi = \pi/2$. Then now we are rotating about $\mathbf{y}$. This is given by Figure 9.4.

The spin vector makes **great circle orbits** on the Bloch sphere. A great circle is the circle formed when you intersect a 2D plane through a sphere's centre - i.e. great circles are the circles of largest diameter on a sphere. We can see that a π pulse will transfer $|0\rangle \rightarrow |1\rangle$.

Suppose you stop the pulse as the vector intersects the xy plane. Then you have an coherent superposition of $|0\rangle$ and $|1\rangle$.

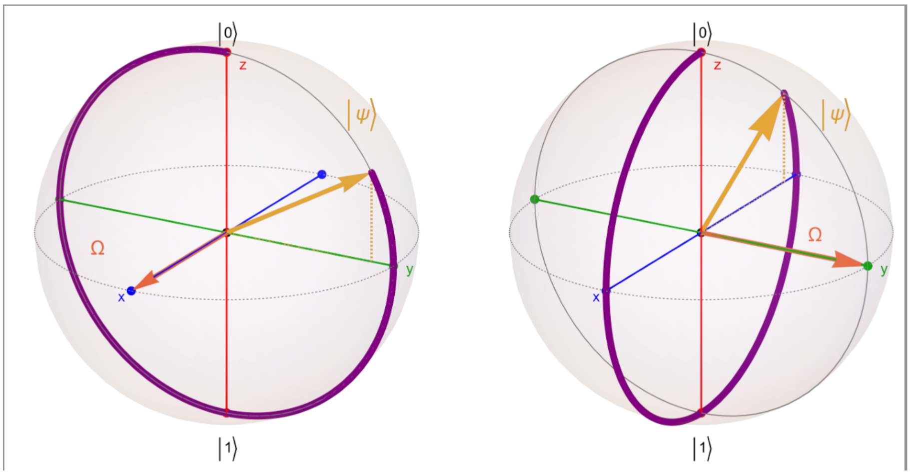

Figure 9.4: Rabi oscillations viewed in the rotating frame. We see as ϕ changes, it changes the orbit through the z axis. Reproduced from the lecture notes.

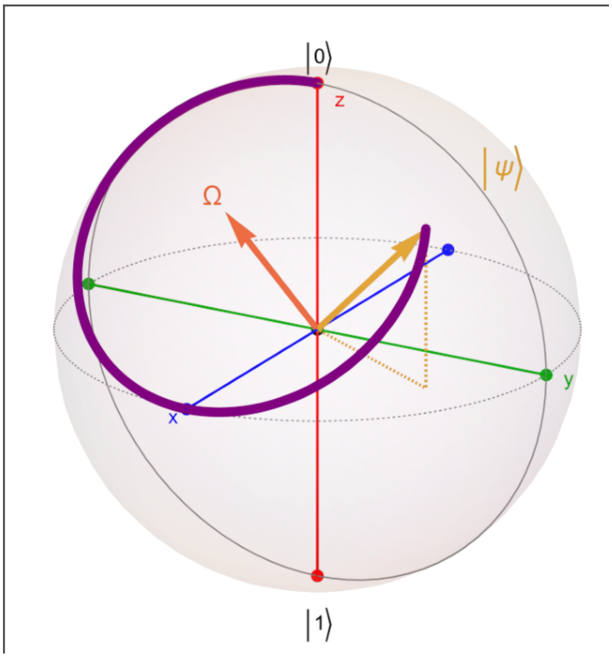

Figure 9.5: Off-resonance rotations in the rotating frame when $-\Delta = \Omega$

Rotating frame, off resonance

Now $\Delta \neq 0$ and now $\hat{\Omega}$ has a $\mathbf{z}$ component, which angles the rotation axis towards the north or south ($|0\rangle$ or $|1\rangle$) poles. We can extract some useful information out of this

