Contents

1 Symmetry

We begin the course with a discussion of symmetry. In QM, symmetry plays an important role. We will discuss several types of symmetry:

- Space rotation symmetry
- Parity
- Time-reversal symmetry

We look for symmetries in order to simplify problems. Space-time has a symmetry as well, relativity, which we sometimes call a Lorentz symmetry. If we take QM and add the spacetime symmetry of relativity, we get QFT. We will not consider relativity in this course, we cover non-relativistic quantum mechanics.

There are also internal symmetries, which is the foundation of the Standard Model, the gauge symmetries (such as $SU(3)$, $U(1)$, etc).

1.1 Group Theory Basics

In mathematics, the field that discusses symmetry is called group theory, invented in 1830, by (18 year old) Galois. So what is a group? A group is a set of elements with a multiplication. This operation must satisfy 4 different conditions.

1. Closure: $g_1 \cdot g_2 = g_3 \in G$
2. Associativity: $g_1 \cdot g_2 \cdot g_3 = (g_1 \cdot g_2) \cdot g_3 = g_1 \cdot (g_2 \cdot g_3)$
3. Existence of an Identity: $\exists e$ such that $e \cdot g = g$
4. Existence of an Inverse: $\forall g, \exists g^{-1}$ such that $g \cdot g^{-1} = e$

There are many classifications of groups. There are finite and infinite groups. Finite groups have a finite number of elements, and infinite groups have an infinite number of elements. Examples of finite groups are the symmetry of crystals. Infinite groups can be either discrete (such as integers under addition), or continuous (rotations). Continuous groups are also known as Lie groups.

We also have Abelian and non-Abelian groups, which are based on whether $g_1 \cdot g_2 = g_2 \cdot g_1$. If the order of the operation does not matter, then we have an Abelian group, otherwise we have a non-Abelian group.

1.2 SO(3)

The group that we will be looking at will be the non-Abelian, Lie group $SO(3)$, which describes spatial rotations.

Suppose we have an experimental apparatus. We will pick some point, and define a coordinate system with 3 axes, x, y, and z. We can define points via their coordinates, $\boldsymbol{r} = (x, y, z)$, and we can rotate these points:

$$\boldsymbol{r}' = R\boldsymbol{r}$$

Where R is a 3 by 3 real orthogonal matrix:

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} R_{11} & R_{12} & \\ R_{21} & & \\ & & \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

Where $RR^T = \mathbb{I}$, the definition of an orthogonal matrix. How many rotations can we define using these matrices? Suppose we have our coordinate axes, and we rotate around the z axis by angle ϕ:

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} \cos\phi & -\sin\phi & 0 \\ \sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

We also note that the determinants of these rotation matrices are always 1, which we denote as special, and thus we have $SO(3)$. How do we characterize all of the rotations we have in three dimensions? We can consider an arbitrary axis $\boldsymbol{n} = (\theta, \phi)$, and specify a rotation amount. We can create a matrix $R_{\boldsymbol{n}}(\alpha)$ that characterizes the rotation by α about the axis specified by $\boldsymbol{n}$. We have a 3 dimensional space, since we have 3 parameters, α, θ, and ϕ. These create what is known as the group manifold. Every point in the group manifold corresponds to a specific rotation. Lie noted that we can use calculus to study the geometry of the group manifold. There is also another way to write down all rotations. The second method provides a simpler representation of the 3 by 3 matrices for the rotations. This method is known as Euler angles, which we have used in classical mechanics for the rotation of rigid bodies. The way that these angles work is to represent successive rotations as matrix multiplications (from the left). We can rotate about the z axis by α, and then rotate along the new y axis by β, and then rotate along the new z axis by γ:

$$R_{z'}(\gamma) R_{y'}(\beta) R_z(\alpha) = R(\alpha, \beta, \gamma)$$

Using this prescription, we can generate arbitrary rotations in 3 dimensions. We know how to write out $R_z(\alpha)$:

$$R_z(\alpha) = \begin{bmatrix} \cos\alpha & -\sin\alpha & 0 \\ \sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

We can come up a relationship for the rotation along the new y' axis:

$$R_{y'}(\beta) = R_z(\alpha) R_y(\beta) R_z^T(\alpha)$$

This relation is not easy to intuit, but it is true. From this, we can write down any rotation using simple matrices that we know:

$$R(\alpha, \beta, \gamma) = R_z(\alpha) R_y(\beta) R_z(\gamma)$$

Note that we already know that matrix multiplication is not commutative, $R_1 R_2 \neq R_2 R_1$, which is why this is a non-Abelian group. To study the non-Abelian character of this group, we will use Lie's method. Lie's method is that in order to understand a finite rotation, we need to study infinitesimal rotations. Consider the z axis rotation, but by a very small angle α:

$$R_z(\alpha) = \begin{bmatrix} 1 & -\alpha & 0 \\ \alpha & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$= \mathbb{I} - i\alpha G_z$$

Where G_z is defined as

$$G_z = \begin{bmatrix} 0 & -i & 0 \\ i & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

G_z is known as the generator of R_z. Consider a finite rotation. We can think of this as N smaller rotations:

$$R_z(\alpha) = R\left(\frac{\alpha}{N}\right) \dots R\left(\frac{\alpha}{N}\right)$$
$$= \left(\mathbb{I} - i\frac{\alpha}{N} G_z\right)^N$$

If we let $N \to \infty$, then we have that

$$R_z(\alpha) = e^{-i\alpha G_z}$$

This is not unique, any rotation can be determined via a generator:

$$R_{\boldsymbol{n}}(\alpha) = e^{-i\boldsymbol{n}\cdot G_n \alpha}$$

We are studying the properties of the group manifold near the identity, which means that we can linearize, and we use the G_ns to form a linear vector space. From this, we can describe the noncommutativity as a property of the linear vector space.

Consider the rotations:

$$R_x(\epsilon)R_y(\epsilon) \qquad R_y(\epsilon)R_x(\epsilon)$$

Since these are noncommutative, the difference will not be zero:

$$R_x(\epsilon)R_y(\epsilon) - R_y(\epsilon)R_x(\epsilon) \neq 0$$

It turns out that the difference is equal to another rotation:

$$R_x(\epsilon)R_y(\epsilon) - R_y(\epsilon)R_x(\epsilon) = R_z(\epsilon^2) - 1$$

If we do this with generators:

$$G_x G_y - G_y G_x = iG_z$$

Thinking about this in terms of commutators:

$$[G_x, G_y] = iG_z$$

This additional operation that this gives us is what gives us a Lie algebra. Algebra's have two operations, a multiplication and an addition. For example, taking the integers, we have an algebra, since we can define addition and multiplication that are closed.

Lie's method says that we can just study the Lie algebra, rather than the group itself, since we can generate any group element using the generators.

We have 3 basis vectors in our space, $[G_x, G_y, G_z]$, and we have commutation relations:

$$[G_i, G_j] = i\epsilon_{ijk}G_k \qquad i = 1, 2, 3$$

This is the Lie algebra for $SO(3)$.

A mathematician might ask how many Lie algebras there are. It turns out that we can classify Lie algebras, but we don't really need to know about that stuff.

Now let us discuss quantum mechanics. In QM, the first thing we need to realize is that we have a Hilbert space (a complex vector space), and any quantum state is defined by a ket in that space. Suppose we have an apparatus that is described by a ket in the Hilbert space, $|\psi\rangle$. A rotation of the apparatus will be described by a different ket, $|\psi'\rangle$. These are related via a unitary operator U:

$$|\psi'\rangle = U\,|\psi\rangle$$

Given R, the real-space rotation matrix, how can we get the unitary rotation? First, we note that for different physical systems, we must have different unitary matrices. Now we can ask, can we find all the different possible unitary matrices? The answer is yes, and it turns out to not be that hard. Every one of these unitary matrices that represents a rotation is denoted a **representation**. What is a representation? We have a "faithful" mapping, if we have $R = R_1 \cdot R_2$, then $U(R) = U(R_1) \cdot U(R_2)$. These unitary matrices form the same group as the rotation matrices, $SO(3)$, they are a representation of the group. What we are interested in are irreducible representations of the group. An irreducible representation means that we cannot write $U(R)$ in the form:

$$U(R) = \begin{bmatrix} U_1(R) & 0 \\ 0 & U_2(R) \end{bmatrix}$$

We cannot decompose the representation into multiple simpler representation.

Let us try to find all the representations of the Lie group $SO(3)$. To do this, we use Lie's method, to look at the group elements near the identity:

$$R(\hat{n}, \Delta\phi) = \mathbb{I} - i\Delta\phi G_{\hat{n}}$$

Where G are the generators of rotations, and they form a Lie algebra, they are closed under both multiplication (the commutator) and addition (matrix multiplication). This Lie algebra has a basis:

$$\{G_x, G_y, G_z\}$$

With the commutation relation:

$$[G_i, G_j] = i\epsilon_{ijk}G_k$$

Using this Lie algebra, we can construct any group element via the generators:

$$R(n, \phi) = e^{-i\phi G_n}$$

In the Hilbert space, we will have the unitary matrix:

$$U(R) = e^{-i\phi J_n/\hbar}$$

Where J_n are the generators in Hilbert space:

$$[J_i, J_j] = i\hbar\epsilon_{ijk}J_k$$

To find all representations of $SO(3)$ in Hilbert space is to find all possible J_i that satisfy the commutation relations.

We will do this later, for now let us just look at examples.

Consider a 2D Hilbert space. Can we find a set of 3 matrices that satisfy this commutation relation? The answer is yes, the Pauli matrices, $\sigma_x, \sigma_y, \sigma_z$:

$$J_i = \frac{\hbar}{2}\sigma_i$$

In this case, we can get unitary rotation operators via exponentiation. Consider a rotation along the $\hat{n}$ direction by an angle α:

$$\begin{aligned}
U(\hat{n}, \alpha) &= e^{-i\alpha\hat{n}\cdot\boldsymbol{J}/\hbar} \\
&= e^{-i\hat{n}\cdot\boldsymbol{\sigma}\alpha} \\
&= \cos\left(\frac{\alpha}{2}\right)\mathbb{I} - i\boldsymbol{\sigma}\cdot\hat{n}\sin\left(\frac{\alpha}{2}\right)
\end{aligned}$$

We can also use Euler angles, α, β, γ:

$$U(\alpha, \beta, \gamma) = U_z(\alpha)U_y(\beta)U_z(\gamma)$$

These matrices are also known as Wigner D-matrices.

What can we use these rotation matrices for?

Consider a spin along the z direction. In the Hilbert space, this is:

$$\chi(z) = \begin{bmatrix} 1 \\ 0 \end{bmatrix}$$

What if we rotate this along the y axis by some angle θ, and then rotate along the original z axis by angle ϕ?

$$\chi(\theta, \phi) = U_z(\phi)U_y(\theta)\chi(z)$$

We know how to write down these matrices:

$$\begin{aligned}
\chi(\theta, \phi) &= e^{-i\sigma_z\phi}e^{-i\sigma_y\theta}\begin{bmatrix} 1 \\ 0 \end{bmatrix} \\
&= \begin{bmatrix} \cos\frac{\theta}{2}e^{-i\phi/2} \\ \sin\frac{\theta}{2}e^{i\phi/2} \end{bmatrix}
\end{aligned}$$

Let us look at a spin. The magnetic moment can be written as:

$$\begin{aligned}\boldsymbol{\mu} &= -g_e\frac{e}{2m_e c}\boldsymbol{s}\\ &= -\frac{g_e}{2}\mu_B\boldsymbol{\sigma}\end{aligned}$$

If we now place this in a magnetic field:

$$\begin{aligned}H &= -\boldsymbol{\mu}\cdot\boldsymbol{B}\\ &= \frac{g_e}{2}\mu_B\boldsymbol{\sigma}\cdot\boldsymbol{B}\end{aligned}$$

Where $\mu_B = \frac{e\hbar}{2m_e c}$ (the Bohr magneton).

Let us look at the evolution of the spin at time 0, $\chi(t=0)$. This will evolve according to the time evolution operator:

$$\chi(t) = e^{-iHt/\hbar}\chi(t=0)$$

Plugging in the Hamiltonian:

$$\chi(t) = e^{-i\left(\frac{g_e}{2}\mu_B\boldsymbol{\sigma}\cdot\boldsymbol{B}\right)t/\hbar}\chi(0)$$

We can rewrite this, and have the time evolution operator be written as

$$U(t) = e^{-i(\boldsymbol{B}\cdot\boldsymbol{\sigma})\omega t/2}$$

Where $\omega = \frac{g_e eB}{2m_e c}$ is the Lamor frequency (classical precession frequency). We look at this and notice that this is the exact same thing as an $SO(3)$ rotation. The magnetic field is rotating the spin with the Lamor frequency. We can use this to experimentally measure g_e, the gyromagnetic ratio. Dirac predicted that this was 2, but it turns out to not be exactly 2, due to the effects of QED. Schwinger was the first to obtain QED corrections to g_e:

$$g_e = 2\left(1+\frac{\alpha}{2\pi}+\dots\right)$$

Which was confirmed by experiment (very precisely).

Recall that we had the rotation:

$$\chi(\theta,\phi) = \begin{bmatrix}\cos\frac{\theta}{2}e^{-i\phi/2}\\ \sin\frac{\theta}{2}e^{i\phi/2}\end{bmatrix}$$

Consider a rotation $\chi(0,2\pi)$. Instead of returning us to our original state, this picks up a negative sign:

$$\chi(0,2\pi) = \begin{bmatrix}-1\\ 0\end{bmatrix}$$

Only after a rotation of 4π do we go back to the original state. In the 1970's, this was verified. We have a beam of neutrons, which have magnetic moments:

$$\mu_n = g_n\boldsymbol{s}$$

We can split the neutron beam into 2 beams. The first travels through the vacuum, and the other goes through a magnetic field. We then combine the two beams together, and then measure the intensity of the beam. This is a variant of the double slit experiment. The change in phase between the rotated and the non-rotated neutrons is proportional to the magnetic field, $\Delta\phi \propto \frac{B}{2}$. We can look at the interference pattern, and see if it reflects the factor of $\frac{1}{2}$ in the phase difference.

Now let us look at the connection between $SU(2)$ and $SO(3)$. We have an infinite number of rotations in real space, and an infinite number of rotations in the Hilbert space. It turns out that there are twice as many rotations in the Hilbert space. Each realspace rotation corresponds to two rotations in the Hilbert space:

$$R = \begin{bmatrix} 1 & & \\ & 1 & \\ & & 1 \end{bmatrix} \to \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \text{ and } \begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix}$$

Thus the realspace rotations, $SO(3)$, is different from the group of Hilbert space rotations, which is actually $SU(2)$, the group of two dimensional special unitary matrices. These share the exact same Lie algebra, and thus when talking about the Lie algebra, we can interchangeably call it the $SO(3)$ Lie algebra or the $SU(2)$ Lie algebra. We can say that $SO(3)$ is a subgroup of $SU(3)$, or we can say that $SU(2) = SO(3) \otimes \mathbb{Z}_2$.

Let us now consider the Hilbert space of 3D particles. Suppose we have a coordinate $\boldsymbol{r}$, and we represent the state in the Hilbert space as $|\psi\rangle$. We represent the position space wavefunction via the inner product:

$$\psi(\boldsymbol{r}) = \langle \boldsymbol{r}|\psi\rangle$$

Suppose we rotate to a new state $|\psi'\rangle$, via a realspace rotation R. We will relate the new state to the old state via a unitary matrix:

$$|\psi'\rangle = U(R)\,|\psi\rangle$$

We can also think about the change in realspace:

$$\begin{aligned} |\boldsymbol{r}'\rangle &= U(R)\,|\boldsymbol{r}\rangle \\ &= |R\boldsymbol{r}\rangle \end{aligned}$$

We expect the new wavefunction in the rotated basis to be the same as the old wavefunction in the old basis:

$$\begin{aligned} \langle \boldsymbol{r}'|\psi'\rangle &= \langle \boldsymbol{r}|\psi\rangle \\ \psi'(\boldsymbol{r}') &= \psi(\boldsymbol{r}) \end{aligned}$$

We know that $\boldsymbol{r}' = R\boldsymbol{r}$, or $\boldsymbol{r} = R^{-1}\boldsymbol{r}'$:

$$\psi'(\boldsymbol{r}) = \psi(R^{-1}\boldsymbol{r})$$

Let us consider a simple rotation, about the z axis. Suppose we rotate by a small angle $\Delta\phi$:

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} 1 & -\Delta\phi & 0 \\ \Delta\phi & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

$$= \begin{bmatrix} x \\ y \\ z \end{bmatrix} + \begin{bmatrix} -\Delta\phi y \\ \Delta\phi x \\ 0 \end{bmatrix}$$

For small rotations:

$$R^{-1}\boldsymbol{r} = \boldsymbol{r} + \begin{bmatrix} \Delta\phi y \\ -\Delta\phi x \\ 0 \end{bmatrix}$$

We can now look at $\psi'(\boldsymbol{r})$:

$$\begin{aligned}\psi'(\boldsymbol{r}) &= \psi\left(\boldsymbol{r} + \begin{bmatrix} \Delta\phi y \\ -\Delta\phi x \\ 0 \end{bmatrix}\right) \\ &= \psi(\boldsymbol{r}) + \left(-\Delta\phi y\partial_x + \Delta\phi x\partial_y\right)\psi(\boldsymbol{r}) \\ &= \left(1 - i\Delta\phi L_z/\hbar\right)\psi(\boldsymbol{r})\end{aligned}$$

Where L_z is the z generator of rotation:

$$L_z = -i\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

And similarly for L_x and L_y:

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

Where $\boldsymbol{p} = -i\hbar\nabla$.

These generators follow the same Lie algebra that we have been looking at:

$$[L_i, L_j] = i\epsilon_{ijk}L_k$$

We see that we have found an infinite dimensional representation for the generators. However, this is not an irreducible representation, it consists of a sum of irreducible representations.

If we look at spherical coordinates, $\boldsymbol{r} = (x, y, z) \to (\theta, \phi, r)$ we can rewrite the generators:

$$L_z = -i\hbar\frac{\partial}{\partial\phi}$$

When we have a symmetry in a system, there is a conservation law as well. For systems with rotational symmetry, we have angular momentum conservation. In fact, all conservation laws can be traced to certain symmetries of the system. This is known as Noether's theorem.

There are 3 ways in which symmetries can affect QM systems. The first is the degeneracy of energy levels. The second is spontaneous symmetry breaking. The third way that symmetry manifests are quantum anomalies. In this course, we will focus on the relationship between conservation laws and symmetries.

Let us discuss how we can determine all possible irreps of $U(R)$, rotations in Hilbert space. One clue that we have is that we can represent any rotation as:

$$U(R) = e^{-i\theta\hat{n}\cdot\boldsymbol{J}/\hbar}$$

Where the three generators obey the commutation relation:

$$[J_i, J_j] = i\epsilon_{ijk}\hbar J_k$$

Looking at 2D, we found that these generators could be represented by the Pauli matrices:

$$J_i = \frac{\hbar}{2}\sigma_i$$

Let us now introduce the total angular momentum:

$$\boldsymbol{J}^2 = J_x^2 + J_y^2 + J_z^2$$

We can (through the commutation relations above) show that:

$$\left[\boldsymbol{J}^2, J_i\right] = 0$$

Let us now choose $\{\boldsymbol{J}^2, J_z\}$ as commuting observables, and find the eigenstates, $|a, b\rangle$:

$$\begin{aligned}\boldsymbol{J}^2 |a, b\rangle &= a |a, b\rangle \\ J_z |a, b\rangle &= b |a, b\rangle\end{aligned}$$

We have two eigenrelations to solve.

Now let us define ladder operators:

$$J_\pm = J_x \pm iJ_y$$

Note that

$$\left[\boldsymbol{J}^2, J_\pm\right] = 0$$

Now consider:

$$\begin{aligned}\boldsymbol{J}^2 (J_+ |a, b\rangle) &= J_+ \left(\boldsymbol{J}^2 |a, b\rangle\right) \\ &= a (J_+ |a, b\rangle)\end{aligned}$$

We can also look at a similar expression for J_z:

$$J_z (J_+ |a, b\rangle)$$

To work with this, we need to know the commutator of J_z and J_+:

$$[J_z, J_+] = \hbar J_+$$

From this, we know that $J_zJ_+ = J_+\left(J_z + \hbar\right)$. We can insert this into our previous expression:

$$\begin{aligned} J_z\left(J_+\left|a,b\right\rangle\right) &= J_+\left(J_z+\hbar\right)\left|a,b\right\rangle \\ &= \left(b+\hbar\right)\left(J_+\left|a,b\right\rangle\right) \end{aligned}$$

We see that $J_+\left|a,b\right\rangle$ is also an eigenvector of J_z, but with eigenvalue $b+\hbar$. This we have that $J_+\left|a,b\right\rangle$ is proportional to $\left|a,b+\hbar\right\rangle$.

Now let us look at the constraints on a and b. First, let us look at

$$\boldsymbol{J}^2 - J_z^2 = J_x^2 + J_y^2$$

Since a squared operator must have positive eigenvalues, if we look at the matrix element:

$$\langle a,b|\boldsymbol{J}^2 - J_z^2|a,b\rangle$$

This must be greater than 0, and if we apply the operators to the right ket, we find that $a \geq b^2$, in order for this matrix element to always be greater than 0.

This constraint tells us that there must be a b_{max}, we cannot just keep applying J_+ to states and increasing b:

$$J_+\left|a,b_{max}\right\rangle = 0$$

Similarly, we can also consider $J_-\left|a,b\right\rangle$, and we see that this maps us to a state proportional to $\left|a,b-\hbar\right\rangle$. We are also constrained on how far down we can go:

$$J_-\left|a,b_{min}\right\rangle = 0$$

Suppose we apply J_- to the b_{max} state:

$$\left(J_-\right)^n\left|a,b_{max}\right\rangle \propto \left|a,b_{max}-n\hbar\right\rangle$$

At some point, we must be able to hit the minimum, and so after n applications, we hit b_{min}:

$$b_{max} - n\hbar = b_{min}$$

Rewriting this:

$$b_{max} - b_{min} = n\hbar$$

Where $n \in \mathbb{Z}$.

Recall that

$$\begin{aligned} \boldsymbol{J}^2 - J_z^2 &= J_x^2 + J_y^2 \\ &= J_\mp J_\pm \pm \hbar J_z \end{aligned}$$

Let us now look at the matrix element:

$$\begin{aligned} \langle a,b_{max}|\left(\boldsymbol{J}^2 - J_z^2\right)\left|a,b_{max}\right\rangle &= \langle a,b_{max}|J_-J_+ + \hbar J_z|ab_{max}\rangle \\ &= \hbar b_{max} \end{aligned}$$

Now recall that this left side must be $a - b_{max}^2$, and thus we have that

$$a = b_{max}\left(b_{max} + \hbar\right)$$

Using the other set of signs, we have that $a = b_{min}\left(b_{min} - \hbar\right)$. From these, we find that $b_{max} = -b_{min}$. Thus, we have that $b_{max} = \left(\frac{n}{2}\right)\hbar$.

Now let us redefine a and b:

$$\begin{aligned} a &= \hbar^2 j\left(j+1\right) \\ b_{max} &= j\hbar \\ b_{min} &= -j\hbar \end{aligned}$$

Where $j = 0, \frac{1}{2}, 1, \frac{3}{2}, \dots$. We can write out the states as:

$$\begin{aligned} \boldsymbol{J}^2 \left|j, m\right\rangle &= \hbar^2 j\left(j+1\right)\left|j, m\right\rangle \\ J_z \left|j, m\right\rangle &= \hbar m \left|j, m\right\rangle \end{aligned}$$

Where $m = j, j-1, \dots, -j$, and $b = m\hbar$. This provides us all possible irreps of the $SO(3)$ generators. Let us try to write out the matrices for the case where $j = \frac{117}{2}$. We know that m can take on the values $m = \frac{117}{2}, \frac{115}{2}, \dots, -\frac{117}{2}$. We can write J_z by placing the values of m along the diagonal, and having zeros everywhere else. Now let us consider the action of the ladder operators:

$$J_\pm \left|j, m\right\rangle = c_\pm \left|j, m \pm 1\right\rangle$$

If we can work out $J_\pm$, then we can work out J_x and J_y. Let us now note that $J_+^\dagger = J_-$, and vice versa. Now looking at the matrix element:

$$\langle j, m | J_\mp J_\pm | j, m\rangle = \mid c_{jm}^\pm \mid^2 \langle j, m \pm 1 | j, m \pm 1\rangle$$

From this, we find that

$$c_\pm = \hbar\sqrt{\left(j \mp m\right)\left(j \pm m + 1\right)}$$

This will provide us with a matrix for $J_\pm$, from which we can determine J_x and J_y.

Let us start with some simple cases. If $j = 0$, then

$$J_x = J_y = J_z = 0$$

Under the rotation, the wavefunction doesn't change, $\psi \to \psi$. Consider the ground state of an oxygen-16 atom. This has 8 electrons, with total angular momentum equal to 0, the entire atom has spin 0. The wavefunction does not change under the rotation.

Now what about $j = \frac{1}{2}$. We have two basis states:

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

In this case, we have the Pauli matrices, $J_z = \frac{\hbar}{2}\sigma_z$. We can also look at the ladder relations:

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

$$J_+ \left|\frac{1}{2}, -\frac{1}{2}\right\rangle = \hbar \left|\frac{1}{2}, \frac{1}{2}\right\rangle$$

We can find that

$$J_+ = \hbar \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix} \qquad J_- = \hbar \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix}$$

From this, we can construct:

$$J_x = \frac{\hbar}{2}\sigma_x \qquad J_y = \frac{\hbar}{2}\sigma_y$$

Now we can generate any Hilbert space rotation:

$$U(R) = e^{-i\theta\hat{n}\cdot\boldsymbol{J}/\hbar}$$

Now what about $j = 1$. This is a 3 dimensional representation. We have the basis:

$$|1,1\rangle \quad |1,0\rangle \quad |1,-1\rangle$$

For simplicity, we will call these states $|1\rangle, |0\rangle$, and $|-1\rangle$ respectively. We can then write out J_z:

$$J_z = \hbar \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

We can write out the J_+ matrix:

$$J_+ = \hbar\sqrt{2} \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{bmatrix}$$

And similarly:

$$J_- = \hbar\sqrt{2} \begin{bmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix}$$

We can work out J_x and J_y:

$$\begin{aligned} J_x &= \frac{1}{2}\left(J_+ + J_-\right) \\ &= \frac{\hbar}{\sqrt{2}} \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix} \\ J_y &= \frac{1}{2i}\left(J_+ - J_-\right) \\ &= -\frac{i\hbar}{\sqrt{2}} \begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 1 \\ 0 & -1 & 0 \end{bmatrix} \end{aligned}$$

Note that this is the only set of matrices that obey these commutation relations. Any other set of matrices must be related to these.

Now how do we construct the unitary matrices in arbitrary dimensions? What we want to do is compute $\langle j, m'|U(\alpha,\beta,\gamma)|j,m\rangle$. This is the matrix element of a $2j+1$ dimensional matrix. We denote this as the Wigner matrix:

$$\mathcal{D}^{(j)}_{m'm}\left(\alpha,\beta,\gamma\right) = \langle j, m'|U(\alpha,\beta,\gamma)|j,m\rangle$$

We can use the Euler angle decomposition:

$$U(R) = e^{-i\alpha J_z/\hbar}e^{-i\beta J_y/\hbar}e^{-i\gamma J_z/\hbar}$$

$$\begin{aligned}\mathcal{D}^{(j)}_{m'm}\left(\alpha,\beta,\gamma\right) &= \langle j, m'|U(\alpha,\beta,\gamma)|j,m\rangle \\ &= e^{-i(m'\alpha+\gamma m)}\left\langle j, m'|e^{-iJ_y\beta/\hbar}|j,m\right\rangle \\ &= e^{-i(m'\alpha+\gamma m)}d^{(j)}_{m'm}\left(\beta\right)\end{aligned}$$

Schwinger was the first to find a closed form for these matrix elements.

