5260 Quantum Mechanics II

University of Colorado, Boulder (Fall 2019)

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This is the second in a series of 3 graduate level classes on quantum mechanics taught at the University of Colorado, Boulder. The textbook that will be referenced in this course is J. J. Sakurai's and Jim Napolitano's, "*Modern Quantum Mechanics*", where Cohen-Tannoudji's "*Quantum Mechanics*" is a useful supplementary reading along with the Feynman lectures found here. As an overview, the topics we will be aiming to cover this semester are listed below.

1. Theory of Angular Momentum;
2. Density Matrix Formulation;
3. Approximate Methods in Quantum Mechanics;
4. Quantum Scattering Theory;
5. Many-Particle Systems;
6. Quantum Simulation.

All notes were taken real-time in the class (i.e. there are bound to be typos) taught by Professor Ana Maria Rey. For information on this class, refer to this link.

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Chapter 1

Introduction

Quantum mechanics has been the basis of many of the current day technologies we use and interact with (e.g. lasers, MRI, semiconductors, etc). It is not just theoretical physics, but many other fields in STEM such as chemistry, computer science and others that are also having to better understand quantum mechanics to better their fields. We are also entering the second quantum revolution in which we can achieve extremely precise measurement and control of quantum systems, which will eventually allow us understand quantum materials and dynamics, and to build quantum computers, quantum networks and many other quantum technologies. What is taught in course will build the foundations to understand the advanced concepts required to eventually materialize the quantum future of society.

§1.1 Broad Overview

To give a very coarse grained gist of what we will be touching on in this class, we will be starting with angular momentum, but with emphasis on application of the its theory on specific problems and visualization schemes such as the *Bloch sphere*. We will also be diving deeper into 2-level systems and interesting phenomena such as Rabbi oscillations and Ramsay spectroscopy. We will then be looking at density matrices, which is a more general treatment of quantum states that will give us a way to understand open-quantum systems. Following this, we will then get into perturbative schemes in quantum theory.

Chapter 2

Theory of Angular Momentum

This chapter gives a brief refresher about rotations and spin-1/2, then dives into more complex examples of these systems to allow us a better understanding of related concepts.

§2.1 Classical Rotations Recap

Rotations in classical theory form a group $O(3)$, and are well represented by 3×3 real, orthogonal matrices. Orthogonality of matrices is defined as:

$$R^T R = RR^T = \mathbb{I} \tag{2.1}$$

$$\Rightarrow \quad \det(R) = \pm 1 \tag{2.2}$$

This implies that for a vector in $\mathbb{R}^3$, a rotation applied to such a vector preserves the norm of the vector ($\|\vec{v} = \|R\vec{v}\|\|$). The matrix representation of rotations matrices are written as:

$$R_x(\alpha) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos\alpha & -\sin\alpha \\ 0 & \sin\alpha & \cos\alpha \end{bmatrix}, \quad R_y(\beta) = \begin{bmatrix} \cos\beta & 0 & \sin\beta \\ 0 & 1 & 0 \\ -\sin\beta & 0 & \cos\beta \end{bmatrix}, \quad R_z(\gamma) = \begin{bmatrix} \cos\gamma & -\sin\gamma & 0 \\ \sin\gamma & \cos\gamma & 0 \\ 0 & 0 & 1 \end{bmatrix} \tag{2.3}$$

These applied to vectors in $\mathbb{R}^3$ are known as *active rotations*, where we are keeping the coordinate systems fixed and rotating the vector. Alternatively, if we were keeping the vector fixed and rotating the coordinate frame, these are known as *passive transformations.* These 2 types of rotations differ by a sign in the angle of rotation. In fact, any rotation in 3-dimensions can be performed by 3 rotations along the axes ZYZ in this order parameterized by what are known as *Euler angles* (well-known in classical mechanics). We can also consider the commutation relation of these operators under differential rotations (by angle $\delta\phi \ll 1$), which work out to be:

$$[R_i(\delta\phi), R_j(\delta\phi)] = \epsilon_{ijk} R_k(\delta\phi^2) - \mathbb{I} \tag{2.4}$$

where we used the fact that $\cos(\delta\phi) \approx 1 - \delta\phi^2/2$ and $\sin(\delta\phi) \approx \delta\phi$. This already alludes to the generators of rotation in quantum mechanics, with the eventual goal to show that the expectation of quantum observables behave just like classical observables. Now let us get into quantum mechanics.

§2.2 Rotations in Quantum Mechanics

The rotation operator, written as $\hat{\mathscr{D}}(R)$, is analogous to classical rotations but that act on quantum states:

$$\left|\alpha\right\rangle_R = \hat{\mathscr{D}}(R)\left|\alpha\right\rangle \tag{2.5}$$

We want now to connect this to classical systems. To do this, we are going to define the generator of rotations. Since we know that the generator of translation is the momentum operator, it is not too far fetched to imagine the generators of rotation being the angular momentum operator:

$$\hat{\mathscr{D}}(\hat{z}, \delta\phi) = 1 - i\left(\frac{\hat{\vec{J}}\cdot\hat{z}}{\hbar}\right)\delta\phi + \dots \tag{2.6}$$

where $\hat{\vec{J}}$ is the angular momentum vector operator (general form and not necessarily $\hat{\vec{r}} \times \hat{\vec{p}}$). In the limit of large rotations (raising to the power of N and taking $N \to \infty$), we get:

$$\hat{\mathscr{D}}(\hat{z}, \phi) = \exp\left\{-i\frac{\hat{J}_z\phi}{\hbar}\right\} \tag{2.7}$$

In general for a rotation about any axis $\hat{n}$, we have:

$$\boxed{\hat{\mathscr{D}}(\hat{n}, \phi) = \exp\left\{-i\frac{\hat{\vec{J}}\cdot\hat{n}}{\hbar}\phi\right\}} \tag{2.8}$$

To check if differential rotations of the form above indeed agree with the commutator relations we found for that with classical rotations, we check:

$$\left[\hat{\mathscr{D}}(R_i, \delta\phi), \hat{\mathscr{D}}(R_j, \delta\phi)\right] = \epsilon_{ijk}\hat{\mathscr{D}}(R_k, \delta\phi) - \mathbb{I} \tag{2.9}$$

indeed agreeing with what we had earlier. From this, we can infer that the commutation relation for the generators of rotation is required to be:

$$\boxed{\left[\hat{J}_i, \hat{J}_j\right] = i\hbar\epsilon_{ijk}\hat{J}_k} \tag{2.10}$$

§2.3 Spin-1/2 Systems

In 1922, Stern and Gerlach we trying to measure the magnetic moment of silver atoms by sending them through an inhomogeneous magnetic field. Classically, such a particle would experience a force:

$$\vec{F} = -\boldsymbol{\nabla}\left(-\vec{\mu}\cdot\vec{B}\right) \tag{2.11}$$

If we have $\vec{B} = B(\vec{r})\hat{z}$, then the force becomes:

$$\vec{F} = \mu_z \boldsymbol{\nabla} B(\vec{r}) \tag{2.12}$$

In the classical picture, we would expect no distinct signal since everything would be averaged out. Classically, we know that:

$$\vec{\mu} = \frac{q}{2mc}\vec{L} \tag{2.13}$$

where $\vec{L}$ is the angular momentum of the particle, q is the charge, m is its mass and c is the speed of light, in a simple model of the spinning spherical charged ball. Back in 1922, they in fact knew of the quantization of energy levels in the *Bohr model*, so they were actually expecting a *space quantization* of $2l+1$ lines to appear on the detector. However, as we all know this is not what they observed, but a 2-peak signal instead. This indicated that their current theory was not describing this system accurately, but some discretized 2-level system was hidden in the physical system.

The first 2 postulates on these results were given by the students of Ehrenfest as follows.

1. An electron has a magnetic moment defined by:

$$\mu_z = \frac{e\hbar}{2m_e c} \tag{2.14}$$

2. This magnetic moment is proportional to some intrinsic spin quantum number $\vec{\mu} \propto \vec{S}$

These turned out to be completely wrong! It also works out that the second postulate was off by a factor of 2. This intrinsic quantum spin $\vec{S}$ follows most of the properties of the orbital angular momentum and has quantum numbers $\hbar^2 s(s+1)$. As such, the total wavefunction of an electron would then be written as:

$$\begin{aligned} &|s;m_s\rangle \otimes |x,y,z\rangle \\ \Rightarrow \quad &|\psi\rangle = \sum_{m_s} \int d^3r \, (|s;m_s\rangle \otimes |x,y,z\rangle)\,(\langle s;m_s| \otimes \langle x,y,z|)\,|\psi\rangle \\ &\quad = \vec{\alpha}\psi_{1/2}(x,y,z) + \vec{\beta}\psi_{-1/2}(x,y,z) \end{aligned} \tag{2.15}$$

where

$$\vec{\alpha} = \begin{bmatrix} 1 \\ 0 \end{bmatrix}, \quad \vec{\beta} = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \tag{2.16}$$

It also works out that:

$$\hat{\vec{S}}\,|s;m_s\rangle = \hbar^2 s(s+1)\,|s;m_s\rangle \tag{2.17}$$

$$\hat{S}_z\,|s;m_s\rangle = \hbar m_s\,|s;m_s\rangle \tag{2.18}$$

$$\hat{S}_\pm\,|s;m_s\rangle = \hbar\sqrt{s(s+1) - m_s(m_s \pm 1)}\,|s;m_s\rangle \tag{2.19}$$

Example:

Consider a spin-1/2 particle in a constant external magnetic field $\vec{B} = B\hat{z}$, we can write the Hamiltonian as:

$$\hat{H} = -\hat{\vec{\mu}} \cdot \vec{B} \tag{2.20}$$

$$\text{where} \quad \hat{\vec{\mu}} = -g\frac{e}{2m_e c}\hat{\vec{S}} \tag{2.21}$$

where g is known as the *gyromagnetic number*. The *Bohr magneton* is also defined as $\mu_B = e\hbar/(2m_e c) \approx 5.7883 \times 10^{-5}$ eV/J. In Dirac's relativistic theory of quantum mechanics, we in fact that $g = 2$ which matches nicely with the experimental result. Further in quantum electrodynamics (QED), it is found that electrons interact with quantum fluctuations which gives:

$$\frac{g-2}{2\pi} = \frac{\alpha}{2\pi} + \mathcal{O}(\alpha^2) \approx 0.00116 \tag{2.22}$$

where $\alpha \approx 1/137$ is the fine-structure constant. Now, we can write the Hamiltonian in terms of the *Pauli matrices*:

$$\begin{aligned} \hat{H} &= \mu_B B\hat{\sigma}_z \\ &= \frac{\hbar\omega_0}{2}\hat{\sigma}_z \end{aligned} \tag{2.23}$$

where $\omega = eB/(m_e c)$ is the *larmor frequency* famous in NMR. The time-evolution of the initial state is then:

$$\begin{aligned} |\psi(t)\rangle &= \exp\left\{-\frac{i\hat{H}t}{\hbar}\right\}|\psi(0)\rangle \\ &= \exp\left\{-\frac{i\phi\hat{S}_z}{\hbar}\right\}|\psi(0)\rangle \\ &\equiv \hat{\mathscr{D}}_z(\phi)\,|\psi(0)\rangle \end{aligned} \tag{2.24}$$

where is just a rotation about an angle $\phi = \omega_0 t$. So indeed the spin operators are also generators of rotation in *spin-space*. Now let's try and connect this to classical mechanics by taking expectation values $\langle\hat{\vec{S}}(t)\rangle$. Considering first the x-component, we have:

$$\begin{aligned} \langle\hat{S}_x(t)\rangle &= \langle\psi(t)|\,\hat{S}_x\,|\psi(t)\rangle \\ &= \langle\psi(0)|\,\hat{\mathscr{D}}_z^\dagger(\phi)\hat{S}_x\hat{\mathscr{D}}_z(\phi)\,|\psi(0)\rangle \end{aligned} \tag{2.25}$$

where we moved to the Heisenberg picture in the second line above. To compute the operator above inside the bra-ket, we use the *Baker-Campbell-Hausdorff* identity:

$$e^{i\hat{O}\lambda}\hat{A}e^{-i\hat{O}\lambda} = \hat{A} + i\lambda\left[\hat{O},\hat{A}\right] + \frac{i^2\lambda^2}{2!}\left[\hat{O},\left[\hat{O},\hat{A}\right]\right] + \ldots \tag{2.26}$$

to get the result in the Heisenberg picture as:

$$\begin{aligned}\hat{\mathscr{D}}_z^\dagger(\phi)\hat{S}_x\hat{\mathscr{D}}_z(\phi) &= \hat{S}_x\left[1-\frac{\phi^2}{2}+\dots\right]-\hat{S}_y\left[\phi-\frac{\phi^3}{3!}+\dots\right]\\ &= \hat{S}_x\cos\phi-\hat{S}_y\sin\phi\\ \Rightarrow\quad \langle\hat{S}_x(t)\rangle &= \langle\hat{S}_x\rangle\cos\phi-\langle\hat{S}_y\rangle\sin\phi\end{aligned}\tag{2.27}$$

Doing this for the other spin operators gives:

$$\langle\hat{S}_y(t)\rangle = \langle\hat{S}_y\rangle\cos\phi+\langle\hat{S}_x\rangle\sin\phi \tag{2.28}$$

$$\langle\hat{S}_z(t)\rangle = \langle\hat{S}_z\rangle \tag{2.29}$$

This in turn grants us the equation of motion for the expectation values of the spin operators as:

$$\begin{aligned}\frac{d}{dt}\hat{\vec{S}} &= \frac{i}{\hbar}\left[\hat{H},\hat{\vec{S}}\right]\\ \Rightarrow\quad \frac{d}{dt}\langle\hat{\vec{S}}\rangle &= -\frac{e}{m_e c}\vec{B}\times\langle\hat{\vec{S}}\rangle\end{aligned}\tag{2.30}$$

which is indeed the classical equations of motion for a charged particle in a magnetic field.

§2.3.1 The Bloch Sphere

The *Bloch sphere* is a geometric visualization of any 2-level system by considering the decomposition:

$$|\psi\rangle = \cos\left(\frac{\theta}{2}\right)|\uparrow\rangle + e^{i\phi}\sin\left(\frac{\theta}{2}\right)|\downarrow\rangle \tag{2.31}$$

where θ tells us the occupation and ϕ tells us the coherence between the 2 states. This can be seen by computing the expectation values of the Pauli matrices with respect to the state above, which gives us:

$$\begin{bmatrix}\langle\hat{\sigma}_x\rangle\\ \langle\hat{\sigma}_y\rangle\\ \langle\hat{\sigma}_z\rangle\end{bmatrix} = \begin{bmatrix}\sin\theta\cos\phi\\ \sin\theta\sin\phi\\ \cos\theta\end{bmatrix} \tag{2.32}$$

A nice online visualization tool for the Bloch sphere can be found in the link. Today, we are now going try and understand how to visualize on the Bloch sphere a rotation about an arbitrary axis $\hat{n}$. To do so, consider the Hamiltonian:

$$\hat{H} = \frac{\hbar\omega}{2}\hat{n}\cdot\hat{\vec{\sigma}} \tag{2.33}$$

We want now to see how an initial state $|\psi(0)\rangle$ evolved according to this Hamiltonian by unitary time-evolution:

$$|\psi(t)\rangle = \exp\left\{-i\frac{\phi}{2}\left(\hat{n}\cdot\hat{\vec{\sigma}}\right)\right\}|\psi(0)\rangle \tag{2.34}$$

where $\phi = \omega t$. For exponentiated Pauli matrices, we can always write these unitary operators as:

$$\boxed{\exp\left\{-i\frac{\phi}{2}\left(\hat{n}\cdot\hat{\vec{\sigma}}\right)\right\} = \hat{\mathbb{I}}\cos\left(\frac{\phi}{2}\right) - i\left(\hat{n}\cdot\hat{\vec{\sigma}}\right)\sin\left(\frac{\phi}{2}\right)} \tag{2.35}$$

In its matrix representation, we have:

$$\exp\left\{-i\frac{\phi}{2}\left(\hat{n}\cdot\hat{\vec{\sigma}}\right)\right\} = \begin{bmatrix} \cos\left(\frac{\phi}{2}\right) - in_z\sin\left(\frac{\phi}{2}\right) & (in_x - n_y)\sin\left(\frac{\phi}{2}\right) \\ -(in_x + n_y)\sin\left(\frac{\phi}{2}\right) & \cos\left(\frac{\phi}{2}\right) + in_z\sin\left(\frac{\phi}{2}\right) \end{bmatrix} \tag{2.36}$$

§2.3.2 Time-Dependent to Time-Independent Pictures

To better develop a physical intuition for this, we consider a 2-level system with a transition frequency of ω_a that is illuminated with light of frequency ω_L. It turns out that the Hamiltonian for such a system can be effectively written as:

$$\hat{H}_{\text{eff}} = \frac{\hbar\Omega}{2}\hat{\sigma}_x - \frac{\hbar\delta}{2}\hat{\sigma}_z \tag{2.37}$$

where $\delta = \omega_L - \omega_a$. In this case, we see that:

$$\hat{n} = \frac{1}{\hbar\sqrt{\Omega^2 + \delta^2}}[\hbar\Omega,\ 0,\ -\hbar\delta]^T \tag{2.38}$$

What we are going to observe, is that Ω is going to be proportional to the groundstate energy E_0 and the dipole moment d ($\Omega \propto E_0 d$). We call Ω the *Rabi* frequency. To see this, we start with the actual physical system written as:

$$\hat{H} = -\frac{\hbar\delta}{2}\hat{\sigma}_z + \frac{\hbar\Omega}{2}\left[\hat{\sigma}^+ e^{-i\omega_L t} + \hat{\sigma}^- e^{i\omega_L t}\right] \tag{2.39}$$

where the $\hat{\sigma}^+$ is associated with a excitation and $\hat{\sigma}^-$ is associated to a downward energy transition of the 2-level system. To move from this Hamiltonian to the one we initially had, we need to move to the *rotating frame* of the laser by applying a rotation:

$$\hat{\mathscr{D}} = \exp\left\{-\frac{i\omega_L t}{2}\hat{\sigma}_z\right\} \tag{2.40}$$