- The space of available states is restricted - we cannot have total population transfer between $|0\rangle$ and $|1\rangle$ (i.e. the spin vector's rotation cycle will never intersect with *both* the north and south poles, it may intersect with one of them).
- the **Rabi angle**, the angle made by $\hat{\Omega}_t$ to the $\mathbf{z}$ axis is given by

$$\boxed{\tan\theta_R = \frac{\Omega}{-\Delta}} \tag{9.138}$$

See Figure 9.5 We can perform the same mathematical analysis to derive the eigenvectors and whatnot. It will be nearly identical except your secular determinant is now

$$\begin{vmatrix} -\frac{\hbar\Delta}{2} - \lambda & \frac{\hbar\Omega}{2}\exp(-i\phi) \\ \frac{\hbar\Omega}{2}\exp(i\phi) & \frac{\hbar\Delta}{2} - \lambda \end{vmatrix} = 0 \implies \left(\frac{\hbar\Delta}{2} - \lambda\right)\left(-\frac{\hbar\Delta}{2} - \lambda\right) - \frac{\hbar^2\Omega^2}{4} = 0 \tag{9.139}$$

and the eigenvalues now become

$$\lambda_\pm = \pm\frac{\hbar}{2}\sqrt{\Delta^2+\Omega^2}$$

Lab (Schrödinger) Frame, on resonance

We perform the unitary transformation back to the lab frame. We therefore must add back what we eliminated, namely the Larmor precession. Since we are on resonance, the drive and Larmor frequency are the same, so the spin is phase coherent with the driving field. Therefore as the spin vector moves between the poles, it also precesses in the xy-plane, giving some really nice spiral patterns as seen in Figure 9.6

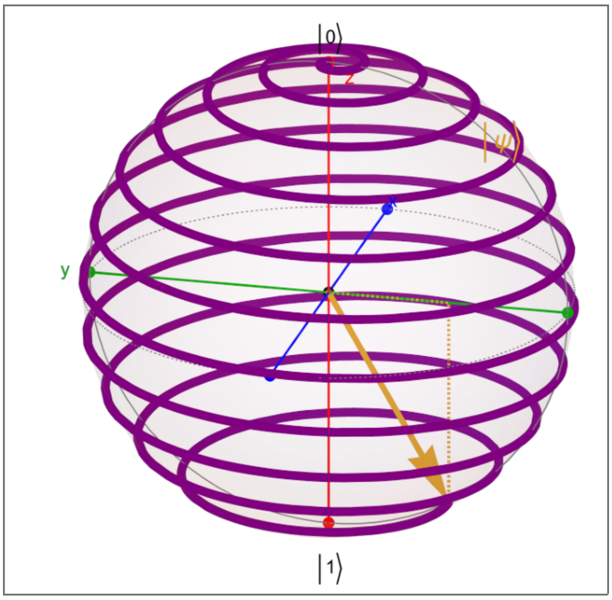

Figure 9.6: Lab frame, on resonance Rabi oscillations of the spin vector. This graphic assumes **x** rotation from $|0\rangle \to |1\rangle$. Reproduced from lecture notes.

9.8 Key Results

Two-level systems (at time of this guide) has rarely appeared in exams. Therefore it is our best guess as to what could appear and what is explicitly worth remembering or not. That being said, a two-level system question will probably follow the examples we've seen previously.

The Algorithm

1. Identify your orthonormal wavefunctions and write your state as a linear combination of these wavefunctions with a vector representation and choose what frame of reference you are working in.
2. Formulate the TDSE as a matrix equation in terms of the amplitudes
3. Solve the secular determinant of the Hamiltonian to find eigenvalues and eigenvectors. Do not forget to use the normalisation condition as part of your system of equations to find the wavefunction coefficients.
4. Determine your final state and compute whatever the question asks you for (expectation values, probability of transitions etc)

Moreover, know what a Bloch sphere is and how to use it.

Also, it is worth recalling the different shapes of Rabi oscillations.

- Rotating frame, on resonance produce great circle orbits.

- Rotating frame, off resonance restrict movement to segments of the Bloch sphere.
- Lab Frame, on resonance: pretty spirals.