Recall that we discussed a single particle moving in 3 dimensions. We have some $\psi(\boldsymbol{r}) = \langle \boldsymbol{r}|\psi\rangle$. We have an infinite dimensional representation of $SO(3)$:

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

The unitary matrices that perform the rotation will be of the form:

$$U(\boldsymbol{n}) = e^{-i\boldsymbol{n}\cdot\boldsymbol{L}/\hbar}$$

We can look at this through spherical coordinates, $|\boldsymbol{r}\rangle = |r,\theta,\phi\rangle$. When we do rotations, we only affect the θ and ϕ portions of the wavefunction. It turns out that the rotations can be described using spherical harmonics:

$$\langle\theta,\phi|l,m\rangle = Y_{l,m}(\theta,\phi)$$

Where l must be an integer, not half-integers.

There are some special cases in which the Wigner $\mathcal{D}$ matrix is more easily solvable. Suppose that we have some ket in the z direction, and we want to rotate it to an arbitrary direction. We apply a rotation matrix to the ket:

$$|\boldsymbol{r}\rangle = U(R)\left|\hat{z}\right\rangle$$

We can write this out as a set of Euler angle rotations, starting with a rotation by ϕ:

$$U(\alpha=\phi,\beta=\theta,\gamma=0)$$

Now let us look at

$$\langle l, m'|\boldsymbol{r}\rangle = \sum_m \langle l, m'|U|l,m\rangle\left\langle l,m|\hat{z}\right\rangle$$

Where we have inserted unity. Now noting that

$$\langle\boldsymbol{r}|l,m\rangle = Y_{l,m}\left(\theta,\phi\right)$$

We see that we have just computed the conjugate of the spherical harmonics:

$$Y^*_{l,m'}\left(\theta,\phi\right)=\sum_m \mathcal{D}^{(l)}_{m,m'}\left(0,\theta,\phi\right)Y^*_{l,m}\left(\hat{z}\right)$$

It turns out that $Y^*_{l,m}\left(\hat{z}\right)=\delta_{m,0}\sqrt{\frac{2l+1}{4\pi}}$. Because of this, the sum over m can be replaced:

$$Y^*_{l,m'}\left(\theta,\phi\right)=\mathcal{D}^{(l)}_{m',0}\left(\phi,\theta,0\right)\sqrt{\frac{2l+1}{4\pi}}$$

From this, we can solve for $\mathcal{D}$:

$$\mathcal{D}^{(l)}_{m',0}=\sqrt{\frac{4\pi}{2l+1}}Y^*_{l,m'}\left(\theta,\phi\right)$$

Also note that when we have spherical harmonics where $m=0$, we have that associated Legendre polynomials.

1.3 Applications

Consider a particle in a central potential $V(r)$. This has the Hamiltonian:

$$\hat{H}=\frac{\boldsymbol{p}^2}{2m}+V(r)$$

Classically, this system is spherically symmetric. Translating this to QM, this means that our Hamiltonian is invariant under rotations:

$$U^\dagger(R)\hat{H}U(R)=\hat{H}$$

This is invariance, or symmetry. We know that all rotations in Hilbert space are generated by the angular momentum:

$$U(R)=e^{-i\boldsymbol{J}\cdot\boldsymbol{n}/\hbar}$$

If we insert this into the previous expression, and then Taylor expand for small rotations, we find that the Hamiltonian commutes with the generators of rotations:

$$[H,\boldsymbol{J}]=0$$

If the system is symmetric under rotation, then the Hamiltonian commutes with the generator of rotations.

Recall the time evolution of operators:

$$\begin{aligned}\frac{d\boldsymbol{J}}{dt}&=[H,\boldsymbol{J}]\\&=0\end{aligned}$$

This relates our symmetry to a conservation law, the operators do not change over time.

What does the Hamiltonian commuting with $\boldsymbol{J}$ mean?

The Hamiltonian commutes with every single generator, which means that when we are trying to solve the Schrodinger equation, we can find a set of commuting observables. There are an infinite set of choices, but there are standard choices. For example, we have the set $\{H, \boldsymbol{J}^2, J_z\}$, of which all 3 operators commute with each other.

Let us try to find the common eigenstates of these three. We assume we have spinless particles, so we are discussing orbital angular momentum, so we have

$$H\left|n, l, m\right\rangle = E_{n,l}\left|n, l, m\right\rangle$$

Because of the symmetry of our system, we have more explicitly written out our $\left|\psi\right\rangle$, this is the gain of discussing symmetries in our system. We can obtain a coordinate space representation:

$$\psi_{n,l,m}(\boldsymbol{r}) = \langle \boldsymbol{r}|n, l, m\rangle$$

And we can write out the Schrodinger equation:

$$\left[\frac{\boldsymbol{p}^2}{2m} + V(\boldsymbol{r})\right]\psi_{n,l,m}\left(\boldsymbol{r}\right) = E_{n,l}\psi_{n,l,m}\left(\boldsymbol{r}\right)$$

Now consider spherical coordinates:

$$\frac{\boldsymbol{p}^2}{2m} = -\frac{\hbar^2}{2mr^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) + \frac{\boldsymbol{L}^2}{2mr}$$

Note that we know that $\boldsymbol{L}^2$ commutes with L_x, L_y, and L_z. This is known as a Casimir operator, an operator that commutes with all the generators of a group.

From this, we can write down ψ, separating it into a radial part and a spherical part:

$$\psi_{nlm}\left(\boldsymbol{r}\right) = R_{nl}\left(\boldsymbol{r}\right)Y_{lm}\left(\theta, \phi\right)$$

Now looking at the radial part:

$$\left[-\frac{\hbar^2}{2mr^2}\frac{d}{dr}\left(r\frac{d}{dr}\right) + \frac{l\left(l+1\right)\hbar^2}{2mr^2} + V\left(\boldsymbol{r}\right)\right]R_{nl}\left(\boldsymbol{r}\right) = E_{nl}\psi_{nl}$$

Since the energy does not depend on m, we have a degeneracy in our spectrum. Since m takes values from $-l$ to $+l$, we have $2l+1$ degeneracy. Symmetry leads to degeneracy in our spectrum.

Let us find the radial part. We rewrite this using $U(r)$, a scaled version of the radial part:

$$U(r) = \frac{R(r)}{r}$$

Which makes the radial equation:

$$-\frac{\hbar^2}{2m}\frac{d^2U_{nl}(r)}{dr^2} + V_{\text{eff}}(r)U_{nl}(r) = E_{nl}U_{nl}(r)$$

And we have redefined the potential to be the effective potential:

$$V_{\text{eff}}\left(\boldsymbol{r}\right) = V(\boldsymbol{r}) + \frac{l\left(l+1\right)\hbar^2}{2mr^2}$$

We can think of this added force as the effect of the angular inertia pushing an orbiting particle away from the center.

Note that this potential restricts the value of r, to $0 < r < \infty$. Note that this also imposes the condition that $U_{nl}(r) \to 0$ as $r \to 0$.

Let us assume that the potential, as $r \to 0$, is not as divergent as $\frac{1}{r^2}$. If we assume this, then the inertia term dominates. In this case, as $r \to 0$, $U_{nl}(r) \to r^{l+1}$.

Now let us consider the case where $r \to \infty$, and we make the assumption that $V_{\text{eff}}(r \to \infty) = 0$. In this case, we have the classic harmonic oscillator equation:

$$U \sim e^{-\kappa r}$$

Where $\kappa = \sqrt{\frac{2m|E|}{\hbar^2}}$.

Let us now look at the relationship between symmetry and degeneracy. Symmetry leads to conservation laws, and in quantum mechanics, will lead to degeneracies. If a system is invariant under $SO(3)$ symmetries, then the Hamiltonian will depend on the Casimir operator, L^2. This means that the energy can only be a function of l, since l is the eigenvalue of the L^2 operator. This means that we will have a degeneracy of $2l+1$, we cannot escape this.

Now let us look at some examples.

Consider a 3D finite well. We have a potential, $V(\boldsymbol{r})$, and some well of height $-V_0$. In the $l = 0$ case, we have an eigenvalue equation. Note that in 3D, the potential well has to be larger than a certain amount to have a bound state:

$$V_0 \geq \frac{\pi^2\hbar^2}{8mR^2}$$

Let us look at another example.

Consider a 3D harmonic oscillator:

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

If we solve this, we have the energy spectrum:

$$E_n = \hbar\omega\left(n + \frac{3}{2}\right) \qquad n = 0, 1, 2, \ldots$$

For even n, we have that $l = 0, 2, 4, \ldots, n$. For odd n, we have that $l = 1, 3, 5, \ldots, n$.

In this case, we actually have more degeneracy than we expected, we have a degeneracy of

$$\frac{(n+1)(n+2)}{2}$$

This means that we have another symmetry, other than just the rotational symmetry. What is the symmetry? The simplest way to solve the 3D harmonic oscillator is to split the Hamiltonian:

$$H = H_x(x) + H_y(y) + H_z(z)$$

We can introduce creation and annhilation operators for each of the directions:

$$\begin{aligned} H &= \hbar\omega\left(a_x^\dagger a_x + a_y^\dagger a_y + a_z^\dagger a_z + \frac{3}{2}\right) \\ &= \hbar\omega\left(\boldsymbol{a}^\dagger \boldsymbol{a} + \frac{3}{2}\right) \end{aligned}$$

This Hamiltonian has $SU(3)$ symmetry. Let us imagine that a_x, a_y, and a_z span a 3 dimensional space. We can rotate in this space via 3 by 3 unitary matrices, and we get another set of creation and annhilation operators.

It turns out that if we limit these rotation matrices to be real and orthogonal, we get $SO(3)$, $SU(3)$ contains $SO(3)$ as a subgroup. This provides more degeneracies than just $SO(3)$.

Let us look at a third example, the Hydrogen atom.

The potential for the Hydrogen atom is given by

$$V(r) = \frac{e^2}{r} z$$

After inserting this into the 1D Schrodinger equation, the spectrum is given by :

$$E_n = -\frac{\alpha}{2n^2}\left(m_e c^2\right) \qquad n = 1, 2, \dots$$

Where $\alpha = \frac{1}{137}$, and $m_e c^2 = 0.505$ MeV, the rest mass of the electron.

For a given n, l takes the values of $0, 1, 2, \dots n-1$, and $m_l = -l, \dots, l$. The degeneracy of the hydrogen atom is n^2. This is not $2l+1$, so there must be another symmetry in the Hydrogen atom.

The symmetry is $SO(4)$, the 4 dimensional rotation group. It takes 6 independent parameters to specify a rotation in 4 dimensions, so we have 6 generators for the rotations. 3 of the generators are the L operators. The other 3 are in $\boldsymbol{M} = (M_x, M_y, M_z)$, known as the Laplace-Runge-Lenz vector.

Consider the Sun and the Earth. We know that the potential between them goes as $\frac{1}{r}$. Central potentials always have orbits that precess. However, this is not true for 1 central potential, specifically the $\frac{1}{r}$ potential, which is why the orbit of the Earth does not precess. To be more specific, the semi-major axis of the orbit is constant. However, this is sort of a lie, since there is the effect of the moon, as well as GR. This breaks the symmetry, but this is still good, because we can look at symmetry breaking in terms of perturbation theory, as we will see later.

Let us consider a fourth example. Consider an atomic nucleus, made up of protons and neutrons, which have almost the same mass, the proton has mass 938.5 MeV, and the neutron has mass 940.3 MeV. Why do these two particles have almost the exact same mass? Heisenberg was the first to think about this. If we consider a 2D vector space, with a neutron wavefunction and a proton wavefunction (isospin), this has symmetry under $SU(2)$ rotations. The Hamiltonian must be in terms of the Casimir operator for the isospin generators. The isospin symmetry is the first example of an internal symmetry.

In the 1950's, people discovered the brothers and sisters of the proton and neutron, with a total of 8 particles, with almost the same masses. This gives us more degeneracies, which indicates we have more symmetries, which turns out to be $SU(3)$. Gell-Mann worked out why it was $SU(3)$ symmetry, and his solution was the 3 quarks, up, down, and strange. He initially posited these as mathematical constructs, not necessarily physical objects. In 1991, the Nobel prize was awarded for the discovery of the quarks, done at SLAC, via deep inelastic scattering.

This is why we start with the idea of looking for symmetries, and discussing how they simplify our systems.

1.4 Many Body Systems

Consider a system of two spins. Each of the spins has a Hilbert space, which in the case of spin $\frac{1}{2}$ particles, is 2 dimensional. The combined Hilbert space is a product of the two spaces, and we end up with a 4D Hilbert space. If we added on another spin, we would have a resulting 8 dimensional Hilbert space, the dimensions multiply to obtain the resulting space.

How do we multiply Hilbert spaces? Let us say that we have two Hilbert spaces, H_1 and H_2. Each has its own representation in a basis, with H_1 having the representation $|j_1, m_1\rangle$, where $m_1 = j_1, j_1 - 1, \cdots - j_1$, and thus has resulting dimension $2j + 1$. Likewise, we have a basis $|j_2, m_2\rangle$ for H_2, with dimension $2j_2 + 1$. The combined Hilbert space will have dimension $(2j_1 + 1)(2j_2 + 1)$, and we want to find out how we can do calculations in this combined Hilbert space.

First, how do we get the basis vectors for the combined Hilbert space? We define them to be the "product" of the two bases:

$$|j_1, m_1\rangle |j_2, m_2\rangle$$

To simplify the notation, we can place them in the same ket:

$$|j_1, m_1, j_2, m_2\rangle$$

Since j_1 and j_2 are fixed, we can further simplify this down to

$$|m_1, m_2\rangle$$

with $m_1 = j_1, j_1 - 1, \ldots, -j_1$and $m_2 = j_2, j_2 - 1, \ldots, -j_2$. The total number of basis vectors is $(2j_1 + 1)(2j_2 + 1)$.

What about operators? We will have operators in the first space, such as $\mathcal{O}_1$, and operators in the other space, such as $\mathcal{O}_2$. When we do the multiplication of the spaces, we just place them next to each other:

$$\mathcal{O}_1\mathcal{O}_2$$

Each operator only acts on the original Hilbert space that it is defined in, so an operation in just H_1 is written as

$$\mathcal{O}_1\mathbb{I}$$

And similarly for an operation acting only in H_2:

$$\mathbb{I}\mathcal{O}_2$$

What about the operator $\mathcal{O}_1 + \mathcal{O}_2$? This is implicitly:

$$\mathcal{O}_1 + \mathcal{O}_2 = \mathcal{O}_1\mathbb{I} + \mathbb{I}\mathcal{O}_2$$

Now how do the operations work? Suppose we have

$$\mathcal{O}_1\mathcal{O}_2 \left|1\right\rangle \left|2\right\rangle$$

The operations are independent, they only act on their own space:

$$\mathcal{O}_1\mathcal{O}_2 \left|1\right\rangle \left|2\right\rangle = \mathcal{O}_1 \left|1\right\rangle \mathcal{O}_2 \left|2\right\rangle$$

Now consider $\boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2$. We have a dot product, since they are vectors:

$$\boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2 \left|1\right\rangle \left|2\right\rangle = (\sigma_1^x\sigma_2^x + \sigma_1^y\sigma_2^y + \sigma_1^z\sigma_2^z) \left|1\right\rangle \left|2\right\rangle$$

Are we allowed to switch the spaces around? We aren't allowed to switch the ordering of the spaces midway through, but the choice of which one is space 1 and which is space 2 is arbitrary at the start of the computation.

Let us return to the 2 spin case. When we multiply our spaces, we are multiplying two spaces that rotate via $SO(3)$ transformations. How does the product space transform under $SO(3)$ rotations?

Consider two spin operators, one from each subsystem, and we add them to generate a total spin operator:

$$\begin{aligned}\boldsymbol{S} &= \boldsymbol{S}_1 + \boldsymbol{S}_2 \\ &= \boldsymbol{S}_1\mathbb{I} + \mathbb{I}\boldsymbol{S}_2\end{aligned}$$

This is how we define the addition of operators from different spaces.

It turns out that the total angular momentum operator $\boldsymbol{S}$ obeys the regular angular momentum commutation relations:

$$[S_i, S_j] = i\epsilon_{ijk}\hbar S_k$$

For notational simplicity, let us denote the basis states of each subspace as $\left|+\right\rangle$ and $\left|-\right\rangle$, which provides us with the 4 basis vectors of the total space:

$$\left|++\right\rangle \quad \left|+-\right\rangle \quad \left|-+\right\rangle \quad \left|--\right\rangle$$

Let us first construct the state

$$\frac{1}{\sqrt{2}}\left[\left|+-\right\rangle - \left|-+\right\rangle\right]$$

Now looking at the S_z operator:

$$S_z = S_{1z} + S_{2z}$$

We see that this state has 0 net spin in the z direction. We can also compute $\boldsymbol{S}^2$ in this state:

$$\boldsymbol{S}^2 = \boldsymbol{S}_1^2 + \boldsymbol{S}_2^2 + 2\boldsymbol{S}_1 \cdot \boldsymbol{S}_2$$

Applying this to the state:

$$\begin{aligned}\boldsymbol{S}^2\frac{1}{\sqrt{2}}\left[|{+-}\rangle-|{-+}\rangle\right]&=\hbar^2\frac{1}{2}\left(1+\frac{1}{2}\right)-\hbar^2\frac{1}{2}\left(1+\frac{1}{2}\right)+0\\&=0\end{aligned}$$

Where the last term corresponds to the $2\boldsymbol{S}_1\cdot\boldsymbol{S}_2$, which we write out the operator in terms of the $S_\pm$ operators, in both spaces.

We can also define other states:

$$\begin{aligned}|S=1,S_z=1\rangle&=|{++}\rangle\\|S=1,S_z=-1\rangle&=|{--}\rangle\\|S=1,S_z=0\rangle&=\frac{1}{\sqrt{2}}\left(|{+-}\rangle+|{-+}\rangle\right)\end{aligned}$$

This is the set of triplet states, and the first state is the singlet state, $|S=0,S_z=0\rangle$. We see that the space is actually a 1 dimensional subspace added to a 3 dimensional subspace, which is why we have $3+1=4$ dimensions. Our $SO(3)$ representation is not irreducible, it can be represented as a set of block diagonal matrices, with one block being a 1 dimensional matrix, and the other block being a 3 by 3 matrix. Note that this is not the same as the $j=\frac{3}{2}$ irrep of $SO(3)$, since it is not irreducible.

Now let us consider a more general system. Consider two Hilbert spaces. H_1 has angular-momentum vector $\boldsymbol{J}_1$, and is of dimension $2j_1+1$. H_2 has angular momentum vector $\boldsymbol{J}_2$, and is of dimension $2j_2+1$. We can put these two spaces together, and we have the basis vectors:

$$|j_1,m_1\rangle\,|j_2,m_2\rangle\to|m_1,m_2\rangle$$

And the product Hilbert space is of dimension $(2j_1+1)(2j_2+1)$.

We have similar operators as before:

$$\boldsymbol{J}=\boldsymbol{J}_1+\boldsymbol{J}_2$$

And they obey the same commutation relations:

$$[J_i,J_j]=i\epsilon_{ijk}\hbar J_k$$

We want to find the common eigenstates of $\boldsymbol{J}^2$ and J_z in the product Hilbert space.

We have that $J_z=J_{1z}+J_{2z}$, and we can apply this against a basis vector:

$$\begin{aligned}J_z\,|m_1,m_2\rangle&=\hbar m_1\,|m_1,m_2\rangle+\hbar m_2\,|m_1,m_2\rangle\\&=\hbar\,(m_1+m_2)\,|m_1,m_2\rangle\end{aligned}$$

We see that the joint basis is already an eigenstate of the J_z operator.

Now let us find the eigenstates of $\boldsymbol{J}^2$. We can represent each basis vector in terms of a point in a 2D space, with axes given by m_1 and m_2. This provides a rectangular lattice, with height $2j_1+1$ and width $2j_2+1$. Each of these states is already an eigenstate of J_z, and has eigenvalue $m=m_1+m_2$. The largest m that we can get is $m=j_1+j_2$, given by the point with the largest m_1 and m_2.

We can create “bands” of states in the 2D space that have the same J_z eigenvalue, ranging from $m = j_1 + j_2$ down to $m = -j_1 - j_2$. Let us start with the maximum case, $m = j_1 + j_2$, which is given by the state

$$|j_1, j_1, j_2, j_2\rangle$$

We claim that this is also an eigenstate of $\boldsymbol{J}^2$, with eigenvalue $j\,(j+1)\,\hbar$, where $j = j_1 + j_2$.

Let us apply $\boldsymbol{J}^2$:

$$\begin{aligned}
\boldsymbol{J}^2 |j_1, j_1, j_2, j_2\rangle &= \left(\boldsymbol{J}_1^2 + \boldsymbol{J}_2^2 + 2\boldsymbol{J}_1 \cdot \boldsymbol{J}_2\right)|j_1, j_2\rangle \\
&= \left[\hbar^2 j_1\,(j_1+1) + \hbar^2 j_2\,(j_2+1) + 2\left(J_1^z J_2^z + J_1^+ J_2^- + J_1^- J_2^+\right)\right]|j_1, j_2\rangle \\
&= \hbar^2\left((j_1+j_2)^2 + (j_1+j_2)\right)|j_1, j_2\rangle \\
&= \hbar^2\,(j_1+j_2)\,(j_1+j_2+1)\,|j_1, j_2\rangle
\end{aligned}$$

Where we have rewritten $|j_1, j_1, j_2, j_2\rangle$ as $|j_1, j_2\rangle$, representing $|m_1, m_2\rangle$, and we remove the ladder operator terms using the fact that j_1 and j_2 are the maximum values of m. From this result, we see that $j = j_1 + j_2$.

Thus we have that

$$|j_1, j_2\rangle = |j_1 + j_2, j_1 + j_2\rangle$$

Where the first ket is $|m_1, m_2\rangle$, and the second ket is $|j, m\rangle$.

From this, we can easily find all other states with the same j by applying the lowering operator:

$$J^- |j_1 + j_2, j_1 + j_2\rangle \sim |j_1 + j_2, j_1 + j_2 - 1\rangle$$

We already know the raising and lowering relations:

$$J^\pm |j, m\rangle = \sqrt{(j \mp m)\,(j \pm m + 1)}\,|j, m \pm 1\rangle$$

So we can apply these to find that

$$J^- |j_1 + j_2, j_1 + j_2\rangle = \sqrt{2\,(j_1 + j_2)}\,|j_1 + j_2, j_1 + j_2 - 1\rangle$$

Flipping this statement, we have that:

$$|j_1 + j_2, j_1 + j_2 - 1\rangle = \frac{1}{\sqrt{2\,(j_1 + j_2)}} J^- |j_1 + j_2, j_1 + j_2\rangle$$

Writing this out as an operation on $|m_1, m_2\rangle$:

$$\begin{aligned}
&= \frac{1}{\sqrt{2\,(j_1 + j_2)}}\left(J_1^- + J_2^-\right)|j_1, j_2\rangle \\
&= \sqrt{\frac{j_1}{j_1 + j_2}}\,|j_1 - 1, j_2\rangle + \sqrt{\frac{j_2}{j_1 + j_2}}\,|j_1, j_2 - 1\rangle
\end{aligned}$$

We can construct an orthogonal state by switching the two kets and changing the sign:

$$|x\rangle = \sqrt{\frac{j_2}{j_1 + j_2}}\,|j_1 - 1, j_2\rangle - \sqrt{\frac{j_1}{j_1 + j_2}}\,|j_1, j_2 - 1\rangle$$

This turns out to be exactly equal to the state

$$|j = j_1 + j_2 - 1, m = j_1 + j_2 - 1\rangle$$

The way to prove this is to apply $\boldsymbol{J}^2$, and show that it is an eigenstate. We will not prove this. From here, we can apply another J^-, and we will see that we have a linear combination of two states, along with an independent state, and they will correspond to $j = j_1 + j_2 - 2$, and $m = j_1 + j_2 - 2$. We can continue to do this, and we will find every single state in our space.

When we continue this algorithm, we have the states given by

$$|j, m\rangle \qquad j = j_1 + j_2, j_1 + j_2 - 1, \dots, |j_1 - j_2|$$

With $m = -j, -j + 1, \dots, j$. We see that the total angular momentum works the same way that the single spin angular momenta worked.

From this, we have that the spin systems, when coupled, will have dimensionality given by:

$$j_1 \otimes j_2 = j_1 + j_2 \oplus j_1 + j_2 - 1 \oplus \cdots \oplus |j_1 - j_2|$$

In the case of two spins, this gets us the $2\times 2 = 3+1$. This gives us a trick to find new representations, by multiplying together the 2 dimensional representations:

$$\begin{aligned} 2 \times 3 &= 4 + 2 \\ 3 \times 3 &= 5 + 3 + 1 \end{aligned}$$

Essentially, when we multiply two Hilbert spaces, we have the $|m_1, m_2\rangle$ basis, and we have that summed basis, $|j, m\rangle$, where $j = j_1 + j_2, \dots |j_1 - j_2|$. The unitary matrix that transforms between the two is given by the Clebsch Gordan coefficients, or the Wigner 3j symbol:

$$|j, m\rangle = \sum_{m_1, m_2} U(j, m, m_2, m_3) \, |m_1, m_2\rangle$$

Where $U(j, m, m_1, m_2) = \langle m_1, m_2 | j, m\rangle$.

We can also transform back:

$$|m_1, m_2\rangle = \sum_{j,m} \langle j, m | m_1, m_2\rangle \, |j, m\rangle$$

Note that these are unitary:

$$\begin{aligned} \sum_{m_1, m_2} \langle j, m | m_1, m_2\rangle \langle m_1, m_2 | j', m'\rangle &= \delta_{j,j'} \delta_{m,m'} \\ \sum_{j,m} \langle m_1, m_2 | j, m\rangle \langle j, m | m_1', m_2'\rangle &= \delta_{m_1, m_1'} \delta_{m_2, m_2'} \end{aligned}$$

Suppose we have two spaces, and the angular-momentum operators in each space obey the usual commutation relations. The product space has the operator

$$\boldsymbol{J} = \boldsymbol{J}_1 + \boldsymbol{J}_2$$

We can look at the Clebsch Gordan coefficients:

$$|jm\rangle = \sum_{m_1,m_2} \langle m_1 m_2 | jm\rangle \, |m_1 m_2\rangle$$

Let us do an example. Consider a Hydrogen atom. The electron can have angular-momentum $l = 0, 1, 2, \ldots \infty$, and the spin is $s = \frac{1}{2}$. The total angular momentum is then $\boldsymbol{j} = \boldsymbol{l} + \boldsymbol{s}$. If $l = 0$, then $j = \frac{1}{2}$. If $j \neq 0$, then $j = l \pm \frac{1}{2}$.

Now let us look at the energy levels of the Hydrogen atom. The ground state, $n = 1$, corresponds to $l = 0$, and thus $j = \frac{1}{2}$. Using spectroscopic notation, labelling states using n, L, and j, we have that the ground state is $1, S, \frac{1}{2}$. If we go to the $n = 2$ state, we have that $l = 0$ or $l = 1$. If $l = 0$, then we are in the $2, S, \frac{1}{2}$ state. When $l = 1$, we have that $j = \frac{3}{2}$ or $j = \frac{1}{2}$. Therefore the state is $2, P, \frac{3}{2}$ or $2, P, \frac{1}{2}$.