This will bring our states from:

$$|\psi(t)\rangle \quad \to \quad \left|\tilde{\psi}(t)\right\rangle \tag{2.41}$$

by a passive rotation $\hat{\mathscr{D}}$ acting on $|\psi(t)\rangle$. Plugging this to the Schrödinger's equation, we get:

$$\begin{aligned} i\hbar\frac{\partial}{\partial}\left|\tilde{\psi}\right\rangle &= i\hbar\frac{\partial}{\partial}\left(\hat{\mathscr{D}}^{\dagger}\left|\psi\right\rangle\right) \\ &= i\hbar\left(\frac{\partial}{\partial}\hat{\mathscr{D}}^{\dagger}\right)\left|\psi\right\rangle + i\hbar\hat{\mathscr{D}}^{\dagger}\left(\frac{\partial}{\partial}\left|\psi\right\rangle\right) \\ &= i\hbar\left(\frac{\partial}{\partial}\hat{\mathscr{D}}^{\dagger}\right)\left|\psi\right\rangle + \hat{\mathscr{D}}^{\dagger}\hat{H}\left|\psi\right\rangle \\ &= \left[i\hbar\left(\frac{\partial}{\partial}\hat{\mathscr{D}}^{\dagger}\right) + \hat{\mathscr{D}}^{\dagger}\hat{H}\right]\hat{\mathscr{D}}\left|\tilde{\psi}\right\rangle \end{aligned} \tag{2.42}$$

So we have the effective Hamiltonian in the rotating frame written as:

$$\hat{H}_{eff} = i\hbar\left(\frac{\partial}{\partial}\hat{\mathscr{D}}^{\dagger}\right)\hat{\mathscr{D}} + \hat{\mathscr{D}}^{\dagger}\hat{H}\hat{\mathscr{D}} \tag{2.43}$$

Considering first the term:

$$\hat{\mathscr{D}}^{\dagger}\hat{H}\hat{\mathscr{D}} = \exp\left\{\frac{i\omega_L t}{2}\hat{\sigma}_z\right\}\hat{H}\exp\left\{-\frac{i\omega_L t}{2}\hat{\sigma}_z\right\} \tag{2.44}$$

Only the terms in the Hamiltonian that raises and lowers the state is affected by this rotation since the other commutes with the rotations. Then since these operators we are sandwiching the raising and lowering Pauli's by rotations about the z-axis, we can simply rotate the operator in the Bloch sphere by an Azimuthal angle $\omega_L t$ to get:

$$\begin{aligned} \exp\left\{\frac{i\omega_L t}{2}\hat{\sigma}_z\right\}\hat{\sigma}^{\pm}\exp\left\{-\frac{i\omega_L t}{2}\hat{\sigma}_z\right\} &= \hat{\sigma}_x\cos(\omega_L t) + \hat{\sigma}_y\sin(\omega_L t) \\ &\pm i\left[\hat{\sigma}_y\cos(\omega_L t) - \hat{\sigma}_x\sin(\omega_L t)\right] \\ &= \hat{\sigma}_{\pm}e^{\pm i\omega_L t} \end{aligned} \tag{2.45}$$

As for the other term, we have:

$$i\hbar\left(\frac{\partial}{\partial}\hat{\mathscr{D}}^{\dagger}\right)\hat{\mathscr{D}} = -\hbar\omega_L\hat{\sigma}_z \tag{2.46}$$

Plugging these results into the effective Hamiltonian, we indeed get the first Hamiltonian we said we would which is:

$$\hat{H}_{\text{eff}} = \frac{\hbar\Omega}{2}\hat{\sigma}_x - \frac{\hbar\delta}{2}\hat{\sigma}_z = \frac{\hbar\Omega_{\text{eff}}}{2}\left(\hat{n}\cdot\hat{\vec{\sigma}}\right) \tag{2.47}$$

where $\Omega_{\text{eff}} = \sqrt{\delta^2 + \Omega^2}$ and $\hat{n}$ is the unit vector defined earlier. What we have done here is made a time-dependent problem into a time-independent one by moving into the rotating frame of the laser which is a much easier problem to solve! This effective Hamiltonian is now simply a rotation about the $\hat{n}$ axis by an angle $\phi = \Omega_{\text{eff}}t$. So to think about how to *Bloch vector* $\hat{n}$ rotates in the Bloch sphere, we can write the rotation matrix:

$$R = \begin{pmatrix} \cos\phi + \frac{\Omega^2}{\Omega^2+\delta^2}(1-\cos\phi) & 0 & -\frac{\delta\Omega}{\Omega^2+\delta^2}(1-\cos\phi) \\ -\frac{\delta}{\sqrt{\Omega^2+\delta^2}}\sin\phi & \cos\phi & -\frac{\Omega}{\sqrt{\Omega^2+\delta^2}}\sin\phi \\ -\frac{\delta\Omega}{\Omega^2+\delta^2}(1-\cos\phi) & \frac{\Omega}{\sqrt{\Omega^2+\delta^2}}\sin\phi & \frac{\Omega^2\cos\phi+\delta^2}{\Omega^2+\delta^2} \end{pmatrix} \tag{2.48}$$

which is constructed by finding the axis-angle rotation matrix that comes from classical mechanics, for which it can be applied to the Bloch vector to rotate it appropriately. This is a great way to think about the problem since we can now imagine time-evolution of this 2-level system in terms of a classical rotation. So in general, after time-evolution of the system with the Hamiltonian above for some arbitrary amount of time from initial state $|\downarrow\rangle$, we have:

$$\begin{bmatrix} \langle\hat{S}_x\rangle \\ \langle\hat{S}_y\rangle \\ \langle\hat{S}_z\rangle \end{bmatrix} = \begin{bmatrix} \frac{\Omega\delta(1-\cos\phi)}{2(\Omega^2+\delta^2)} \\ \frac{\Omega\sin\phi}{2\sqrt{\Omega^2+\delta^2}} \\ -\frac{\Omega^2\cos\phi+\delta^2}{2(\Omega^2+\delta^2)} \end{bmatrix} \tag{2.49}$$

From this, we can get the the probability of finding the state in the up state $|\uparrow\rangle$, which can be computed as:

$$\boxed{\mathbb{P}(|\uparrow\rangle) = |\langle\uparrow|\psi(t)\rangle|^2 = \frac{\Omega^2}{\Omega^2+\delta^2}\sin^2\left(\frac{\Omega_{\text{eff}}t}{2}\right)} \tag{2.50}$$

This probability can also be physical thought of as the probability of the 2-level system *population* being in the excited state. There are now 2 regimes of interest with respect to the Ω and δ frequencies. First, we have the regime where $\Omega \ll \delta$ known as the *large detuning regime* (driving frequency is “detuned” far away from the 2-level energy difference). In this regime, we have:

$$\begin{bmatrix} \langle\hat{S}_x\rangle \\ \langle\hat{S}_y\rangle \\ \langle\hat{S}_z\rangle \end{bmatrix} \approx \begin{bmatrix} \frac{\Omega}{\delta}\sin^2\left(\frac{\delta t}{2}\right) \\ \frac{\Omega}{2\delta}\sin(\delta t) \\ -\frac{1}{2} + \frac{\Omega^2}{\delta^2}\sin^2\left(\frac{\delta t}{2}\right) \end{bmatrix} \tag{2.51}$$

$$\Rightarrow \quad \mathbb{P}(|\uparrow\rangle) \approx \frac{\Omega^2}{\delta^2}\sin^2\left(\frac{\delta t}{2}\right) \tag{2.52}$$

The other regime is where $\delta = 0$, known as the *zero-detuning regime* (also referred to as the *resonant regime*), which leads to:

$$\begin{bmatrix} \langle\hat{S}_x\rangle \\ \langle\hat{S}_y\rangle \\ \langle\hat{S}_z\rangle \end{bmatrix} = \begin{bmatrix} 0 \\ \frac{1}{2}\sin(\Omega t) \\ -\frac{1}{2}\cos(\Omega t) \end{bmatrix} \tag{2.53}$$

which leads to **only** sinusoidal oscillations of these expectation with frequency Ω. These type of oscillations are known in the community as *Rabi oscillations.* The probability is then:

$$\mathbb{P}(|\uparrow\rangle) = \sin^2\left(\frac{\Omega t}{2}\right) \tag{2.54}$$

As such, we can characterize important "pulses" that one could apply to a 2-level system such that we either have a fully excited or groundstate system.

- π-*Pulse* ($\Omega t = \pi$): fully excited population, $\mathbb{P}(|\uparrow\rangle) = 1$;
- 2π-*Pulse* ($\Omega t = 2\pi$): fully groundstate population, $\mathbb{P}(|\uparrow\rangle) = 0$;
- $\frac{\pi}{2}$-*Pulse* ($\Omega t = \pi/2$): even distribution of states in the population, $\mathbb{P}(|\uparrow\rangle) = 1/2$.

Having this formalism can in fact be applied to quantum computing and act as unitary gate operations on qubits!

§2.4 Density Matrices

Before jumping into this concept, we start with some motivation for this formalism we are going to study. A good motivation in view of having studied 2-level systems is atomic clocks.

§2.4.1 Atomic Clocks

In general, clocks consist of something that ticks (e.g. pendulum) and something that tracks the ticking (a counter). In atomic clocks, the light (electromagnetic waves) does the ticking and the atom counts those ticks. Mathematically, these are essentially once again just 2-level systems. What an experimentalist would want to measure then, is of course the population of excited states:

$$\mathbb{P}(|\uparrow\rangle) = \frac{\Omega^2}{\Omega^2 + \delta^2} \sin^2\left(\frac{t\sqrt{\Omega^2 + \delta^2}}{2}\right) \tag{2.55}$$

The coefficient (distribution envelop) in front of this probability distribution is just a *Lorentzian* and known as the *Lamb shape*. In principle, we want that a clock over long times remains coherent so that the time-keeping is kept consistent. Decoherence (which occurs in physical clock implementations due to interactions with the environment) causes variations in the sinusoidal function, eventually leading to a smearing of the distribution into a Gaussian. Decoherence is common in all quantum open systems and to gain a better picture of decoherence, the best way is via the formalism of *density matrices*.

§2.4.2 Statistical Mixtures

In real physical systems, it is extremely difficult to truly isolate a quantum system from its environment. As such, we usually refer to the system we are concerned with a subsystem of the total system, whereby the subsystem is coupled to its environment. Density matrices allows us to talk about the subsystem in the language of *statistical mixtures*. To base this in a concrete picture, consider the polarization of a photon.

Example:

Let's say that there is a photon emitted along the $\hat{z}$-direction, for which it then has a $50 - 50\%$ probability of polarization along $\hat{x}$ or $\hat{y}$ (unpolarized light). We can thus write the state of this system as:

$$|\psi\rangle = \frac{|x\rangle + |y\rangle}{\sqrt{2}} \tag{2.56}$$

Let us also define:

$$p_x \equiv \mathbb{P}(|x\rangle), \quad p_y \equiv \mathbb{P}(|y\rangle) \tag{2.57}$$

First, recall that for unitary evolution of closed systems, recall that if we assume the photon is along some state $|j\rangle$, we can evolve the state as a function of time according to the associated Hamiltonian of the system via unitary time-evolution which will give the probability to stay in the state j as:

$$P_j = \left|\langle j|\, \hat{U}(t)\, |j\rangle\right|^2 \tag{2.58}$$

As such, we can write the probabilities by weighting each possible initial state by their probabilities with their associated final probabilities after time-evolution:

$$\mathbb{P} = \sum_j p_j P_j \tag{2.59}$$

With the intuition from the example above, we can have a general formulation of statistical mixtures. A mixed system is a basis of states $\{|\psi^{(k)}\rangle\}$ (not necessarily an orthogonal basis) with probabilities p_k associated to each of these states. For a mixed system, we can take expectation values via the formula:

$$\begin{aligned}\langle\hat{Q}\rangle &= \sum_k p_k \left\langle \psi^{(k)} \middle| \hat{Q} \middle| \psi^{(k)} \right\rangle \\ &= \sum_{n,n'} Q_{n,n'} \sum_k p_k \left(c_{n'}^{(k)}\right)^* c_n^{(k)}\end{aligned} \tag{2.60}$$

The term that sums over k allows us to define a density matrix with indices $\{n, n'\}$:

$$\begin{aligned}[\hat{\rho}]_{n,n'} &= \sum_k p_k \left(c_{n'}^{(k)}\right)^* c_n^{(k)} \\ \Rightarrow &\boxed{\hat{\rho} = \sum_k p_k \left|\psi^{(k)}\right\rangle \left\langle\psi^{(k)}\right| = \sum_{n,n'} [\hat{\rho}]_{n,n'} |u_n\rangle \langle u_{n'}|}\end{aligned} \tag{2.61}$$

where $|u_n\rangle$ are the orthonormal basis states of the Hilbert space. so we can say that the expectation value of the operator $\hat{Q}$ is given by:

$$\boxed{\langle\hat{Q}\rangle = \mathrm{tr}\left(\hat{\rho}\hat{Q}\right) = \mathrm{tr}\left(\hat{Q}\hat{\rho}\right)} \tag{2.62}$$

Some useful **properties of density matrices** are given below.

1. <u>Trace Preservation</u>: $\mathrm{tr}(\hat{\rho}) = 1$ or equivalently $\sum_n \rho_{n,n} = 1$;

2. Hermiticity: $\hat{\rho} = \hat{\rho}^\dagger$;
3. Purity: $0 \leq \mathrm{tr}\big(\hat{\rho}^2\big) \leq 1$, and is equal to unity **only** for *pure states*.
4. Positive-Semidefiniteness: All eigenvalues of $\hat{\rho}$ are non-negative, and $\rho_{n,n} \geq 0$.
5. Time-Evolution: Given that $\big|\psi^{(k)}(0)\big\rangle = \sum_n c_n^{(k)}(0)\,|u_n\rangle$ for some orthonormal basis $\{|u_n\rangle\}$, then the coefficients evolve as:

$$c_n^{(k)}(t) = \sum_{n'} \left[e^{-i\frac{\hat{H}t}{\hbar}}\right]_{n,n'} c_{n'}^{(k)}(0) \tag{2.63}$$

Exploring a little deeper the time-evolution of the density matrix, we first write it out in its operator form as:

$$\begin{aligned} \left|\psi^{(k)}(t)\right\rangle &= e^{-i\frac{\hat{H}t}{\hbar}}\left|\psi^{(k)}(0)\right\rangle \\ \Rightarrow \quad & \boxed{\hat{\rho}(t) = e^{-i\frac{\hat{H}t}{\hbar}}\hat{\rho}(0)e^{i\frac{\hat{H}t}{\hbar}}} \end{aligned} \tag{2.64}$$

we can then take a time derivative of the above boxed expression which will give us the density operator equation of motion:

$$\boxed{\frac{d\hat{\rho}(t)}{dt} = -\frac{i}{\hbar}\left[\hat{H}, \hat{\rho}(t)\right]} \tag{2.65}$$

Note: A generalization of the equation above to open-systems would make use of another operator known as the *Liouville operator*, $\mathcal{L}$ which gives us:

$$\frac{d\hat{\rho}(t)}{dt} = \mathcal{L}\left(\hat{\rho}(t)\right) \tag{2.66}$$

The Liouville operator allows for us to account for the loss of information from a quantum subsystem to its environment.

Recall that in the Heisenberg picture, we had the time-evolution of operators governed by:

$$\frac{d\hat{Q}(t)}{dt} = +\frac{i}{\hbar}\left[\hat{H}, \hat{O}(t)\right] \tag{2.67}$$

The difference in sign comes from the fact that density matrices are in fact the state of the system, so we are actually in the Schrödinger picture and **not** evolving the observables in time but the state.

Note: Density matrices have a connection to classical mechanics in that its time-evolution can be mapped in phase-space just as a classical trajectory would, but the density matrix phase-space evolution would have quantum noise associated to it.

Density matrices can have a diagonal representation by transforming into the appropriate basis, just as operators can. That is, we can find a othonormal set of eigenstates associated to a density matrix $\{|u_n\rangle\}$ such that:

$$\hat{\rho} = \sum_n p_n |u_n\rangle \langle u_n| \tag{2.68}$$

is diagonal. The unitaries that transform a density matrix into this diagonal representation is generally **not** unique. We now considering several cases.

1. Pure States:

   In the case of **pure states**, we can always find a basis such that:

   $$\hat{\rho} = |v\rangle \langle v| \tag{2.69}$$

   which indicates that it is separable in **any** basis.

2. States at Thermal Equilibrium:

   Consider a system with a fixed number of particles that is in thermal contact with a bath at temperature T. The particles would follow a canonical ensemble which maximizes the entropy:

   $$\begin{aligned} &\max\left\{S = -k_B \sum_k p_k \ln p_k\right\} \\ \text{s.t.} \quad &\sum_k p_k E_k = U; \quad \sum_k p_k = 1 \end{aligned} \tag{2.70}$$

   where U is the total energy of the system. To do this, we adopt the use of Lagrange multipliers which grants us the result:

   $$p_k = \frac{1}{Z} e^{-\beta E_k} \tag{2.71}$$

   where $e^{-\beta E_k}$ are known as *Boltzmann factors*, $\beta = 1/k_B T$ and Z is known as the *partition function* defined as:

   $$\begin{aligned} &Z = \sum_k e^{-\beta E_k} \\ \Rightarrow \quad &\langle H \rangle = -\frac{\partial}{\partial \beta} \ln Z = \frac{\sum_k E_k e^{-\beta E_k}}{\sum_k e^{-\beta E_k}} \end{aligned} \tag{2.72}$$

   where H is the Hamiltonian.

Note: Computing the partition function can often be reduced to computing a geometric series (indexed by the quantization index n) for which it is known that:

$$\sum_n r^n = \frac{1}{1-r}. \tag{2.73}$$

However, to instead compute the energy function weight by the Boltzmann factors is a little harder but can be compute by using the following trick:

$$\sum_k E_k e^{-\beta E_k} = -\frac{\partial}{\partial \beta} \sum_k e^{-\beta E_k} \tag{2.74}$$

However, in quantum mechanics, we compute $\langle \hat{H} \rangle$ as:

$$\langle \hat{H} \rangle = \operatorname{tr}\left\{\hat{\rho}\hat{H}\right\} \tag{2.75}$$

using the fact that the density matrix can be written as:

$$\hat{\rho} = \frac{\sum_k e^{-\beta E_k} \left|k\right\rangle \left\langle k\right|}{\sum_k e^{-\beta E_k}} \tag{2.76}$$

As such, we can also quantize the entropy as follows:

$$\boxed{S = -k_B \operatorname{tr}\left\{\hat{\rho}\ln\hat{\rho}\right\}} \tag{2.77}$$

This is known as the *Von Neumann entropy.*

Note: In the diagonal basis, the Von Neumann entropy simply reduces again to the classical definition of entropy.

In fact, any mean observable $\hat{Q}$ in a thermal system can always be computed as:

$$\boxed{\langle \hat{Q} \rangle = \operatorname{tr}\left\{\hat{\rho}\hat{Q}\right\}} \tag{2.78}$$

§2.4.3 Mixed-States in 2-Level Systems

The first thing to note is that the Pauli matrices and the identity span the space for all 2 × 2-Hermitian matrices. We also list some other useful properites of Pauli matrices below.

1. $\operatorname{tr}\hat{\sigma}_j = 0$
2. $\operatorname{tr}\left[\hat{\sigma}_i, \hat{\sigma}_j\right] = 2\delta_{ij}$
3. $\operatorname{tr}\hat{\sigma}_j^2 = 2$

Furthermore, any density matrix in a 2-level system can be written as:

$$\hat{\rho} = \frac{1}{2}\left(p_0\hat{\mathbb{I}} + p_x\hat{\sigma}_x + p_y\hat{\sigma}_y + p_z\hat{\sigma}_z\right) \tag{2.79}$$

Using the form above and the properties of the Pauli matrices we have listed above, we get that $p_0 = 1$ and:

$$\begin{aligned} &\langle \hat{\sigma}_j \rangle = \mathrm{tr}\left\{ \hat{\rho} \hat{\sigma}_j \right\} \\ \Rightarrow \quad &\boxed{\hat{\rho} = \frac{1}{2}\left(\hat{\mathbb{I}} + \langle \hat{\vec{\sigma}} \rangle \cdot \hat{\vec{\sigma}} \right)} \end{aligned} \tag{2.80}$$

Writing this in its 2 × 2 matrix representation, we have:

$$\hat{\rho} = \begin{pmatrix} 1 + \langle \hat{\sigma}_z \rangle & \langle \hat{\sigma}_x \rangle - i \langle \hat{\sigma}_y \rangle \\ \langle \hat{\sigma}_x \rangle + i \langle \hat{\sigma}_y \rangle & 1 - \langle \hat{\sigma}_z \rangle \end{pmatrix} \tag{2.81}$$

where the off-diagonal entries are usually denoted as *coherences* and the diagonal entries as *populations.*

Note: The fully mixed state is simply the identity can be written as:

$$\hat{\rho} = \frac{|\uparrow\rangle\langle\uparrow| + |\downarrow\rangle\langle\downarrow|}{2} = \hat{\mathbb{I}} \tag{2.82}$$

This also corresponds to the state with maximum entropy. The biggest problem in quantum computation is that in open-systems, the state of the system will always revert to a fully mixed state which is trivial.

Consider the pure state:

$$|\psi\rangle = c_\uparrow e^{i\phi} |\uparrow\rangle + c_\downarrow |\downarrow\rangle \tag{2.83}$$

where the phase ϕ is random. In an experiment, the density matrix we can describe the system by would then be having a sum over all possible phases, but since the phase is continuous, we have an integral instead:

$$\hat{\rho} = \int d\phi p_\phi |\psi_\phi\rangle \langle \psi_\phi| \tag{2.84}$$

But in the case where $p_\phi = 1/2\pi$, we have that all the coherence terms are going to cancel which leaves only:

$$\hat{\rho} = |c_\uparrow|^2 |\uparrow\rangle\langle\uparrow| + |c_\downarrow|^2 |\downarrow\rangle\langle\downarrow| \tag{2.85}$$

bringing us back to a state that is only concerned with the populations.

§2.4.4 Purity

We now want a means to quantify how "pure" a state is. The measure the community has adopted is known as the *purity*, which is defined as:

$$\boxed{\mathrm{tr}\left\{ \hat{\rho}^2 \right\} = \frac{1}{2}\left(1 + \langle \hat{\sigma}_x \rangle^2 + \langle \hat{\sigma}_y \rangle^2 + \langle \hat{\sigma}_z \rangle^2 \right)} \tag{2.86}$$

In the Bloch sphere picture, the quantity above represents the **length of the Bloch vector**, for which if it lies on the surface of the Bloch sphere (unit length), it is a pure state. A fully mixed state then would have zero length, and any value in between indicates a degree of entanglement in the state. In the bra-ket notation, any state that can be written as a *product-state* is pure. Otherwise, the state is entangled, for which we can use the formalism of *partial traces* to see this.

§2.5 General Quantum Rotation Systems

As seen before, rotations can be defined by the a rotation axis (unit vector) $\hat{n}$ and an angle of rotation ϕ in the *axis-angle representation.* The Wigner D-matrix for rotations was also defined earlier, for which we can define the *Wigner-function* as:

$$\boxed{\mathscr{D}^{(j)}_{m',m}(\hat{R}) = \langle j;m'|\, e^{-i\frac{\hat{\vec{J}}\cdot\hat{n}}{\hbar}\phi}\, |j;m\rangle} \tag{2.87}$$

which are basically the matrix elements of the Wigner D-matrix in the total angular momentum basis. These functions appear as coefficients of a rotation applied to a state:

$$\hat{\mathscr{D}}(R)\,|j;m\rangle = \sum_{m'} |j;m'\rangle \langle j;m'|\, \hat{\mathscr{D}}^{(j)}(R)\,|j;m\rangle = \sum_{m'} \mathscr{D}^{(j)}_{m',m}(R)\,|j;m'\rangle \tag{2.88}$$

As per classical mechanics, these Wigner-functions can also be written in the Euler angle representation as:

$$\begin{aligned} \mathscr{D}^{(j)}_{m',m}(\hat{R}) &= \langle j;m'|\, e^{-i\frac{\hat{J}_z\alpha}{\hbar}} e^{-i\frac{\hat{J}_y\beta}{\hbar}} e^{-i\frac{\hat{J}_z\gamma}{\hbar}}\, |j;m\rangle \\ &= e^{-i(m'\alpha+m\gamma)} \langle j;m'|\, e^{-i\frac{\hat{J}_y\beta}{\hbar}}\, |j;m\rangle \end{aligned} \tag{2.89}$$

where the simplification in the last line comes from the fact that the states we are closing the bra-ket with are eigenstates of $\hat{J}_z$, which simply allows us to pull out a phase, leaving only the y-axis rotation operator.

Note: Literature often refers to the y-rotation function as the Wigner (small) d matrix with elements:

$$\begin{aligned} d^{(j)}_{m',m}(\beta) &= \langle j;m'|\, e^{-i\frac{\hat{J}_y\beta}{\hbar}}\, |j;m\rangle \\ &= \sum_k (-1)^{k-m+m'} \frac{\sqrt{(j+m)!(j-m)!(j+m')!(j-m')!}}{(j+m-k)!k!(j-k-m')!(k-m+m')!} \\ &\qquad \times\ \cos^{2j-2k+m-m'}\left(\frac{\beta}{2}\right) \sin^{2k-m+m'}\left(\frac{\beta}{2}\right) \end{aligned} \tag{2.90}$$

We have also seen before that rotation matrices have a relation to *spherical harmonics.* Recalling the orbital angular momentum operators:

$$\left[\hat{L}_i, \hat{L}_j\right] = i\varepsilon_{ijk}\hat{L}_k \tag{2.91}$$

We have that any spherically symmetric system can have states written in the position-space representation as:

$$\langle\vec{r}|n,l,m\rangle = R_{n,l,m}(r)Y_l^m(\theta,\phi) \tag{2.92}$$

where $R_{n,l,m}(r)$ is the radial wavefunction and $Y_l^m(\theta,\phi)$ is indeed the famed spherical harmonics. Picking out just the angular wavefunction, we have:

$$\langle\hat{n}|l,m\rangle = Y_l^m(\theta,\phi) \tag{2.93}$$

However, we also know that we can write:

$$\begin{aligned} |\hat{n}\rangle &= \hat{\mathscr{D}}^{(l)}(\phi,\theta,0)\,|\hat{z}\rangle \\ &= \sum_m \hat{\mathscr{D}}^{(l)}(\phi,\theta,0)\,|l,m\rangle\,\langle l,m|\hat{z}\rangle \\ \Rightarrow \quad Y_l^{m'}(\theta,\phi) &= \sum_m \mathscr{D}^{(l)}_{m',m}(\phi,\theta,0)Y_l^0(\theta=0,\phi) \end{aligned} \tag{2.94}$$

Then by the selection rules, we have the relation:

$$\boxed{Y_l^m(\theta,\phi) = \sqrt{\frac{2l+1}{4\pi}}\mathscr{D}^{(l)}_{m',0}(\phi,\theta,0)} \tag{2.95}$$

§2.6 Schwinger Bosons

The idea behind *Schwinger Bosons* is the formulation of a mapping from 2, single harmonic oscillators to angular momentum operators. This is commonly adopted in systems like the *Bose-Einstein condenstate* (BEC) and ultracold Bosons. the formulation is as follows. Consider we have 2 types of harmonic oscillators, called *right* (R) and *left* (L) *oscillators.* For both of these, we define the creation and annihilation operators as:

$$\begin{aligned} &\left\{\hat{a}_R, \quad \hat{a}_R^\dagger, \quad \hat{N}_R\right\} \\ &\left\{\hat{a}_L, \quad \hat{a}_L^\dagger, \quad \hat{N}_L\right\} \end{aligned} \tag{2.96}$$

Furthermore, we assert that these oscillators are complete decoupled, so we have the commutation relations:

$$\begin{aligned} &\left[\hat{a}_j, \hat{a}_j^\dagger\right] = 1 \\ &\left[\hat{N}_j, \hat{a}_j^\dagger\right] = \hat{a}_j^\dagger, \quad \left[\hat{N}_j, \hat{a}_j\right] = -\hat{a}_j \\ &\left[\hat{a}_i, \hat{a}_j^\dagger\right] = 0, \quad i \neq j \end{aligned} \tag{2.97}$$

Due to this decoupling, we are able to have a basis for this system with the states $|n_L;n_R\rangle$. In this basis, we have that:

$$\begin{aligned} &\hat{n}_R\,|n_L;n_R\rangle = n_R\,|n_L;n_R\rangle\,, \quad \hat{n}_L\,|n_L;n_R\rangle = n_L\,|n_L;n_R\rangle \\ &\hat{a}_R^\dagger\,|n_L;n_R\rangle = \sqrt{n_R+1}\,|n_L;n_R+1\rangle\,, \quad \hat{a}_L^\dagger\,|n_L;n_R\rangle = \sqrt{n_L+1}\,|n_L+1;n_R\rangle \\ &\hat{a}_R\,|n_L;n_R\rangle = \sqrt{n_R}\,|n_L;n_R-1\rangle\,, \quad \hat{a}_L\,|n_L;n_R\rangle = \sqrt{n_L}\,|n_L-1;n_R\rangle \end{aligned} \tag{2.98}$$

It works out that this operator algebra, is exactly equivalent to that of angular momentum operators if we define:

$$\begin{aligned} \hat{J}_+ &\equiv \hbar \hat{a}_R^\dagger \hat{a}_L, \quad \hat{J}_- \equiv \hbar \hat{a}_L^\dagger \hat{a}_R \\ \hat{J}_z &\equiv \frac{\hbar}{2}\left(\hat{a}_R^\dagger \hat{a}_R - \hat{a}_L^\dagger \hat{a}_L\right) = \frac{\hbar}{2}\left(\hat{N}_R - \hat{N}_L\right) \end{aligned} \tag{2.99}$$

It works out that these indeed satisfy the angular momentum Lie algebra relations:

$$\begin{aligned} \left[\hat{J}_z, \hat{J}_\pm\right] &= \pm\hbar \hat{J}_\pm \\ \left[\hat{J}_+, \hat{J}_-\right] &= 2\hbar \hat{J}_z \end{aligned} \tag{2.100}$$

which can easily be checked using the properties of the creation and annihilation operators. It can also be checeked that these operators satisfy the relation:

$$\boxed{\hat{J}^2 = \hat{J}_z^2 + \frac{1}{2}\left(\hat{J}_+\hat{J}_- + \hat{J}_-\hat{J}_+\right) = \hbar^2 \frac{\hat{N}}{2}\left(\frac{\hat{N}}{2} + 1\right)} \tag{2.101}$$

where $\hat{N} = \hat{N}_L + \hat{N}_R$. So we see that we have mapped the total angular momentum operator to the number operator as:

$$J \to \frac{N}{2} \tag{2.102}$$

which is saying we have mapped a system of N spin-1/2 particles to the system of 2-uncouple harmonic oscillators. So we are connecting the excitations in the R or L harmonic oscillators to the $|\uparrow\rangle$ or $|\downarrow\rangle$ states at each of the N indistinguishable sites! Now, where the name Schwinger Bosons come from, is that the creation and annihilation operators are Bosonic operators which move particles in the R and L sites in the second quantization picture with the mapping to angular momentum being called the *Schwinger mapping*. With this mapping, we get that every energy eigenstate of the system can be written as:

$$|j, m\rangle = \frac{\left(\hat{a}_x^\dagger\right)^k \left(\hat{a}_y^\dagger\right)^n}{\sqrt{k!n!}} |0, 0\rangle \tag{2.103}$$

with $k = j + m$ and $n = j - m$. In this angular momentum picture, we have the $\hat{J}_x$ and $\hat{J}_y$ angular momentum operators representing site hopping between the left and right sites. An application of this is to the *Bose-Hubbard model*, where we have a 2-site harmonically trapped system of Bosons. The Hamiltonian is then written as:

$$\begin{aligned} \hat{H} &= -\tau\left(\hat{a}_R^\dagger \hat{a}_L + \hat{a}_L^\dagger \hat{a}_R\right) + \frac{U}{2}\left[\hat{N}_R\left(\hat{N}_R - 1\right) + \hat{N}_L\left(\hat{N}_L - 1\right)\right] \\ &= \tau\left(\hat{J}_+ + \hat{J}_-\right) + \frac{U}{2}\left(2\hat{J}_z^2 + \text{constant}\right) \\ \Rightarrow \quad \hat{H}_{eff} &= -2\tau \hat{J}_x + U \hat{J}_z^2 \end{aligned} \tag{2.104}$$

where τ is the hopping energy, U is the interaction potential and we noted that constants in the Hamiltonian just contribute a global phase so the effective Hamiltonian ignores constants. The term on the left is responsible for site hopping, and the term on the right for interactions within site. This Hamiltonian is complicated, but can indeed be understood using the Schwinger mapping as rotations! If we look at the interaction term in the Hamiltonian only, the eigenstates for this term are just $|n_R, n_L\rangle$.

Note: If the tunneling term is switched off, the states corresponding to zero energy are:

$$E = 0 : \quad |0,0\rangle\,, \;\; |1,0\rangle\,, \;\; |0,1\rangle \tag{2.105}$$

However, once we turn on tunneling, things get more complicated and we indeed need the Schwinger mapping to simplify things.

As an aside, another way to write these are by defining:

$$\hat{J}_\alpha = \frac{1}{2}\hat{a}_i^\dagger \hat{\sigma}_{ij}^\alpha \hat{a}_j \tag{2.106}$$

where $\hat{\sigma}_{ij}^\alpha$ are Pauli matrices where the subscript indicate R and L sites. This allows a generalization to $SU(N)$ by swapping out the Pauli matrix to higher dimensional Lie algebra representations.