Let us look more closely at the $n = 2$ case. If $l = 1$, then we can have 3 possible values for m_l, $\pm, 0$. We can also have up spin or down spin, $m_s = \pm\frac{1}{2}$. Thus when we combine these:

$$|l = 1, m_l = \pm_1, 0\rangle \otimes |s = \frac{1}{2}, m_s = \pm\frac{1}{2}\rangle = |m_l, m_s\rangle$$

This is a $3 \times 2 = 6$ dimensional space, and we can represent this in terms of a $4 + 2$ representation. If we want to find the relationship between the two bases, we can relate $|j, m\rangle$ to $|m_l, m_s\rangle$, via the Clebsch Gordan coefficients:

$$|j = l + \frac{1}{2}, m\rangle = \sqrt{\frac{l + m + \frac{1}{2}}{2l + 1}} \underbrace{|m_l = m_l - \frac{1}{2}, m_s = \frac{1}{2}\rangle}_{Y_{l.m_l - \frac{1}{2}}(\theta,\phi)\begin{pmatrix}1\\0\end{pmatrix}} + \sqrt{\frac{l - m + \frac{1}{2}}{2l + 1}} \, |m_l = m_l + \frac{1}{2}, m_s = -\frac{1}{2}\rangle$$

Thus we have that

$$\Psi_{j=\frac{3}{2}, l=1, m} = \begin{pmatrix} \sqrt{\frac{l+m+\frac{1}{2}}{2l+1}} Y_{l, m_l - \frac{1}{2}}(\theta, \phi) \\ \sqrt{\frac{l-m+\frac{1}{2}}{2l+1}} Y_{l, m_l + \frac{1}{2}}(\theta, \phi) \end{pmatrix}$$

Consider a Hamiltonian:

$$H = \underbrace{H_0}_{\frac{p^2}{2m} + V(r)} + V_{SO}$$

Where V_{SO} is the spin orbital term:

$$V_{SO} = V(r) \boldsymbol{s} \cdot \boldsymbol{l}$$

In order to compute the matrix elements of this, it is easier to do so in the states $|j, m\rangle$:

$$\begin{aligned} \langle j, m | \boldsymbol{s} \cdot \boldsymbol{l} | j, m\rangle &= \frac{1}{2} \langle j, m | \left(\boldsymbol{s} + \boldsymbol{l}\right)^2 - \boldsymbol{s}^2 - \boldsymbol{l}^2 | j, m\rangle \\ &= \frac{\hbar^2}{2} \left(j\left(j + 1\right) - l\left(l + 1\right) - \frac{1}{2}\left(\frac{1}{2} + 1\right)\right) \end{aligned}$$

Where we have noted that $\left(\boldsymbol{s} + \boldsymbol{l}\right)^2$ is just the total angular momentum squared.

1.5 Tensor Operators

So far, we have discussed how rotations in real space correspond to rotations of the wavefunction in Hilbert space. The natural question arises, how do we rotate operators in Hilbert space? It turns out that there is a bunch of math that goes into this, we will do simple cases, and then generalize that using tensor operators.

Let us start with something that we know. Consider a system that is rotationally symmetric. In this case, the Hamiltonian, an operator in Hilbert space, is rotationally invariant:

$$UHU^\dagger = H$$

The Hamiltonian is a scalar under rotation. Note that all atomic nuclei, with no external fields, are invariant under rotation. This is because the space that we live in places equal weight on each of the 3 directions, there is no difference between the x, y, and z axes.

However, we have operators that are not invariant under rotation, such as the position operators.

How do we transform the position operator in Hilbert space? This is key when defining tensor operators. When we consider the rotation of vectors, we generate a new vector via the application of a rotation matrix:

$$\boldsymbol{r}' = R\boldsymbol{r}$$

where $R \in SO(3)$.

When we consider the Hilbert space rotation:

$$|\psi'\rangle = U(R)\,|\psi\rangle$$

We expect that if we compute $\langle\psi'|\boldsymbol{r}|\psi'\rangle$, the expectation value of the position in the rotated state, this should be equal to the expectation value of the rotated vector in the original state:

$$\langle\psi'|\boldsymbol{r}|\psi'\rangle = \langle\psi|R\boldsymbol{r}|\psi\rangle$$

What does this tell us? We know that $|\psi'\rangle = U(R)\,|\psi\rangle$, so we can replace the left side of the expression:

$$\langle\psi|U^\dagger\boldsymbol{r}U|\psi\rangle = \langle\psi|R\boldsymbol{r}|\psi\rangle$$

From this, we know that, since this should apply for any $|\psi\rangle$, we have that

$$U^\dagger\boldsymbol{r}U = R\boldsymbol{r}$$

The left side denotes that $\boldsymbol{r}$ is an operator, and it transforms like an operator, and the right side states that $\boldsymbol{r}$ is a vector, and it transforms like a vector. In order for our formalism to be solid, we need these both to match.

If this is true, it must also be true for infinitesimal transformations:

$$U = 1 - i\boldsymbol{\theta}\cdot\boldsymbol{L}/\hbar$$

with its associated realspace rotation matrix:

$$R = 1 - i\boldsymbol{G}\cdot\boldsymbol{\theta}$$

We can insert these two rotations into our expression:

$$(1 - i\boldsymbol{\theta} \cdot \boldsymbol{L}/\hbar)\, \boldsymbol{r}\, (1 - i\boldsymbol{\theta} \cdot \boldsymbol{L}/\hbar) = (1 - i\boldsymbol{G} \cdot \boldsymbol{\theta})\, \boldsymbol{r}$$

If we go through all of this, we will find that

$$[\hat{r}_i, L_j] = i\hbar\epsilon_{ijk} r_k$$

Let us make a concrete definition.

If we have 3 vectors V_1, V_2, and V_3, and they obey the commutation relations:

$$[V_i, J_j] = i\epsilon_{ijk}\hbar V_k$$

Then V_i is a vector operator in Hilbert space.

As a consequence, we have that

$$U\boldsymbol{V}U^\dagger = R\boldsymbol{V}$$

There are many things that obey this commutation relation, such as position, momentum, angular momentum, the Pauli $\boldsymbol{\sigma}$ vector, etc.

Let us now try to generalize this, to tensor operators.

Suppose instead of 3 operators, we have 9 operators:

$$T^{i,j}$$

Where $i = 1, 2, 3$ and $j = 1, 2, 3$. Suppose that the spatial rotation applies to T^{ij} as it did for the vector operators:

$$UT^{ij}U^\dagger = \sum_{i',j'} R^{ii'} R^{jj'} T^{i'j'}$$

If this is true, then T^{ij} is known as a second order tensor operator. We can generalize this to an operator with e^n components:

$$T^{i_1,i_2,\ldots,i_n}$$

Where each index goes from 1 to 3. If we apply a rotation, and it transforms as follows:

$$UT^{i_1,i_2,\ldots,i_n}U^\dagger = \sum_{i'_1,\ldots i'_n} R^{i_1 i'_1} \ldots R^{i_n i'_n} T^{i_1,i_2,\ldots,i_n}$$

Then T is an nth order tensor operator in Cartesian coordinates.

Let us look at an example. The quadropole moment of a system is represented as a second order tensor. Systems can also have the octopole moment, which is a 3rd order tensor.

Let us consider a second order tensor operator, T^{ij}. What if we look at:

$$T^{11} + T^{22} + T^{33}$$

This sum does not change under rotation:

$$U\left(T^{11}+T^{22}+T^{33}\right)U^{\dagger}=\left(T^{11}+T^{22}+T^{33}\right)$$

This is also written in Einstein notation as T^{ii}, which gives a 1 dimensional representation.

Now consider:

$$V^{i}=\epsilon^{ijk}T^{jk}$$

This transforms like a vector, and this is the only vector operator that we can get out of this tensor. This is a 3 dimensional representation.

Now consider:

$$W^{ij}=T^{ij}+T^{ji}-\frac{2}{3}\delta^{ij}T^{kk}$$

When we do this, we find that $W^{kk}=0$. If we look at the vector operator representation of W^{ij} , we see that it is also 0, therefore W only has 5 independent components, and we have our 5 dimensional representation. As we can see, $3\times 3=1+3+5=9$. Thus we see that our definition of tensors are reducible, which is not what we want. We want an irreducible representation of tensor operators. An irreducible tensor of order k will have $2k+1$ components

$$UT^{kq}U^{\dagger}=\sum_{q'}\mathcal{D}^{(k)}_{qq'}(R)T^{(k)q'}$$

Where $q=-k,-k+1,\ldots,k$, and $\mathcal{D}$ is the Wigner D matrix. This is a spherical tensor operator of order k.

We see that the operators that make up the tensor are shuffled around by the Wigner D matrix.

We seem to be able to form the vector

$$\begin{bmatrix} T^{(k)}_{k} \\ T^{(k)}_{k-1} \\ T^{(k)}_{k-2} \\ \vdots \\ T^{(k)}_{-k} \end{bmatrix}$$

and we have a rotation that acts on this vector of operators, to form the rotated $T^{(k)}_{q}$. Thus, $T^{(k)}_{q}$ forms a $2k+1$ dimensional representation of $SO(3)$.

Now let us look at some examples of tensor operators. The simplest is the scalar, an operator that doesn't transform under rotation. These correspond to $k=0$, $q=0$.

We can then go to $k=1$. In this case, $q=\pm_1,0$, so we have 3 operators. Recall that we defined a vector operator, that had 3 operators, which rotate under a spatial rotation, and obey certain commutation relations with the components of $\boldsymbol{J}$. Note that these are defined in the Cartesian basis. What is the relationship between vector operators and the rank 1 spherical tensor operator? It turns out that they are given as

$$T^{(1)}_{0}=V^{z}$$

$$T^{(1)}_{\pm 1} = \mp \frac{1}{\sqrt{2}} \left(V^x \pm iV^y\right)$$

This can be thought of as a general form of the relationship between spherical harmonics $Y^1_m(\theta, \phi)$ and x, y, and z.

1.5.1 Product of Tensor Operators

Now let us consider the product of tensor operators. Consider two tensor operators $X^{(k_1)}_{q_1}$ and $Y^{(k_2)}_{q_2}$, with $2k_1 + 1$ and $2k_2 + 1$ operators respectively. To get the new tensor operator, we will use Clebsch-Gordan coefficients:

$$Z^{(k)}_q = \sum X^{(k_1)}_{q_1} Y^{(k_2)}_{q_2} \langle k_1 q_1 k_2 q_2 | kq \rangle$$

Note that the Clebsch-Gordan coefficients will vanish unless we have the relationship that $|k_1 - k_2| < k < k_1 + k_2$. We are essentially treating the operators as if they are a basis in Hilbert space, we are treating them the way that we treated the addition of representations.

Suppose we look at the coupling between two rank 1 tensors. We can expect either a rank 0, rank 1, or rank 2 tensor operator as a result. Let us construct the rank 0, scalar operator:

$$Z^0 = \sum_{q_1, q_2} X^{(1)}_{q_1} Y^{(1)}_{q_2} \langle 0, 0 | 1, q_1, 1, q_2 \rangle$$

Note that we can flip the inner product because Clebsch-Gordan coefficients are all real.

Now looking at the Clebsch-Gordan coefficients, we know that $q_1 + q_2 = 0$ for the nonvanishing coefficients. Thus we have that $q_1 = -q_2$, and q_1 can only take 3 values, $\pm_1$ and 0:

$$Z^{(0)} = \frac{1}{\sqrt{3}} X^{(1)}_{+1} Y^{(1)}_{-1} + \frac{1}{\sqrt{3}} X^{(1)}_{-1} Y^{(1)}_{+1} - \frac{1}{\sqrt{3}} X^{(1)}_0 Y^{(1)}_0$$

Where the coefficients are obtained from the Clebsch-Gordan table.

Why are we doing this? We know another way to get a scalar out of two vectors, the dot product. It turns out that if we convert the operators to Cartesian, $Z^{(0)}_0$ is just the dot product of the two vectors.

Now consider the rank 2 result:

$$\begin{aligned}
Z^{(2)}_{q=\pm 2} &= X^{(1)}_{\pm 1} Y^{(1)}_{\pm 1} \\
Z^{(2)}_{q=\pm 1} &= \frac{1}{\sqrt{2}} \left(X^{(1)}_{\pm 1} Y^{(1)}_0 + X^{(1)}_0 Y^{(1)}_{\pm 1} \right) \\
Z^{(2)}_{q=0} &= \frac{1}{\sqrt{6}} \left(X^{(1)}_{+1} Y^{(1)}_{-1} + X^{(1)}_{-1} Y^{(1)}_{+1} \right) + \sqrt{\frac{2}{3}} X^{(1)}_0 Y^{(1)}_0
\end{aligned}$$

Now let's do another check. If we let these two operators be just some position vectors, $\boldsymbol{r}$ and $\boldsymbol{r}'$, then $Z^{(2)}_m \sim Y^2_m$.

Now let's see why the past 3 weeks of lectures have been useful, and how we can use symmetries and tensor operators to simplify our computations.

1.5.2 Wigner-Eckart Theorem

In quantum mechanics, at the end of the day, we are calculating matrix elements:

$$\langle \phi | \hat{O} | \varphi \rangle$$

Sometimes this matrix element is 0, and we want to know when the matrix element is 0. These are known as selection rules. The only way that a transition probability matrix element will be zero is if there is a symmetry. Suppose we have nothing that breaks rotational symmetry in our system, so we can write our states in terms of a spherical angular-momentum basis. We can also write any operator in terms of spherical tensor operators.

$$\langle \phi | \hat{O} | \varphi \rangle = \langle \alpha', j', m' | T_q^{(k)} | \alpha, j, m \rangle$$

This means that we have to calculate a lot of matrix elements, because $= -j, -j+1, \dots, j$, $q = -k, -k+1, \dots, k$, and similarly for m'. Even if we fix α, k, and α', we have to calculate $(2j+1)(2j'+1)(2k+1)$ matrix elements.

Suppose we have a Hydrogen atom, in the $n = 2$, $l = 2$ state. It makes a transition to the $l = 1$ state. This is a dipole transition, with dipole operator $\boldsymbol{p}$. Suppose we want to compute the transition probability of this. We start with 5 possible magnetic quantum numbers, and we have 3 components of the operator, and we have 3 final possible states. This means that we have to calculate 45 matrix elements. Using the tools that we have developed over the last 3 weeks, we can reduce this down to doing only 1 matrix element, using the Wigner-Eckart theorem.

Theorem 1.1. *Wigner-Eckart Theorem Consider the matrix element $\langle \alpha', j', m' | T_q^{(k)} | \alpha, j, m \rangle$. This matrix element is equal to*

$$\langle \alpha', j', m' | T_q^{(k)} | \alpha, j, m \rangle = \langle j, m, k, q | j', m' \rangle \left(\frac{\langle \alpha', j' || T^{(k)} || \alpha, j \rangle}{\sqrt{2j+1}} \right)$$

Where the first term is a Clebsch-Gordan coefficient, and the second coefficient is known as the reduced matrix element, and is independent of j', j, and q.

In atomic physics, the most important transition is the dipole transition, whose operator $\boldsymbol{d}$ can be represented with a rank 1 spherical tensor.

We can, via the Wigner-Eckart theorem, immediately see that $l = 0$ to $l = 0$ dipole transition cannot happen:

$$\begin{aligned} \langle j = 0 | T^{(k=1)} | j = 0 \rangle &\sim \langle 001m | 00 \rangle \\ &= 0 \end{aligned}$$

Since the Clebsch-Gordan constraints are not satisfied, and thus the coefficient vanishes. This is a selection rule, we didn't need to calculate anything. (Note that this transition can actually happen, its called a 2 photon transition, but it takes a very long time, on the order of minutes rather than nanoseconds).

We know that

$$\langle \alpha, j', m' | T^{(1)} | \alpha, j, m \rangle \sim \langle j, m, 1, q | j', m' \rangle$$

We see that we can only have $j - j' = 0$ or $j - j' = \pm 1$, otherwise the Clebsch-Gordan coefficient will be zero. If we start at $l = 2$, we cannot make a transition to anything other than $l = 1, 2, 3$. This is a selection rule:

$$\begin{aligned} |j - j'| &\leq 1 \\ m' &= m + q \end{aligned}$$

We can also have operators of higher rank, such as the octopole transition, which is a rank 3 tensor operator.

1.5.3 Translational Symmetry

Suppose we have that the Hamiltonian commutes with the operator U:

$$[H, U] = 0$$

If we have this, then we have degeneracies. To show this, we look at the energy eigenstates:

$$H \left|\psi_n\right\rangle = E_n \left|\psi_n\right\rangle$$

It is easy to show that $U \left|\psi_n\right\rangle$ is also an energy eigenstate, with the same energy:

$$\begin{aligned} H(U \left|\psi_n\right\rangle) &= UH \left|\psi_n\right\rangle \\ &= UE_n \left|\psi_n\right\rangle \\ &= E_n \left(U \left|\psi_n\right\rangle\right) \end{aligned}$$

We see that the symmetry has led to degeneracies. What is the relationship between $U \left|\psi_n\right\rangle$ and $\left|\psi_n\right\rangle$. If we look at the application of all possible U to the eigenstate, this gives us a subspace of states, each of which is degenerate with that energy eigenstate. Thus the dimension of this subspace, $\mathrm{Dim}\{U \left|\psi_n\right\rangle\}$ is the degeneracy.

Sometimes this dimension is 1. In this case, we call the state **symmetric under** $\{U\}$, we have no degeneracy.

For example, consider the ground state of the Hydrogen atom, ψ_{100}. U is a continuous symmetry ϵ_i, where $i = 1, \ldots, n$:

$$U = 1 - i \sum_i \epsilon_i \frac{G_i}{\hbar}$$

Where G_i are Hermitian, and correspond to physical observables. Note that these generators are also time-independent:

$$\begin{aligned} i\hbar \frac{dG_i}{dt} &= [H, G_i] \\ &= 0 \end{aligned}$$

We see that the G_i are conserved. This is exactly what we found before, the degeneracy is the dimension of the group of rotations, $2l + 1$.

Consider starting from the state $\left|n = 2, l = 1, m = 0\right\rangle$, and rotating it:

$$U \left|n = 2, l = 1, m = 0\right\rangle = \sum_{m=-1,0,1} \lambda_m \left|l = 1, m\right\rangle$$

We have a triple degeneracy, $2l+1=3$. We essentially fix an eigenstate, and then apply all possible rotations, and we have a linear superposition of different possible wavefunctions, giving us the degeneracy. The ground state however, is symmetric, $|n=1,l=0,m=0\rangle$ will only ever be rotated to itself.

Now let us consider a spatial translation. Suppose we have some physical system that we shift by $\boldsymbol{a}$. The transformation that we applied to the system is mapping $\boldsymbol{r}$ to $\boldsymbol{r}'=\boldsymbol{r}+\boldsymbol{a}$, and we are mapping the wavefunction to some new wavefunction, $|\psi\rangle \rightarrow |\psi'\rangle$:

$$U(\boldsymbol{a})\,|\psi\rangle = |\psi'\rangle$$

We have that $\psi(\boldsymbol{r}) = \langle \boldsymbol{r}|\psi\rangle$, and similarly for $\psi(\boldsymbol{r}')$. We also have $\psi'(\boldsymbol{r}) = \langle \boldsymbol{r}|\psi'\rangle$. We alos have the condition that the new wavefunction at the new coordinate should be the same as the original wavefunction at the original coordinates, since we are just shifting everything over:

$$\psi'\left(\boldsymbol{r}'\right) = \psi\left(\boldsymbol{r}\right)$$

From this, we have that

$$\psi'\left(\boldsymbol{r}\right) = \psi\left(\boldsymbol{r}-\boldsymbol{a}\right)$$

Now let us attempt to Taylor expand the right side around $\boldsymbol{a}=0$:

$$\begin{aligned}\psi'\left(\boldsymbol{r}\right) &= \psi\left(\boldsymbol{r}-\boldsymbol{a}\right)\\ &= e^{-\boldsymbol{a}\cdot\boldsymbol{\nabla}}\psi(\boldsymbol{r})\end{aligned}$$

Where we have omitted steps, but it boils down to the Taylor series being a series of derivatives of ψ. Now let us define a new operator:

$$\boldsymbol{p} = \frac{\hbar}{i}\boldsymbol{\nabla}$$

From this, we have that

$$\psi'\left(\boldsymbol{r}\right) = e^{-i\boldsymbol{a}\cdot\boldsymbol{p}}\psi(\boldsymbol{r})$$

We see that $\boldsymbol{p}$ is the vector of generators of translations. This translation is Abelian, translating by $\boldsymbol{b}$ and $\boldsymbol{a}$ in any order is the same:

$$U(\boldsymbol{a})U(\boldsymbol{b}) = U(\boldsymbol{b})U(\boldsymbol{a})$$

We can write any translation using the generators:

$$U = 1 - i\hbar\boldsymbol{a}\cdot\boldsymbol{p} + \dots$$

And the generators commute, $[p_i,p_j]=0$. We also see that the generators are the momentum operators. Since the translation operators commute with the Hamiltonian, by our previous statements about generators, the momentum must be conserved:

$$[H,U(\boldsymbol{a})] = 0 \rightarrow [H,\boldsymbol{p}] = 0$$

This tells us that if our system is translationally invariant, the momentum must be conserved, we have a conservation law that comes out of a property of the Hamiltonian.

Now let us see how we get translational symmetry in a Hamiltonian. Consider:

$$H = \frac{\boldsymbol{p}^2}{2m} + V\left(\boldsymbol{r}\right)$$

This first term is translationally invariant, but the second term need not be:

$$U\left(\boldsymbol{a}\right)^{\dagger} HU\left(\boldsymbol{a}\right) = \frac{\boldsymbol{p}^2}{2m} + V\left(\boldsymbol{r} - \boldsymbol{a}\right)$$

If $V = 0$, then $[H, \boldsymbol{p}] = 0$, and we have the free particle case. In crystals, where we have periodic potentials, this gives rise to the Bloch theorem.

If we have that $[H, \boldsymbol{p}] = 0$, we have plane wave states:

$$\psi_{\boldsymbol{p}}\left(\boldsymbol{r}\right) = e^{i\boldsymbol{p}\cdot\boldsymbol{r}/\hbar}$$

We can apply a translation operator to this, and try to find the dimension of the space, to get the degeneracy.

$$\begin{aligned} U(\boldsymbol{a})\psi_{\boldsymbol{p}}\left(\boldsymbol{r}\right) &= e^{-\boldsymbol{a}\cdot\boldsymbol{\nabla}}\psi_{\boldsymbol{p}}\left(\boldsymbol{r}\right) \\ &= \psi_{\boldsymbol{p}}\left(\boldsymbol{r} - \boldsymbol{a}\right) \\ &= e^{-i\boldsymbol{p}\cdot\boldsymbol{a}}e^{i\boldsymbol{p}\cdot\boldsymbol{r}/\hbar} \\ &\sim e^{i\boldsymbol{p}\cdot\boldsymbol{r}/\hbar} \end{aligned}$$

We see that this is equal to the original state, up to an overall phase. This means that we don't really have degeneracies, since we only end up with the same state. However, we know that we have degeneracies, but those turn out to come from the rotation operators, not the translation operators:

$$\text{Dim}\left[U\left(\boldsymbol{\theta}\right)\psi_{\boldsymbol{p}}\left(\boldsymbol{r}\right)\right] = \infty$$

1.6 Discrete Symmetries

So far we have just discussed continuous symmetries, with an infinite number of transformations. Let us now consider discrete symmetries, those with a finite number of symmetric transformations. We will discuss parity, also known as mirror or left/right symmetry, as well as time-reversal symmetry.

1.6.1 Parity

Let us now consider parity transformations. A parity transformation maps $\boldsymbol{r}$ to $-\boldsymbol{r}$:

$$(x, y, z) \to (-x, -y, -z)$$

This can be considered a mirror transformation, $(x, y, z) \to (x, y, -z)$, followed up with a 180 degree rotation about the z axis.

We can consider this transformation as a matrix:

$$R_p = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

Note that this matrix has determinant -1, unlike the rotation matrices, which has determinant 1. Together with the $SO(3)$ rotations, we can tack on the matrices with negative determinants, to form the group $O(3)$:

$$\{SO(3), SO(3) \times R_p\} = O(3)$$

We want to find the corresponding unitary operator in Hilbert space, π:

$$\pi \left|\psi\right\rangle = \left|\psi'\right\rangle$$

And it acts on the position:

$$\pi^\dagger \boldsymbol{r} \pi = -\boldsymbol{r}$$

Since π is unitary, $\pi^\dagger \pi = 1$.

Theorem 1.2. *The parity operator π acting on a basis vector maps states as follows:*

$$\pi \left|\boldsymbol{r}\right\rangle \to \left|-\boldsymbol{r}\right\rangle$$

Proof. Note that since $\pi^\dagger \boldsymbol{r} \pi = -\boldsymbol{r}$, we have that $\boldsymbol{r}\pi = -\pi\boldsymbol{r}$. We also have, by the definition of a position eigenstate:

$$\boldsymbol{r} \left|\boldsymbol{r}\right\rangle = \boldsymbol{r} \left|\boldsymbol{r}\right\rangle$$

Now consider $\boldsymbol{r} \left(\pi \left|\boldsymbol{r}\right\rangle\right)$:

$$\begin{aligned} \boldsymbol{r} \left(\pi \left|\boldsymbol{r}\right\rangle\right) &= -\pi \boldsymbol{r} \left|\boldsymbol{r}\right\rangle \\ &= \left(-\boldsymbol{r}\right) \pi \left|\boldsymbol{r}\right\rangle \end{aligned}$$

And thus this state must be equal to $\left|-\boldsymbol{r}\right\rangle$, up to a phase factor $e^{i\delta}$. ☐

Thus we have that

$$\pi \left|\boldsymbol{r}\right\rangle = e^{i\delta} \left|-\boldsymbol{r}\right\rangle$$

We make the choice that this phase factor is 0:

$$\pi \left|\boldsymbol{r}\right\rangle = \left|-\boldsymbol{r}\right\rangle$$

Now what happens with we apply this twice:

$$\begin{aligned} \pi^2 \left|\boldsymbol{r}\right\rangle &= \pi \left|-\boldsymbol{r}\right\rangle \\ &= \left|\boldsymbol{r}\right\rangle \end{aligned}$$

Thus we have that $\pi^2 = 1$, and thus

$$\pi^{-1} = \pi = \pi^\dagger$$

Moreover, this tells us that the eigenvalues of π are only ±1.

We have discussed how states have transformed under parity, now let us consider how operators transform under the parity transformation.

First, we note that if the position flips under parity, then so too must the momentum:

$$\pi^\dagger \boldsymbol{r} \pi = -\boldsymbol{r} \qquad \pi^\dagger \boldsymbol{p} \pi = -\boldsymbol{p}$$

From this, we can define a vector, something that transforms as we have discussed before, and it transforms like position under parity:

$$U^\dagger (R)\, \boldsymbol{V} U (R) = R_{ij} V_k \qquad \pi^\dagger \boldsymbol{V} \pi = -\boldsymbol{V}$$

Let us look at angular momentum. Consider the application of a rotation and a parity operation, we see that the parity operator must commutate with everything, since its just $-\mathbb{I}$:

$$R(\alpha, \beta, \gamma)\, R_\pi = R_\pi R(\alpha, \beta, \gamma)$$

Thus, we have that

$$\boldsymbol{J}\pi = \pi \boldsymbol{J} \qquad \pi^\dagger \boldsymbol{J} \pi = \boldsymbol{J}$$

We see that $\boldsymbol{J}$ is not a vector, it is instead an **axial vector**, which transforms under parity as:

$$\pi^\dagger \boldsymbol{A} \pi = +\boldsymbol{A}$$

We can also define scalars:

$$\pi^\dagger s \pi = s$$

We can also define a pseudo-scalar, which has one component, and changes sign under parity:

$$\pi^\dagger p \pi = -p$$

An example of a pseudo-scalar would be the product of a vector and an axial vector:

$$\pi^\dagger \boldsymbol{V} \cdot \boldsymbol{A} \pi = -\boldsymbol{V} \cdot \boldsymbol{A}$$

Now let us ask a question. Does the Hamiltonian of nature commute with parity?

$$[H, \pi] = 0 \quad (?)$$

Before 1957, we thought that the answer was yes. However, in 1957, Lee and Yang proved that this was true for electromagnetism, gravity, and strong interactions, but it turns out to be not true for weak interactions.

Consider the Sun, which has a lot of protons inside. The interaction between protons is based on the weak interaction :

$$p + p \to d + e^{+} + V_e$$

Two protons turn into a deuteron, an electron, and a neutrino.