Chapter 3

Approximation Methods in Quantum Mechanics

In general, we can divide up approximations in quantum mechanics as perturbative or non-perturbative. In perturbative cases, we usually introduce a small parameter which allows us to divide up the Hamiltonian as some main (hopefully analytically solvable) term $\hat{H}_0$*, and a perturbative term* $\lambda\delta\hat{H}$ *where* λ *is the perturbative parameter and* $\delta\hat{H}$ *is generally not exactly solvable. In perturbative approximations, we also have to consider time-dependent and time-independent scenarios, along with degenerate and non-degenerate perturbation theory. Some instances of the tools used in time-dependent perturbation theory are Fermi's golden rule, Floquet theory and the rotating-wave approximation. As for non-perturbative approximations, there are techniques such as the variational principle, adiabatic methods and the WKB approximation. We will first be getting into approximation schemes with perturbation theory.*

§3.1 Time-Independent Perturbation Theory

We will be starting in particular, with *non-degenerate perturbation theory.*

§3.1.1 Non-Degenerate Perturbation Theory

In perturbation theory, we asserted in the introductory paragraph above that we assume we can write the Hamiltonian as:

$$\hat{H} = \hat{H}_0 + \lambda\delta\hat{H} \tag{3.1}$$

where we usually take $\left\|\lambda\delta\hat{H}\right\| \ll 1$. We also assume that we know the spectrum of $\hat{H}_0$ which allows us to write:

$$\hat{H}_0 \left|\psi_n^{(0)}\right\rangle = E_n^{(0)} \left|\psi_n^{(0)}\right\rangle \tag{3.2}$$

Having these, how then can be construct that solutions to the full Hamiltonian? Well, we can consider an expansion about the λ parameter about the zeroth order Hamiltonian which since it forms a basis over the entire Hilbert space, allowing us to write:

$$\begin{aligned} &\left|\psi_n\right\rangle = \left|\psi_n^{(0)}\right\rangle + \lambda\left|\psi_n^{(1)}\right\rangle + \lambda^2\left|\psi_n^{(2)}\right\rangle + \dots \\ \Rightarrow\quad &E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \end{aligned} \tag{3.3}$$

As assumption asserted here is that the function is analytic around $\lambda = 0$, otherwise this expansion would not work. Now if we plug in the solution above and collect the terms that are the same order in λ, we get the terms in first few orders as:

$$\begin{aligned} \mathcal{O}(\lambda^0): &\quad \hat{H}_0\left|\psi_n^{(0)}\right\rangle = E_n^{(0)}\left|\psi_n^{(0)}\right\rangle \\ \mathcal{O}(\lambda^1): &\quad \hat{H}_0\left|\psi_n^{(1)}\right\rangle + \delta\hat{H}\left|\psi^{(0)}\right\rangle = E_n^{(0)}\left|\psi_n^{(1)}\right\rangle + E_n^{(1)}\left|\psi^{(0)}\right\rangle \\ \mathcal{O}(\lambda^2): &\quad \hat{H}_0\left|\psi_n^{(2)}\right\rangle + \delta\hat{H}\left|\psi^{(1)}\right\rangle = E_n^{(0)}\left|\psi_n^{(2)}\right\rangle + E_n^{(1)}\left|\psi^{(1)}\right\rangle + E_n^{(2)}\left|\psi^{(0)}\right\rangle \\ &\qquad\qquad\vdots \end{aligned} \tag{3.4}$$

From this, we see a pattern and we see that we can write:

$$\left|\psi_n^{(1)}\right\rangle = \sum_j c_{n,j}^{(1)}\left|\psi_j^{(0)}\right\rangle \tag{3.5}$$

If we plug this into the equation for $\mathcal{O}(\lambda^1)$ and apply the bra $\left\langle\psi_i^{(0)}\right|$, we get:

$$\begin{aligned} &c_{n,i}^{(1)}E_i^{(0)} + \left\langle\psi_i^{(0)}\right|\delta\hat{H}\left|\psi_j^{(0)}\right\rangle = c_{n,i}^{(1)}E_n^{(0)} + \delta_{n,i}E_n^{(1)} \\ \Rightarrow\quad &\boxed{E_n^{(1)} = \left\langle\psi_n^{(0)}\right|\delta\hat{H}\left|\psi_n^{(0)}\right\rangle}, \quad \text{if } n = i \\ \Rightarrow\quad &\boxed{c_{n,i}^{(1)} = \frac{\left\langle\psi_n^{(0)}\right|\delta\hat{H}\left|\psi_i^{(0)}\right\rangle}{E_n^{(0)} - E_i^{(0)}}}, \quad \text{if } n \neq i \end{aligned} \tag{3.6}$$

which grants us the first order energy correction to the full Hamiltonian. From these results, we also get the wavefunction up to first order in the perturbation parameter as:

$$\left|\psi_n\right\rangle \approx \left|\psi_n^{(0)}\right\rangle + \lambda\sum_{j\neq n}\frac{\left\langle\psi_n^{(0)}\right|\delta\hat{H}\left|\psi_i^{(0)}\right\rangle}{E_n^{(0)} - E_i^{(0)}}\left|\psi_j^{(0)}\right\rangle + \lambda c_{n,n}^{(1)}\left|\psi_n^{(0)}\right\rangle \tag{3.7}$$

where $c_{n,n}^{(1)}$ is found by state normalization which is just 0 if we ignore all terms in order λ^2 and above, which gives the result of first order perturbation theory as:

$$\boxed{\left|\psi_n\right\rangle \approx \left|\psi_n^{(0)}\right\rangle + \lambda\sum_{j\neq n}\frac{\left\langle\psi_n^{(0)}\right|\delta\hat{H}\left|\psi_i^{(0)}\right\rangle}{E_n^{(0)} - E_i^{(0)}}\left|\psi_j^{(0)}\right\rangle} \tag{3.8}$$

The result above allows us to better formalize the condition in which we can apply perturbation theory, which is:

$$\boxed{\left|\frac{\left\langle \psi_n^{(0)}\middle| \delta\hat{H} \middle|\psi_i^{(0)}\right\rangle}{E_n^{(0)} - E_i^{(0)}}\right| \ll 1, \quad \forall n \neq i} \tag{3.9}$$

Now if we consider second-order perturbation theory, which is keeping track of terms up to order λ^2. To do this, we want to expand the second order correction in terms of the zeroth order Hamiltonian eigenbasis states:

$$\left|\psi_n^{(2)}\right\rangle = \sum_i c_{n,i}^{(2)} \left|\psi_i^{(0)}\right\rangle \tag{3.10}$$

Applying the full Hamiltonian on this, we get:

$$\hat{H}_0 \sum_i c_{n,i}^{(2)} \left|\psi_i^{(0)}\right\rangle + \lambda\delta\hat{H} \sum_i c_{n,i}^{(1)} \left|\psi_i^{(0)}\right\rangle = E_n^{(0)} \sum_i c_{n,i}^{(2)} \left|\psi_i^{(0)}\right\rangle + E_n^{(1)} \sum_i c_{n,i}^{(1)} \left|\psi_i^{(0)}\right\rangle + E_n^{(2)} \left|\psi_i^{(0)}\right\rangle \tag{3.11}$$

Then closing the bra-ket with a bra state $\left\langle \psi_j^{(0)}\right|$, we get:

$$E_j^{(0)} c_{n,j}^{(2)} + \sum_i c_{n,i}^{(1)} \left\langle \psi_n^{(0)}\middle| \delta\hat{H} \middle|\psi_i^{(0)}\right\rangle = E_n^{(0)} c_{n,j}^{(2)} + E_n^{(1)} c_{n,j}^{(1)} + E_j^{(2)} \delta_{n,j} \tag{3.12}$$

Then considering the case where $n = j$, we get:

$$\begin{aligned} E_n^{(2)} &= \sum_i c_{n,i}^{(1)} \left\langle \psi_n^{(0)}\middle| \delta\hat{H} \middle|\psi_i^{(0)}\right\rangle \\ \Rightarrow \quad & \boxed{E_n^{(2)} = \sum_{i\neq n} \frac{\left|\left\langle \psi_n^{(0)}\middle| \delta\hat{H} \middle|\psi_i^{(0)}\right\rangle\right|^2}{E_n^{(0)} - E_i^{(0)}}} \end{aligned} \tag{3.13}$$

So we have the energy up to second order corrections is given by:

$$\boxed{E_n = E_n^{(0)} + \left\langle \psi_n^{(0)}\middle| \delta\hat{H} \middle|\psi_n^{(0)}\right\rangle + \sum_{i\neq n} \frac{\left|\left\langle \psi_n^{(0)}\middle| \delta\hat{H} \middle|\psi_i^{(0)}\right\rangle\right|^2}{E_n^{(0)} - E_i^{(0)}}} \tag{3.14}$$

What this shows is that in matrix representation, the first-order correction only adds diagonal elements to the zeroth order Hamiltonian. All other higher perturbative corrections will start to consider off-diagonal elements. We will not derive the second-order corrected wavefunction since it is messy and usually unnecessary (only the first-order wavefunction and second-order energies are relevant) in practice.

Remarks:

1. The true groundstate of the full Hamiltonian always has an energy that is less than or equal to that of the energy computed in perturbation theory (this comes from the variational principle which we will prove).

2. Additionally, if the system has a continuum of states, integrals will have to be taken instead of sums (or both depending on the spectrum of the Hamiltonian).

3. When there are 2 energy levels such that there is a non-vanishing coupled term in the perturbative Hamiltonian ($\left\langle \psi_n^{(0)} \middle| \delta\hat{H} \middle| \psi_i^{(0)} \right\rangle \neq 0$), there will be *level repulsion* between those 2 energy levels from the zeroth order spectrum. If the term vanishes however, there can be level crossing.

§3.1.2 Degenerate Perturbation Theory

Suppose we have N degenerate states in the zeroth order Hamiltonian that for a subspace of states $\{|\phi_i\rangle\}_{i\in[1,N]}$. This allows us to write:

$$\begin{aligned} &\hat{H}_0 |\psi_\mu\rangle = E_0 |\psi_\mu\rangle \\ \text{where} \quad &|\psi_\mu\rangle = \sum_{i=0}^{N} c_{\mu,i} |\phi_i\rangle \end{aligned} \tag{3.15}$$

So moving into a basis where we have $|\psi_\mu\rangle$ instead other $|\phi_i\rangle$ will allow us to break the degeneracy (in most situations). That is, computing the perturbative correction on the zeroth-order degenerate energy will split this degeneracy. We note that $c_{\mu,j} = \langle\phi_i|\psi_\mu\rangle$, so we can convert the energies into this new basis by:

$$\begin{aligned} &\sum_{i,j} \left\langle \psi_i^{(0)} \middle| \delta\hat{H} \middle| \psi_j^{(0)} \right\rangle c_{\mu,j} = c_{\mu,i} W_\mu \\ \Rightarrow \quad &E_\mu = E_0 + W_\mu + \dots \end{aligned} \tag{3.16}$$

where $\mu \in [1, N]$ now indexes the split energies of the initially degenerate subspace. In practice, a methodical way in which we can do this is by first constructing a matrix representation of the energies in the degenerate subspace with entries being:

$$\left[\hat{E}_{deg}\right]_{i,j} = \left\langle \psi_i^{(0)} \middle| \delta\hat{H} \middle| \psi_j^{(0)} \right\rangle . \tag{3.17}$$

We then diagonalize this matrix, for which its eigenvalues W_μ, give us the split energies, and eigenvectors give us the coefficients $c_{\mu,i}$ that brings us to the new non-degenerate basis. These energy corrections however, are only the first order-corrections. Fortunately, the second-order corrections are found just as we did for non-degenerate perturbation theory but ignoring all states in the degenerate subspace. In summary, we have the energy corrections for degenerate-perturbation theory up to second-order written as:

$$\boxed{E_{n,\mu} = E_n^{(0)} + W_{n,\mu} + \sum_{i\neq n} \frac{\left|\left\langle \psi_{n,\mu}^{(0)} \middle| \delta\hat{H} \middle| \psi_i^{(0)} \right\rangle\right|^2}{E_n^{(0)} - E_i^{(0)}}} \tag{3.18}$$

Let's now look at some famous examples of this.

§3.1.3 The Stark Shift

A *Stark shift* is the shifting and splitting of energy levels in atoms/molecules when in the presence of an external electric field. It is analogous to the *Zeeman effect* but for electric fields. To understand how this occurs, consider a Hydrogen atom in an external electric field. We want to study how the atom responds to this external field, so we use the dipole approximation which gives the perturbative Hamiltonian term:

$$\begin{aligned}\delta\hat{H} &= -\hat{\vec{d}}\cdot\vec{E} \\ &= q\hat{\vec{r}}\cdot\vec{E} = qrE\cos\theta\end{aligned} \tag{3.19}$$

where q is the dipole charge and θ is the angle between $\vec{r}$ and $\vec{E}$. We know that to minimize energy, the atoms would want to align the dipole moment along the external field. First, we note that without the spin degrees of freedom, the Hydrogen atom ground state is non-degenerate and can be characterized by the quantum numbers $\{n, l, m\}$. The excited state however, can be degenerate if we consider $|n = 2, l, m\rangle$. The zeroth order Hamiltonian is written as:

$$\hat{H} = \left(-\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 - \frac{e^2}{r}\right) + Eq\hat{z} \tag{3.20}$$

Some essential parameters for this zeroth order Hamiltonian in Hydrogen are:

$$E_{1s}^{(0)} = -\frac{e^2}{2a_{Br}}, \quad a_{Br} = \frac{\hbar^2}{e^2\mu}, \quad \mu = \frac{m_p m_e}{m_e + m_p} \approx m_e, \tag{3.21}$$

where a_{Br} is the Bohr radius and the groundstate wavefunction is given by:

$$\begin{aligned}\psi^{(0)}(\vec{r}) &= \frac{u_{1s}(r)}{r}Y_{0,0}(\Omega) \\ \text{where} \quad u_{1s}(r) &= \sqrt{a_{Br}}\left(\frac{2r}{a_{Br}}\right)e^{-r/a_{Br}}\end{aligned} \tag{3.22}$$

Now using perturbation theory, we can compute the energy correction terms as expectations on the pertrubative Hamiltonian over the unperturbed ground state:

$$\begin{aligned}E_{1s}^{(1)} &= 0 \\ E_{1s}^{(2)} &= -\frac{1}{2}\alpha_{1s}E^2\end{aligned} \tag{3.23}$$

where α_{1s} is known as the *polarizability*, and written as:

$$\alpha_{1s} = 2e^2\sum_{n,l,m}\frac{\langle 1s|\, r\cos\theta\, |n,l,m\rangle\, \langle n,l,m|\, r\cos\theta\, |1s\rangle}{E_{n,l}^{(0)} - E_{1s}^{(}0)}. \tag{3.24}$$

technically, the integral over the unbound continuum of states needs to be included above, but if we only care about the boundstates, the sum above over $\{n, l, m\}$ will suffice. To compute the terms in the sum, we need to perform integrals:

$$\begin{aligned} \langle n, l, m| \, r\cos\theta \, |1s\rangle &\propto \int R_{n,l}(r) R_{1,0}(r) r^2 dr \int d\Omega Y^*_{l,m}(\Omega) Y_{1,0}(\Omega) \\ &= \int R_{n,l}(r) R_{1,0}(r) r^2 dr \times \delta_{l,1}\delta_{m,0} \end{aligned} \tag{3.25}$$

So the second order energy correction simplifies to:

$$E^{(2)}_{1s} = \sum_{n=2}^{\infty} \frac{|\langle n, 1, 0| \, eEs \, |1s\rangle|^2}{E^{(0)}_{1s} - E^{(0)}_{n,1,0}} + \int_0^{\infty} \frac{|\langle \epsilon, 1, 0| \, eEs \, |1s\rangle|^2}{E^{(0)}_{1s} - \epsilon} d\epsilon \tag{3.26}$$

We notice that:

$$\begin{aligned} & E^{(0)}_{1s} - E^{(0)}_{n,1,0} \leq E^{(0)}_{1s} - E^{(0)}_{2,1,0} \\ \Rightarrow \quad & E^{(0)}_{1s} \geq \frac{1}{E^{(0)}_{1s} - E^{(0)}_{2,1,0}} \sum_{n=2}^{\infty} |\langle 1s| \, eEz \, |n, l, m\rangle|^2 \\ \Rightarrow \quad & E^{(0)}_{1s} \geq \frac{|\langle 1s| \, eEz \, |1s\rangle|^2}{E^{(0)}_{1s} - E^{(0)}_{2,1,0}} = -\frac{8}{3} a^3_{Br} E^2 \end{aligned} \tag{3.27}$$

So this gives us an approximation that:

$$\alpha_{1s} \approx \frac{16}{3} a^3_{Br} \tag{3.28}$$

This however, works out to not be correct. We thus need to perform a more exact calculation. So do this, we make use of *Green's functions* by considering:

$$\alpha_{1s} = 2e^2 \langle 1s| \, \hat{r}\cos\theta \cdot \hat{\mathcal{G}} \cdot \hat{r}'\cos\theta' \, |1s\rangle \tag{3.29}$$

where $\hat{\mathcal{G}}$ is the Green's function defined as:

$$\boxed{\hat{\mathcal{G}} = \sum\!\!\!\!\!\!\!\int \frac{|n, l, m\rangle \langle n, l, m|}{E^{(0)}_{n,l} - E^{(0)}_{1s}}} \tag{3.30}$$

which obeys:

$$\begin{aligned} & \left[\hat{H} - E^{(0)}_{1s}\right] \hat{\mathcal{G}} = \hat{\mathbb{I}} \\ \Rightarrow \quad & \left[\hat{H} - E^{(0)}_{1s}\right] \mathcal{G}(r, r') = \delta(r - r') \end{aligned} \tag{3.31}$$

where $\mathcal{G}(r, r') = \langle r| \, \hat{\mathcal{G}} \, |r'\rangle$. We then define $\hat{w} = \hat{r}\cos\theta$, and now define an auxiliary state:

$$\begin{aligned} & |\Phi\rangle = \hat{\mathcal{G}}\hat{w} \, |1s\rangle \\ \Rightarrow \quad & \boxed{\Phi(r) = \int_0^{\infty} G_{l=1}(r, r') r' u_{1s}(r') dr'} \end{aligned} \tag{3.32}$$

where the second line comes from close the state with $\langle r|$. This grants us the new equation to solve:

$$\boxed{\left[\hat{H}_0 - E_{1s}^{(0)}\right]|\Phi\rangle = \hat{w}\,|1s\rangle}, \quad \alpha_{1s} = 2\,\langle 1s|\,\hat{w}\,|\Phi\rangle \tag{3.33}$$

which gives us an equation to solve in just one variable. Another key aspect of solving this analytically, is by utilizing the spherical symmetry of the problem. Spherical symmetry then allows us to separate the radial and angular coordinates:

$$\alpha_{1s} = 2e^2|\langle Y_{0,0}|\cos\theta\,|Y_{1,0}\rangle|^2\left[\sum + \int\right]\frac{|\langle \epsilon,1,0|\,\hat{r}\,|1s\rangle|^2}{E_{n,1,0}^{(0)} - E_{1s}^{(0)}} \tag{3.34}$$

For the rest of this, we will work in units such that $\hbar = a_{Br} = e = 1$. As such, the radial equation we are concerned with becomes:

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} + \left.\frac{l(l+1)}{2r}\right|_{l=1} - E_{1s}^{(0)}\right] G_{l=1}(r,r') = \delta(r-r') \tag{3.35}$$

Plugging the form of $\Phi(r)$ we had into the radial Green's function equation gives:

$$-\frac{1}{2}\Phi''(r) + \left(\frac{1}{r^2} - \frac{1}{r} + \frac{1}{2}\right)\Phi(r) = 2r^2e^{-r} \tag{3.36}$$

To solve this, we consider asymptotic solutions.

1. $\underline{r \to \infty}$:

   The equation we are solving now becomes:

$$\begin{aligned} &-\frac{1}{2}\Phi'' + \frac{1}{2}\Phi = 0 \\ \Rightarrow\quad &\Phi(r) \sim e^{-r} \end{aligned} \tag{3.37}$$

2. $\underline{r \to 0}$:

   The equation then becomes:

$$\begin{aligned} &-\frac{1}{2}\Phi'' + \frac{1}{r^2}\Phi = 0 \\ \Rightarrow\quad &\Phi(r) \sim r^2 \end{aligned} \tag{3.38}$$

We then need to match these 2 asymptotic solutions, which gives us:

$$\Phi(r) = F(r)e^{-r}r^2 \tag{3.39}$$

To find $F(r)$, we plug the ansatz above back into the differential equation to get:

$$\begin{aligned} &-\frac{1}{2}F''(r) + (r-2)F(r) + F(r) = 2r \\ \Rightarrow\quad &F(r) = 2 + r \\ \Rightarrow\quad &\boxed{\Phi(r) = (2r^2 + r^3)e^{-r}} \end{aligned} \tag{3.40}$$

Plugging this back into α_{1s}, we get:

$$\begin{aligned}\alpha_{1s} &= 2\left\langle 1s\right| \hat{w} \left|\Phi\right\rangle \\ &= 2|\left\langle Y_{0,0}\right| \cos\theta \left|Y_{1,0}\right\rangle|^2 \left\langle 1s\right| r \left|\Phi\right\rangle \\ &= 2 \cdot \frac{1}{3} \cdot \frac{27}{4}\end{aligned} \tag{3.41}$$

Plugging back the units, we get:

$$\boxed{\alpha_{1s} = \frac{9}{2} a_{Br}^3} \tag{3.42}$$

Now, if we want to consider the excited state ($n = 2$), we are going to need degenerate perturbation theory. The $n = 2$ state will have the following $|n, l, m\rangle$ degenerate states:

$$\begin{aligned}&\left|2,0,0\right\rangle \\ &\left|2,1,-1\right\rangle, \quad \left|2,1,0\right\rangle, \quad \left|2,1,1\right\rangle\end{aligned} \tag{3.43}$$

So to perform perturbation on these states, we again sandwich the perturbative term between these states which will form a matrix, but we note that the only non-trivial terms will be for the terms:

$$V_{1,0} \equiv \left\langle 2,1,0\right| eE\hat{z} \left|2,0,0\right\rangle, \quad V_{0,1} \equiv \left\langle 2,0,0\right| eE\hat{z} \left|2,1,0\right\rangle \tag{3.44}$$

So we get the subspace of energies in matrix representation:

$$\hat{E} = \begin{bmatrix} E_2^{(0)} & V_{0,1} \\ V_{1,0} & E_2^{(0)} \end{bmatrix} \tag{3.45}$$

Diagonalizing this matrix gives us the splitting energies:

$$E_\pm = E_2^{(0)} \pm 2eEa_{Br}; \quad \psi_\pm^{(E)} = \frac{1}{\sqrt{2}}[1, \quad \pm 1]^T \tag{3.46}$$

We notice that:

$$\lim_{E\to 0} \left| \frac{dE_\pm^{(1)}}{dE} \right| = 3ea_{Br} \neq 0 \tag{3.47}$$

so there seems to be a *permanent dipole moment*. However, taking the same limit above for the second order energy correction indeed causes the energy correction to vanish. So the second order energy correction is referred to as in *induced dipole moment*. If we look at the potential energy curve of this perturbed system, the boundstates in the original Hamiltonian are no longer strictly boundstates after the perturbative term is added. Hence, the states are now called *metastable states*. This is best understood when we see how the Stark effect changes the potential energy curve as shown in figures 3.1 and 3.2 below.

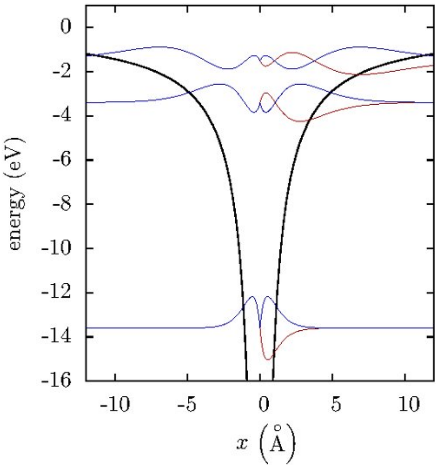

Figure 3.1: Potential without Stark shift.

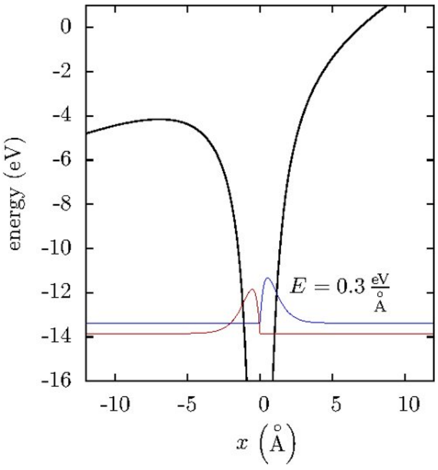

Figure 3.2: Potential with Stark shift.

The images above were taken from this website.

§3.2 Quasi-Degenerate Perturbation Theory

We recall that in non-degenerate perturbation theory, we required the condition:

$$\left| \frac{\langle i| \delta\hat{H} |n\rangle}{E_n^{(0)} - E_i^{(0)}} \right| \ll 1 \tag{3.48}$$

and for the degenerate case, we had:

$$E_n^{(0)} = E_i^{(0)} \tag{3.49}$$

for some i. But what if the first condition is not satisfied? That is we are looking at strongly coupled systems.

§3.2.1 Lamb-Shift

The *Lamb-shift* is an energy difference between the $2s_{1/2}$ and $2p_{1/2}$ eigenstates of Hydrogen that was not predicted by Dirac's equation, but experimentally measure by Lamb and Retherford in 1947. To see this, we consider the inclusion of the spin-orbit coupling term in the Hamiltonian. So we have the relevant quantum numbers:

$$|n, j(s,l), m_j\rangle \tag{3.50}$$

where $s = 1/2$. For the case where $n = 2$, we have $l = 1$ so $j = 3/2$ and we can get:

$$m_j = -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2} \tag{3.51}$$

We know that the unpertrubed (zeroth order) Hydrogen system as energy:

$$\begin{aligned} E_n &= -\frac{1}{2}\frac{Z^2}{n^2}\frac{e^2}{a_{Br}} \\ &= -\frac{1}{2}mc^2\left(\frac{Z\alpha}{n}\right)^2 \end{aligned} \tag{3.52}$$

where $\alpha = e^2/\hbar c \approx 1/137$ is the *fine structure constant*. Why we need to care about these relativisitc corrections is through a quick classical calculation. Classically, we have:

$$\langle T\rangle = \frac{1}{2}mv^2, \quad \langle V\rangle = -\left\langle \frac{e^2}{r}\right\rangle \tag{3.53}$$

for which we can use the Virial theorem to get the velocity of the particle:

$$\langle v\rangle \sim c\alpha \tag{3.54}$$

which is about 1% the speed of light. So we indeed need to input relativistic corrections. Why we can treat this perturbatively though, is because $Z\alpha \ll 1$.

Note: If we want the exact solution to the Hydrogen atom, we need to use the *Dirac equation* which gives:

$$\begin{aligned} E &= mc^2\sqrt{1+\frac{(Z\alpha)^2}{(n-\delta j)^2}} \\ \text{where} \quad \delta j &= j+\frac{1}{2}-\sqrt{\left(j+\frac{1}{2}\right)^2-(Z\alpha^2)} \end{aligned} \tag{3.55}$$

and $j = l + s$ with $s = 1/2$.

Recall that from perturbation theory, we got:

$$E_n = mc^2\left[1-\frac{1}{2}\frac{(Z\alpha)^2}{n^2}-\frac{1}{2}(Z\alpha)^4\left(\frac{n}{j+1/2}-\frac{3}{4}\right)+\dots\right] \tag{3.56}$$

which was gotten from expanding $E = \sqrt{mc^2 + p^2c^2}$. Nonetheless, the basis for the treatment of spin-orbit coupling is by considering charged particles (such as electrons) and relativistic effects during orbit. We know form relativity that when we boost to the frame of the electron, instead of seeing a electric field, the electron would experience a magnetic field:

$$\vec{B} = -\frac{1}{c}\vec{v}\times\vec{E} \tag{3.57}$$

which is derived by applying Lorentz transformation to the Faraday tensor. So for an electric orbiting a central positively charged center, we have that the magnetic field will be radial and:

$$\vec{B} = \frac{Ze}{mcr^3}\vec{L} \tag{3.58}$$

where $\vec{L}$ is the angular momentum. This tells us that the magnetic field is proportional to the angular momentum! So the key of spin-orbit coupling is that in the frame of the electron, it will experience a magnetic field instead of the electric field from the central potential which causes it to feel $\vec{L}$ effects.

Now where the *Lamb shift* comes into play, is when it was experimentally found that there was another degeneracy splitting in addition to that from the spin-orbit coupling. Essentially, Lamb and Rutherford used microwaves to measure this splitting of the degeneracy in 1947. The energy splitting structure (including the hyperfine structure present when in external fields) is illustrated in figure 3.3 below.

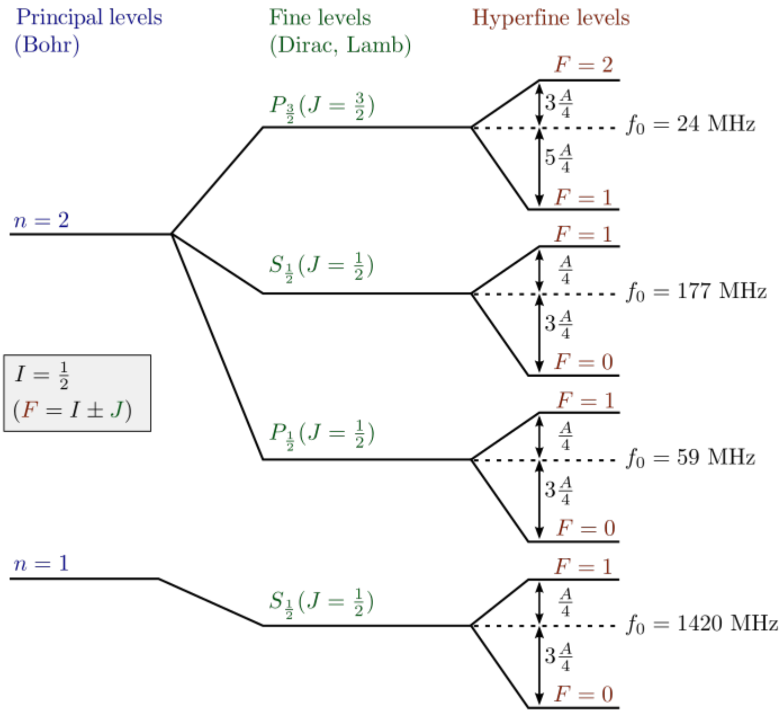

Figure 3.3: Energy spectrum structure in Hydrogen (picture credits).

In the figure above, I indicates the nuclear spin, $J = S + L$ with S being the spin angular momentum and L the orbital angular momentum, while F denotes the total angular momentum.

§3.3 The Variational Method

Variational methods are very useful as tools to dealing with complex and large quantum systems where exact methods are intractable. Variational methods are based on the *variational theorem*. The statement of the theorem is as follows.

Theorem 3.3.1. *Given an arbitrary "trial" wavefunction $|\psi\rangle$ and a Hamiltonian $\hat{H}$, we have the inequality*:

$$E[\psi] = \frac{\langle\psi|\,\hat{H}\,|\psi\rangle}{\langle\psi|\psi\rangle} \geq E_0 \tag{3.59}$$

where E_0 is the true groundstate energy of the Hamiltonian $\hat{H}$.

Proof. We can always write the state $|\psi\rangle$ as:

$$|\psi\rangle = \sum_n c_n\,|\psi_n\rangle \tag{3.60}$$

where the set of $|\psi_n\rangle$ are the orthonormal energy eigenstates of $\hat{H}$. From this we note that:

$$E[\psi] = \frac{\sum_n \langle\psi_n|\,\hat{H}\,|\psi_n\rangle}{\sum_n \langle\psi_n|\psi_n\rangle} = \frac{\sum_n |c_n|^2 E_n}{\sum_n E_n} \geq \frac{\sum_n |c_n|^2 E_0}{\sum_n |c_n|^2} = E_0 \tag{3.61}$$

☐

The variational theorem then allows us to use the *variational principle* which is that if we consider a variation from the true wavefunction of a Hamiltonian:

$$\hat{H} = -\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + V(r), \quad |\psi\rangle = |\psi_E\rangle + |\delta\psi\rangle \tag{3.62}$$

where the subscript E indicates the exact solution. We can take the expectation of this Hamiltonian with the variational ansatz to get:

$$\delta E = \frac{\Delta\delta V - \mathcal{N}\delta\Delta}{\Delta^2} \tag{3.63}$$

from the chain rule, where

$$\Delta = \int d^3r|\psi(r)|^2, \quad \mathcal{N} = \int d^3r\psi^*(r)\hat{H}\psi(r) \tag{3.64}$$

So we have the variational terms as:

$$\delta\Delta = 2\int d^3r\psi^*\delta\psi \tag{3.65}$$

$$\delta N = \int d^3r\left[\delta\psi^*\hat{H}\psi_E + \psi_E^*\hat{H}\delta\psi\right] \tag{3.66}$$

To simplify δN, we perform integration by parts and use the divergence theorem (noticing that all surface integrals at infinity vanishes for normalized wavefunctions) to get:

$$\delta N = 2\int d^3r\;\delta\psi^*\hat{H}\psi_E \tag{3.67}$$

This gives us the result that:

$$\delta E \sim (\delta\psi)^2 \tag{3.68}$$

which tells us that all corrections to the energy when using an ansatz that is a small perturbation away from the true wavefunction, we get energy corrections that are one the order of $(\delta\psi)^2$! However, the trouble now is how do we pick a good variational ansatz? There are several ways to do this.

1. Brute-Force Ansatz: Pick a trial wavefunction that is dependent on some free parameters $\vec{\alpha}$, giving $|\psi(\vec{\alpha})\rangle$ and have the form of this trial function appropriate to the physical system from some intuition. Then minimize with respect to these parameters.
2. Rayleigh-Ritz Variational Method: Choose a particular linear combination of some basis $\{|u_j\rangle\}$ and optimize the coefficients of this linear combinations. Explicitly, the *Rayleigh-Ritz variational method* is done in the following few steps.
   (a) We postulate a wavefunction solution $|\psi\rangle$ to the problem.
   (b) We pick a finite (usually truncated to reduce the size of the Hilbert space for computational feasibility) basis set $|u_j\rangle$ and write the postulated wavefunction as a linear combination of these basis vectors:

$$|\psi\rangle = \sum_j c_j \, |u_j\rangle \tag{3.69}$$

   (c) We minimize the energy with this linear combination of basis vectors with respect to the set $\{c_j\}$:

$$\frac{\partial E}{\partial c_j^*} = 0, \qquad \sum_j |c_j|^2 = 1 \tag{3.70}$$

$$\Rightarrow \quad (\hat{H} - E\hat{\mathbb{I}})\vec{c}_n = \vec{0} \tag{3.71}$$

   and solve the resulting linear system for all the c_j coefficients.

Note: The Rayleigh-Ritz variational method reduces to just diagonalizing the Hamiltonian of the system in some reduced Hilbert space (truncated set of basis states).

Example:

We are now going to try and apply the brute-force variational method to an actual system. Let's say we want to find the groundstate of a 2-electron atom/ion (bound to a nucleus). The Hamiltonian for this system can be written as:

$$\begin{aligned} \hat{H} &= \hat{h}_1 + \hat{h}_2 + \frac{e^2}{\|\vec{r}_1 - \vec{r}_2\|} \\ \text{where} \quad \hat{h}_j &= -\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 - \frac{Ze^2}{r_j} \end{aligned} \tag{3.72}$$

What we are going to do now is to treat the electron-coupling term $e^2/\|\vec{r}_1 - \vec{r}_2\|$ as small (perturbative Hamiltonian), so we have the zeroth order energy for the groundstate as:

$$E_{1s}^{(0)} = -2\left(\frac{Z^2 e^2}{2a_{Br}}\right) \tag{3.73}$$

As such, we have that the “good quantum numbers” to adopt for this problem as $\{n, l, m\}$, for which we can treat the wavefunction solution as separable and write:

$$\psi(\vec{r}_1, \vec{r}_2) = \psi_{1,0,0}(\vec{r}_1)\psi_{1,0,0}(\vec{r}_2) \tag{3.74}$$

It works out that that in a Helium system ($Z = 2$), we have from perturbation theory that the energy works out to be $E_{1s} \approx -74.8$ [eV]. However, the actual measured total groundstate energy value in experiment is in fact -78.995 [eV]. This is actually due to fermionic interactions between the electrons (the wavefunction has to be antisymmetrized).