The weak force Hamiltonian was determined to not go back to itself. The weak interaction Hamiltonian has two parts, one part that is a scalar, and another that is a pseudo-scalar:

$$H_W = H_s + H_p \to \pi^\dagger H_W \pi = H_s - H_p$$

Nature breaks parity due to the weak interaction.

This was first experimentally determined by Wu, using Cobalt-60. Cobalt-60 can undergo β decay, which turns it into Nickel-60, electrons, and neutrinos. The electrons that are emitted by the decay can come out in any set of directions. If we look at this process under a parity transformation, the angular momentum does not change, the spin of the Nickel-60 nucleus will be the same direction, but the electron momentum will flip via parity. Now, due to the fact that we have rotational symmetry, we can see whether the number of electrons emitted in the $\boldsymbol{n}$ direction and the flipped direction, and if they are not the same, then we have violated parity symmetry.

We have seen how the parity operator applies to position eigenstates, so we know how it works on wavefunctions:

$$\psi'(\boldsymbol{r}) = \psi(-\boldsymbol{r})$$

Consider a particle in a central potential. The wavefunction is given as:

$$\psi_{nlm}(\boldsymbol{r}) = R_{nl}(r)\, Y_m^l(\theta, \phi)$$

When we do a parity transformation and take $\boldsymbol{r} \to -\boldsymbol{r}$, we have that r remains the same, $\theta \to \pi - \theta$, and $\phi \to \phi + \pi$.

Now we can see how the wavefunction changes:

$$\psi_{nlm}(\boldsymbol{r}) \to \psi_{nlm}(-\boldsymbol{r})$$

Looking at the spherical harmonics:

$$Y_m^l(\theta - \pi, \phi + \pi) = Y_m^l(\theta, \phi)(-1)^l$$

From this, we see that the wavefunction is an eigenstate of the parity operator. Note that if the eigenvalue of an eigenstate of the parity operator is $+1$, then we have whats known as an even parity, and if we have -1, then we have an odd parity state.

Consider a Hamiltonian that is symmetric under parity:

$$\pi^\dagger H \pi = H$$

Now consider the energy eigenstates:

$$H\,|\psi_n\rangle = E_n\,|\psi_n\rangle$$

These (if there is no energy degeneracy) are eigenstates of the parity operator:

$$\pi\left|\psi_n\right\rangle = e^{i\theta}\left|\psi_n\right\rangle$$

Consider the infinite square well, which has a Hamiltonian of the form:

$$H = \frac{p^2}{2m} + V\left(x\right)$$

And we have parity invariance, $[\pi, H] = 0$. Since the system is 1-D, we have no degeneracies. As such, each energy eigenstate will be a parity eigenstate, either even or odd. The ground state is even, the first excited is odd, the second excited is even, so on and so forth.

What is the benefit of considering the parity eigenstates? The nice thing is that we can make statements about these states in regards to parity. For example, consider atomic transitions. Suppose we start with an $l = 1$ start, and we are considering a dipole transition to a lower energy level with $l = 1$:

$$\langle\alpha', l = 1|e\boldsymbol{r}|\alpha, l = 1\rangle$$

We can use parity to argue that this is equal to 0. We can insert the identity:

$$\begin{aligned}\langle\alpha', l = 1|\pi^\dagger\pi e\boldsymbol{r}\pi^\dagger\pi|\alpha, l = 1\rangle &= \left(-1\right)^l\left\langle\alpha', l = 1\right|\left(-e\boldsymbol{r}\right)\left|\alpha, l = 1\right\rangle\left(-1\right)^l \\ &= -\left\langle\alpha', l = 1|e\boldsymbol{r}|\alpha, l = 1\right\rangle\end{aligned}$$

We see that the matrix element is equal to the negative of itself, and thus the only possibility is that it is 0.

Note that if parity is conserved, any isolated system cannot have a dipole moment.

1.6.2 Time-Reversal Symmetry

Time-reversal symmetry maps $t \to -t$.

Consider classical mechanics, where we have that $\boldsymbol{F} = m\boldsymbol{a}$, and we have some potential:

$$m\frac{d^2\boldsymbol{r}}{dt^2} = -\nabla V\left(\boldsymbol{r}\right)$$

If we apply a time-reversal symmetry, we see that Newton's equations are invariant under time-reversal:

$$m\frac{d^2\boldsymbol{r}}{dt^2} = -\nabla V\left(\boldsymbol{r}\right) \to m\frac{d^2\boldsymbol{r}}{d\left(-t\right)^2} = -\nabla V\left(\boldsymbol{r}\right)$$

We have an original solution that moves forwards through time:

$$\boldsymbol{r} = \boldsymbol{r}(t)$$

and the time-reversal gives us a new solution that is the same solution but parameterized with time inverted:

$$\boldsymbol{r}' = \boldsymbol{r}\left(-t\right)$$

However, what if we have frictional forces? In this case, Newton's equations will also have a dependence on the velocity, and the equation is no longer invariant under time-reversal, we have a non-physical solution (objects moving backwards with friction pushing them, rather than slowing them down).

It turns out that it is hard to find interactions that violate time-reversal symmetry (E&M, gravity, and strong interactions all obey time-reversal symmetry), but the weak interaction might violate this symmetry. In fact, this asymmetry might be the reason for the existence of matter.

What happens in quantum mechanics? We have the Schrodinger equation:

$$i\hbar\frac{\partial}{\partial t}\psi\left(\boldsymbol{x},t\right)=H\psi\left(\boldsymbol{x},t\right)\to -i\hbar\frac{\partial}{\partial t}\psi\left(\boldsymbol{x},-t\right)=H\psi\left(\boldsymbol{x},-t\right)$$

This seems like its not time-reversal symmetric, but luckily we have the imaginary component. If we take the complex conjugate of the time-reversed equation, we see that we get back almost the original equation:

$$i\hbar\frac{\partial}{\partial t}\psi^{*}\left(\boldsymbol{x},t\right)=H\psi^{*}\left(\boldsymbol{x},t\right)$$

We see that a solution to the time-reversed equation is the same as the transpose of the original solution:

$$\psi^{T}\left(\boldsymbol{x},t\right)=\psi^{*}\left(\boldsymbol{x},-t\right)$$

The main issue now is that the time-reversal operator is not a unitary operator in the Hilbert space. The reason we like unitary operators is because it preserves the scalar product $\langle\psi|\phi\rangle$. This is actually a more stringent condition than we need! Experimentally, we only observe the norm, the square of these scalar products. Thus we are allowed to have scalar products that are complex conjugates, since this still preserves the norm:

$$\langle\psi|U^{\dagger}U|\phi\rangle=\langle\psi|\phi\rangle^{*}$$

In this case, U is known as an anti-unitary operator. What are the properties of an anti-unitary operator Θ? First, let us see the application on a linear combination:

$$\Theta\left(c_1\left|\psi_1\right\rangle+c_2\left|\psi_2\right\rangle\right)=c_1^{*}\Theta\left|\psi_1\right\rangle+c_2^{*}\Theta\left|\psi_2\right\rangle$$

This is known as anti-linearity.

The time-reversed solution corresponds to anti-unitary transformations. To prove this, we first note that for stationary position eigenstates, we expect this to be an eigenstate:

$$\Theta\left|\boldsymbol{r}\right\rangle=\boldsymbol{r}$$

Now consider a state $|\psi\rangle$, which we can expand in terms of the position basis:

$$\left|\psi\right\rangle=\int d\boldsymbol{r}\,\left\langle\boldsymbol{r}|\psi\right\rangle\left|\boldsymbol{r}\right\rangle$$

Now consider the time-reversed wavefunction:

$$\Theta\left|\psi\right\rangle=\int d^{3}\boldsymbol{r}\psi^{*}\left(\boldsymbol{r}\right)\Theta\left|\boldsymbol{r}\right\rangle$$

$$= \int d^3\boldsymbol{r}\, \psi^*\left(\boldsymbol{r}\right) \left|\boldsymbol{r}\right\rangle$$

It can be shown that any anti-unitary operator can be written as a unitary operator U multiplied by K, which does nothing except complex conjugate everything it is applied on:

$$\Theta = UK$$

Applying this to the $\boldsymbol{r}$ operator:

$$\Theta\boldsymbol{r}\Theta^{-1} = \boldsymbol{r}$$

However, it has an effect on the momentum, the momentum should flip directions when we reverse time. We also have the fact that

$$\boldsymbol{p} = \frac{\hbar}{i}\frac{\partial}{\partial\boldsymbol{r}}$$

Thus we have that

$$\Theta\boldsymbol{p}\Theta^{-1} = -\boldsymbol{p}$$

We can also argue that the angular-momentum should behave the same way:

$$\Theta\boldsymbol{J}\Theta^{-1} = -\boldsymbol{J}$$

From this, we can verify whether a Hamiltonian has time-reversal invariance.

For example, consider the Hamiltonian:

$$H = \frac{\boldsymbol{p}^2}{2m} + V\left(\boldsymbol{r}\right)$$

Applying the operator:

$$\Theta H\Theta^{-1} = \frac{\boldsymbol{p}^2}{2m} + V^*\left(\boldsymbol{r}\right)$$

We see that if the interaction is real, then we have time-reversal invariance, and if the potential has an imaginary part, then we lose that invariance. This is the same idea as the friction in classical mechanics. This is true in the case of electromagnetism, gravity, and the strong interaction, but we have complex parameters in the weak interaction Hamiltonian.

Let us again consider a particle in a central potential, and we have the wavefunction:

$$\psi_{nlm}\left(\boldsymbol{r}\right) = R_{nl}\left(r\right)Y^l_m\left(\theta,\phi\right)$$

What happens under a time-reversal transformation? Well we know that this maps $\psi_{nlm}\left(\boldsymbol{r}\right)$ to $\psi^*_{nlm}\left(\boldsymbol{r}\right)$. This means that we have to look at the complex conjugates of the spherical harmonics:

$$\left(Y^l_m\left(\theta,\phi\right)\right)^* = \left(-1\right)^m Y^l_{-m}\left(\theta,\phi\right)$$

We have a physical interpretation as to why this is the case. Consider a spherical harmonic. As we rotate, m is the projection of the angular-momentum along the z direction. When we reverse time, the direction of rotation goes backwards, and thus the angular-momentum will flip, and instead we will have $-m$ as our projection.

Thus we have that

$$\Theta\left|l,m\right\rangle = \left(-1\right)^m\left|l,-m\right\rangle$$

Theorem 1.3. *If H is invariant under time-reversal, and the state $|\phi_n\rangle$ is non-degenerate, then the eigenfunction is real.*

Proof. If we find an eigenstate $H|\phi_n\rangle = E_n|\phi_n\rangle$, then we have that $|\phi_n^*\rangle$ must also be an eigenstate, under time-reversal symmetry. Since we had no degeneracy, we have that they must be the same, $\phi_n = \phi_n^*$, and the eigenfunction is real. □

We see that this works for $l \in \mathbb{Z}$, but we can generalize this to fractional l, by saying that $(-1)^m = (i)^{2m}$:

$$\Theta|j,m\rangle = i^{2m}|j,-m\rangle \qquad j = 0, \frac{1}{2}, 1, \frac{3}{2}, \dots$$

In quantum computing, we use $j = \frac{1}{2}$, and we see that

$$\begin{aligned}\Theta|\frac{1}{2},\frac{1}{2}\rangle &= i|\frac{1}{2},-\frac{1}{2}\rangle \\ \Theta|\frac{1}{2},\frac{1}{2}\rangle &= -i|\frac{1}{2},\frac{1}{2}\rangle\end{aligned}$$

Now applying Θ^2, we see that we are left with the original state:

$$\begin{aligned}\Theta^2|\frac{1}{2},\frac{1}{2}\rangle &= \Theta\left(i|\frac{1}{2},-\frac{1}{2}\rangle\right) \\ &= -i\Theta|\frac{1}{2},-\frac{1}{2}\rangle \\ &= -|\frac{1}{2},\frac{1}{2}\rangle\end{aligned}$$

And similarly, $\Theta^2|\frac{1}{2},-\frac{1}{2}\rangle = -|\frac{1}{2},-\frac{1}{2}\rangle$. Generalizing this, we see that if j is a half-integer, then we have that $\Theta^2 = -1$, and if j is an integer, we have that $\Theta^2 = +1$.

What does this mean? Suppose we have a Hamiltonian that is invariant under time-reversal. If the system has half-integer spin, then the energy levels will have double degeneracies:

$$H|\psi_n\rangle = E_n|\psi_n\rangle$$

E_n, will have at least degeneracy 2, because if we have $|\psi_n\rangle$, we can apply time-reversal once , and we will have to end up at a different state, which has the same energy (since $[H,\Theta] = 0$). This is known as a Kramer degeneracy.

Now what is the time-reversal operator? In the spin $\frac{1}{2}$ case:

$$\Theta = e^{-i\pi J_y}K$$

It is a rotation by π degrees in the y direction, followed up by a complex conjugation.

As a quick aside, we can actually argue that no atom has a dipole moment. We note that the dipole is defined as:

$$\boldsymbol{d} = \sum_i e_i\boldsymbol{r}_i + Z\left(\boldsymbol{r} = 0\right)$$

Now we note that the dipole is an eigenstate of the parity operator:

$$\pi^\dagger \boldsymbol{d}\pi = -\boldsymbol{d}$$

Now we note that the Hamiltonian for the atom will be invariant under parity:

$$\pi^\dagger H\pi = H$$

Now look at the ground state of the atom:

$$H\left|g\right\rangle = E\left|g\right\rangle$$

Now because of this, we have that

$$\pi\left|g\right\rangle = \pm\left|g\right\rangle$$

Due to the fact that it is an eigenstate of the Hamiltonian, which is invariant under parity.

Now looking at the dipole moment:

$$\begin{aligned}\boldsymbol{d} &= \langle g|\boldsymbol{d}|g\rangle \\ &= \langle g|\pi^\dagger\pi\boldsymbol{d}\pi^\dagger\pi|g\rangle \\ &= \langle g|-\boldsymbol{d}|g\rangle \\ &= -\boldsymbol{d}\end{aligned}$$

And thus we have that $\boldsymbol{d} = 0$.

2 Perturbation Theory

At the simplest level, perturbation theory is based on a Taylor expansion:

$$f(x+a) = f(x) + af'(x) + \frac{a^2}{2!}f''(x) + \dots$$

If we allow a to be small, then we can cut off higher order terms (depending on the accuracy needed).

In physics, we consider effective theories, which are essentially idealized models. In thermodynamics and statistical mechanics, we have the ideal gas, which doesn't exist. We need to add interactions, but oftentimes the ideal gas serves as a good approximation for gases. An effective theory is a model that neglects the small effects that are present in the real world. To include these effects, we use a Taylor expansion, and this is known as an effective theory expansion, and is very common in theory.

2.1 Time-independent Perturbation Theory

Consider a Hamiltonian H_0. We assume that we have computed the spectrum of H_0:

$$H_0\left|n^{(0)}\right\rangle = E_n^{(0)}\left|n^{(0)}\right\rangle \qquad n^{(0)} = 0, 1, 2, \dots$$

Physically, our system has some additional potential, parametrized by λ:

$$H = H_0 + \lambda V$$

Where λ is an expansion parameter, and is very small. We want to find the spectrum of H:

$$H\left|n\right\rangle = E_n\left|n\right\rangle$$

However, suppose we don't know how to solve for the spectrum of H. To solve this, we use perturbation theory. We say that the exact eigenenergy will be approximately the unperturbed energy, plus corrections:

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots$$

We hope that this expansion converges, and we want to compute these corrections to the energy.

We can also expand the eigenstates:

$$\left|n\right\rangle = \left|n^{(0)}\right\rangle + \lambda\left|n^{(1)}\right\rangle + \lambda^2\left|n^{(2)}\right\rangle + \dots$$

Now let us look at the Schrodinger equation that we want to solve:

$$\left(H_0 + \lambda V\right)\left|n\right\rangle = E_n\left|n\right\rangle$$

From this, we can plug in what we have already expanded out, then match terms of equal order in λ, to get our result (We skip the derivation because everyone has already seen it). This is known as Rayleigh-Schrodinger perturbation theory. We can write out the energy corrections:

$$\begin{aligned}\Delta_n &= E_n - E_n^{(0)} \\ &= \lambda\left\langle n^{(0)}\middle|V\middle|n\right\rangle\end{aligned}$$

Which gives us a recursion relation:

$$\begin{aligned}\Delta_n^{(1)} &= \lambda\left\langle n^{(0)}\middle|V\middle|n^{(0)}\right\rangle \\ \Delta_n^{(2)} &= \lambda\left\langle n^{(0)}\middle|V\middle|n^{(1)}\right\rangle \\ \Delta_n^{k+1} &= \lambda\left\langle n^{(0)}\middle|V\middle|n^{(k)}\right\rangle\end{aligned}$$

Looking at the corrections to the wavefunctions, we first introduce a projection operator Q_n:

$$Q_n = \mathbb{I} - P_n$$

Where $P_n = \left|n^{(0)}\right\rangle\left\langle n^{(0)}\right|$. Note that $P_n + Q_n = \mathbb{I}$, the two projection operators separate the Hilbert space into two parts. Using this, we can write out the corrections to the wavefunction:

$$\left|n\right\rangle = \left|n^{(0)}\right\rangle + \frac{Q_n}{E_n^{(0)} - H_0}\left(\lambda V - \Delta_n\right)\left|n\right\rangle$$

This equation also allows us to iterate to get the solutions of higher order. Let us introduce the technique of power counting, which is basically asking "How many powers of λ do we have?" We see that $\left|n\right\rangle$ is a very complicated function of λ. $\left|n^{(0)}\right\rangle$ has no dependence on λ, and neither do $E_n^{(0)}$ or H_0. λV has one power of λ, and Δ_n contains all the powers of λ. If we wanted to get the first order corrections, we only look for the first order terms:

$$\left|n^{(1)}\right\rangle = \frac{Q_n}{E_n^{(0)} - H_0}\left(\lambda V - \Delta_n^{(1)}\right)\left|n^{(0)}\right\rangle$$

We have only the terms that would be first order in λ. However, we note that the second term in this is actually 0:

$$|n^{(1)}\rangle = \frac{Q_n}{E_n^{(0)} - H_0} (\lambda V) |n^{(0)}\rangle$$

However, this is a bit of a formal result, so let us rewrite this. Looking at Q_n:

$$Q_n = \sum_{k \neq n} |k^{(0)}\rangle \langle k^{(0)}|$$

Thus we can rewrite the result as:

$$\begin{aligned} |n^{(1)}\rangle &= \frac{Q_n}{E_n^{(0)} - H_0} (\lambda V) |n^{(0)}\rangle \\ &= \sum_{k \neq n} \frac{|k^{(0)}\rangle \langle k^{(0)}|\lambda V|n^{(0)}\rangle}{E_n^{(0)} - E_k^{(0)}} \end{aligned}$$

Which is the result that can be found in undergraduate quantum mechanics.

We have the second order energy corrections, and we can insert the first order wavefunction corrections to work it out explicitly in terms of known states and energies:

$$\begin{aligned} E_n^{(2)} &= \lambda \langle n^{(0)}|V|n^{(1)}\rangle \\ &= \lambda^2 \sum_{k \neq n} \frac{|\langle k^{(0)}|V|n^{(0)}\rangle|^2}{E_n^{(0)} - E_k^{(0)}} \end{aligned}$$

Now pushing on to the second order wavefunction corrections, we can once again use power counting:

$$\begin{aligned} |n^{(2)}\rangle &= \frac{Q_n}{E_n^{(0)} - H_0} \left[\lambda V |n^{(1)}\rangle - \Delta_n^{(2)} |n^{(0)}\rangle - \Delta_n^{(1)} |n^{(1)}\rangle\right] \\ &= \frac{Q_n}{E_n^{(0)} - H_0} \left[\lambda V |n^{(1)}\rangle - \Delta_n^{(2)} |n^{(0)}\rangle\right] \end{aligned}$$

Where once again, Q_n kills off $|n^{(0)}\rangle$. From this, we have

$$|n^{(2)}\rangle = \frac{Q_n}{E_n^{(0)} - H_0} \left(\lambda V - \Delta_n^{(1)}\right) |n^{(1)}\rangle$$

2.1.1 Polarizability of Hydrogen Atom

Recall that we have $\boldsymbol{P} = \chi_e \boldsymbol{E}$, where $\boldsymbol{E}$ is the external electric field, and χ_e is the susceptibility. We also have that the energy is given via:

$$\begin{aligned} \mathcal{E} &= -\boldsymbol{P} \cdot \boldsymbol{E} \\ &= -\frac{1}{2}\chi_e \boldsymbol{E}^2 \end{aligned}$$

Let us try to compute this for the Hydrogen atom, using perturbation theory.

Suppose we have a proton, with an orbiting electron, and an external magnetic field $\boldsymbol{E}$ in the z direction. For the electron, the Hamiltonian will be

$$H = \frac{\boldsymbol{p}^2}{2m} + \underbrace{\left(\frac{-Ze^2}{r}\right)}_{\text{Coulomb}} - \underbrace{e|\boldsymbol{E}|z}_{\text{Electric Potential}}$$

This Hamiltonian can be solved analytically, and is not terribly difficult, but it is definitely hard, we lose the spherical symmetry due to the electric field, giving us just cylindrical symmetry.

Let us assume that the electric potential felt by the electron is small. How small? The electron feels the electric field of the nucleus, which is kind of large. As long as the external field is smaller than the internal electric field of the atom, it can be considered small.

Thus, we can use perturbation theory:

$$H = H_0 + H' \qquad H' \ll H_0$$

We can compute the first order energy corrections:

$$\begin{aligned} E_n^{(1)} &= \langle n^{(0)}|H'|n^{(0)}\rangle \\ &= \langle n^{(0)}|\left(-e|\boldsymbol{E}|\right)z|n^{(0)}\rangle \\ &= -e|\boldsymbol{E}|\,\langle n^{(0)}|z|n^{(0)}\rangle \end{aligned}$$

Now arguing from a parity perspective ($z = \pi^\dagger z \pi$), this matrix element should be zero by inspection:

$$E_n^{(1)} = 0$$

Thus, we have to look at the second order energy corrections:

$$E_n^{(2)} = \sum_{k \neq n} \frac{|\,\langle k^{(0)}|V|n^{(0)}\rangle\,|^2}{E_n^{(0)} - E_k^{(0)}}$$

Let us focus on the $n = 1$ case:

$$E_1^{(2)} = \sum_{k=2,3,\ldots;\, l;\, m} \frac{|\,\langle 100|\left(-e|\boldsymbol{E}|z\right)|nlm\rangle\,|^2}{E_1^{(0)} - E_n^{(0)}}$$

Note that this energy correction is always negative, the numerator is positive and the denominator is negative, since the ground state energy minus all the excited state energies must be negative. The second observation that we can make is that the energy is proportional to $\boldsymbol{E}^2$:

$$E_1^{(2)} = -\frac{\alpha}{2}\boldsymbol{E}^2$$

Where α is the polarizability, and is equal to:

$$\alpha = 2e^2 \sum_{n,l,m} \frac{|\,\langle 100|z|nlm\rangle\,|^2}{E_n^{(0)} - E_1^{(0)}}$$

Now, via the Wigner-Eckart theorem, we have a selection rule. z is a rank 1 spherical tensor, with $q = 0$, and thus $q + m = 0$, and thus we have that $m = 0$:

$$\alpha = 2e^2 \sum_{n,l} \frac{|\langle 100|z|nl0\rangle|^2}{E_n^{(0)} - E_1^{(0)}}$$

We also have a constraint on l, since the total l is 0, and z has $l = 1$, so l must be 1, via the triangular relation. Thus we have that

$$\alpha = 2e^2 \sum_{n} \frac{|\langle 100|z|n10\rangle|^2}{E_n^{(0)} - E_1^{(0)}}$$

Now let us see if parity gets us any more simplification. We have the matrix element:

$$\begin{aligned}\langle 100|z|n10\rangle &= \langle 100|\pi^\dagger \pi z \pi^\dagger \pi|n10\rangle \\ &= \langle 100|\left(-z\right)\left(-1\right)|n10\rangle \\ &= \langle 100|z|n10\rangle\end{aligned}$$

Where we have used the fact that the ground state is invariant under parity, z maps to $-z$, and the right side gives us a factor of $(-1)^l$. However, we see that we just have the same matrix element, we don't get any more information.

Thus we have the infinite sum:

$$\alpha = 2e^2 \sum_{n} \frac{|\langle 100|z|n10\rangle|^2}{E_n^{(0)} - E_1^{(0)}}$$

We can look at just the first term of this summation, in the hope of getting an estimate. Another thing we can do is smarter, we can compute the matrix element as a function of n, and then attempt the summation. This works, but it takes a while. The third method is to do the following. What we do is to replace the $E_n^{(0)}$ in the denominator with $E_2^{(0)}$, and this provides an upper bound for the energy correction:

$$\alpha = 2e^2 \frac{1}{E_2^{(0)} - E_1^{(1)}} \underbrace{\sum_n |\langle 100|z|n10\rangle|^2}_{\langle 100|z^2|100\rangle}$$

This summation also (via some very difficult math) be solved exactly, with no approximation:

$$\alpha = \frac{9a_0^3}{2}$$

Where a_0 is the Bohr radius.

When we move to more complicated atoms, we can compute their polarizability, but they are not solvable analytically, and must be done either experimentally or via approximations.

An Aside about Perturbative QFT

For a long time, perturbation theory was the only way to do QFT, we would have Hamiltonians that had solvable free fields (plane waves), and we would have interactions among fields as perturbations. The key thing is to keep this Lorentz invariant, because QFT needs to describe relativistic theories. This development of perturbation theory for QFT got Feynman, Schwinger, and Tomonaga the Nobel Prize. Feynman developed a language to describe perturbation theory, known as Feynman diagrams. Essentially, he was able to write down all possible orders of corrections via diagrams, with rules on how to calculate them, known as Feynman rules.

Perturbative QFT was used to match theory to experiment, with an accuracy of over 9 digits after the decimal point, indicating that QFT was a very useful model.

Dyson was the first one to notice that Schwinger, Feynman, and Tomonaga, while their formalisms seemed different, they were all doing the same thing. He was interested in finding the radius of convergence for the expansion of the muon $g-2$, and he found that it was zero. He never touched QED again. The reason that the radius of convergence is zero has a very interesting argument. The expansion of the muon $g-2$ is in terms of α, the fine structure constant, which is the coupling. If we say that α is complex, we can look at the complex plane for α. The physical value of α lies on the real axis, at $\frac{1}{137}$. What we do when we have the perturbative expansion is to look at the circle around the origin that represents the radius of convergence, and hope that everything is well defined in that circle. However, things break down if we let $\alpha < 0$ (no stable physical systems exist). Thus, an expansion of α around 0 doesn't exist, and perturbation theory does not work.

Then how does the pertubation theory match the experiment so well? It turns out that the perturbation expansion is asymptotic. If we have expansion variable n, an asymptotic expansion means that as we take higher orders of n, at some point, the corrections begin to diverge. What we do is to calculate up until the minimum of the corrections, and then stop, with uncertainties in the next order of n.

The question is, at what order of the expansion does QED start to break down? It turns out that this happens at about order $\frac{1}{\alpha} = 137$.

2.1.2 Radius of Convergence of Perturbative Expansions

Let us take a simple system:

$$H = H_0 + V$$

Where H_0 is diagonal:

$$H_0 = \begin{bmatrix} E_1^{(0)} & 0 \\ 0 & E_2^{(0)} \end{bmatrix}$$

And let us suppose that V has some real off-diagonal terms:

$$V = \begin{bmatrix} 0 & V_{12} \\ V_{12} & 0 \end{bmatrix}$$

This is a simple enough system that we can solve exactly. We can first compute the eigenvalues of the Hamiltonian:

$$H = \begin{bmatrix} E_1^{(0)} & V_{12} \\ V_{12} & E_2^{(0)} \end{bmatrix}$$

We can then compute $\det\left[H-\lambda\mathbb{I}\right]$, and we find that the eigenvalues are:

$$\lambda_{1,2}=\frac{E_1^{(0)}+E_2^{(0)}}{2}\pm\sqrt{\frac{\left(E_1^{(0)}-E_2^{(0)}\right)^2}{4}+\left(V_{12}\right)^2}$$

This is the exact result.