Instead of including these antisymmetrized solutions, what we will attempt to do here is pick and ansatz and perform the variational method. We write this ansatz as:

$$\psi_{Z^*}(\vec{r}_1, \vec{r}_2) \sim \exp\left(-\frac{Z^*(r_1 + r_2)}{a_{Br}}\right)\left(\frac{Z^*}{a_{Br}}\right)^3 \tag{3.75}$$

where Z^* is some modified value of Z which we will be varying and minimizing with respect to, that allows us to mimic an effective charge. with some constant prefactors being dropped above. We also modify the Hamiltonian to include Z^* by defining:

$$\begin{aligned} \hat{h}_j^* &\equiv -\frac{\hbar^2}{2m}\nabla^2 - \frac{Z^* e^2}{r_j} \\ \Rightarrow \quad \hat{H} &= \hat{h}_1^* + \hat{h}_2^* + \delta\hat{H}^* \\ \text{where} \quad \delta\hat{H}^* &= \left[(Z^* - Z)\left(\frac{e^2}{r_1} + \frac{e^2}{r_2}\right) + \frac{e^2}{r_{1,2}}\right] \end{aligned} \tag{3.76}$$

where $r_{1,2} = \|\vec{r}_1 - \vec{r}_2\|$. To now find $\langle\psi_{Z^*}|\,\hat{H}\,|\psi_{Z^*}\rangle$, we need to take integrals over $\vec{r}_1$ and $\vec{r}_2$. To do this, we first recall the identity:

$$\frac{1}{r_{1,2}} = \sum_{l,m} \frac{4\pi}{2l+1} Y_{l,m}^*(\hat{r}_1) Y_{l,m}(\hat{r}_2) \frac{r_<^l}{r_>^{l+1}} \tag{3.77}$$

which allows us to perform the integral:

$$\begin{aligned} V(Z^*) &= \int d^3 r_1 r^3 r_2 \psi_{Z^*}^*(\vec{r}_1)\delta\hat{H}^*\psi_{Z^*}^*(\vec{r}_2) \\ &= \frac{e^2}{a_{Br}}\left[-(Z^*)^2 + 2Z^*(Z^* - Z) + \frac{5}{8}Z^*\right] \end{aligned} \tag{3.78}$$

Minimizing this energy with respect to Z^* then gives:

$$\begin{aligned} Z^* &= Z - \frac{5}{16} \\ \Rightarrow \quad E(Z^*) &= E^{(0)} + V(Z^*) = -77.5 \text{ [eV]} \end{aligned} \tag{3.79}$$

which is indeed a better result that using perturbation theory!

§3.4 Time-Dependent Perturbation Theory

From now, we are going to move away from static problems and touch on systems that are intrinsically time-dependent. To do so , we consider the Hamiltonian:

$$\hat{H}(t) = \hat{H}_0 + \delta\hat{H}(t) \tag{3.80}$$

where $\hat{H}_0$ is time-independent and solvable, that is we know the spectrum and energy eigenstates of $\hat{H}_0$:

$$\begin{aligned} \left|\psi^{(0)}(t)\right\rangle &= \exp\left(-\frac{i\hat{H}_0 t}{\hbar}\right)\left|\psi^{(0)}(0)\right\rangle \\ &= \sum_n e^{-iE_n t/\hbar} c_n \left|u_n\right\rangle \end{aligned} \tag{3.81}$$

Furthermore, we will once again treat $\delta\hat{H}(t)$ as "small" compared to $\hat{H}_0$. Before proceeding, we note a few important features of time-dependent perturbation theory. With time-dependent perturbation theory, the total system we are working with is no longer *Hamiltonian* (i.e. the total energy of the system is **not** conserved). This implies that for a system governed by a Hamiltonian with explicit time-dependence $\hat{H} = \hat{H}(t)$, the notion of energy eigenstates no longer applies. To deal with this, what we often do is consider 3 temporal regions of analysis.

1. $\underline{t < t_0}$: Here, the time-dependent perturbation is turned **off**. That is to say:

$$\delta\hat{H}(t)\Big|_{t<t_0} = 0 \tag{3.82}$$

   allowing us to describe the traditional eigenstates/eigen-energy description of the system.

2. $\underline{t_0 \leq t \leq t_f}$: Here, the time-dependent perturbation is turned **on**:

$$\delta\hat{H}(t)\Big|_{t_0 \leq t \leq t_f} \neq 0, \tag{3.83}$$

   giving a non-trivial $\delta\hat{H}(t)$ for which the notions of energy eigenstates is lost.

3. $\underline{t > t_f}$: Here, the time-dependent perturbation is once again turned **off**:

$$\delta\hat{H}(t)\Big|_{t>t_f} = 0, \tag{3.84}$$

   and we regain the ability to talk about energy eigenstates and eigenvalues.

The question to now ask is then "*given some finite-time interval for which the system is perturbed by a time-varying Hamiltonian, how will the system transition away from its initial state by the time the perturbation is turned off?*" To solve the time-dependent problem, we are going to assert that we can write:

$$\left|\psi(t)\right\rangle = \sum_n e^{-iE_n t/\hbar} c_n(t) \left|u_n\right\rangle \tag{3.85}$$

That is all the time-dependence is taken into the expansion coefficients in the initial $\hat{H}_0$ basis. Furthermore, we assume that the perturbation series:

$$c_n(t) = c_n^{(0)} + c_n^{(1)}(t) + c_n^{(2)}(t) + \dots \tag{3.86}$$

is convergent. To approach this, we plug this ansatz into the Schrödinger's equations and look at the terms order-by-order in the perturbation as we did before. First, we write:

$$\begin{aligned} & i\hbar\frac{\partial}{\partial t}\left|\psi(t)\right\rangle = \hat{H}_0\left|\psi(t)\right\rangle + \delta\hat{H}(t)\left|\psi(t)\right\rangle \\ \Rightarrow\quad & i\hbar\frac{\partial}{\partial t}c_m(t) = \sum_n e^{i\omega_{m,n}t}\left\langle u_m\right|\delta\hat{H}(t)\left|u_n\right\rangle c_n(t) \end{aligned} \tag{3.87}$$

where we define $\omega_{m,n} \equiv (E_m - E_n)/\hbar$. Now looking at the first few order terms, we have:

$$\begin{aligned} \mathcal{O}(0):\quad & i\hbar\frac{\partial}{\partial t}c_m^{(0)} = 0 \\ \mathcal{O}(1):\quad & i\hbar\frac{\partial}{\partial t}c_m^{(1)} = \sum_n e^{i\omega_{m,n}t}V_{m,n}(t)c_n^{(0)} \\ & \Rightarrow c_m^{(1)} = \frac{1}{i\hbar}\int_{t_0}^{t}\sum_n e^{i\omega_{m,n}\tau}V_{m,n}(\tau)c_n^{(0)}d\tau \\ \mathcal{O}(2):\quad & i\hbar\frac{\partial}{\partial t}c_m^{(2)} = \sum_n e^{i\omega_{m,n}t}V_{m,n}(t)c_n^{(1)} \\ & \Rightarrow c_m^{(2)} = \left(\frac{1}{i\hbar}\right)^2\int_{\tau}^{t}d\tau\sum_l e^{i\omega_{m,l}\tau}V_{m,l}(\tau)\int_{\tau_0}^{\tau}\sum_n e^{i\omega_{m,n}\tau}V_{m,n}(\tau)c_n^{(0)}d\tau \\ & \quad\vdots \end{aligned} \tag{3.88}$$

§3.4.1 Fermi's Golden Rule

We will see that the above series will lead to a result known as "*Fermi's golden rule*" when considering harmonic perturbations. To get a picture of what this is, we consider the harmonic field perturbation:

$$\delta\hat{H}(t) = \delta\hat{H}e^{-i\omega t} \tag{3.89}$$

where $\delta\hat{H}$ is time-independent. Firstly, we are going to work with the assumption that at $t = 0$, we start in an eigenstate $\left|u_{n^*}\right\rangle$ of the $\hat{H}_0$ Hamiltonian. As such, this makes the coefficients at $t = 0$ to be Kronecker-delta functions $c_n = \delta_{n,n^*}$. The expression for the first order time-dependent coefficient then simplifies to:

$$\begin{aligned} c_m^{(1)} &= \frac{1}{i\hbar}\int_{t_0}^{t}e^{i\omega_{m,n^*}\tau}\delta H_{m,n^*}(\tau)d\tau \\ &= \frac{\delta H_{m,n^*}}{i\hbar}\times\frac{e^{i(\omega_{m,n^*})-w)t}-1}{i(\omega_{m,n^*}-\omega)} \end{aligned} \tag{3.90}$$

where $\delta\hat{H}_{m,n^*} \equiv \langle u_m| \delta\hat{H} |u_{n^*}\rangle$ (time-**independent** term) and we set $t_0 = 0$. This then allows us to compute the probability of transitioning from state $|n^*\rangle$ at time $t = t_0$ to state $|m\rangle$ at time $t = t_f$ to first-order in the perturbation as:

$$\boxed{\mathbb{P}_{m\leftarrow n^*} \approx |c_{m^{(1)}}|^2 = \frac{|\delta H_{m,n^*}|^2}{\hbar^2}\left[\frac{\sin^2\left(\frac{(\omega_{m,n^*}-\omega)t}{2}\right)}{\left(\frac{(\omega_{m,n^*}-\omega)}{2}\right)^2}\right]}. \tag{3.91}$$

Now, we consider the long-time behavior of this probability term. First we define:

$$\Delta \equiv \frac{(\omega_{m,n^*} - \omega)}{2}. \tag{3.92}$$

So when we consider the time-dependent factor:

$$\frac{\sin^2(\Delta t)}{\Delta^2} \tag{3.93}$$

we realize it is in fact a Bessel function in Δ for which at long times ($t \to \infty$), this tends toward a delta-function-like distribution. Now, we know that delta-functions must be normalized to 1, so to truly write the Bessel function in the long-time limit as a delt-function, we need to find this normalization factor as follows:

$$\begin{aligned} &\int_{-\infty}^{\infty} \frac{\sin^2(\Delta t)}{t\Delta^2} d\Delta = \pi \,\mathrm{sign}(t) \\ \Rightarrow \quad &\lim_{t\to 0} \frac{\sin^2(\Delta t)}{\Delta^2} = \pi t \delta(\Delta), \quad \text{for } t > 0 \end{aligned} \tag{3.94}$$

where the integral above was evaluated using contour integration (refer to appendix section .1 for details on this). So we have that:

$$\boxed{\lim_{t\to 0}\left|c_m^{(1)}(t)\right|^2 = |\delta H_{m,n^*}|^2\left(\frac{2\pi t}{\hbar}\right)\delta(E_m - E_{n^*} - \hbar\omega)}. \tag{3.95}$$

This result is known as *Fermi's golden rule*, and tell us that the long-time behavior of a system is only going to have a response when the injected energy via the time-dependent perturbation matches the innate spectrum of the unperturbed Hamiltonian $\hat{H}_0$ (at least to first-order, which applies to systems with a dense spectrum/continuum of energy states). Additionally, we can then get that the rate of transition between 2 states $R_{m\leftarrow n^*}$, defined as the time derivative of the transition probability will be, in the long-time limit, written as:

$$\boxed{R_{m\leftarrow n^*} = |\delta H_{m,n^*}|^2\left(\frac{2\pi}{\hbar}\right)\delta(E_m - E_{n^*} - \hbar\omega)} \tag{3.96}$$

Remark: Recall that for 2-level systems, we had that the probability of being in the excited state when we apply some time-dependent Hamiltonian:

$$\hat{H}(t) = \hbar\Omega\hat{\sigma}^{+}\exp\left(-i\omega t\right) \tag{3.97}$$

$$\Rightarrow \quad \mathbb{P}_{\uparrow} = \frac{\Omega^2}{\Omega^2+\delta^2}\sin^2\left(\frac{t}{2}\sqrt{\Omega^2+\delta^2}\right). \tag{3.98}$$

This gives us a probability that goes like $\sim t^2$ at short times, however we had that the Fermi's golden rule gave us a probability that goes like $\sim t$. Why? It turns out that this is due to the fact that Fermi's golden rule **only** applies to system with a *dense spectrum* (where we use the notion of a density of states).

More specifically, we see that for this system, Fermi's golden rule would break down because the resonance (as a function of the detuning δ) is going to follow a Lorentzian $\sim \frac{\Omega^2}{\Omega^2+\delta^2}$, which cannot be effectively squeezed and approximated as a δ-function since the uncertainty principle ($\Delta t\Delta E \sim \hbar$) asserts that we will have to wait arbitrarily long to get it arbitrarily narrow (unlike the $\frac{\sin^2(\Delta t)}{\Delta^2}$ function we got for dense spectra).

The remark above then motivates us to consider problems with dense energy spectra. One such system is a Hydrogen atom that is irradiated by a photon γ, which ionizes it (into a proton and an electron):

$$\mathrm{H}+\gamma \quad \rightarrow \quad p+e^{-} \tag{3.99}$$

The wavefunction of the exiting electron after this process is well-described by a plane wave solution, which as we know can have a continuum of energies characterized by k^2. To approach solving this continuum of states, we use a formalism known as *box regularization/normalization* which would result in some density of energy states $\rho(E)$.

§3.4.2 Box Regularization

Consider a finite-sized box of edge length L with periodic-boundary conditions such that we can normalize the wavefunction inside the box and write it as:

$$\begin{aligned} \phi_{\vec{k}}(\vec{r}) &= \frac{1}{L^{3/2}}e^{i\vec{k}\cdot\vec{r}} \\ \text{where} \quad \vec{k} &= \frac{2\pi}{L}\left[n_x\hat{x},\ n_y\hat{y},\ n_z\hat{z}\right]^T. \end{aligned} \tag{3.100}$$

We also assert that within this box, we have a complete set of orthonormal states in the basis ϕ_k, for which k is now discrete due to the finite-sized box boundary conditions. We can then define a "*density distribution function*" $F(n_x,n_y,n_z)$, as a means to count the number of states, for which we want in some limit that we get:

$$\sum_{n_x,n_y,n_z} F(n_x,n_y,n_z)\Delta n_x\Delta n_y\Delta n_z \quad \rightarrow \quad \left(\frac{L}{2\pi}\right)^3\int F(\vec{k})d^3k. \tag{3.101}$$

So we see that the real motivation of defining this finite-sized box is so that we can work with tools we are familiar with for discrete spectra, then appropriately take limits to retrieve results for continuous spectra. Using the fact that $p = \hbar k$, we can do a change of variable such that integral above becomes:

$$\left(\frac{L}{2\pi}\right)^3 \int F(\vec{k})d^3k = \left(\frac{L}{2\pi\hbar}\right)^3 \int F(\vec{p})d^3p \tag{3.102}$$

If we apply this to Fermi's golden rule, we get:

$$\begin{aligned}\lim_{t\to 0}\left|c_f^{(1)}(t)\right|^2 &= \left(\frac{L}{2\pi\hbar}\right)^3 \int d^3p_f|\delta H_{f,i}|^2\left(\frac{2\pi t}{\hbar}\right)\delta(E_f - E_i - \hbar\omega) \\ &= \left(\frac{L}{2\pi\hbar}\right)^3 \int d\Omega_f \int p_f^2 \frac{dp_f}{dE_f}dE_f|\delta H_{f,i}|^2\left(\frac{2\pi t}{\hbar}\right)\delta(E_f - E_i - \hbar\omega)\end{aligned} \tag{3.103}$$

where the subscripts f and i denote the final and initial states respectively. We can then define a *density of final states*:

$$\boxed{\rho_f(E_f) \equiv \left(\frac{L}{2\pi\hbar}\right)^3 \frac{p_f^2 dp_f d\Omega_f}{dE_f}} \tag{3.104}$$

which is a measure of the number of states per unit interval of final energy E_f. This is in fact analogous to the density of state commonly used in statistical mechanics. With this definition, we are now able to write the Fermi's golden rule for a continuum of states as:

$$\boxed{dR_{E_f\leftarrow E_i} = \frac{2\pi}{\hbar}\left|\langle\psi_f|\,\delta\hat{H}\,|\psi_i\rangle\right|^2\rho_f(E_f)} \tag{3.105}$$

keeping in mind that $\delta\hat{H}$ here is the time-independent perturbation associated to perturbing harmonic fields. Another means of arriving at this same result is through the use of *energy normalization* of the δ-function in energy-space to change coordinates where:

$$\frac{\delta(\vec{p}-\vec{p}\,')}{p^2} = \frac{\delta(E-E')}{p^2}\frac{dE}{dp}, \tag{3.106}$$

which allows us to once again arrive at the same result as in equation (3.105).

Example (The Photoelectric Effect in Hydrogen):

Let us consider an application of Fermi's golden rule in the system of Hydrogen. Imagine that we apply an external electric field:

$$\vec{E}(\vec{r},t) = \vec{E}_0\cos\left(\vec{k}\cdot\vec{r} - \omega t\right) \tag{3.107}$$

to a H-atom in its ground $1s$ state, which grants the perturbation term in the Hamiltonian written in terms of complex exponentials to be:

$$\delta\hat{H}(t) = e\vec{E}_0\cdot\vec{r}\left(\frac{e^{i(\vec{k}\cdot\vec{r}-\omega t)} + e^{-i(\vec{k}\cdot\vec{r}-\omega t)}}{2}\right). \tag{3.108}$$

In the experimental set-up, we also have a detector that measures the electrons emitted from the Hydrogen atom when perturbed by this external field that radiate into some differential solid angle $d\Omega$.