Now let us consider a perturbative expansion. First, let us rewrite the square root term:

$$\sqrt{\frac{\left(E_1^{(0)}-E_2^{(0)}\right)^2}{4}+\left(V_{12}\right)^2}=\left(\frac{E_1^{(0)}-E_2^{(0)}}{2}\right)\sqrt{1+\left(\frac{2V_{12}}{E_1^{(0)}-E_2^{(0)}}\right)^2}$$

Now using the expansion for $\sqrt{1+x}$:

$$\sqrt{1+x}=1+\frac{1}{2}x-\frac{1}{4}x^2+\dots$$

Where $x=\frac{2V_{12}}{E_1^{(0)}-E_2^{(0)}}$. What is the radius of convergence of the Taylor series for $\sqrt{1+x}$? We can look at where we can put the branch cut of $\sqrt{1+x}$ if $x\in\mathbb{C}$, and we can choose to put it on the negative real axis, before -1. Now we can see that we can draw a circle of radius 1 around the origin. We can't draw any larger circle, since we run into the negative real axis before -1. Thus this expansion is only defined if $|x|$ is less than 1. Thus we see that if the two unperturbed energy levels are very close to each other, then we cannot consider this with perturbation, since x will be very large, and thus the series will not converge.

Consider a problem where we have sets of energy levels, clumped together. Our non-degenerate perturbation theory will work on energy levels between clumps, but not for the energy levels inside a clump. Thus we will develop a hybrid method to deal with situations like this.

2.1.3 Effective Theory

Consider a Hilbert space, which we partition into two separate spaces, P and Q, such that $P+Q=H$. Suppose that the dimensionality of H is n_{dim}, and we have $n_P+n_Q=n_{\text{dim}}$. The "trick" is to, instead of diagonalizing the $n_{\text{dim}}\times n_{\text{dim}}$ matrix, we instead diagonalize the $n_p\times n_p$ matrix, which is much smaller. We want to do this, and get the same answer. How can we do this? This sounds too good to be true! The matrix $H_{n_p\times n_p}$ is known as the effective Hamiltonian. This is the approach of effective theory, and is used all the time by theorists.

Consider the extremely large matrix for the original Hamiltonian, $H_{n_{\text{dim}}\times n_{\text{dim}}}$. Suppose we have 3 states that have very close energy levels. The effective theory approach is to look at only the 3×3 submatrix, and to diagonalize that. We strip away other parts of the space, and then treat those parts are perturbations, since the energy difference between the three states and the other parts of the system are large. This approach is also known as degenerate perturbation theory.

We have the Schrodinger equation:

$$\left(H_0+V\right)\left|\psi_n\right\rangle=E_n\left|\psi_n\right\rangle$$

We will try to write $\left|\psi_n\right\rangle$ in terms of the P part of the system, plus the Q part of the system:

$$\left|\psi_n\right\rangle=P\left|\psi_n\right\rangle+Q\left|\psi_n\right\rangle$$

We can then write the Schrodinger equation again:

$$(H_0 + V)\left(P\left|\psi_n\right\rangle + Q\left|\psi_n\right\rangle\right) = E_n\left(P\left|\psi_n\right\rangle + Q\left|\psi_n\right\rangle\right)$$

Schematically, we are decomposing our H:

$$H = \begin{bmatrix} V_{PP} & V_{PQ} \\ V_{QP} & V_{QQ} \end{bmatrix}$$

Where each of these terms is a submatrix, and V_{PP} is what we would like to deal with.

We can then project our equations into P space:

$$\left(E_n^{(0)} + V_{PP}\right) P\left|\psi_n\right\rangle + V_{PQ}Q\left|\psi_n\right\rangle = E_nP\left|\psi_n\right\rangle$$

And project it into Q space:

$$V_{QP}P\left|\psi_n\right\rangle + \left(E_n^{(0)} + V_{PQ}\right) Q\left|\psi_n\right\rangle = E_nQ\left|\psi_n\right\rangle$$

Where $V_{PP} = PVP$, and similarly for V_{QP} and V_{PQ}. We can now solve this, and we find that

$$Q\left|\psi_n\right\rangle = \frac{1}{E_n - \left(E_n^{(0)} + V_{QQ}\right)} V_{PP}P\left|\psi_n\right\rangle$$

Now substituting this back into our equation, we find that

$$\underbrace{\left(E_n^{(0)} + V_{PP} + V_{PQ}\frac{1}{E_n - \left(E_n^{(0)} + V_{QQ}\right)}V_{QP}\right)}_{H_{\text{effective}}}\left(P\left|\psi_n\right\rangle\right) = E_n\left(P\left|\psi_n\right\rangle\right)$$

We see that we have a matrix equation that only operators in the 3×3 space, we have an effective Hamiltonian that only lives in the P space, which we can diagonalize more easily than the original Hamiltonian. Note that if we say that the P space is only 1 dimensional, we recover the perturbation theory that we discussed before. However, there is an issue, this $n_P \times n_P$ matrix depends on E_n, which we don't know, so this diagonalization process is not linear. It also gets worse, H_{eff} is not in general Hermitian.

When V is small, we can write our effective Hamiltonian as:

$$H_{\text{eff}} = H_0 + V_{PP}$$

Let us deal with this case.

2.1.4 Linear Stark Effect

Consider the Hydrogen atom. We previously discussed the $n = 1$ ground state, now let us consider the $n = 2$ excited state. Ignoring spin degeneracy, we have 4 degenerate states with energy E_2, sude to the possible values of l. Now suppose we stick the atom in a constant electric field $\boldsymbol{E}$:

$$H = H_0 - Ze|\boldsymbol{E}|$$

If we wanted to compute the corrections to the Bohr energy levels for the $n = 2$ case, we could not use non-degenerate perturbation theory, since we have degeneracies in energy. Let us instead use effective theory.

The total number of dimensions is infinite, $n_{\text{dim}} = \infty$. Let us take the 4 degenerate states as our P space, so $n_P = 4$, and $n_Q = \infty - 4$.

Let us write out our 4 states:

$$l = 0 \qquad l = 1, m = 0 \qquad l = 1, m = +1 \qquad l = 1, m = -1$$

Let us now claim that there is no perturbation to the diagonal elements, due to the fact that z is odd under parity, and each of our 4 states are odd under parity as well. Parity also allows us to immediately note that all the states with $l = 1$ will have no interaction terms between each other. This leaves us with 6 unknown matrix elements. Now using the fact that H is Hermitian, we only need to focus on 3 of them. We claim that only one of these 3 is nonzero. This is because V is a tensor of the form $T^{(1)}_{q=0}$, and thus by Wigner-Eckart, only the $l = 1, m = 0$ state will have nonzero Clebsch-Gordan coefficients. Putting this all together:

$$H = \begin{bmatrix} E_2^{(0)} & & 0 & 0 \\ & E_2^{(0)} & 0 & 0 \\ 0 & 0 & E_2^{(0)} & 0 \\ 0 & 0 & 0 & E_2^{(0)} \end{bmatrix}$$

We only have one matrix element that we actually have to compute (Behold the power of symmetry). It turns out that this is $3ea_0|\boldsymbol{E}|$:

$$H = \begin{bmatrix} E_2^{(0)} & 3ea_0|\boldsymbol{E}| & 0 & 0 \\ 3ea_0|\boldsymbol{E}| & E_2^{(0)} & 0 & 0 \\ 0 & 0 & E_2^{(0)} & 0 \\ 0 & 0 & 0 & E_2^{(0)} \end{bmatrix}$$

We started with 4 states that are degenerate, and it turns out that two of the states are not affected by the external field, the $l = 1, m = \pm 1$ states. Thus we effectively have 3 non-degenerate states.

It can be found that the 3 states are given by:

$$\begin{cases} \frac{1}{\sqrt{2}} \left(|2s, m = 0\rangle - |2p, m = 0\rangle \right) \\ |2p, l = 0, m = \pm 1\rangle \\ \frac{1}{\sqrt{2}} \left(|2s, m = 0\rangle + |2p, m = 0\rangle \right) \end{cases}$$

Looking at this state, we note that we have coherent superpositions of the p and s states. We have that the states are not parity eigenstates, and in fact if we enact a parity transformation, we map from one of the state to the other. We have that our parity symmetry is broken. Therefore, this state will have a dipole moment. Once we have a dipole moment, we will have the dipole aligning or anti-aligning with the external field, each of which corresponds to one of the two superposition states. The middle states cannot have a dipole moment, and thus the energy remains the same. This is known as the Stark effect. If we take an atom with degeneracies and place it in an external electric field, we split the degenerate states and generate a dipole moment.

Now let us look at some more examples of the application of perturbation theory.

2.1.5 Relativistic Kinematic Effects

Consider the energy momentum relation:

$$E = \sqrt{\boldsymbol{p}^2 c^2 + m^2 c^4}$$

Which in natural units becomes

$$E = \sqrt{\boldsymbol{p}^2 + m^2}$$

In atomic physics, we often have that the momentum is much less than the mass, $p \ll m$, where we have implicit powers of c attached to each term to make the units work. We can then Taylor expand for small $\boldsymbol{p}$:

$$\begin{aligned} E &= \sqrt{\boldsymbol{p}^2 + m^2} \\ &\approx m + \frac{\boldsymbol{p}^2}{2m} - \frac{\boldsymbol{p}^4}{8m^3} + \dots \end{aligned}$$

The first term is the rest mass, the energy the particle has as long as it exists. This *can* turn into energy (electron and positron annhilating into gamma rays), when the mass disappears. However, for our calculation, we will say that the mass will remain no matter what, so let us ignore this term. This is why our Hamiltonians generally start with the $\frac{\boldsymbol{p}^2}{2m}$ term, rather than the m term.

However, this $\frac{\boldsymbol{p}^2}{2m}$ term is not 100% correct, we assume that the higher order terms are negligible. What if we instead, took these into account as perturbations? For example, take the Hydrogen atom Hamiltonian:

$$\begin{aligned} H &= \frac{\boldsymbol{p}^2}{2m} - \frac{\boldsymbol{p}^4}{8m^3} + \dots + V_c(r) \\ &= H_0 + V \end{aligned}$$

Where $V = -\frac{\boldsymbol{p}^4}{8m^3}$.

We have the unperturbed energy eigenstates:

$$H_0 \left|nlm\right\rangle = E_n \left|nlm\right\rangle$$

With Bohr energy levels:

$$E_n = -\frac{\alpha^2}{2n^2}\left(mc^2\right)$$

The only scale for the energy that we have in this system is the mass of the electron, and for that reason the mass of the electron (really $\left(mc^2\right)$) is the yardstick used in atomic/molecular/biophysics, and is roughly 500 keV.

Looking at the other terms in the energy levels, we have $\alpha \sim \frac{1}{137} \sim 10^{-2}$, and thus we have that $E_1 \approx 25$ eV.

Now let us consider the extra interaction:

$$V = -\frac{\boldsymbol{p}^4}{8m^3}$$

Now we need to figure out whether or not V is diagonal in the basis of states $|nlm\rangle$, which determines whether we need to use degenerate or non-degenerate perturbation theory. It turns out that $[\boldsymbol{L}, V] = 0$, and thus V is diagonal in the nlm basis, and thus, even though the $|nlm\rangle$ states are highly degenerate, we can use non-degenerate perturbation.

How do we show that $[\boldsymbol{L}, V] = 0$? The easiest way is to note that V is a scalar operator, and any scalar operator commutes with the angular momentum operator. In fact, this also gives us the commutation relationships:

$$\left[\boldsymbol{L}^2, V\right] = 0$$
$$\left[L_z, V\right] = 0$$

We can now compute the first order energy corrections:

$$\Delta_n^{(1)} = \langle nlm| - \frac{\boldsymbol{p}^4}{8m^3}|nlm\rangle$$

We don't actually need to do much calculation to get the result for this, because we can see that $V \sim \left(\frac{\boldsymbol{p}^2}{2m}\right)^2$, the kinetic energy applied twice. More specifically, we have that $V = -\frac{T^2}{2m}$, where T is the kinetic energy $\frac{\boldsymbol{p}^2}{2m}$. Now we leverage the Schrodinger equation:

$$\left(T + V\right)|\psi_n\rangle = E_n^{(0)}|\psi_n\rangle$$

We can then write the correction as:

$$\begin{aligned}\Delta_n^{(1)} &= -\frac{1}{2m}\langle nlm|\left(E_n^{(0)} - V_c\right)^2|nlm\rangle \\ &= -\frac{1}{2m}\left[\left(E_n^{(0)}\right)^2 - 2E_n^{(0)}\langle nlm|V_c|nlm\rangle + \langle V_c^2\rangle\right]\end{aligned}$$

We can now leverage the virial theorem, which states that

$$2\langle T\rangle = -\langle V\rangle$$

Which gives us that:

$$\langle V\rangle = 2E_n^{(0)}$$

For the $\langle V_c^2\rangle$ term, we can use the precalculated values from Sakurai, and we find that:

$$\begin{aligned}\Delta_n^{(1)} &= -\frac{1}{2m}\left[\left(E_n^{(0)}\right)^2 - 2E_n^{(0)}\langle nlm|V_c|nlm\rangle + \langle V_c^2\rangle\right] \\ &= -\frac{1}{2m}\left[\left(E_n^{(0)}\right)^2 - \left(2E_n^{(0)}\right)^2 + \langle V_c^2\rangle\right] \\ &= -\frac{1}{2}\left(m_ec^2\right)\alpha^4\left(-\frac{3}{4n^4} + \frac{1}{n^3\left(l+\frac{1}{2}\right)}\right)\end{aligned}$$

We see that not only do we depend on n, we also depend on l, which gives us splitting between the degenerate states with the same n but different l.

However, the most important thing to notice is that this correction is proportional to α^4. This means that the splitting between the degenerate energy levels is incredibly small, of the order of 10^{-4} of the original energy of the level.

2.1.6 Spin-Orbit Splitting

The Coulomb interaction holds for two charges that are stationary. In the case of an atom, we have that the electron is moving, and also has spin. This spin produces a magnetic moment. This moving magnetic moment also experiences a magnetic field, generated by the relativistic effect of the change of frame from static to moving:

$$\boldsymbol{B} \approx \frac{\boldsymbol{v}}{c} \times \boldsymbol{E}$$

Which interacts with the magnetic moment:

$$H = -\boldsymbol{\mu}_e \cdot \boldsymbol{B}_p$$

However, if we go through this calculation, we find that we are off by a factor of 2. This is because the electron is accelerating, since it is changing directions constantly. We have that our inertial frames are rotating at every moment, which is known as Thomas precession, derived in 1926. This provides us the factor of $\frac{1}{2}$ that we were missing:

$$H = -\frac{1}{2}\boldsymbol{\mu}_e \cdot \boldsymbol{B}_p$$

How can we derive this?

We have that the total Hamiltonian for the Hydrogen atom has the basic Hydrogen Hamiltonian, H_0, the p^4 corrections, given by V_{p^4}, and the spin-orbit effects, given by V_{SO}. For now, let us look only at the spin-orbit interaction:

$$H_{SO} = \frac{1}{2m^2c^2}\left(\frac{1}{r}\frac{dV_c}{dr}\right)(\boldsymbol{L} \cdot \boldsymbol{s})$$

Now we note that $[\boldsymbol{L}, H_{SO}] \neq 0$, and $[H_{SO}, \boldsymbol{S}] \neq 0$. This means that in the $|nlm\rangle$ basis, H_{SO} is not diagonal. Because of this, we need to use degenerate perturbation theory. However, we can make our lives easier if we notice that

$$\begin{aligned}
\boldsymbol{L} \cdot \boldsymbol{S} &= \frac{1}{2}\left(2\boldsymbol{L} \cdot \boldsymbol{S} + \boldsymbol{L}^2 + \boldsymbol{S}^2 - \boldsymbol{L}^2 - \boldsymbol{S}^2\right) \\
&= \frac{1}{2}\left((\boldsymbol{L} + \boldsymbol{S})^2 - \boldsymbol{L}^2 - \boldsymbol{S}^2\right) \\
&= \frac{1}{2}\left(\boldsymbol{J}^2 - \boldsymbol{L}^2 - \boldsymbol{S}^2\right)
\end{aligned}$$

Now we note that $\left[H_{SO}, \boldsymbol{L}^2\right] = \left[H_{SO}, \boldsymbol{S}^2\right] = 0$, because $\boldsymbol{L}^2$ and $\boldsymbol{S}^2$ commute with their components. This means that if we work in the basis of the common eigenstates of $\boldsymbol{J}^2, \boldsymbol{L}^2, \boldsymbol{S}^2$, and J_z, we will automatically diagonalize H_{SO}. We can write out the first order energy corrections:

$$\Delta_n^{(1)} = \frac{1}{2m^2c^2}\left\langle\frac{1}{r}\frac{dV}{dr}\right\rangle\frac{1}{2}\left(j(j+1) - l(l+1) - \frac{1}{2}\left(\frac{1}{2}+1\right)\right)$$

This is done in the textbook, and it turns out that it is also proportional to α^4. This is of the same order as the relativstic corrections.

These are not the only corrections, there is another term that is proportional to α^4, known as the Darwin term. This correction takes into account the deBroglie wavelength of the electron, and takes into account the fact that the electron is fluctating, it is not at a single point, which varies the Coulomb interaction.

After the second world war, Rabi's lab at Columbia observed another splitting in the levels, known as the Lamb Shift. This can be derived only from relativistic QFT, which provides corrections of the order α^5 (actually to infinite orders of α). This was more evidence that QFT was a correct framework.

2.1.7 Zeeman Effect

Consider a uniform magnetic field $\boldsymbol{B}$, interacting with the Hydrogen atom. In mechanics, the Hamiltonian would be of the form:

$$H = \frac{\left(\boldsymbol{p}^2 - \frac{e\boldsymbol{A}}{c}\right)}{2m} + V$$

We see that we have a new form of momentum, rather than the canonical momentum $\boldsymbol{p} \sim \frac{\hbar}{i}\nabla$, we have the mechanical momentum[1]:

$$\boldsymbol{p}_m = \boldsymbol{p}_c - \frac{e\boldsymbol{A}}{c}$$

The magnetic vector potential is related to $\boldsymbol{B}$ via:

$$\nabla \times \boldsymbol{A} = \boldsymbol{B}$$

Recall that $\boldsymbol{A}$ is not unique, we have a gauge symmetry:

$$\boldsymbol{A} \to \boldsymbol{A} + \nabla\phi$$

We will work in the Coulomb gauge:

$$(A_x, A_y, A_z) = \left(-\frac{1}{2}B_y, \frac{1}{2}B_x, 0\right)$$

Which obeys the property that $\nabla \cdot \boldsymbol{A} = 0$.

We can now write down the Hamiltonian for a Hydrogen atom in an external $\boldsymbol{B}$ field:

$$H = H_0 + \frac{1}{2m}\left[\boldsymbol{p} \cdot \left(-\frac{e}{c}\right)\boldsymbol{A} + \left(-\frac{e}{c}\boldsymbol{A}\right) \cdot \boldsymbol{p}\right] + \frac{1}{2m}\left(-\frac{e}{c}\boldsymbol{A}\right)^2$$

This last term is small, and is known as Landau dimagnetism. This is also related to Lenz's law. The middle term has cross terms, which are related to L_z:

$$\begin{aligned} H &= H_0 - \frac{e}{2mc}\left(\boldsymbol{B} \cdot \boldsymbol{L}\right) \\ &\sim H_0 - \boldsymbol{B} \cdot \boldsymbol{\mu} \end{aligned}$$

Where $\boldsymbol{\mu} = \mu_B \cdot \boldsymbol{L}$. We see that we have generated a magnetic moment, which isn't surprising, we have a charge rotating in a magnetic field. Putting this together with the spin magnetic moment that we had before, we have that

$$H = H_0 - \frac{e}{2mc}\boldsymbol{B} \cdot (\boldsymbol{L} + 2\boldsymbol{S})$$

---

[1] For a further discussion of mechanical momentum, see Feynman's Lectures, Vol. III.

What we have derived is that an external magnetic field, we have a magnetic moment interaction proportional to $\boldsymbol{L}+2\boldsymbol{S}$.

For the Hydrogen atom, the magnetic moment is split up into two parts, the spin magnetic moment and the orbital magnetic moment:

$$\boldsymbol{\mu}=\boldsymbol{\mu}_s+\boldsymbol{\mu}_l$$

The spin magnetic moment is given by the Bohr magneton:

$$\boldsymbol{\mu}_s=-\mu_B\frac{(2\boldsymbol{s})}{\hbar}$$

And the orbital angular momentum is given by:

$$\boldsymbol{\mu}_l=-\mu_B\frac{\boldsymbol{l}}{\hbar}$$

Thus we have the magnetic field Hamiltonian:

$$H_B=-\frac{\mu_B\boldsymbol{B}}{\hbar}\left(2\boldsymbol{S}+\boldsymbol{L}\right)$$

Assuming that the $\boldsymbol{B}$ field is in the z direction:

$$H_B=-\frac{\mu_B}{\hbar}\left(2S_z+L_z\right)$$

Thus the Hamiltonian for the Hydrogen atom with the factors that we are taking into account will be:

$$H=H_0+H_{SO}+H_B$$

For the moment, let us consider the weak field limit. This is the case where $H_B \ll H_{SO}$. In this case, we know that the basis for the system will be the basis that fits the case of just the spin-orbit splitting, which is the $|nljm_j\rangle$ basis. In this basis, we want to compute the effects of the H_B perturbation. We now note that the energy levels of what we are considering the unperturbed system are degenerate in j, with degeneracy $2j+1$.

We want to compute the corrections due to the Zeeman splitting:

$$\begin{aligned}\Delta^{(1)}_{\text{Zeeman}}&=\langle nljm|H_B|nljm\rangle\\&=-\frac{H_B}{\hbar}B\left\langle nljm|2S_z+L_z|nljm\right\rangle\end{aligned}$$

We can always write that

$$2S_z+L_z=J_z+S_z$$

Since $\boldsymbol{J}=\boldsymbol{L}+\boldsymbol{S}$. From this, we can use the fact that $J_z\left|jm\right\rangle=m\left|jm\right\rangle$, to compute $\langle S_z\rangle$. There are two ways to do this. The first way is to use Clebsch-Gordan coefficients to write out $|jm\rangle$ in terms of the uncoupled states, and we would find that:

$$\langle S_z\rangle=\frac{\hbar}{2}\left(|C_+|^2-|C_-|^2\right)$$

The second method is to use the Wigner-Eckart theorem, to prove the equation:

$$\langle jm|V_z|jm\rangle = \frac{(\boldsymbol{V}\cdot\boldsymbol{J})\,\langle J_z\rangle}{\boldsymbol{J}^2}$$

Where $\boldsymbol{V}$ is a vector operator[2]. From this, we can compute the Zeeman shift:

$$\Delta^{(1)}_{\text{Zeeman}} = m\mu_B B\left(1 \pm \frac{1}{2l+1}\right)$$

The upper sign denotes the $j = l + \frac{1}{2}$ state, and the lower sign denotes the $j = l - \frac{1}{2}$ state. This is the Zeeman splitting.

Let us consider the the Zeeman effect on the $n = 1$ 1S $\frac{1}{2}$ state. In this case, we split into two, corresponding to $m = \frac{1}{2}$ and $m = -\frac{1}{2}$. This splitting is due to the projection of the magnetic moment into the direction of the magnetic field. If the magnetic moment goes against the field, we get one case, and if its aligned we get the other case.

For the $n = 2$, 2P$\frac{3}{2}$ state, we have $j = \frac{3}{2}$, so we split into 4 different energy levels, corresponding to the different ms, $m = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$.

Now let us consider the strong field limit[3], the case where $H_B \gg H_{SO}$, the magnetic field is much stronger than the magnetic field due to the proton. In this case, the leading order Hamiltonian will be

$$H = H_0 + H_B$$

Note that we lose full rotational symmetry, since $[H, \boldsymbol{J}] \neq 0$. However, we still have z axis rotational symmetry. The good quantum numbers are the original basis, $|nlm_l sm_s\rangle$. The Hamiltonian is diagonal in this uncoupled basis, where the spins and the orbitals don't interact.

In this case, our energy levels will be given by:

$$E^{(1)}_n = E^{(0)}_n + \left(-\frac{\mu_B B}{\hbar}\right)(2m_s + m_l)$$

This takes minimal work, since the Hamiltonian is already diagonal in this basis.

Let us look at the spectrum for this case. Consider the $n = 2$ case, where $l = 1$ or $l = 0$. We see that the maximal value of $2m_s + m_l$ is 2, when $m_l = 1$ and $m_s = \frac{1}{2}$. Looking at all the possible values of $2m_s + m_l$, we see that we can have integer values between -2 and 2. Thus the energy level splits into these 5 possibilities, and three of them are degenerate. Thus we have a total of 8 states.

What happens if the $\boldsymbol{B}$ field is somewhere in between? In this case, we have to diagonalize an 8×8 matrix, in either of the two bases. If we do this for $n = 2$, we could see how the energy levels change as we vary $\boldsymbol{B}$ from weak to strong.

Now let us consider the spin orbit corrections, which we can treat as a small perturbation on top of the Zeeman splitting:

$$\Delta^{(1)}_{SO} = \langle nlm_l sm_s|H_{SO}|nlm_l sm_s\rangle$$

---

[2] Page 239 of Sakurai.

[3] Also known as the Paschen-Back limit.

$$= \frac{1}{2m^2c^2}\left\langle\frac{1}{r}\frac{dV}{dr}\right\rangle \langle lm_l sm_s|\boldsymbol{L}\cdot\boldsymbol{S}|lm_l sm_s\rangle$$

The Zeeman effect is the basis for research into cold atoms, as the Zeeman effect can be used to convert the kinetic energy into internal energy, by inducing phase transitions in split energy levels using lasers. This cools down the atoms, hence the term cold ion trapping.