Labeling the groundstate energy as E_{1s} and the stipulated final state energy after the perturbation as E_f, we have that Fermi's golden rule will grant us probabilities that go like:

$$\mathbb{P}_{E_f \leftarrow E_{1s}} \sim \delta(E_f - E_{1s} \pm \hbar\omega) \tag{3.109}$$

where the $\pm\hbar\omega$ is determined by the sign of $i\omega t$ in the complex exponential. It turns out that the term in $\exp(-i\omega t)$ corresponds to a *stimulated emission* process which vanishes in first order perturbation theory, so we just consider the $\exp(-i\omega t)$ term. For this, we have that the transition rate per unit solid angle works out to be:

$$\frac{dR}{d\Omega}(E_f \leftarrow E_{1s}) = \frac{2\pi}{\hbar}\left| \langle E_f, \vec{p}_f| \, \frac{e\vec{E}_0 \cdot \vec{r}}{2} e^{i\vec{k}\cdot\vec{r}} \, |E_{1s}\rangle \right|^2 . \tag{3.110}$$

From here, we are going to adopt an approximation known as the *electric dipole approximation*, which assumes that the wavelength of the incoming harmonic field is much longer than the length scale relevant to the atom ($\lambda \gg r_0 \Rightarrow \frac{\omega}{c} \ll \frac{1}{r_0}$). This allows us to write:

$$\exp\left(i\vec{k}_f \cdot \vec{r}\right) \approx 1 + i\vec{k}_f \cdot \vec{r} \tag{3.111}$$

or in fact just simply $e^{i\vec{k}\cdot\vec{r}} \approx 1$ (for all intends and purposes) granting the result:

$$\frac{dR}{d\Omega}(E_f \leftarrow E_{1s}) \approx \frac{2\pi}{\hbar}\left| \langle E_f, \vec{p}_f| \, \frac{e\vec{E}_0 \cdot \vec{r}}{2} \, |E_{1s}\rangle \right|^2 . \tag{3.112}$$

To then compute the matrix element, we use the box regularized plane-wave function and adopt the energy normalization of the δ-function to get:

$$\langle \vec{r} | E_f, \vec{p}\rangle = \frac{1}{(2\pi)^{3/2}} \left(\frac{p_f^2 dp_f}{dE_f} \right)^{1/2} \exp\left(i\frac{\vec{p}_f \cdot \vec{r}}{\hbar} \right) \tag{3.113}$$

This calculation simplifies if we use the identity:

$$\exp\left(i\vec{k}_f \cdot \vec{r}\right) = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} Y^*_{l,m}(\hat{k}_f) Y_{l,m}(\hat{r}) j_l(k_f r) \tag{3.114}$$

where $j_l(k_f r)$ is the spherical Bessel function of the first kind. Plugging this back into the transition rate per unit solid angle formula, we get:

$$\begin{aligned} \frac{dR}{d\Omega}(E_f \leftarrow E_{1s}) \approx & \frac{2\pi}{\hbar} \left(\frac{1}{2\pi}\right)^3 \left(\frac{p_f^2 dp_f}{dE_f} \right) \\ & \times \left| 4\pi \sum_{l,m} Y^*_{l,m}(\hat{k}_f) \, \langle Y_{l,m}(\hat{r}) j_l(k_f r)| \, \frac{eE_0 r \cos\theta}{2} \, |R_{1s}(r) Y_{0,0}\rangle \right|^2 . \end{aligned} \tag{3.115}$$

Since we know that $E_f = p_f^2/2m$, we can plug this into the equation above to get:

$$\frac{dR}{d\Omega}(E_f \leftarrow E_{1s}) \approx \frac{e^2E_0^2}{\hbar^4}m\hbar k_f\left|Y_{1,0}(\hat{k}_f)\right|^2\left[\int_0^\infty j_1(k_fr)rR_{1s}(r)r^2dr\right]^2 \tag{3.116}$$

which gives us a formula for the "*probability rate per unit solid angle subtended by some detector to detect a photon in direction $\hat{k}_f$*". From this, we can now ask, what is the cross-section which will give us a measure of the probability of emitted electrons into some solid angle given some incident flux of photons injected into the system. To do so, we consider the incoming flux incident on the H-atom by using the Poyting vector:

$$\begin{aligned}\langle S\rangle &= c\langle u\rangle \\ &= \frac{c}{2}\left[\frac{|E_0|^2}{8\pi}+\frac{|B_0|^2}{8\pi}\right]^2 = c\frac{|E_0|^2}{8\pi}\end{aligned} \tag{3.117}$$

The Pyonting vector gives us a measure of the power flux, so to get the photon number flux, we simply divide this by $\hbar\omega$, for the differential scattering cross-section is then:

$$\begin{aligned}\frac{d\sigma}{d\Omega} &= \frac{\hbar\omega}{\langle S\rangle}\times\frac{dR}{d\Omega}(E_f \leftarrow E_{1s}) \\ &= \frac{8\pi m\omega e^2}{\hbar^2c}k_f\left|Y_{1,0}(\hat{k}_f)\right|^2\left[\int_0^\infty j_1(k_fr)rR_{1s}(r)r^2dr\right]^2\end{aligned} \tag{3.118}$$

which works out indeed to have units of length-squared over radians if some dimensional analysis is performed.

A question we can now ask is, in what situations can we actually consider the Fermi's golden rule where the final energy density function is indeed a δ-function (as in what we saw when we first derived the Fermi's golden rule)? Well, one way of thinking about this is to first consider the full system of the perturbation and the zeroth order Hamiltonian (e.g. atom in a photon field). The state of this total system will then have to account for both the state of the zeroth-order system and the excitations of the perturbation (e.g. the tensor state of the atom and the photon field $|\text{atom}\rangle\otimes|\text{photon}\rangle$). The full formal way of doing this is by working with a *master equation* with a *Liouville superoperator*, however this is not in the scope of this course and what we are going to do is look at a simplified model. Recall that the first order transition amplitude for time-dependent harmonic fields derived earlier was given as:

$$c_f^{(1)} = -\frac{i}{\hbar}\int_0^t dt'e^{i(\omega_f-\omega_i)t'}e^{-i\omega t'}\langle f|\hat{V}|i\rangle \tag{3.119}$$

To consider a spontaneous emission process, we can possibly try adding some "damping" term in the above expression to give:

$$\begin{aligned}c_f^{(1)} &= -\frac{i}{\hbar}\int_0^t dt'e^{i(\omega_f-\omega_i)t'}e^{-i\omega t'}\langle f|\hat{V}|i\rangle e^{-\Gamma(t-t')} \\ \Rightarrow\quad c_f^{(1)} &= -\frac{i}{\hbar}\langle f|\hat{V}|i\rangle e^{-\Gamma t}\left[\frac{e^{i(\omega_f-\omega)t}e^{-\Gamma t}-1}{i(\omega_f-\omega)+\Gamma}\right]\end{aligned} \tag{3.120}$$

From here, if we take the limit where time goes to infinity, we see that we in fact get a probability that follows a Lorentzian:

$$\left|c_f^{(1)}\right|^2 = \frac{\left|\langle f|\,\hat{V}\,|i\rangle\right|^2}{\hbar} \times \frac{1}{(\omega_f - \omega)^2 + \Gamma^2} \tag{3.121}$$

This is **not** good since we want to retrieve a δ-function type behavior! The simplest means to fix this is by considering a classical picture of things. In classical mechanics, we have equations of motion (EOM), so let's try to model the probability via some EOM. Without spontaneous emission, we would have:

$$\frac{d\left|c_f^{(1)}\right|^2}{dt} = R\left(\left|c_i^{(1)}\right|^2 - \left|c_f^{(1)}\right|^2\right) \tag{3.122}$$

where R is short hand for $R_{f\leftarrow i}$. We can then try to add some damping term to the which will give a coupling between the initial and final states:

$$\begin{aligned} \frac{d\left|c_f^{(1)}\right|^2}{dt} &= R\left(\left|c_i^{(1)}\right|^2 - \left|c_f^{(1)}\right|^2\right) - 2\Gamma\left|c_f^{(1)}\right|^2 \\ \frac{d\left|c_i^{(1)}\right|^2}{dt} &= R\left(\left|c_f^{(1)}\right|^2 - \left|c_i^{(1)}\right|^2\right) - 2\Gamma\left|c_i^{(1)}\right|^2. \end{aligned} \tag{3.123}$$

We can then consider the point of *detailed balance* (stationary point where all "velocities" are zero) which gives:

$$\begin{aligned} (R + 2\Gamma)\left|c_f^{(1)}\right|^2 &= R\left|c_i^{(1)}\right|^2 \\ \Rightarrow \quad \left|c_f^{(1)}\right|^2 &= \frac{R\left|c_i^{(1)}\right|^2}{R + 2\Gamma}. \end{aligned} \tag{3.124}$$

Now we consider the limit where $\Gamma \ll R$, and plugging this back into the approximate solution we had for $\left|c_i^{(1)}\right|^2$, we get the rate:

$$R_{f\leftarrow i} \approx \frac{\left|\langle f|\,\hat{V}\,|i\rangle\right|^2}{\hbar} \times \frac{2\Gamma}{(\omega_f - \omega)^2 + \Gamma^2} \tag{3.125}$$

which in the limit where $\Gamma \to 0$, we indeed get:

$$\lim_{\Gamma\to 0} \frac{2\Gamma}{(\omega_f - \omega)^2 + \Gamma^2} = 2\pi\delta(\omega_f - \omega), \tag{3.126}$$

the Fermi's golden rule! Of course, this was a very hand-wavy way of doing things, so let's consider another approach to this, where we *adiabatically* tune the perturbation.

§3.4.3 The Wigner-Weisskopf Approximation

This more rigorous treatment that we are about to do is known as the *Wigner-Weisskopf approach* derived in 1930. What they did was to consider an extremely slowly varying perturbation:

$$\delta\hat{H}(t) = e^{\eta t}\hat{V} \tag{3.127}$$

where η is a very small parameter which we will later take the its limit to 0, such that there is a very slow and gradual growth of the time-independent potential $\hat{V}$. In general, $\hat{V}$ can in fact be time-dependent, we for now we simply set this as time-independent (so it is just a shift in the energy levels). From time-dependent perturbation theory, we have that in general:

$$\begin{aligned} & c_n^{(0)}(t) = 0 \\ & c_n^{(1)(t)} = -\frac{i}{\hbar}V_{n,i}\lim_{t_0\to-\infty}\int_{t_0}^{t} e^{i\omega_{n,i}t'}e^{\eta t'}\,dt' = -\frac{iV_{n,i}}{\hbar}\frac{e^{\eta t+i\omega_{n,i}t}}{\eta+i\omega_{n,i}} \\ \Rightarrow\quad & \left|c_n^{(1)}(t)\right|^2 = \frac{|V_{n,i}|^2}{\hbar^2}\frac{e^{2\eta t}}{\eta^2+\omega_{n,i}^2} \end{aligned} \tag{3.128}$$

If we now take the limit as $\eta\to 0$, we have:

$$\begin{aligned} \lim_{\eta\to 0} R_{n\leftarrow i} &= \frac{|V_{n,i}|^2}{\hbar^2}\lim_{\eta\to 0}\frac{2\eta e^{2\eta t}}{\eta^2+\omega_{n,i}^2} \\ &= \frac{2\pi|V_{n,i}|^2}{\hbar^2}\delta(\omega_{n,i}) \end{aligned} \tag{3.129}$$

which indeed gives us the form of Fermi's golden rule. In the $\hat{V}$ being time-independent case, we have the first-order energy correction as:

$$c_i^{(0)} = -\frac{iV_{i,i}}{\hbar}\lim_{t_0\to-\infty}\int_{t_0}^{t} e^{\eta t'}\,dt' = -\frac{iV_{ii}}{\hbar}\frac{e^{\eta t}}{\eta} \tag{3.130}$$

As for the second-order energy correction, we have:

$$\begin{aligned} c_i^{(2)} &= \left(-\frac{i}{\hbar}\right)^2\sum_m |V_{m,i}|^2\lim_{t_0\to-\infty}\int_{t_0}^{t} e^{i\omega_{i,m}t'+\eta t'}\,dt' \\ &= \left(-\frac{i}{\hbar}\right)^2\frac{|V_{i,i}|^2}{2\eta^2}e^{2\eta t} + \left(-\frac{i}{\hbar}\right)\sum_{m\neq 1}\frac{|V_{i,m}|^2 e^{2\eta t}}{2\eta(E_i-E_m+i\hbar\eta)} \end{aligned} \tag{3.131}$$

Now considering the time derivatives up to second-order, we have:

$$\begin{aligned} \frac{\dot{c}_i(t)}{c_i} &= \frac{-\frac{i}{\hbar}V_{i,i} + \left(-\frac{i}{\hbar}\right)^2\frac{V_{i,i}^2}{\eta} + \left(-\frac{i}{\hbar}\right)\sum_{m\neq i}\frac{|V_{mi}|^2}{E_i-E_m-i\hbar\eta}}{1-\frac{iV_{i,i}}{\hbar\eta}} \\ &\approx -\frac{i}{\hbar}V_{i,i} + \left(-\frac{i}{\hbar}\right)\sum_{m\neq i}\frac{|V_{m,i}|^2}{E_i-E_m-i\hbar\eta} \end{aligned} \tag{3.132}$$

So we see that the time derivative of the transition amplitude is being "corrected" by the decay parameter η. Then taking the limit $\eta \to 0$ and using contour integration, we are going to see that we have second order energy corrections with a real and imaginary part:

$$\lim_{\eta\to 0} E_i^{(2)} = P \sum_{m\neq i} \frac{|V_{m,i}|^2}{E_i - E_m} - i\pi \sum_{m\neq i} |v_{m,i}|^2 \delta(E_i - E_m) \tag{3.133}$$

where P is the Cauchy-principle value. Defining the above result as Δ_i and comparing this to the result in Fermi's golden rule, we have that:

$$\begin{aligned} \sum_{m\neq i} R_{m\leftarrow i} &= -\frac{2}{\hbar} \operatorname{Im}[\Delta_i] \\ \Rightarrow \quad c_i(t) &= e^{-\frac{i}{\hbar}\operatorname{Re}[\Delta_i]} e^{-\frac{\Gamma_i t}{2\hbar}} \quad \text{where} \quad \Gamma_i = 2\operatorname{Im}[\Delta_i] \end{aligned} \tag{3.134}$$

§3.5 The Adiabatic Approximation

Now, we will look to systems in which Hamiltonians vary with extreme time-dependence (extremely rapid and short-lived, or extremely slow and long-lived). In recent years, the study of *quench dynamics* have been of great interest. A quench is a very sudden change in the parameters in the Hamiltonian, where the notion of "sudden" is governed by some time-scale T such that:

$$\frac{1}{T} \gg \frac{E_n}{\hbar} = \omega_n. \tag{3.135}$$

That is, the time-scale is fast enough such that the Hamiltonian is unable to vary within that time-interval of the parameter change. The converse of such processes, is known as the *adiabatic approximation* whereby we vary the parameters in the Hamiltonian extremely slowly, such that the eigenstates transit adiabatically from the initial to the final Hamiltonian and entropy is conserved ($\Delta S = 0$). The condition for such a process is given by:

$$\frac{1}{T} \ll \omega_{a,b} \tag{3.136}$$

where the subscript denotes any relative energy splitting in the system $\omega_b - \omega_a$. This will be the extreme time-dependence of interest to us for the time being.

Firstly, a few considerations. In the adiabatic regime, conservation of entropy implies that there is also a conservation of the number of energy eigenstates by multiplicity considerations. This invokes the main statement of the adiabatic approximation (theorem).

The Adiabatic Theorem

Given a system that starts in an instantaneous energy eigenstate, it will remains in the same instantaneous eigenstate throughout the time-varying adiabatic process so long as the associated energy eigenvalue is gapped with respect to the rest of the spectrum.

An application of this is adiabatic quantum computing or *quantum annealing.* To formalize this, we first consider the initial system with energy eigenstates denoted by n:

$$\hat{H} |\psi_n\rangle = E_n |\psi_n\rangle \tag{3.137}$$

For time-independent Hamiltonians, we know that time-evolution is encoded as a phase associated with each eigenstate. Now if we turn-on time-dependence, we now assert that in the adiabatic limit, we have:

$$\hat{H}(t)\left|\psi_n(t)\right\rangle = E_n(t)\left|\psi_n(t)\right\rangle \tag{3.138}$$

where each of these *instantaneous eigenstates* are orthonormal (this is the assertion $\langle\psi_m(t)|\psi_n(t)\rangle = \delta_{m,n}$). Any linear combination of these eigenstates also have to be solutions of the time-depdendent Schrödinger equation, so we can write:

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\left|\psi(t)\right\rangle &= \hat{H}(t)\left|\psi(t)\right\rangle \\ \Rightarrow \quad \left|\psi(t)\right\rangle &= \sum_n c_n(t)e^{i\theta_n(t)}\left|\psi(t)\right\rangle \\ \text{where} \quad & \boxed{\theta_n(t) = -\frac{1}{\hbar}\int_0^t E_n(t')dt'}. \end{aligned} \tag{3.139}$$

The boxed quantity above is known as the *dynamical phase* in an adiabatic process. Plugging the solution back into the time-depdendent Schrödinger equation gives:

$$\sum_n \left[\dot{c}_n(t)e^{i\theta_n(t)}\left|\psi_n(t)\right\rangle + c_n(t)e^{i\theta_n(t)}\left|\dot{\psi}_n(t)\right\rangle + i\dot{\theta}_n(t)\left|\psi_n(t)\right\rangle\right] = \sum_n c_n(t)e^{i\theta_n(t)}\hat{H}(t)\left|\psi_n(t)\right\rangle. \tag{3.140}$$

Using the relation in equation (3.138), we can get that by construction:

$$\begin{aligned} \sum_n \dot{c}_n(t)e^{i\theta_n(t)}\left|\psi_n(t)\right\rangle &= \sum_n c_n(t)e^{i\theta_n(t)}\left|\dot{\psi}_n(t)\right\rangle \\ \Rightarrow \quad & \boxed{\dot{c}_m(t) = \sum_n c_n(t)e^{i[\theta_n(t)-\theta_m(t)]}\left\langle\psi_m(t)\middle|\dot{\psi}_n(t)\right\rangle} \end{aligned} \tag{3.141}$$

where the final expression is obtained by contraction with $\langle\psi_m(t)|$. Now, let's also consider taking the time-derivative of the equation (3.138) then contracting again with $\langle\psi_m(t)|$ which gives:

$$\begin{aligned} \dot{\hat{H}}(t)\left|\psi_n(t)\right\rangle + \hat{H}(t)\left|\dot{\psi}_n(t)\right\rangle &= \dot{E}_n(t)\left|\psi_n(t)\right\rangle + E_n(t)\left|\dot{\psi}_n(t)\right\rangle \\ \Rightarrow \quad & \boxed{\left\langle\psi_m(t)\right|\dot{\hat{H}}\left|\psi_n(t)\right\rangle = [E_n(t) - E_m(t)]\left\langle\psi_m(t)\middle|\dot{\psi}_n(t)\right\rangle} \end{aligned} \tag{3.142}$$

Comparing the 2 boxed equations above gives us that:

$$\dot{c}_m(t) = -c_m(t)\left\langle\psi_m(t)\middle|\dot{\psi}_m(t)\right\rangle - \sum_{n\neq m} c_n(t)\frac{\left\langle\psi_m(t)\right|\dot{\hat{H}}\left|\psi_n(t)\right\rangle}{E_n(t) - E_m(t)}e^{i[\theta_n(t)-\theta_m(t)]}. \tag{3.143}$$

The above derivation allows us to speak more rigorously and say that the adiabatic approximation is the approximation whereby we vary the Hamiltonian so slowly that we can ignore the second term in the expression for $\dot{c}_m$.