2.2 Time-Dependent Perturbation Theory

We have so far been concerned with time-independent Hamiltonians, but let us consider the time-dependent Schrodinger equation:

$$i\hbar\frac{\partial}{\partial t}|\psi\rangle = H|\psi\rangle$$

Let us consider the case where we have a time-independent Hamiltonian, with a time-dependent perturbation:

$$i\hbar\frac{\partial}{\partial t}|\psi\rangle = (H_0 + V(t))|\psi\rangle$$

Where H_0 already has a solution:

$$H_0|n\rangle = E_n|n\rangle$$

To do this, let us introduce something known as the intermediate picture. In the Schrodinger picture, the states evolve using the unitary time evolution operator, and the operators are time-independent:

$$\begin{aligned}|\psi(t)\rangle &= e^{-iH(t)t/\hbar}|\psi(0)\rangle\\ \mathcal{O}(t) &= \mathcal{O}(0)\end{aligned}$$

In the Heisenberg picture, the states don't evolve in time, but the operators do:

$$\begin{aligned}|\psi(t)\rangle &= |\psi(0)\rangle\\ \mathcal{O}(t) &= e^{iHt/\hbar}\mathcal{O}(0)e^{-iHt/\hbar}\end{aligned}$$

In the intermediate frame, the states rotate backwards, using H_0:

$$|\psi(t)\rangle = e^{iH_0t/\hbar}|\psi(t)\rangle$$

And the operators evolve according to the unperturbed Hamiltonian:

$$\mathcal{O}(t) = e^{iH_0t/\hbar}\mathcal{O}(t)\,e^{-iH_0t/\hbar}$$

Now let us consider the Schrodinger equation:

$$\begin{aligned}i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle &= \left(-H_0|\psi(t)\rangle + e^{iH_0t/\hbar}(H_0+V)\,e^{-iH_0t/\hbar}\right)|\psi(t)\rangle\\ &= e^{iH_0t/\hbar}V(t)e^{-iH_0t/\hbar}|\psi(t)\rangle\end{aligned}$$

Now from the definition of how operators evolve in the intermediate picture, this is

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

Now let us expand out intermediate states in terms of time-dependent coefficients and the unperturbed eigenstates:

$$\left|\psi\left(t\right)\right\rangle = \sum_n c_n\left(t\right)\left|n\right\rangle$$

Inserting this into the Schrodinger equation we have, we obtain a matrix equation:

$$i\hbar\frac{\partial}{\partial t}\begin{pmatrix} c_1\left(t\right) \\ c_2\left(t\right) \\ \vdots \end{pmatrix} = \begin{pmatrix} V_{11}(t) & e^{i(E_1-E_2)t/\hbar}V_{12}\left(t\right) & \dots \\ e^{i(E_2-E_1)t/\hbar} & \ddots & \\ \vdots & & \end{pmatrix}\begin{pmatrix} c_1\left(t\right) \\ c_2\left(t\right) \\ \vdots \end{pmatrix}$$

2.2.1 Rabi Oscillations

Now let us consider a 2 by 2 case, where:

$$H_0 = \begin{bmatrix} E_1 & 0 \\ 0 & E_2 \end{bmatrix} \qquad V\left(t\right) = \begin{bmatrix} 0 & \gamma e^{i\omega t} \\ \gamma^* e^{-i\omega t} & 0 \end{bmatrix}$$

and $V \ll H_0$. We can set up the matrix equation:

$$i\hbar\frac{\partial}{\partial t}\begin{pmatrix} c_1\left(t\right) \\ c_2\left(t\right) \end{pmatrix} = \begin{pmatrix} 0 & \gamma e^{i(\omega-\omega_{21})t} \\ \gamma^* e^{-i(\omega-\omega_{21})} & 0 \end{pmatrix}\begin{pmatrix} c_1\left(t\right) \\ c_2\left(t\right) \end{pmatrix}$$

Where $\omega_{21} = \frac{E_2-E_1}{\hbar}$, and similarly for the other term. This set of equations is well known, it has solution given by the Rabi formula:

$$\left|c_2\left(t\right)\right|^2 = \frac{\frac{\gamma^2}{\hbar^2}}{\Omega^2}\sin^2\Omega t$$

Where $\Omega = \sqrt{\frac{(\omega-\omega_{21})^2}{4}+\frac{\gamma^2}{\hbar^2}}$ is the Rabi frequency.

We have a two-level system, and the period of oscillations between the two levels generated by our perturbation is $T = \frac{2\pi}{\Omega}$.

We have the probabiltiy distribution

$$P_2(t) = \frac{\gamma^2}{\gamma^2 + \frac{(\omega-\omega_{21})^2}{4}}$$

Now plotting this, we see that it is at a maximum at resonance, when $\omega = \omega_{21}$. Looking at the limit, we see that it is proportional to a delta function, and γ is a damping factor, which determines the width of the resonance peak. We define the quality factor $Q \sim \frac{1}{\gamma}$.

2.2.2 Nuclear Magnetic Resonance

The basic idea of NMR imaging is to look at the water distribution inside your body. How does this work?

Consider a proton, a spin-$\frac{1}{2}$ particle. It has a magnetic moment, proportional to the spin:

$$\boldsymbol{\mu} = g_p \mu_N \boldsymbol{s}_p$$

Where μ_N is the nuclear magneton, $\mu_N = \frac{e\hbar}{2m_p c}$, and $g_p = 5.6$. Now we apply a strong magnetic field B_0, say in the z-direction. Our unperturbed Hamiltonian is given by $H_0 = -\boldsymbol{\mu} \cdot \boldsymbol{B}$. The direction of the magnetic moment causes a split in the energy levels:

$$\begin{aligned} \frac{E_2 - E_1}{\hbar} &= \omega_{21} \\ &= B_z' \end{aligned}$$

We now look at a perturbation, $V(t)$:

$$\begin{aligned} V(t) &= B_1 \cos \omega t \hat{x} \\ &= \hat{S}_x B_1 \cos \omega t \end{aligned}$$

If the incoming oscillation has $\omega = \omega_{21}$, then we have maximal absorption, we have maximum resonance. The incoming photon is absorbed by the proton, and the proton transitions between energy levels and flips spin directions. The photons that are not absorbed scatter, and then we can determine the proton distribution based on the scattering of the photons (caused by spontaneous emission), producing an image.

2.2.3 Sudden Approximation

Let us consider the special case where the Hamiltonian as a function of time has a sudden jump in a very short span of time.

For example, suppose we have an infinite square well, inhabited by a particle in the ground state, and we, in an instant, double the width of the well, suddenly changing the Hamiltonian.

The solution is very simple. If we can solve the Hamiltonian prior to the sudden change, and solve it after the sudden change, we can leverage the fact that the wavefunction is continuous in time, and treat the wavefunction before the change as the initial condition for the Hamiltonian after the change, we can decompose the original wavefunction in terms of the eigenstates of the new Hamiltonian. This relies on the change happening over a suitably short time period.

For example, consider the decay of tritium (2 neutrons, one proton, and an electron outside) via beta decay. The beta decay changes the system into Helium 3, a neutron turns into a proton, plus an electron and a neutrino (which have so much energy they just leave the atom). In the US, Helium 3 is in part obtained through the waste product of aging hydrogen bombs.

2.2.4 Adiabatic Approximation

The adiabatic approximation is the exact opposition of the sudden approximation. We have a Hamiltonian that is a function of time, but it changes incredibly slowly. We can then solve the equation at any given time:

$$H\left(t\right)\left|\psi_n\left(t\right)\right\rangle = E_n\left(t\right)\left|\psi_n\left(t\right)\right\rangle$$

Suppose we have a magnetic moment, and we insert a magnetic field parallel to the magnetic moment. We now very slowly rotate the direction of the magnetic field. Thus we know the eigenstates at every point during the rotation, since we can solve the Hamiltonian at every point in time.

We then can decompose the wavefunction as

$$\left|\psi\right\rangle\left(t\right) = \sum c_n\left(t\right)e^{-i\int E_n(t)\,dt}\left|\psi_n\left(t\right)\right\rangle$$

We can now insert this into the Schrodinger equation and solve it.

The condition for the adiabatic approximation is that the change of the Hamiltonian in time is not comparable to the Hamiltonian itself. More precisely, looking at the matrix element of the time derivative of the Hamiltonian:

$$\frac{\left\langle m\left(t\right)\right|\dot{H}\left|n\left(t\right)\right\rangle}{E_{nm}\left(t\right)} \ll \frac{E_n\left(t\right)}{\hbar}$$

This is the condition for the adiabatic approximation.

We can consider the change in the value of $c_m\left(t\right)$:

$$\frac{dc_m\left(t\right)}{dt} = -c_m\left(t\right)\left\langle m\left(t\right)\right|\frac{\partial}{\partial t}\left|m\left(t\right)\right\rangle$$

This differential question gives us that $c_n\left(t\right) = c_n\left(0\right)e^{i\gamma_n(t)}$, where

$$\gamma_n\left(t\right) = i\int_0^t \left\langle n\left(t'\right)\right|\frac{\partial}{\partial t'}\left|n\left(t'\right)\right\rangle dt'$$

This leads to Berry phase. Consider parameterizing the time-dependence of the Hamiltonian:

$$H\left(t\right) = H\left(\boldsymbol{R}\left(t\right)\right)$$

Suppose that, in the space of possible parameters, we make a loop, our ending parameter is the same as the starting parameter. If we have this condition, then we can compute the phase factor γ_n, by changing $\left\langle n\left(t\right)\right|\frac{\partial}{\partial t}\left|n\left(t\right)\right\rangle \to \frac{\partial \boldsymbol{R}}{\partial t}\cdot\left\langle n\left(t\right)\right|\nabla_{\boldsymbol{R}}\left|n\left(t\right)\right\rangle$. From this, we can compute the phase factor γ:

$$\gamma_n\left(t\right) = i\int_0^t \underbrace{\left\langle n\left(t\right)\right|\nabla_{\boldsymbol{R}}\left|n\left(t\right)\right\rangle}_{\boldsymbol{A}(\boldsymbol{R})} d\boldsymbol{R}$$

This can be thought of as a path integral in parameter space, and thus if we have a loop, then this becomes an integral of a loop in parameter space:

$$\gamma_n = i\oint \boldsymbol{A}\left(\boldsymbol{R}\right)\,d\boldsymbol{R}$$

Now applying Stoke's theorem, we have that

$$\gamma_n(t) = i \oiint \boldsymbol{B} \cdot d\boldsymbol{S}$$

Where $\boldsymbol{B} = \nabla \times \boldsymbol{A}$.

One application of the Berry phase is the Aharanov-Bohm effect, where charged particles pick up a phase based on the loop around the solenoid, even though they are moving through a region with no magnetic field (just nonzero magnetic vector potential, which is in the Hamiltonian for a charged particle).

2.2.5 Fermi's Golden Rule

Consider a system decribed by H_0, and we perturb the system with a time-dependent perturbation $V(t)$, and the system makes a transition. We assume that the external perturbation is harmonic, that is, of the form

$$V(t) = V_{ni} e^{i\omega t} + V_{ni}^{\dagger} e^{-i\omega t}$$

The Fermi Golden Rule tells us the transition rate is given by

$$w_{i \to n} = \left(\frac{2\pi}{\hbar}\right) |V_{ni}|^2 \delta\left(E_f - E_i + \omega\hbar\right) |V_{ni}^{\dagger}|^2 \delta\left(E_f - E_i - \omega\hbar\right)$$

Note that the terms of the form $e^{i\omega t}$ in the perturbation are taking energy away from the system, and terms of the form $e^{-i\omega t}$ are adding energy to the system.

Consider an atom in a laser field. The laser field is an EM wave, so we have $\boldsymbol{E}$ and $\boldsymbol{B}$, and in a laser, these two are the same, they share the same amount of energy. Thus, we generally describe them in terms of the $\boldsymbol{E}$ field, since we generally work with charge interactions. We describe the electromagnetic field using the gauge potential. Working in the Coulomb gauge, we have that

$$\phi = 0 \quad \boldsymbol{A} \neq 0 \quad \nabla \cdot \boldsymbol{A} = 0$$

Thus we have 2 physical degrees of freedom for the EM field:

$$\boldsymbol{A} = 2A_0 \cos\left(\omega t - \boldsymbol{k} \cdot \boldsymbol{x}\right) \boldsymbol{\epsilon}$$

Where $\boldsymbol{\epsilon}$ is the polarization vector. This is a plane wave. If we compute the $\boldsymbol{E}$ field:

$$\begin{aligned} \boldsymbol{E} &= -\nabla\phi - \frac{\partial \boldsymbol{A}}{\partial t} \\ &= 2A_0\omega \sin\left(\omega t - \boldsymbol{k} \cdot \boldsymbol{x}\right) \boldsymbol{\epsilon} \end{aligned}$$

Note that $\boldsymbol{k} \cdot \boldsymbol{\epsilon} = 0$, and thus the polarization is orthogonal to the direction of propagation. We can compute the $\boldsymbol{B}$ field:

$$\begin{aligned} \boldsymbol{B} &= \nabla \times \boldsymbol{A} \\ &= 2A_0 \left(\boldsymbol{k} \times \boldsymbol{\epsilon}\right) \sin\left(\omega t - \boldsymbol{k} \cdot \boldsymbol{x}\right) \end{aligned}$$

From this, we can compute the time-average energy density in the laser:

$$U = \frac{1}{2\pi}\frac{\omega^2}{c^2}|A_0|^2$$

We can also think about the intensity of the laser, the energy flux:

$$\begin{aligned} I &= Uc \\ &= \frac{\omega^2}{2\pi c}|A_0|^2 \end{aligned}$$

This is how much energy is transmitted per unit area per unit time. This is what is labelled on lasers.

Now let us consider placing a Hydrogen atom in this laser field. The Hamiltonian will be

$$\hat{H} = \frac{(\boldsymbol{p} - e\boldsymbol{A})^2}{2m} + e\phi$$

Where the ϕ is not the $\phi = 0$ of the laser, but of the proton interacting with the electron. Expanding this (noting that in the Coulomb gauge, $\boldsymbol{p}$ and $\boldsymbol{A}$ commute), we have

$$H = \underbrace{\left(\frac{\boldsymbol{p}^2}{2m} + e\boldsymbol{\phi}\right)}_{H_0} - \frac{e}{m}\boldsymbol{\phi}\cdot\boldsymbol{A} + \mathcal{O}\left(\boldsymbol{A}^2\right)$$

We see that the interaction of the laser with the electron will be

$$\begin{aligned} V(t) &= -\frac{e}{m}\boldsymbol{p}\cdot\boldsymbol{A}(t) \\ &= -\frac{e}{m}\boldsymbol{\epsilon}\cdot\boldsymbol{p}\,(2A_0)\cos(\omega t - \boldsymbol{k}\cdot\boldsymbol{x}) \\ &= -\frac{eA_0}{m}\boldsymbol{\epsilon}\cdot\boldsymbol{p}\left(e^{i(\omega t - \boldsymbol{k}\cdot\boldsymbol{x})} + e^{-i(\omega t - \boldsymbol{k}\cdot\boldsymbol{x})}\right) \\ &= V_{ni}e^{i\omega t} + V_{ni}^{\dagger}e^{-i\omega t} \end{aligned}$$

Where

$$V_{ni} = \left\langle n \left| -\frac{eA_0}{m}\boldsymbol{\epsilon}\cdot\boldsymbol{p}e^{i\boldsymbol{k}\cdot\boldsymbol{x}} \right| i \right\rangle$$

We see that we have converted this into a harmonic perturbation. We can now apply Fermi's Golden Rule and compute the transition rate:

$$\omega_{i\to n} = \frac{2\pi}{\hbar}\left|\left\langle n \left| -\frac{eA_0}{m}\boldsymbol{\epsilon}\cdot\boldsymbol{p}e^{\pm i\boldsymbol{k}\cdot\boldsymbol{x}} \right| i \right\rangle\right|^2 \delta\left(E_f - E_i \pm \omega\hbar\right)$$

Consider the case where the wavelength of the laser is about 800 nanometers. The size of the Hydrogen atom is about 0.1 nanometers. For this reason, as a very good approximation, we can drop the $e^{\pm - \boldsymbol{k}\cdot\boldsymbol{x}}$ term, since the variation in $\boldsymbol{x}$ will not cause a meaningful change in the phase of the plane wave. This is the dipole approximation.

This makes the matrix element a lot easier to calculate:

$$\omega_{i\to n} = \frac{2\pi}{\hbar}\left(\frac{e^2A_0^2}{m^2}\right)|\langle n|\boldsymbol{\epsilon}\cdot\boldsymbol{p}|i\rangle|^2\,\delta\left(E_f - E_i \pm \omega\hbar\right)$$

We see that the transition probability is dependent on the intensity of the laser, since we have a relation between A_0 and I:

$$|A_0|^2 = \frac{2\pi c}{\omega^2} I$$

Thus we can rewrite the transition rate:

$$\begin{aligned}\omega_{i\to n} &= \frac{4\pi^2 e^2 c I}{\hbar m^2 \omega^2} \left|\langle n|\boldsymbol{\epsilon}\cdot\boldsymbol{p}|i\rangle\right|^2 \delta\left(E_f - E_i \pm \omega\hbar\right) \\ &= \frac{4\pi^2 \alpha I}{c^2 m^2 \omega^2} \left|\langle n|\boldsymbol{\epsilon}\cdot\boldsymbol{p}|i\rangle\right|^2 \delta\left(E_f - E_i \pm \omega\hbar\right)\end{aligned}$$

Where we have used the fact that we can rewrite this using the fine structure constant, $\alpha = \frac{e^2}{\hbar c}$.

Let us now consider the matrix element

$$\langle n|\boldsymbol{\epsilon}\cdot\boldsymbol{p}|i\rangle$$

Suppose that the laser is travelling in the z direction. In this case, we only have the components in the x direction:

$$\begin{aligned}\langle n|\boldsymbol{\epsilon}\cdot\boldsymbol{p}|i\rangle &= \langle n|p_x|i\rangle \\ &= \frac{m}{i\hbar}\langle n|\left[H_0, x\right]|i\rangle \\ &= \frac{m}{i\omega_{ni}}\omega_{ni}\langle n|x|i\rangle\end{aligned}$$

Where we leverage the fact that

$$\begin{aligned}\left[\boldsymbol{H}_0, x\right] &= \left[\frac{\boldsymbol{p}^2}{2m} + V\left(\boldsymbol{x}\right), x\right] \\ &= \frac{p}{m}\left[p, x\right] \\ &= \frac{i\hbar p_x}{m}\end{aligned}$$

Now inserting this into the transition rate:

$$\omega_{i\to n} = \frac{4\pi^2 \alpha I}{c^2} |\langle n|x|i\rangle|^2 \delta\left(\omega_{ni} \pm \omega\right)$$

We see that $\langle n|x|i\rangle$ is the dipole operator.

2.2.6 Spontaneous Emission

Let us now consider the case of spontaneous emission, where an atom starts at an excited state, emits a photon, and drops down to a lower energy level. Suppose we have a box of width L, and we place an excited atom in the box. The total energy in the box, after the photon is emitted, is the quantized energy of one photon, $\hbar\omega$:

$$\frac{1}{2\pi}\frac{\omega^2}{c^2}|A_0|^2 L^3 = \hbar\omega$$

And thus we have that

$$|A_0|^2 = \frac{2\pi\hbar c^2}{\omega L^3}$$

We see that if $L \to \infty$, $A_0 \to 0$, but let's not take this limit yet. We can compute the transition probability:

$$\begin{aligned} \omega_s &= \frac{2\pi e^2 2\pi\hbar c^2}{\hbar\omega L^3 m^2}\omega^2 m^2 |\langle n|\overline{\boldsymbol{\epsilon}\cdot\boldsymbol{r}}|i\rangle|^2 \delta\left(E_f - E_i - \hbar\omega\right) \\ &= \frac{4\pi^2 e^2 c^2}{L^3}\omega |\langle n|\overline{\boldsymbol{\epsilon}\cdot\boldsymbol{r}}|i\rangle|^2 \delta\left(E_f - E_i - \hbar\omega\right)\Delta n_\gamma \end{aligned}$$

Where, since we don't know which direction the emitted photon will go, we have to sum this over the density of states of the photon:

$$\Delta n_\gamma = \frac{1}{\hbar}\left(\Delta y \Delta z \Delta x \Delta p_x \Delta p_y \Delta p_z\right)$$

Integrating the $\Delta x \Delta y \Delta z$, we get the volume of the box, L^3. The momenta of the photon integrate to the wavevector:

$$L^3 \frac{d^3\boldsymbol{k}}{8\pi^3}$$

Thus we can write the transition rate as

$$\begin{aligned} \omega_s &= \frac{4\pi^2 e^2 c^2}{L^3}\omega |\langle n|\overline{\boldsymbol{\epsilon}\cdot\boldsymbol{r}}|i\rangle|^2 \delta\left(E_f - E_i - \hbar\omega\right) V \frac{d^3\boldsymbol{k}}{8\pi^3} \\ &\sim \int d\omega\, \omega |\langle n|\overline{\boldsymbol{\epsilon}\cdot\boldsymbol{r}}|i\rangle|^2 \delta\left(\frac{E_f - E_i}{\hbar} - \omega\right) \frac{4\pi}{c^3}\omega^2 \end{aligned}$$

Where we have used that $d^3\boldsymbol{k} = \frac{4\pi}{c^3}\omega^2\, d\omega$, and we have dropped some constants temporarily. The final result gives us that

$$\omega_s = 2\alpha \frac{\omega^3}{c^2} |\langle n|\boldsymbol{\epsilon}\cdot\boldsymbol{r}|i\rangle|^2$$

This is the probability of an excited atom undergoing spontaneous emission, and dropping to a lower energy state and emitting a photon. This can be linked to statistical mechanics, the phase space of states with an emitted photon is larger than the phase space of states without a photon, and the tendency of a system to increase the entropy leads to these transitions.

We can also consider the lifetime of the excited state:

$$\tau_{\text{lifetime}} = \frac{\hbar}{\omega_s}$$

If we go through with the computation, it can be found that the lifetime for a p state of Hydrogen is measured on the order of a nanosecond.

2.2.7 Black Body Radiation

Consider an atom with 2 energy levels, E_1 and E_2. A laser with some intensity I shines on the atom, and we want to find the transition rate, the probability per unit time, of the transition:

$$w = \frac{|c_n\left(t\right)|^2}{T}$$

We can compute the transition rate from the first excited state to the second:

$$\begin{aligned} w_{12} &= \frac{2\pi}{\hbar}|V_{fi}|^2\delta\left(\hbar\omega - \left(E_f - E_i\right)\right) \\ &= \frac{4\pi^2\alpha}{m^2\omega^2}I|\left\langle n|\boldsymbol{p}\cdot\boldsymbol{\epsilon}|i\right\rangle|^2\delta\left(\hbar\omega - \left(E_f - E_i\right)\right) \end{aligned}$$

We can also go through and compute ω_{21}, and we find that $\omega_{12} = \omega_{21}$, which is known as detailed balance, and is related to time-reversal symmetry.

We can compute the number of transitions from 1 to 2:

$$\omega_{12}N_1$$

Where N_1 is the number of atoms in state 1. Similarly, the number of transitions from 2 to 1 is given by

$$\omega_{21}N_2$$

We see that they have the same transition rate, but not necessarily the same number of actual transitions. We also have the effect of spontaneous emission:

$$\omega_s = \frac{\omega^3}{c^3m^2\omega^2}\frac{2}{3}|\left\langle 1|\boldsymbol{p}|2\right\rangle|^2$$

So we have that the number of downward transitions is given by

$$\omega_{21}N_2 + \omega_sN_2$$

Einstein's idea was to consider the condition for equilibrium, the number of transitions in either directions were equal:

$$\omega_{12}N_1 = \omega_{21}N_2 + \omega_sN_2$$

This is known as the balance condition. Rewriting this:

$$\omega_{12}\left(\frac{N_1}{N_2}\right) = \omega_{21} + \omega_s$$

Now using some statistical mechanics, applying the Boltzmann distribution:

$$\begin{aligned} \frac{N_1}{N_2} &= e^{-(E_1-E_2)/kT} \\ &= e^{\hbar\omega/kT} \end{aligned}$$

Now inserting the expression for ω_{12} :

$$\begin{aligned}\frac{4\pi^2\alpha c}{m^2\omega^2} I\left(\omega\right) \left| \left\langle n \right| \boldsymbol{p}\cdot\boldsymbol{\epsilon} \left| i \right\rangle \right|^2 \left(e^{\frac{\hbar\omega}{kT}}-1\right) &= \frac{\alpha\omega^3}{c^3m^2\omega^2} \left| \left\langle n \right| \boldsymbol{p}\cdot\boldsymbol{\epsilon} \left| i \right\rangle \right|^2 \\ I\left(\omega\right) &= \frac{\omega^3}{e^{\frac{\hbar\omega}{kT}}-1}\end{aligned}$$

We see that this is the usual black-body radiation formula.

Let us continue looking at a two-level system. Suppose that at $t=0$, the system is in the ground state:

$$c_i^{(0)}\left(0\right)=1$$

What if we look at how this evolves in time (skipping a lot of math and distribution calculus):

$$\frac{1}{c_1\left(t\right)}\frac{dc_i\left(t\right)}{dt} = -\frac{i}{\hbar}\left(V_{ii}+\sum_m \frac{\left|V_{mi}\right|^2}{E_i-E_m+i\epsilon}\right)$$

Note that this looks very familiar, this is the first and second order energy shifts from time-independent perturbation theory, where we have dodged the degeneracy pole by moving around the pole with an $i\epsilon$.

From this, we see that

$$c_i\left(t\right)=e^{-\frac{i}{\hbar}\Delta_i t}$$

Where Δ_i is the ith order energy shift. Note that Δ_i, in order to avoid the poles, need not be real.

We can consider the imaginary part of the energy shift:

$$\begin{aligned}\mathrm{Im}\Delta_i &= -\frac{1}{\hbar}\sum_{m\neq i}\left|V_{mi}\right|^2\delta\left(E_m-E_i\right) \\ &= -\frac{\hbar}{2}\sum_{i\to m}\omega_{i\to m}\end{aligned}$$

From this, we can write out the state amplitude:

$$\begin{aligned}c_i\left(t\right) &= e^{-\frac{i}{\hbar}\left(\Delta_i^{\mathrm{Re}}+i\Delta_i^{\mathrm{Im}}\right)t} \\ &= e^{-\frac{1}{2}\sum_m \omega_{i\to m}t}e^{-\frac{i}{\hbar}\Delta_i^{\mathrm{Re}}t}\end{aligned}$$

We see that $\tau=\frac{1}{\sum_m \omega_{i\to m}}$, which allows us to write that the probability of being in a certain state is given by

$$\begin{aligned}\left|c_i\left(t\right)\right|^2 &= e^{-\sum_m \omega_{i\to m}t} \\ &= e^{-t/\tau}\end{aligned}$$

2.2.8 Width of States

We have shown that states have lifetimes, an atom in an excited state will not remain there forever, the amplitude is given by

$$c_1\left(t\right) = e^{-iE_it/\hbar}e^{-t/2\tau}$$

To combine these two, we introduce Γ, the width of the state:

$$\Gamma = \frac{\hbar}{\tau}$$

This has units of energy, and we can use it to rewrite the amplitude of the state:

$$c_1\left(t\right) = e{-}i\left(E_i - i\frac{\Gamma_i}{2}\right)t$$

From this, we realize that we can think of the energy having an imaginary component:

$$E_i = E_i^{(0)} - i\frac{\Gamma_i}{2}$$

But what does this really mean? We can think of this as saying that the system is not precisely at E_i, but rather there is a Lorentzian[4] distribution of energies around E_i, whose width is given by Γ. This is related to the energy-time uncertainty. Since the state only lives for finite time, we cannot measure the energy with infinite resolution, the uncertainty in the energy is related to the width of the state:

$$\Delta E\Delta t \sim \hbar$$

In the limit where $\Gamma \to 0$, we recover the delta function $\delta\left(E - E_i^{(0)}\right)$.

Consider an atom exposed to light. We have some electron emission, and we would like to apply Fermi's Golden Rule. We have that

$$w = \frac{2\pi}{\hbar}|V_{fi}|^2\delta\left(\left(E_f - E_i\right) \pm \hbar\omega\right)$$

Now let us introduce the idea of a cross-section, which is independent of the source of the light. The energy absorbed per unit time is equal to the probability per unit time of the absorption, w, times the energy absorbed, $\hbar\omega$. If we then divide this by the flux, the energy passing through per unit area per unit time, otherwise known as the intensity, this gives us the cross-section:

$$\sigma_{\text{cross-section}} = \frac{\text{Energy absorbed/unit time}}{\text{Intensity}}$$

If we shine light on an atom, and then look at the cross-section as a function of the frequency of the light, $\sigma\left(\omega\right)$, we see peaks, which indicate the existence of an excited state, which is absorbing the incoming electrons.

---

[4] Lorenz or Lorentz?

We can look at the cross-section explicitly:

$$\begin{aligned}\sigma &= \frac{4\pi^2\hbar\alpha}{m_e^2\omega}\sum_n |\langle n|e^{i\boldsymbol{k}\cdot\boldsymbol{x}}\boldsymbol{\epsilon}\cdot\boldsymbol{p}|i\rangle|^2\delta\left(E_n - E_i - \hbar\omega\right) \\ &= \frac{4\pi^2\hbar\alpha}{m_e^2\omega}V\int\left(\frac{d^3\boldsymbol{k}_f}{h^3}\right)\delta\left(E_n - E_i - \hbar\omega\right)|\langle n|e^{i\boldsymbol{k}\cdot\boldsymbol{x}}\boldsymbol{\epsilon}\cdot\boldsymbol{p}|i\rangle|^2\end{aligned}$$

Now using the fact that $E_e = \frac{k_f^2}{2m}$, an we have that

$$d^3\boldsymbol{k}_f = \frac{d\Omega}{d}k_f^2 dk_f$$

We can write out $d\sigma$:

$$d\sigma = d\Omega\frac{4\pi^2\hbar\alpha}{m_e\omega}\frac{V}{h^3}mk_f|\langle n|e^{i\boldsymbol{k}\cdot\boldsymbol{x}}\boldsymbol{\epsilon}\cdot\boldsymbol{p}|i\rangle|^2$$

From this, we can write out $\frac{d\sigma}{d\Omega}$, the differential cross-section:

$$\frac{d\sigma}{d\Omega} = \frac{4\pi^2\hbar\alpha}{m_e^2\omega}|\langle k_f|e^{i\boldsymbol{k}\cdot\boldsymbol{x}}\boldsymbol{\epsilon}\cdot\boldsymbol{p}|i\rangle|^2\frac{m_e k_f V}{\hbar^2\left(2\pi\right)^3}$$

3 Identical Particles

Consider a stable nucleus with $Z = 82$, which is Lead 208. This has 82 protons and 126 neutrons. We can write down the Hamiltonian for Lead-208, by neglecting the nucleus, and focusing on the electrons. We have 82 electrons, so we will have a label $i = 1, 2, \ldots 82$. We will have the kinetic energies of the electrons, $\frac{p_i^2}{2m}$, and Coulomb potentials, from the central nucleus. We also have the mutual interactions, based on the distance between two particles, $r_{ij} = |\boldsymbol{r}_i - \boldsymbol{r}_j|$:

$$\hat{H} = \sum_{i=1}^{82}\frac{p_i^2}{2m} + \sum_{i=1}^{82}V_c\left(r_i\right) + e^2\sum_{i<j}\frac{1}{r_{ij}}$$

Now we note that the Hamiltonian is dependent on the labels of the 82 electrons, and the electrons are identical particles, so we have exchange symmetry between the different labels. This symmetry forms a group, S_n, the symmetric group of nth order. Note that this is a finite group. In the case of $n = 2$, we can have $H(1, 2)$ and $H(2, 1)$. The group consists of two elements. The first is the identity, there is no swapping of labels. The second is the swap between the first label and the second label, P_{12}. Thus:

$$S_2 = \{\mathbb{I}, P_{12}\}$$

Considering the case of S_3, we have 6 different elements. In S_n, we have $n!$ group elements.

Note that our particles being the same indicate that $[H, S_n] = 0$, permuting the labels in any way does nothing to change the Hamiltonian.

What does this permutation symmetry imply for the wavefunction of the system? We don't require invariance under permutations, but we have a physical requirement for quantum indistinguishability.

This requirement is that the probability density ($|\psi|^2$) should be invariant under permutations. From this, we see that $\psi(1,2)$ and $\psi(2,1)$ can only ever differ by a phase factor:

$$\psi(1,2) = e^{i\alpha}\psi(2,1)$$

Once we do the swapping, we expect to be able to do a swap back to the original permutation of coordinates (only true in 3+ dimensional systems), and therefore

$$e^{i\alpha} = e^{2i\alpha}$$

From this, we have that $e^{i\alpha} = \pm 1$. For quantum mechcanical systems, this means that if we swap any two labels, we pick up a $\pm$:

$$\psi\left(1,2,\ldots,n\right) = \left(\pm 1\right)\psi(i_1,\ldots,i_n)$$

Where $i_1,\ldots,i_n$ differs from $1,2,\ldots,n$ by one permutation.

There are two one-dimensional representations of symmetry group, one of which is totally symmetric, and another that is totally anti-symmetric. These correspond to Bosons and Fermions, respectively.

3.1 Helium Atom

$Z = 82$ is a bit overkill, so let us consider the case of $Z = 2$, the Helium atom:

$$\hat{H} = \sum_{i=1}^{2}\frac{p_i^2}{2m} + \sum_{i=1}^{2}V_c\left(r_i\right) + e^2\sum_{i<j}\frac{1}{r_{ij}}$$

This is not analytically solvable, so let us use perturbation theory to solve this. Let us neglect the electron-electron interaction. We expect the wavefunction to be the same as the Hydrogen wavefunction, except we change Z to 2. This is sometimes known as the independent particle approximation. Let us first consider the state with two electrons in the ground state. We have that

$$\Psi\left(1,2\right) = \psi\left(1\right)\psi\left(2\right)$$

Where $\psi_1 = \psi_{nlm}\left(\boldsymbol{r}\right)\chi_{m_s}$. In order to maintain the quantum indistinguishability, we need the spin section of the wavefunction to be antisymmetric, and therefore we need this to be a spin singlet,

$$\Psi\left(\boldsymbol{r}_1,\boldsymbol{r}_2\right) = \psi_{100}\left(\boldsymbol{r}_1\right)\psi_{100}\left(\boldsymbol{r}_2\right)$$

Let us compute the ground state energy of the Helium atom. We have that

$$H = H_0 + V$$

Where

$$H_0 = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + V\left(r_1\right) + V\left(r_2\right)$$

And $V = \frac{e^2}{r_{12}}$. We have the ground state wavefunction:

$$\psi\left(1,2\right) = \psi_{100}\left(\boldsymbol{r}_1\right)\psi_{100}\left(\boldsymbol{r}_2\right)\frac{1}{\sqrt{2}}\left(\left|\uparrow\right\rangle\left|\downarrow\right\rangle - \left|\downarrow\right\rangle\left|\uparrow\right\rangle\right)$$

We can compute the ground state energy:

$$\begin{aligned} E_0 &= -13.6 \times Z^2 \times 2 \\ &= -108.8 \text{ eV} \end{aligned}$$

This is the binding energy, computed with no perturbation. We can compute the first order energy correction:

$$\begin{aligned} \Delta^{(1)} &= \langle \psi\left(1,2\right) | V_{12} | \psi\left(1,2\right) \rangle \\ &\vdots \\ &= \frac{5}{2}\left(13.6\right) \end{aligned}$$

Note that this correction is positive, because the electron-electron interaction is repulsive. That gives the first order perturbation theory binding energy:

$$E_0 + \Delta^{(1)} = -74.8 \text{ eV}$$

Comparing this to the experimental value of -79 eV, we see that we're not too far off.

Now let us consider some excited states of Helium. The ground state had total spin equal to zero. Let us now promote one of the electron to an excited state. We have possibilities of the form of one particle being in $|100\rangle$ and the other in $|nlm\rangle$.

We can have a symmetric wavefunction, or an antisymmetric wavefunction:

$$\psi_{\pm}\left(1,2\right) = \frac{1}{\sqrt{2}}\left(|100\rangle |nlm\rangle \pm |nlm\rangle |100\rangle\right)$$

For spin, we have either a triplet, which has $m_s = \pm 1, 0$ and is symmetric, or we can have a singlet, which has $m_s = 0$, and is antisymmetric.

We can form what is known as the triplet state:

$$\begin{aligned} \psi^{s=1}\left(1,2\right) &= \chi_{s=1}\psi_{-}\left(1,2\right) \\ &= \chi_{s=1}\left(\psi_{100}\left(\boldsymbol{r}_1\right)\psi_{nlm}\left(\boldsymbol{r}_2\right) - \psi_{nlm}\left(\boldsymbol{r}_1\right)\psi_{100}\left(\boldsymbol{r}_2\right)\right) \end{aligned}$$

Or we can have the singlet state:

$$\psi^{s=0}\left(1,2\right) = \chi_{s=0}\psi_{+}\left(1,2\right)$$

These are the only two wavefunctions we can make that have the correct antisymmetry.

Without any perturbation, we have that the energy is $E_{100} + E_{nlm}$ for both states. We can then compute the first order corrections for both possible wavefunctions. If we go through these computations, we find that the two states give different energy corrections. Thus we will split the original state into two different states. Without calculating, we can argue about which state will have a higher energy. The wavefunction is antisymmetric, which means that when two electrons are on top of each other, the wavefunction vanishes. For this reason, we say that the antisymmetric wavefunction, the triplet state, will have a lower energy than the singlet state.

Thus, we have shown that when we excite one electron, we have a splitting in every single excited energy level, into a higher and lower energy state.

From this, we see that it seems like we can write out an effective Hamiltonian that is proportional to $\boldsymbol{s}_1 \cdot \boldsymbol{s}_2$:

$$H_{\mathrm{E}} = J\boldsymbol{s}_1 \cdot \boldsymbol{s}_2$$

Thus we see that we have an effective model for ferromagnetism, the spins are induced to line up, since that requires less energy. This is known as the Heisenberg interaction or Heisenberg model, as he was the first to use this.

3.2 Higher Order Elements

Now let us jump to Lead-208. We have 82 electrons, and the Hamiltonian will be given by

$$H = \sum_{i=1}^{82} \frac{p_i^2}{2m} + \sum_{i=1}^{82} \frac{Ze^2}{r_i} + \sum_{i<j} \frac{e^2}{r_{ij}}$$

This is obviously not solvable. We can apply perturbation theory, and neglect the interactions between electrons, and we see that the Hamiltonian is just a sum of 82 non-interacting Hamiltonians, each of which are exactly solvable. The lowest energy state will just be to fill up the electron orbitals using the Pauli Exclusion Principle. This turns out to be a good starting point, but we can do better. If we compare the ground state energy to experiment, we are very off, and our ground state wavefunction also doesn't agree with experiment. How do we do better? We assume that the wavefunction is indeed composed of single particle wavefunctions (which are not the non-interacting wavefunctions, they are different), $\{\phi_i\}$, arranged in a Slater determinant:

$$\Psi\left(1, 2, \ldots, 82\right) = \frac{1}{\sqrt{82!}} \begin{vmatrix} \phi_1\left(\boldsymbol{r}_1\right) & \phi_2\left(\boldsymbol{r}_1\right) & \ldots & \phi_{82}\left(\boldsymbol{r}_1\right) \\ \phi_1\left(\boldsymbol{r}_2\right) & \phi_2\left(\boldsymbol{r}_2\right) & \ldots & \phi_{82}\left(\boldsymbol{r}_2\right) \\ \vdots & \vdots & \ldots & \vdots \end{vmatrix}$$

Note that this has an absurd number of terms in the wavefunction (82! terms).

Now how do we get the ϕ functions? We do this via mean field theory. What this entails is to focus on one electron, and say that the other electrons together contribute some mean field $V_{\text{mean field}}\left(\boldsymbol{r}_i\right)$. A very stupid way to calculate this is to assume that all the other electron functions are known, and compute the Coulomb interaction with all the other electrons:

$$V_{\text{mean field}}\left(\boldsymbol{r}_1\right) = \sum_{i=1}^{Z} \int \frac{e^2}{\left|\boldsymbol{r}_i - \boldsymbol{r}\right|} \left|\phi\left(\boldsymbol{r}_2\right)\right|^2 d^3\boldsymbol{r}_2$$

Now let us insert this into the Schrodinger equation:

$$H = \sum_{i=1}^{82} \left(\frac{p_i^2}{2m} + \frac{Ze^2}{r_i}\right) + \sum_{i=1}^{Z} V_{\text{mf}}\left(\boldsymbol{r}\right)$$

Which makes the Schrodinger equation:

$$\left(\frac{\boldsymbol{p}^2}{2m}+\frac{(-e)^2 Z}{r}+V_{\mathrm{mf}}\left(\boldsymbol{r}\right)\right)\phi_i\left(\boldsymbol{r}\right)=\mathcal{E}_i\phi_i\left(r\right)$$

However, note that this is not really the Schrodinger equation, because it's nonlinear, unlike the Schrodinger equation (since V_{mf} depends on the ϕ). We solve this equation using iteration. Also note that our V_{mf} does not take into account the fact that the electrons are identical particles. If we take this into account, the result is the Hartree-Fock equation:

$$\left(\frac{\boldsymbol{p}^2}{2m}+\frac{-e^2 Z}{r}\right)\phi_i\left(\boldsymbol{r}\right)+\sum_{j=1}^{N}\int\frac{e^2}{\left|\boldsymbol{r}_2-\boldsymbol{r}\right|}\left[\underbrace{\left|\phi_j\left(\boldsymbol{r}_2\right)\right|^2\phi_i\left(\boldsymbol{r}\right)}_{\text{Hartree Term}}-\underbrace{\phi_j^*\left(\boldsymbol{r}_2\right)\phi_j\left(\boldsymbol{r}\right)\phi_i\left(\boldsymbol{r}_2\right)}_{\text{Fock Term}}\right]d\boldsymbol{r}_2=\mathcal{E}_i\phi_i\left(\boldsymbol{r}\right)$$

Note that this implicitly deals with self-interaction, since the term where $i=j$ will always be zero. This equation takes into account the particle interchange anti-symmetry for the electrons. It turns out that this mean field theory approximation is very useful and accurate in condensed matter systems, and has been the go-to method for many years. However, recently, systems have been found (called "strongly interacting electron systems") that cannot be described using MFT, such as the quantum Hall effect.

3.3 Periodic Table

We began by discussing Hydrogen. For Helium, the ground state is two electrons in the $1s$ state, with total spin 0 (since we need spin wavefunction antisymmetry). Using notation $^{2s+1}L_j$, we have $^1S_0$ for Helium.

For Lithium, we have one electron in the $2s$ state, so we have $^2S_{1/2}$.

After this, Beryllium fills up the $2s$ state, so we have total spin equal to 0, and total angular momentum equal to 0, so we have $^1S_0$.

Adding another electron in the $2p$ state to get Boron, we have a triplet state, with orbital angular momentum equal to 1, so we have $^2P_{1/2}$ (1/2 because when we compute the spin-orbit splitting, the 1/2 state is lower than the 3/2 state).

Adding another electron to the $2p$ state, we get Carbon. We guess that the ground state will be a triplet state, and we have $m_l=1,0,-1$. Picking the case with the lowest spin-orbit interaction, we get total $j=0$, so we have that the ground state is $^3P_0$.

Up next is Nitrogen. We have 3 electrons, and the lowest energy spin configuration is where all of them are aligned, giving total spin 3/2, which means that $2s+1$ is 4, we have a quadruplet state. What about the orbital angular momentum? Each electron is in a different m_l state, either $1,0$ or -1, and therefore the total orbital angular momentum is 0. Thus this is an S state. Thus we have a $^4S_{3/2}$ state.

Next, Oxygen has 4 electrons in the p state. When we get past Oxygen, we start thinking about holes, rather than what is filled. We have 6 slots, and 4 filled, so we have 2 holes. Thinking about Carbon, which has 2 electrons, Oxygen will be similar to Carbon, except they are hole states. This gives us a triplet P state. However, when we look at the spin-orbit interaction for the holes, the sign is flipped. Thus we instead take the highest possible configuration of the 2 electron spin-orbit interaction. We have $0, 1$, and 2, and therefore we take the highest angular momentum, so we take the 2. This is what we do when over half of a shell is filled. Thus we have that Oxygen is a ${}^3P_2$ state.

Next, Fluorine is very similar to Boron, so we have a ${}^2P_{3/2}$, where we take the 3/2 instead of the 1/2 spin-orbit configuration.

Completely filling the $3p$ state, we get Neon, which is a singlet, ${}^1S_0$.

Looking at Sodium, we get ${}^3S_{1/2}$. After that, Magnesium has ${}^1S_0$. After we get to Calcium, we switch to filling the $3d$ state first, but the rules work the same way.

4 Scattering

4.1 Classical Scattering Theory

We have some incoming particles, scattering off of a solid object. We have some incoming flux, I, which is the number of incoming particles per unit area per unit time. The cross section σ, which represents the the area of the solid object that the particles are scattering off of. For example, in the case of a solid sphere of radius R, the cross section is the maximal cross-sectional area, πR^2.

We also define the event rate, λ, which is the number of scattered particles per unit time. We have the relationship between the three variables:

$$\sigma = \frac{\lambda}{I}$$

Now let us define the differential cross-section. consider a small segment of area in space. We have incoming particles that pass through this area, and they will be scattered off of the object into some solid angle, $d\Omega$. We can compute the differential cross-section

$$\frac{d\sigma}{d\Omega}$$

based on the geometry of the system. Experimentally, this is computed via scattering experiments. The incoming particles through the area $d\sigma$, is related to the infinitesimal event rate and the intensity:

$$d\lambda = I d\sigma$$

Which allows us to write the differential cross section in terms of the infinitesimal event rate and the intensity:

$$\frac{d\sigma}{d\Omega} = \frac{1}{I}\frac{d\lambda}{d\sigma}$$

Let us consider the example of classical hard sphere scattering, with particles directly incident on the sphere. Let us introduce a parameter b, the impact parameter, which tells us the height above/below the center of the sphere a particle is incident, and we label θ to be the angle from the horizontal that the particle scatters at. Let us consider a ring of incident area, centered on the central axis of the sphere, $d\sigma$. We have incident angle α, and in the case of hard sphere scattering, the incident angle is the same as the scattered angle, when measured perpendicular to the sphere. We also know that

$$\begin{aligned} d\lambda &= I d\sigma \\ &= I \cdot 2\pi b \, db \end{aligned}$$

From the angle relations:

$$\begin{aligned} \sin\alpha &= \frac{b}{R} \\ 2\alpha + \theta &= \pi \end{aligned}$$

We have that

$$d\lambda = I\frac{\pi}{2}R^2 d\cos\theta$$

From this, we have that

$$\frac{d\sigma}{d\cos\theta} = \frac{\pi}{2}R^2$$

And we can compute the differential cross-section:

$$\begin{aligned} \frac{d\sigma}{d\Omega} &= \frac{d\sigma}{2\pi d\cos\theta} \\ &= \frac{R^2}{4} \end{aligned}$$

This tells us that the measurement of the number of particles scattered into a particle direction is independent of the angle.

We can also compute the total cross-section, by integrating out the entire solid angle:

$$\begin{aligned} \sigma &= \int d\Omega \frac{R^2}{4} \\ &= \pi R^2 \end{aligned}$$

We see that the cross-section is consistent with the intuitive cross-section of a solid sphere.

Why do we need to introduce this concept? It seems more difficult than just using a ruler or some form of measurement. The reason for this is because that type of measurement is not possible for quantum systems.

4.2 Quantum Scattering Theory

Instead of considering the physical trajectory of incoming particles, we consider incoming plane waves, interacting with a scattering potential. We then look at the reflections of the plane waves, and attempt to find solutions to the Schrodinger equation of the form $\psi(r,\theta) = Ae^{ikz} + Af(\theta)e^{ikr}/r$, where r is the distance from the potential, and θ is the angle from the incident plane. The first term is the incident plane wave, and the second term is the scattering plane wave. The function $f(\theta)$ is known as the scattering amplitude, which is of key importance. Note that the $1/r$ dependence is necessary in order to maintain probability normalization.

We want to find a quantum mechanical analogue of the ideas of intensity and event rate. The analogue of the intensity is the probability flux $\boldsymbol{j}$ in the direction of the incoming plane wave. Recall that the probability flux is defined as:

$$\boldsymbol{j} = \frac{\hbar}{m}\text{Im}\left[\psi^* \nabla \psi\right]$$

Looking at the direction of the incident plane wave:

$$\begin{aligned} j_{i,z} &= \frac{\hbar}{m}\text{Im}\left[A^* e^{-ikz}\frac{\partial}{\partial z}Ae^{ikz}\right] \\ &= \frac{\hbar}{m}|A|^2 k \end{aligned}$$

We can also consider the scattered probability flux:

$$j_{s,r} = \frac{\hbar}{m}|A|^2 |f\left(\theta\right)|^2 \frac{k}{r^2}$$

Note that the outgoing flux goes as $1/r^2$.

Let us compute the total probability of something scattering through a sphere of radius r around the potential:

$$\int d\Omega\, r^2 j_{s,r} = \int d\Omega\, \frac{\hbar}{m}|A|^2 |f\left(\theta\right)|^2 k$$

Note that the probability is independent of r, and therefore if we make a larger sphere, the probability is constant, thus proving that we maintain probability conservation.

Now let us define the quantum mechanical differential cross-section for this case:

$$\frac{d\sigma}{d\Omega} = \frac{1}{j_{i,r}}\frac{j_{s,r}\cdot r^2 d\Omega}{d\Omega}$$

Where we note that the intensity is the incoming flux, and the event rate is the scattered flux times the area of a section of the sphere. If we write this out, we have that

$$\frac{d\sigma}{d\Omega} = |f\left(\theta\right)|^2$$

We see that the differential cross-section is related directly to the scattering amplitude, which is why the scattering amplitude is important.

We can compute the total cross-section:

$$\sigma = \int d\Omega\, |f\left(\theta\right)|^2$$

In the lab, we can conduct scattering experiments to compute $\frac{d\lambda}{d\Omega}$, and then work backwards to compute $f\left(\theta\right)$, $\frac{d\sigma}{d\Omega}$, and σ. These can then be linked to the potential V. Thus the differential cross-section is a link between theoretical models and scattering experiments. Note that our solution to the Schrodinger equation works for potentials that have cylindrical symmetry, and works in the regime of large r. For cases where there is ϕ dependence in the potential, the scattering amplitude becomes a function of θ and ϕ.

4.3 Quantum Hard Sphere

Consider the potential $V(r)$:

$$V(r) = \begin{cases} +\infty & r \ll a \\ 0 & r > a \end{cases}$$

To solve this problem, we introduce a technique known as partial wave analysis. This technique is applicable to problems with spherical symmetry. Since the potential is spherically symmetric, the Hamiltonian is as well, and therefore $\left[H, \boldsymbol{L}^2\right] = [H, L_z] = 0$. In this case, we can check the eigenstates of the Hamiltonian by looking at the eigenstates of the angular momentum operators, spherical harmonics:

$$\psi_{l,m}(r, \theta, \phi) = R_l(r) Y_l^m(\theta, \phi)$$

Recall that if we let $U_l(r) = rR_l(r)$, we can write out the Schrodinger equation that these functions satisfy:

$$-\frac{\hbar^2}{2m}\frac{\partial^2 U_l}{\partial r^2} + \left[V(r) + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right] U_l = EU_l$$

We can write the solution to this equation in terms of a series expansion:

$$\psi = \sum_{l,m} c_{l,m} R_l(r) Y_l^m(\theta, \phi)$$

Where the coefficients $c_{l,m}$ are determined via boundary conditions (similar to solving Laplace's equation in E&M).

Now considering the original potential we were looking at, we have the equation:

$$-\frac{\hbar^2}{2m}\frac{\partial^2 U_l}{\partial r^2} + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2} U_l = EU_l$$

The solutions to this equation are the Hankel functions:

$$U_l(kr) = Arh_l^{(1)}(kr) + Brh_l^{(2)}(kr)$$

Note that $h_l^{(1)}(kr) \sim e^{ikr}/r$, and the second order is proportional to e^{-ikr}/r. Since we only care about outgoing waves, we neglect the second term (incoming waves). Thus we write our solutions as:

$$\psi(r, \theta, \phi) = A\left[e^{ikz} + \sum_{l,m} c_{l,m} h_l^{(1)}(kr) Y_L^m(\theta, \phi)\right]$$

We determine the coefficients in this expression using the boundary conditions, and then apply a large r expansion in the Hankel functions. Now we note that we don't need to sum over m, since the system is ϕ-symmetric (we can apply Wigner-Eckart, since the potential is a rank 0 spherical tensor). Thus we have that

$$\psi(r, \theta) = A\left[e^{ikz} + \sum_{l} c_{l,0}\, h_l^{(1)}(kr) P_l(\cos\theta)\right]$$

The boundary condition for this system is that $\psi(r=a,\theta)=0$. To apply this, it will be convenient to write the incoming wave e^{ikz} in terms of Legendre polynomials[5]:

$$e^{ikz}=\sum_{l=0}^{\infty} i^{l}\left(2l+1\right)J_{l}\left(kr\right)P_{l}\left(\cos\theta\right)$$

Where J_l are the spherical Bessel functions (of the first kind). Now noting that the Legendre polynomials are linearly independent for each l, we can separate the different ls and insert the boundary conditions to determine the coefficients $c_{l,0}$.

If we do this all out, and compute the cross-section in the large r limit, we find:

$$\sigma=4\pi\sum_{l=0}^{\infty}\left(2l+1\right)\frac{1}{k^{2}}\left|\frac{J_{l}\left(ka\right)}{h_{l}^{(1)}\left(ka\right)}\right|^{2}$$

4.3.1 Low Energy Limit

Let us look at the limit where $ka \ll 1$, where we can make approximations for the Bessel and Hankel functions, we find that

$$\begin{aligned}\sigma&\sim 5\pi\sum_{l=0}^{\infty}\ldots\left(ka\right)^{4l+2}\\&=4\pi a^{2}\end{aligned}$$

We see that this is a factor of 4 larger than the classical result. This is due to the fact that we are in the low energy limit, where the wavelengths of incoming plane waves can interact with a larger area of the spherical potential.

4.3.2 High Energy Limit

Now looking at the limit where $ka \gg 1$, we have extremely short wavelengths, meaning that we are closer to the classical picture, where we have particles with many trajectories that scatter across the potential. Looking at the classical picture again, we need trajectories such that the impact parameter b is less than the radius of the sphere, $b<a$, otherwise the particle will just pass by. This means that we have a maximum angular momentum (since $\boldsymbol{L}=\boldsymbol{r}\times\boldsymbol{p}=bp$) $l_{\max}=ak$. Thus, we cut off the sum at $l_{\max}$, rather than ∞. We also apply an approximation for the Bessel and Hankel functions, in the case of large ka, and we find that

$$\sigma\approx 4\pi\sum_{l=0}^{ka}\left(2l+1\right)\frac{1}{k^{2}}\sin^{2}\left[\frac{\pi}{2}l-ka\right]$$

Consider adjacent pairs in this sum. We note that the $\sin^2$ will be shifted by $\frac{\pi}{2}$:

$$\sin^{2}\left[\frac{\pi}{2}l-ka\right]+\sin^{2}\left[\frac{\pi}{2}\left(l+1\right)-ka\right]=1$$

Thus we have that (on average), each term gives $1/2$ from the $\sin^2$:

$$\sigma\approx 4\pi\sum_{l=0}^{ka}\left(2l+1\right)\frac{1}{k^{2}}\frac{1}{2}$$

---

[5] Using Rayleigh's formula.

$$\approx 2\pi a^2$$

We see that we are a factor of 2 off of the classical result. Why is this the case? Well, when we consider the reflected cross-section, we get a factor of πa^2. We also have a shadow area, in which the wavefunction is 0. However, The total wavefunction contains the incoming wavefunction, which is nonzero in the shadow region. Thus we must have destructive interference between the incoming and scattered wavefunction in this area. This shadow scattered wavefunction must contribute to the cross-section, giving us the $2\pi a^2$.

We have two types of scattering. The first is elastic scattering, where we shoot something at a target, and the two collide and then recoil. The second type is inelastic scattering, where the target breaks into other particles after being hit with the incoming particle.

We also have reactions, where we hit a target with something, and we are left with outputs that are not the incoming particle or the target (Think splitting U-235 in a nuclear reaction).

We will cover elastic two-body scattering, the simplest case of scattering.

4.4 Elastic Scattering

We have a potential generated by the target $V(r)$, and we send in a particle/wave, and we want to see how it scatters off of the target. There are several energy scales involved in this. We have an incoming wave, which has a particular energy. We also have an effective size of the potential, at some point we consider the potential to have become negligible. We also have the depth of the potential well, which gives us another scale.

In order to discuss the incoming wave, we have to solve the Schrodinger equation:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right]\psi(r) = E\psi(r)$$

The scattering solution will depend on the boundary conditions. Suppose our experimental setup is such that the incoming beam is moving in the z axis, and we are not close to the potential well yet, we are still far away. We have an incoming plane wave, e^{-ikz}, and we put detectors very far away from where the scattering occurs, and we will measure the incoming plane wave, as well as the scattered wave, which we model as a spherical wave:

$$\psi_s = f(\theta,\phi)\frac{e^{ikr}}{r}$$

Thus, for large r, we are looking for a solution of the form:

$$\psi(r) = e^{ikz} + f(\theta,\phi)\frac{e^{ikr}}{r}$$

Once we have solved for $f(\theta,\phi)$, we then want to compute the differential cross-section:

$$\frac{\partial\sigma}{\partial\Omega} = |f(\theta,\phi)|^2$$

4.4.1 Phase Shift Analysis

The first method that we will introduce is phase shift analysis. This is useful for low-energy scattering.

Mathematically, plane waves, at large r, are the sum of many spherical waves:

$$e^{ikz} \approx \sum_{l=0}^{\infty} \frac{(2l+1)}{2ik} P_l(\cos\theta) \left(\frac{e^{ikr}}{r} - \frac{e^{-i(kr-l\pi)}}{r}\right)$$

Why is this better for low-energy scattering? Even though we have an infinite sum over angular momentum, we will see that only the low values of l will contribute to the summation.

Inserting this summation into our ψ, and assuming that the scattering is spherically symmetric (so $f(\theta)$), and therefore expanding $f(\theta)$ in terms of the Legendre polynomials, we have that

$$\psi(r) = \sum_{l=0}^{\infty} \frac{(2l+1) P_l(\cos\theta)}{2ik} \left[(2ikf_l + 1) e^{ikr} - e^{-i(kr-l\pi)}\right]$$

Recall that in the case of elastic scattering, we do not lose particles, and therefore the magnitude of the incoming plane wave must remain 1, and therefore $|2ikf_l + 1|^2$ must be 1. We denote this quantity S_l, and note that it must be a phase:

$$\begin{aligned} S_l &= 2ikf_l + 1 \\ &= e^{2i\delta_l} \end{aligned}$$

Where δ_l is known as the phase shift. We can solve for f_l, and we find that

$$\begin{aligned} f_l &= \frac{S_k - 1}{2ik} \\ &= \frac{1}{k\cot\delta_l - k} \end{aligned}$$

Working backwards to find $f(\theta)$:

$$f(\theta) = \sum_{l=0}^{\infty} (2l+1) P_l(\cos\theta) f_l$$

We can then compute the cross-section:

$$\sigma_{\text{total}} = \frac{4\pi}{k} \sum_{l=0}^{\infty} (2l+1) \sin^2\delta_l$$

Let us return to hard sphere scattering, and look at the low energy case. Outside of the potential, we will have that $l = 0$, we have only the s-wave scattering. We can solve the Schrodinger equation for this case:

$$-\frac{\hbar^2}{2m} \frac{d^2 U_0}{dr^2} = E U_0$$

Rewriting this with $k = \sqrt{\frac{2mE}{\hbar^2}}$:

$$\frac{d^2U_0}{dr^2} + k^2U_0 = 0$$

This has solution:

$$\begin{aligned} U_0 &= A\sin\left(kr + \delta_0\right) \\ &= A\frac{1}{2i}\left(e^{i(kr+\delta_0)} - e^{-i(kr+\delta_0)}\right) \\ &= A\frac{e^{i\delta_0}}{2i}\left(e^{2i\delta_0}e^{ikr} - e^{-ikr}\right) \end{aligned}$$

In order to compute the phase shift, we need to use the boundary condition at the edge of the potential, when $r = R$. We need the wavefunction to be continuous:

$$A\sin\left(kR + \delta_0\right) = 0$$

Which is true when $\delta_0 = -Rk$. This is a repulsive interaction, we have a negative phase shift. If we had a positive phase shift, then we have an attractive interaction. Note that the phase shift tells us the size of the hard sphere, R.

In general, we can apply the partial wave analysis method if $Rk \ll 1$, we only have the s-wave scattering.

Looking at the cross-section:

$$\begin{aligned} \sigma_{\text{total}} &= \frac{4\pi}{k^2}\sum_{l=0}^{\infty}\left(2l+1\right)\sin^2\delta_l \\ &= \frac{4\pi\delta_0^2}{k^2} \\ &= 4\pi R^2 \end{aligned}$$

Note that this cross-section is maximized when $\delta_l = \frac{\pi}{2}, \frac{3\pi}{2}, \ldots$, which is known as a unitarity constraint. Also note that

$$\begin{aligned} \text{Im}\left[f\left(\theta = 0\right)\right] &= \frac{1}{k}\sum_{l=0}\left(2l+1\right)\sin^2\delta_l \\ &= \frac{k}{4\pi}\sigma_{\text{total}} \end{aligned}$$

Which is known as the optical theorem, derived in Section 4.4.5.

Let us consider the low-energy limit, $k \to 0$, and $\delta_l \sim k^{2l+1}$. We have s-wave scattering ($l = 0$), and we have that

$$\sigma = \frac{4\pi}{k^2}\sin^2\delta_0$$

In order for this not to go to infinity in the low energy limit, we need $\delta_0 \to 0$. Specifically, the phase shift vanishes linearly:

$$\delta_0 \to -ka$$

Where a is known as the scattering length. Writing out the cross-section:

$$\begin{aligned}\sigma &= \frac{4\pi}{k^2}\left(-ka\right)^2 \\ &= 4\pi a^2\end{aligned}$$

We can also look at $k\cot\delta_l$, when looking at f_l, and expand this:

$$k\cot\delta_l = -\frac{1}{a} + \frac{1}{2}r_0k^2 + \mathcal{O}\left(k^4\right) + \dots$$

Where r_0 is called the effective range. This is useful because in the low energy limit, there is a certain universality that can be exploited, much like phase transitions.

Now let us consider a more difficult situation. Instead of a hard sphere, let us consider a soft sphere, the potential inside the sphere is finite, rather than infinite (thinking radially, this is a finite square well). Let us first consider the attractive case, we have a spherical potential well of depth V_0.

Let us again only consider the s-wave scattering. In the $r < R$ region, we have the equation:

$$\left[\frac{\hbar^2}{2m}\frac{d^2}{dr^2} - V_0\right]U_0 = EU_0$$

Now defining $k' = \sqrt{\frac{2m(E+V_0)}{\hbar^2}}$, we have that the inner solution is:

$$\psi_{\text{interior}} = A\sin\left(k'r\right)$$

Similarly, we can compute the outside wavefunction:

$$\psi_{\text{outside}} = B\sin\left(kr+\delta_0\right)$$

Now using the continuity condition, we can compute the derivative of the two solutions, divide by the solution, and then set them equal to each other:

$$\frac{k'\cos k'R}{\sin k'R} = \frac{k\cos\left(kR+\delta_0\right)}{\sin\left(kR+\delta_0\right)}$$

Which can be rewritten:

$$k'\cos k'R = k\cot\left(kR+\delta_0\right)$$

And solving this for δ_0:

$$\delta_0 = -kR + \operatorname{arccot}\left(\frac{k'}{k}\cos\left(k'R\right)\right)$$

We see that the relationship between V_0 and δ_0 is very complicated, but we can get a lot of good information from this.

Let us consider low-energy scattering, the incoming particle has very low energy. In this case, $k \to 0$, $E \to 0$ and if we define $\varrho = \sqrt{\frac{2mV_0}{\hbar^2}}$, we have that

$$k\frac{\cos(kR-ka)}{\sin(kR-ka)} = \varrho\cos\varrho R$$

Now exploiting the fact that k is small, we have that

$$\frac{1}{R-a} = \varrho\cos\varrho R$$

Solving this, we have that

$$a = R - \frac{1}{\varrho}\tan\varrho R$$

We have a formula for the scattering length in terms of the radius and depth of the well. Now let us take the limit where $V_0 \to 0$. We expect there to be no scattering, and we see that we do indeed recover the fact that if there is no potential, there is no scattering.

Next, what if we let V_0 increase, and we see that ϱ increases, and we see that the tangent will go to infinity when $\varrho R = \frac{\pi}{2}$, and therefore we will have $a \to -\infty$. Inserting in the definition of ϱ, we see that this occurs when

$$V_0 = \frac{\hbar^2\pi^2}{8mR^2}$$

We see that we will have an infinite scattering cross-section. This is similar to a phase transition point. This is the point at which we begin to have a bound state, with zero energy. We have an incoming particle, and no outgoing particle, which motivates the cross-section going to infinity.

As we deepen the well past this point, we continue to add bound states, each time with the scattering length going to infinity.

We know that

$$\sigma = \frac{4\pi}{k^2}\sin^2\delta_0$$

And we know that $k\cot(kR+\delta_0) = 0$. When we let $k \to 0$, then we have that $\delta_0 = \frac{\pi}{2}$, which we can then use to show that the cross-section goes like $1/k^2$.

What is the scattering length? The wavefunction decays exponentially as we leave the well:

$$\psi \sim e^{-\tau r}$$

Where

$$\tau = \sqrt{\frac{2m|E_B|}{\hbar^2}}$$

The size of the system is based on the decay rate, it is related to the binding energy. The size is proportional to $1/\tau$, and in fact, this is the scattering length:

$$a \sim \frac{1}{\tau} \sim \sqrt{\frac{\hbar^2}{2m|E_B|}}$$

This provides another length scale in the system, based on the binding energy, and is not in the Hamiltonian.

If we scatter a proton and neutron at low energy, they bind loosely (forming a deuteron), with $E_B = 2.2$ MeV, and scattering length $a_{pn} = 5.4$ fm. This is much larger than anything in nuclear physics (almost 5x $\frac{1}{\Lambda_{\text{QCD}}}$). However, this is small compared to the size of the well.

What happens before the bound state forms? The bound state only forms when we reach a certain point, but the scattering length becomes large even before the bound state forms. The answer is that there is a virtual bound state. Let us make the incoming particle have an energy that has both real and complex components:

$$E = E_R + iE_I$$

If we look at the complex plane of energy, we will find that the S matrix will have poles in the negative real energy axis, as well as a pole that moves towards the origin. The reason that the zero energy bound state has an effect before it appears is because of the influence of this pole.

4.4.2 Resonances

Consider a potential of the form:

$$V(r) = V(r) + \frac{l(l+1)\hbar^2}{2mr^2}$$

We have a potential well $V(r)$, and a centrifugal barrier. If we increase the height of the centrifugal barrier, we will form more and more bound states inside the well. If we then let the barrier decrease, the bound states will not go away. Eventually, the particles will tunnel through the lower barrier, and escape outwards to infinity. This is a resonance. When we have a resonance, the scattering cross-section (plotted against energy) will peak, since the captured particle will increase the cross-section. The width of the peak in the cross-section is related to how long the particle is in the bound state, which is how long the resonance lives for.

4.4.3 Lippmann-Schwinger Equation

We have developed the method of partial wave analysis, which is based on using the solution

$$\psi(r \to \infty) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}} + f(\theta, \phi)\frac{e^{i\boldsymbol{k}\cdot\boldsymbol{r}}}{r}$$

for the Schrodinger equation:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\boldsymbol{r})\right)\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r})$$

Now let us consider the conversion of this differential equation to an integral equation, which is known as the Lippmann-Schwinger equation. To do this, let us rewrite the Schrodinger equation as

$$(E - T)\psi(\boldsymbol{r}) = V\psi(\boldsymbol{r})$$

Where $T = \frac{\hbar^2}{2m}\nabla^2$ is the kinetic term. Now solving this for ψ:

$$\psi(\boldsymbol{r}) = \frac{1}{E - T}V\psi(\boldsymbol{r})$$

Now let us do what we do when we solve Poisson's equation, let us consider the equation

$$(E-T)\,\psi(\boldsymbol{r})=0$$

In general, the solutions to this are:

$$\varphi(\boldsymbol{r})=e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$$

Where $\frac{\hbar^2k^2}{2m}=E$. We now can write out the general solution:

$$\psi(\boldsymbol{r})=\varphi(\boldsymbol{r})+\frac{1}{E-T}V\psi(\boldsymbol{r})$$

We can see that we have an issue when we have $E=T$, and therefore we insert an $i\epsilon$ in the denominator to shift the pole into the complex plane:

$$\psi(\boldsymbol{r})=\varphi(\boldsymbol{r})+\frac{1}{E-T+i\epsilon}V\psi(\boldsymbol{r})$$

This is the Lippmann-Schwinger equation. Now let us look at this second term on the right side. What we actually mean is that we are looking at the entire term in the position basis:

$$\langle\boldsymbol{r}|\frac{1}{E-T+i\epsilon}V|\psi\rangle=\int\underbrace{\langle\boldsymbol{r}|\frac{1}{E-T+i\epsilon}|\boldsymbol{r'}\rangle}_{G(\boldsymbol{r},\boldsymbol{r'})}\langle\boldsymbol{r'}|V|\psi\rangle\;d^3\boldsymbol{r'}$$

Where we have inserted a complete set of states, and denoted the first inner product as the Green's function. We see that we indeed have an integral equation. From this, we have that our general solution is of the form:

$$\psi(\boldsymbol{r})=\varphi(\boldsymbol{r})+\int G\left(\boldsymbol{r},\boldsymbol{r'}\right)V(\boldsymbol{r})\,\psi\left(\boldsymbol{r'}\right)\;d^3\boldsymbol{r'}$$

Looking at the Green's function:

$$\begin{aligned}
G\left(\boldsymbol{r},\boldsymbol{r'}\right)&=\langle\boldsymbol{r}|\frac{1}{E-T+i\epsilon}|\boldsymbol{r'}\rangle\\
&=\int\frac{d^3\boldsymbol{k}}{(2\pi)^3}\langle\boldsymbol{r}|\boldsymbol{k}\rangle\langle\boldsymbol{k}|\frac{1}{E-T+i\epsilon}|\boldsymbol{r'}\rangle\\
&=\int e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\frac{d^3\boldsymbol{k}}{(2\pi)^3}\frac{1}{E-\frac{\hbar^2k^2}{2m}+i\epsilon}e^{-i\boldsymbol{k}\cdot\boldsymbol{r'}}\\
&=\int\frac{d^3\boldsymbol{k}}{(2\pi)^3}e^{i\boldsymbol{k}(\boldsymbol{r}-\boldsymbol{r'})}\frac{1}{E-\frac{\hbar^2k^2}{2m}+i\epsilon}\\
&=\vdots\\
&=\frac{2\pi i}{|\boldsymbol{r}-\boldsymbol{r'}|}\int_{-\infty}^{\infty}\frac{k\,dk}{E-\frac{\hbar^2k^2}{2m}+i\epsilon}e^{-ik|\boldsymbol{r}-\boldsymbol{r'}|}
\end{aligned}$$

We see that this has two poles, at $k=\pm\sqrt{\frac{2mE}{\hbar^2}}$. To solve this, we apply the residue theorem, and make a choice of contour that goes either above or below. We choose to use the contour that goes towards $k = -\infty$, since the exponential will decay, rather than blow up. We care about the pole that is in the lower half plane, inside our contour, which is $k = -\sqrt{\frac{2mE}{\hbar^2}}$.

Now writing out the general wavefunction:

$$\psi\left(\boldsymbol{r}\right) = e^{ikz} - \frac{2m}{\hbar^2}\int d^3\boldsymbol{r}'\frac{e^{ik_0|\boldsymbol{r}-\boldsymbol{r}'|}}{4\pi|\boldsymbol{r}-\boldsymbol{r}'|}\left\langle\boldsymbol{r}'\right|V\left|\boldsymbol{r}\right\rangle$$

where $k_0 = \sqrt{\frac{2mE}{\hbar^2}}$. Now let us consider the case where $r \to \infty$. First we note that we can expand $|\boldsymbol{r}-\boldsymbol{r}'|$ in the large r limit:

$$|\boldsymbol{r}-\boldsymbol{r}'| = r - \frac{\boldsymbol{r}\cdot\boldsymbol{r}'}{|\boldsymbol{r}|^2} + \dots$$

Now looking at the wavefunction:

$$\psi\left(\boldsymbol{r}\to\infty\right) = -\frac{2m}{\hbar^2}\frac{e^{ik_0 r}}{4\pi r}\int e^{-ik_0\boldsymbol{r}\cdot\boldsymbol{r}'}\left\langle\boldsymbol{r}\right|V\left|\psi\right\rangle d^3\boldsymbol{r}'$$

We see that this indeed has the correct asymptotic behavior, we have an outgoing spherical wave. Thus our general solution to the Lippmann-Schwinger equation has the correct boundary conditions. Instead of solving for the general wavefunction, let us instead apply the Born approximation.

From our general wavefunction, we can read off the scattering amplitude:

$$f\left(\theta,\phi\right) = -\frac{2m}{\hbar^2}\frac{1}{4\pi}\int e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}\left\langle\boldsymbol{r}'\right|V\left|\psi\right\rangle\, d^3\boldsymbol{r}'$$

The Born approximation is to replace the dependence on the wavefunction in the scattering amplitude with an incoming plane wave, $\psi \to e^{i\boldsymbol{k}'\cdot\boldsymbol{r}}$:

$$f\left(\theta,\phi\right) = -\frac{2m}{\hbar^2}\frac{1}{4\pi}\int e^{-i\boldsymbol{q}\cdot\boldsymbol{r}}V\left(\boldsymbol{r}\right)\, d^3\boldsymbol{r}'$$

Where $\boldsymbol{q} = \boldsymbol{k}' - \boldsymbol{k}$. We can see that this is just the Fourier transform.

Let us consider a very simple scattering computation, Coulomb scattering. We have a Coulomb potential, $V\left(\boldsymbol{r}\right) = \frac{\alpha}{r}$, and we see that we have the Fourier transform:

$$V\left(\boldsymbol{q}\right) = \int V\left(\boldsymbol{r}\right)e^{i\boldsymbol{q}\cdot\boldsymbol{r}}\, d^3\boldsymbol{r}$$

We can actually solve this without doing much work, using dimensional analysis. We can see that this must be of the form $\frac{1}{\boldsymbol{q}^2}$, since the exponential must be dimensionless, so $\boldsymbol{q}$ and $\boldsymbol{r}$ have opposite dimensions. Thus we have $\frac{1}{r}$ from the Coulomb potential, 3 $\boldsymbol{r}$s in the integration, so we must have $\frac{1}{\boldsymbol{q}^2}$. Thus we have that $f\left(\theta,\phi\right) \sim \frac{1}{|\boldsymbol{q}|^2}$, and we can compute the differential cross-section:

$$\begin{aligned}\frac{d\sigma}{d\Omega} &= |f|^2\\ &\sim \frac{1}{\left(\boldsymbol{q}^2\right)^2}\end{aligned}$$

This is the Rutherford scattering cross-section.

When is the Born approximation a valid approximation? We have that

$$\psi\left(\boldsymbol{r}\right)=e^{i\boldsymbol{k}\cdot\boldsymbol{r}}-\frac{2m}{\hbar^2}\int d^3\boldsymbol{r}'\,\frac{e^{ik|\boldsymbol{r}-\boldsymbol{r}'|}}{4\pi|\boldsymbol{r}-\boldsymbol{r}'|}V\left(\boldsymbol{r}'\right)\psi\left(\boldsymbol{r}'\right)$$

Let us suppose that we have a potential with finite range. The first case in which the Born approximation is valid is when $k\to\infty$, because we are integrating a smooth function over a large oscillating factor, so the integral becomes negligible, and therefore the fact that we are making the Born approximation makes no difference. This is physically intuitive, if the particle has a lot of energy, the impact of the finite potential is negligible. This is the high energy limit. As it turns out, the Born approximation is also good in the low energy limit, where $k\to 0$. In this case, we can more or less neglect the phase factor in the integral. In this case, the second term is just

$$\frac{2m}{\hbar^2}VR^3$$

Where R is the range of the potential. When this value is much less than 1, the Born approximation is valid, we don't have any bound states.

How can we do better than the Born approximation? We can use the Eikonal approximation.

4.4.4 Eikonal Approximation

When we classically scatter a particle, the trajectory of the particle doesn't change very much, this is how we get the Born approximation. However, when we consider the wave behavior, we note that we will obtain some phase factor as the scattering process occurs.

The Eikonal approximation calculates the accumulating phase factor in the scattering. Instead of having $\psi\left(r\right)=e^{ikz}$, we will have some additional phase factor:

$$\psi\left(r\right)=e^{ikz}e^{i\Delta s/\hbar}$$

We denote $S=kz+\Delta s$, so that

$$\psi\left(\boldsymbol{r}\right)=eiS/\hbar$$

We can look at the Schrodinger equation:

$$\left[-\frac{\hbar^2}{2m}\nabla^2+V\left(\boldsymbol{r}\right)\right]\psi\left(\boldsymbol{r}\right)=E\psi\left(\boldsymbol{r}\right)$$

To do this, we are making the "classical" approximation, light travels in a straight line because of the high energy/low wavelength of the photon. If we now take the $\hbar\to 0$ limit to get the classical behavior:

$$\frac{1}{2m}\left(\nabla S\right)^2+V\left(\boldsymbol{r}\right)=E$$

Which is analogous to the Hamilton-Jacobi equation. We find that

$$\nabla S=\sqrt{2m\left(E-V\left(\boldsymbol{r}\right)\right)}$$

Which tells us that

$$S = \int \sqrt{2m\left(E - V\left(r\right)\right)}$$

This is the phase factor that we have accumulated.

To check this, consider the case with no interaction. We will find that $S = kz$, and we have recovered the expected behavior, there is not phase factor added when we don't have scattering.

Consider the case where we have impact parameter $\boldsymbol{b}$, and there is no scattering as the particle moves through the potential. We want to compute the accumulated phase factor, using the formula for S derived above:

$$S\left(z, \boldsymbol{b}\right) = \int_{-\infty}^{z} \sqrt{2m\left(E - V\left(\boldsymbol{r}\right)\right)}\, dz$$

Where $\boldsymbol{b} = \left(x, y\right)$. The energy is much greater than V, so we expand:

$$\begin{aligned} S\left(z, \boldsymbol{b}\right) &= \int_{-\infty}^{z} k\left(1 - \frac{V}{2E}\right)\, dz \\ &= kz - \frac{m}{\hbar^2 k}\int_{-\infty}^{z} V\, dz \end{aligned}$$

Now let us use this to compute the scattering cross-section.

$$f\left(\theta\right) = -\frac{1}{4\pi}\frac{2m}{\hbar^2}\int e^{-i\boldsymbol{k}'\cdot\boldsymbol{r}} V\left(\boldsymbol{b}, z\right) e^{ikz} \underbrace{e^{-\frac{im}{\hbar^2 k}\int_{-\infty}^{z} V\left(\boldsymbol{b}, z'\right) dz}}_{\text{Eikonal Phase}}$$

This extra phase is known as the eikonal phase. In QCD, where the eikonal approximation is used often for high-energy scattering, this is known as a Wilson line[6].

This has solution:

$$f\left(\theta\right) = -ik\int_{0}^{\infty} bJ_0\left(kb\theta\right)\left[e^{2i\Delta\left(b\right)} - 1\right]\, db$$

Where $\Delta\left(b\right)$ is defined as:

$$\Delta\left(b\right) = -\frac{m}{2k\hbar^2}\int_{-\infty}^{\infty} V\left(\sqrt{b^2 + z^2}\right)\, dz$$

We claim that this is a better approximation than the Born approximation. When is the Eikonal approximation valid? It is valid when $E \gg V_0$, the incoming energy is much greater than the depth of the potential, when we can use the classical approximation.

Rewriting this condition, we haev that

$$k^2 a^2 \gg \frac{V_0}{E_0}$$

Where E_0 is the zero-point energy. Note that the Born approximation requires $ka \gg \frac{V_0}{E_0}$, while the Eikonal approximation requires that $\left(ka\right)^2 \gg \frac{V_0}{E_0}$.

---

[6] The list of things named after Ken Wilson increases.

4.4.5 Optical Theorem

Consider light e^{ikz} shining on an infinite slab of thickness d. Two things happen, the first is that the wave slows down as it enters the slab (from c to $\frac{c}{n}$, where n is the index of refraction), and the second is attenuation, the intensity of the light will decay along the direction of propagation along the direction of propagation. Let us try to describe this process using scattering theory, and we can show that the index of refraction and the attenuation will relate to quantities that appear in scattering processes.

Let us assume that there are N atoms per unit volume in the slab. Let us first consider the scattering of the plane wave off of 1 atom. This produces a plane wave plus an outgoing spherical wave:

$$e^{ikz} \to e^{ikz} + \frac{e^{ikr}}{r} f\left(\theta, \varphi\right)$$

Now looking at the slab, we have a bunch of these scattering processes happening, and we want to sit on the other side of the slab and look at the scattered wave. If the atomic positions are random (such as in glass), we actually get 0 scattering, the phases cancel out due to the randomness. If we have a crystal, we have the Bragg condition, with phases interacting based on the lattice structure.

Let us consider the case of glass. If we look at just the forward direction, we don't see cancellation. We can integrate the scattering amplitude over the volume[7]:

$$\int f_{\text{scatter}}\, dV = e^{ikz} \frac{2\pi N d i}{k} f\left(0\right)$$

Where $f\left(0\right)$ is the scattering amplitude in the forward direction. We see that only the forward scattering remains uncancelled.

The total wave, after going through the slab, will be:

$$e^{ikz}\left(1 + \frac{2\pi N d}{k} i f\left(k, 0\right)\right)$$

If $f\left(k, 0\right)$ is imaginary, then the resulting amplitude of the wave will decrease, it will be less than 1. This produces attenuation. Thus the attenuation of the wave is related to the imaginary part of the forward scattering amplitude not being 0.

How much does the wave attenuate? We can consider a unit volume of the slab, and note that the attenuation is given by

$$\text{attenuation} = 1 - \sigma N d$$

The attenuation is impacted by the cross-section, which is multiplied by the number of collisions per unit area.

This is obvious if we look at the wavefunction, if we square it, we see that

$$\frac{4\pi N d}{k} \text{Im}\left(f\left(0\right)\right) = \sigma N d$$

---

[7] see Jackson chapter 15

Which then immediately implies the optical theorem:

$$\sigma = \frac{4\pi}{k}\mathrm{Im}\left(f\left(0\right)\right)$$

We can also note that the propagation of the plane wave changes:

$$k \to k + \frac{2\pi N}{k} f\left(k, 0\right)$$

This gives us a formula for the index of refraction:

$$n\left(k\right) = 1 + \frac{2\pi N}{k^2}\mathrm{Re}\left[f\left(k, 0\right)\right]$$

Let us pivot, and discuss the relationship between bound states and scattering states. Scattering states give us things of the form:

$$\psi\left(r\right) = A\left(E\right)\frac{e^{ikr}}{r} + B\left(E\right)\frac{e^{-ikr}}{r}$$

at large r. When we have bound states, we decay at large r:

$$\psi\left(r\right) \sim e^{-\kappa r}$$

Where $\kappa = \sqrt{2m|E_B|}$, we know how the wavefunction decays. Let us compare these wavefunctions. Let us instead write this as:

$$e^{-\kappa r} \sim e^{-\sqrt{-E}r}$$

Where we neglect the mass term, and explicitly write out the energy dependence. We can do the same thing in the scattering state solutions:

$$\psi\left(r\right) = A\left(E\right)\frac{e^{-\sqrt{-E}r}}{r} + B\left(E\right)\frac{e^{\sqrt{-E}}}{r}$$

If we analytically continue the functions of $\sqrt{-E}$ into the regions where $E > 0$, we will end up seeing that $B\left(E_B\right) = 0$. If we compute the S-matrix, $S\left(E\right) = A\left(E\right)/B\left(E\right)$, we see that the bound states give us poles in the S-matrix.

Let us now consider the Hydrogen atom. Suppose we have the proton and electron in the ground state, and send in a photon, with some energy E_γ. If we look at the complex plane of the energy of the photon, we know that the photon will not have a bound state with the atom. Thus, we expect complete analyticity on the negative real axis. However, if the energy of the photon is exactly equal to $E_1 - E_0$, the energy difference between first excited and ground states, the electron will eat up the photon and excite to the excited state, for some time, after which it will spontaneously emit a photon and decay to the ground state. These peaks in the cross-section are represented by poles in the complex plane, when the energy in the real axis is exactly the energy difference, and the complex component is the lifetime of the resonance:

$$E_\gamma = \left(E_1 - E_0\right) - i\Gamma_1$$

The same thing happens for all of the other excited states of the Hydrogen atom, they are resonances between scattered photons and the electron.