Note: We see that the size of the second term is highly dependent on $E_n(t) - E_m(t)$, which tells us that if we have a system whereby any of the energy gaps between 2 energy levels are very small, the process must proceed extremely slowly in order for us to adopt the adiabatic approximation.

If we ignore the second term, we simply have:

$$\begin{aligned} &\dot{c}_m(t) = -c_m(t)\left\langle \psi_m(t) \middle| \dot{\psi}_m(t) \right\rangle \\ \Rightarrow\quad &\frac{dc_m(t)}{c_m(t)} = -\left\langle \psi_m(t) \middle| \dot{\psi}_m(t) \right\rangle dt \\ \Rightarrow\quad &c_m(t) = c_m(0)e^{i\gamma_m(t)} \end{aligned} \tag{3.144}$$

where

$$\boxed{\gamma_m(t) \equiv i\int_0^t \left\langle \psi_m(t') \middle| \dot{\psi}_m(t') \right\rangle dt'}. \tag{3.145}$$

The quantity defined above is known as *Berry's phase* (a.k.a *geometrical phase*). From this, if the system starts with $c_n(0) = 1$ and $c_{m\neq n}(0) = 0$ (a particular instantaneous eigenstate), then we have that the instantaneous eigenstate of the system at time t can be written as:

$$\begin{gathered} \boxed{|\psi(t)\rangle = \exp\Big(i\theta_n(t)\Big)\exp\Big(i\gamma_n(t)\Big)\,|\psi_n(t)\rangle} \\ \text{where}\quad \theta_n(t) = -\frac{1}{\hbar}\int_0^t E_n(t')dt', \quad \gamma_m(t) = i\int_0^t \left\langle \psi_m(t') \middle| \dot{\psi}_m(t') \right\rangle dt' \end{gathered} \tag{3.146}$$

telling us that any instantaneous eigenstates under adiabatic time-evolution evolves **only** by a (dynamical and Berry) phase.

Example:

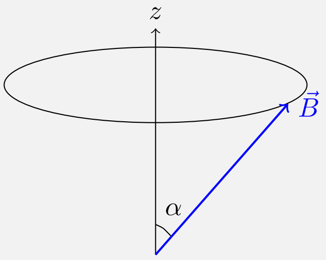

Figure 3.4: Precessing magnetic field about the z-axis.

We are now going try and understand better the notions of the geometric and Berry's phase by means of an example. Consider a spin-1/2 particle in a precessing magnetic field:

$$\vec{B}(t) = B_0 \begin{bmatrix} \sin\alpha\cos(\omega t) \\ \sin\alpha\sin(\omega t) \\ \cos\alpha \end{bmatrix} \tag{3.147}$$

which gives us the Hamiltonian:

$$\hat{H} = -\hat{\vec{\mu}} \cdot \vec{B}(t) \tag{3.148}$$

which grants us that the magnetic field precesses about the $\hat{z}$-axis as shown in figure 3.4. As such, we have the Hamiltonian written explicitly as:

$$\begin{aligned} \hat{H} &= \frac{e\hbar B_0}{2m}\left(b_x\hat{\sigma}_x + b_y\hat{\sigma}_y + b_z\hat{\sigma}_z\right) \\ &= \frac{\hbar\omega_I}{2}\begin{bmatrix} \cos\alpha & e^{-i\omega t}\sin\alpha \\ e^{i\omega t}\sin\alpha & -\cos\alpha \end{bmatrix} \end{aligned} \tag{3.149}$$

where $\omega_I = eB_0/m$ and I denotes "instantaneous". From here, we can in fact obtain the instaneous eigenstates of the system in the adiabatic approximation by applying a rotation into the rotating frame of the magnetic field:

$$\mathscr{D}(\alpha;\omega) = \exp\left(-\frac{i\hat{\sigma}_z\omega t}{2}\right)\exp\left(-\frac{i\hat{\sigma}_y\alpha}{2}\right). \tag{3.150}$$

Applying this to the spin-z eigenstates gives us:

$$\mathscr{D}(\alpha;\omega)\left|\uparrow\right\rangle = \begin{bmatrix} \cos(\alpha/2) \\ e^{i\omega t}\sin(\alpha/2) \end{bmatrix} \equiv \chi_\uparrow(t) \tag{3.151}$$

$$\mathscr{D}(\alpha;\omega)\left|\downarrow\right\rangle = \begin{bmatrix} e^{-i\omega t}\sin(\alpha/2) \\ -\cos(\alpha/2) \end{bmatrix} \equiv \chi_\downarrow(t) \tag{3.152}$$

which will give us that the instantaneous eigen-energies of this system as:

$$E_\pm^{(I)}(t) \pm \frac{\hbar\omega_I}{2} \tag{3.153}$$

$$\Rightarrow \quad \theta(t) = -\frac{1}{\hbar}\int_0^t \frac{\hbar\omega_I}{2}dt' = -\frac{\omega_I t}{2} \tag{3.154}$$

where as a reminder, $\theta(t)$ is the dynamical phase. Having computed the dynamical phase, we can also compute Berry's phase as:

$$\begin{aligned} \dot{\chi}_\uparrow(t) &= \begin{bmatrix} 0 \\ i\omega e^{i\omega t}\sin(\alpha/2) \end{bmatrix} \\ \Rightarrow \quad \gamma_\uparrow(t) &= i\int_0^t \left[\cos\left(\frac{\alpha}{2}\right),\ e^{i\omega t'}\sin\left(\frac{\alpha}{2}\right)\right]\begin{bmatrix} 0 \\ i\omega e^{i\omega t'}\sin(\alpha/2) \end{bmatrix}dt' = -\frac{\omega t}{2}\left[1-\cos(\alpha)\right]. \end{aligned} \tag{3.155}$$

If we consider just one period of precession ($t = 2\pi/\omega$), the Berry's phase is then:

$$\gamma_\uparrow = -\pi\left[1-\cos(\alpha)\right] = -\frac{1}{2}\Omega_\alpha \tag{3.156}$$

where Ω_α is the solid angle traced out by the precession. This link between geometry and the Berry's phase is subtle but significant and will be touched on next.

Of course, we expect that this result holds well in the regime where $\omega_I \gg \omega$ (the rate of precession of the magnetic field is much slower that the intrinsic energy scaling of the system, therefore can be taken as adiabatic) and would fail otherwise.

§3.5.1 Berry's Phase and Configuration Space

We are now going to see an interesting difference between the dynamical and the Berry's phase. To first say what this is, it turns out that the dynamical phase will continuously and increasingly vary with the duration of the adiabatic process, whereas Berry's phase only cares about the geometry of the "path" traversed but not how long it took.

What is this "path" you ask? Well to understand this, we first need to introduce the notion of *configuration space*. In general, we can consider a Hamiltonian that has a set of parameters $\{R_j\}$, which we can group into a vector $\vec{R} \in \mathbb{R}^N$ such that:

$$\hat{H} = \hat{H}(\vec{R}), \tag{3.157}$$

which allows us to write:

$$\hat{H}(\vec{R}) \left| \psi_n(\vec{R}) \right\rangle = E_n(\vec{R}) \left| \psi_n(\vec{R}) \right\rangle . \tag{3.158}$$

These parameters can in general be time-dependent $\vec{R} = \vec{R}(t)$, which then allows us to define the configuration space with axes labelled by R_j, and a trajectory in this space defined by the path $\vec{R}(t)$. An illustration of this for a Hamiltonian with 2 parameters $\{R_1, R_2\}$ is given in figure 3.5 below.

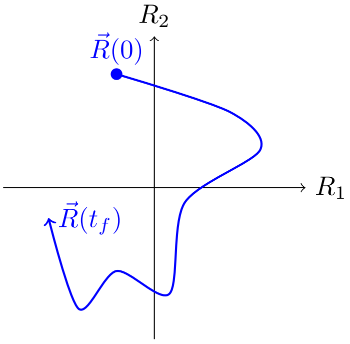

Figure 3.5: Trajectory in configuration space $\vec{R} \in \mathbb{R}^2$.

Imbuing the parameters with time-dependence also causes the Hamiltonian to be time-dependent. The states on the other hand, can have derivatives:

$$\frac{\partial}{\partial t} \left| \psi_n(\vec{R}) \right\rangle = \sum_j \frac{\partial R_j}{\partial t} \frac{\partial}{\partial R_j} \left| \psi_n(\vec{R}) \right\rangle . \tag{3.159}$$

So the Berry's phase for such a system will be written as:

$$\boxed{\gamma_m \equiv i \int_{\vec{R}(0)}^{\vec{R}(t)} \left\langle \psi_m(\vec{R}) \right| \boldsymbol{\nabla}_{\vec{R}} \left| \psi_m(\vec{R}) \right\rangle \cdot d\vec{R}}, \tag{3.160}$$

which allows us to think of this integral as occurring over the trajectory in configuration space! This is why Berry's phase is not duration-dependent, but only concerned with the path traversed in configuration space (time plays no role). The integrand of the Berry phase is commonly referred to as the *Berry connection*:

$$\vec{A}_n(\vec{R}) = i \left\langle \psi_m(\vec{R}) \right| \boldsymbol{\nabla}_{\vec{R}} \left| \psi_m(\vec{R}) \right\rangle . \tag{3.161}$$

What is an interesting and in fact necessary result for the measurement of the Berry's phase, is that for such time-varying adiabatic systems, even if the Hamiltonian returns to its original configuration (trajectory in configuration space is closed), we have that the Berry phase in fact does not necessarily vanish:

$$\gamma_m(t) \equiv i \oint \langle \psi_m(t') | \boldsymbol{\nabla}_{\vec{R}} | \psi_m(t') \rangle \cdot d\vec{R} \neq 0. \tag{3.162}$$

To see why this is necessary, we need to think about gauge invariances. We can work out that the Berry connection in fact transforms as a vector potential under gauge transformations of:

$$\begin{aligned} \left| \psi_n(\vec{R} \right\rangle &\to \exp\Big(-i\beta(\vec{R})\Big) \left| \psi_n(\vec{R} \right\rangle \\ \Rightarrow \quad \vec{A}_n\vec{R} \quad &\to \quad \vec{A}_n\vec{R} + \boldsymbol{\nabla}_{\vec{R}}\beta(\vec{R}) \end{aligned} \tag{3.163}$$

where $\beta(\vec{R}) \in \mathbb{R}$.

Note: The transformation is a gauge transformation as it does not affect the Hamiltonian evolution of the system. That is:

$$\hat{H}(\vec{R})e^{-i\beta(\vec{R})} \left| \psi_n(\vec{R}) \right\rangle = \hat{H}(\vec{R})e^{-i\beta(\vec{R})} \left| \psi_n(\vec{R}) \right\rangle e^{-i\beta(\vec{R})} \hat{H}(\vec{R}) \left| \psi_n(\vec{R}) \right\rangle \tag{3.164}$$

i.e. these instantaneously eigenstates have a gauge degree of freedom in configuration space.

However, the Berry phase itself is **not** gauge invariant since for a given path in configuration space between 2 points $\vec{R}_0$ and $\vec{R}_f$, we have:

$$\begin{aligned} \tilde{\gamma}_n &= \int_{\vec{R}_0}^{\vec{R}_f} \left[\vec{A}_n(\vec{R}) + \boldsymbol{\nabla}_{\vec{R}}\beta(\vec{R}) \right] \cdot d\vec{R} \\ &= \gamma_n + \beta(\vec{R}_f) - \beta(\vec{R}_0) \end{aligned} \tag{3.165}$$

where $\tilde{\gamma}_n$ is the gauge transformed Berry phase. The lack of gauge invariance implies that it **cannot** be measured in an experiment (since measurable quantities cannot be gauge dependent)! However, if the configuration space trajectory is closed, then we indeed have:

$$\tilde{\gamma}_n = \gamma_n \tag{3.166}$$

which makes the Berry phase physically present and measurable.

Comment:

In the special case where $\vec{R} \in \mathbb{R}^3$, it works out that the Berry connection is analogous to the magnetic vector potential $\vec{A}_B$ in classical electrodynamics. Recall, that for a current that flows through a closed path Γ, we have that the magnetic flux Φ_B through the surface of that closed path is given by:

$$\Phi_B = \oint_\Gamma \vec{A}_B \cdot d\vec{\Gamma}. \tag{3.167}$$

By Stoke's theorem, the above equation becomes:

$$\Phi_B = \iint_S (\boldsymbol{\nabla} \times \vec{A}_B) \cdot d\vec{a} = \iint_S \vec{B} \cdot d\vec{a}. \tag{3.168}$$

So indeed by analogy, we have that the Berry phase is the flux associated to the curl of the Berry connection through the area defined by a closed trajectory in configuration space.

Using the result of equation (3.160) that Berry phase is related to the gradient of the wavefunction in configuration space, let us go back and try to apply this to the example of the precessing magnetic field we had earlier. Since we are working in spherical coordinates, we note that the gradient operator in spherical variables is given as:

$$\boldsymbol{\nabla}_{\vec{r}} = \hat{r}\frac{\partial}{\partial r} + \hat{\theta}\frac{1}{r}\frac{\partial}{\partial \theta} + \hat{\phi}\frac{1}{r\sin\theta}\frac{\partial}{\partial \phi}. \tag{3.169}$$

Applying this to the spinor wavefunction and taking the overlap of this with the spinor wavefunction, it can be shown that we have:

$$\langle \chi | \boldsymbol{\nabla}_{\vec{r}} | \chi \rangle = \frac{i\sin^2(\theta/2)}{r\sin\theta}. \tag{3.170}$$

Since we are indeed working with the special case that the configuration space **is** $\mathbb{R}^3$ (as the comment above states), then we can find the Berry phase by taking the curl of the Berry connection which gives:

$$\begin{aligned} \boldsymbol{\nabla}_{\vec{r}} \times \langle \chi | \boldsymbol{\nabla}_{\vec{r}} | \chi \rangle &= \frac{i}{2r^2}\hat{r} \\ \Rightarrow \quad \gamma &= -\int \left(\frac{1}{2r^2}\right) \hat{r} \cdot d\vec{a} \\ &= -\int \left(\frac{1}{2r^2}\right) \hat{r} \cdot r^2 d\Omega_\alpha \hat{r} = -\frac{\Omega_\alpha}{2} \end{aligned} \tag{3.171}$$

which agrees exactly with what we had before. More details of this problem can be found in Griffiths chapter 10. In fact, the result above can be generalized to an arbitrary spin s particle in a precessing magnetic field to get the result:

$$\boxed{\gamma = -s\Omega} \tag{3.172}$$

again with Ω being the solid angle of precession and s being the particle spin.

§3.5.2 The Aharanov-Bohm Effect

The *Aharanov-Bohm effect* is the result of an experiment conceptualized in 1959, for which we saw a treatment of last semester when we were considering the path integral formulation of quantum mechanics. However, we will now look at this phenomenon using the tools from Berry phases. Recall that in classical electromagnetism, we are concerned with electric and magnetic fields from which we can take these as our physical quantities of interest (scalar and vector potentials are not too much of our concern since they are not directly measurable). However, when we do consider these scalar and vector potentials:

$$\vec{E} = -\boldsymbol{\nabla}\Phi - \frac{\partial \vec{A}}{\partial}, \quad \vec{B} = \boldsymbol{\nabla} \times \vec{A}, \tag{3.173}$$

there are some transformations we can perform on these potentials (fields) that leave the electric and magnetic fields (and hence Maxwell's equations) invariant. These are known as *gauge transformations* (already introduced in the section on Berry phases above):

$$\begin{aligned} \Phi \quad &\to \quad \Phi' = \Phi - \frac{\partial \Lambda}{\partial t} \\ \vec{A} \quad &\to \quad \vec{A}' = \vec{A} + \boldsymbol{\nabla}\Lambda \end{aligned} \tag{3.174}$$

Because these transformations leave the electric and magnetic fields unscathed, the physics will also be invariant under them. This however, is not the case in quantum mechanics. In quantum mechanics, it turns out that gauge transformations of the scalar and vector potentials result in a phase $\exp(iq\Lambda/\hbar)$ which can in fact be measured. As such, the vector and scalar potentials are in fact measurables which the Aharanov-Bohm effect will elucidate. In quantum mechanics, we are concerned with the Hamiltonian for which given an external electromagnetic field, it takes the form:

$$\hat{H} = \frac{1}{2m}\left(\frac{\hbar}{i}\boldsymbol{\nabla} - q\vec{A}\right)^2 + q\Phi. \tag{3.175}$$

The set-up of the experiment is as follows. Consider an infinitely long ideal solenoid of radius a with current I flowing through it. This would result in the production of a uniform magnetic field within the coil, but no field outside the coil. For this problem, we are going to pick the Coulomb gauge which is defined as:

$$\boldsymbol{\nabla} \cdot \vec{A} = 0. \tag{3.176}$$

Now consider the magnetic vector potential, we are going to have that outside the solenoid $(r > a)$:

$$\begin{aligned} \vec{A} &= \frac{\Phi_B}{2\pi r}\hat{\phi} \\ \text{where} \quad \Phi_B &= \pi a^2 B \end{aligned} \tag{3.177}$$

where Φ_B is the magnetic flux. Now consider a particle confined to move in a circle of radius $b > a$ around the solenoid in the Azimuthal plane. The Hamiltonian for this particle would thus be:

$$\begin{aligned}
\hat{H} &= \frac{1}{2m}\left[-\hbar^2\boldsymbol{\nabla}^2 + q^2\vec{A}^2 + 2i\hbar q\vec{A}\cdot\boldsymbol{\nabla}\right] \\
&= \frac{1}{2m}\left[-\frac{\hbar^2}{b^2}\frac{\partial^2}{\partial\phi^2} + \left(\frac{q\Phi_B}{2\pi b}\right)^2 + 2i\hbar q\left(\frac{\Phi_B}{2\pi b}\frac{1}{b}\frac{\partial}{\partial\phi}\right)\right] \\
\Rightarrow \quad \frac{1}{2m}&\left[-\frac{\hbar^2}{b^2}\frac{\partial^2}{\partial\phi^2} + \frac{i\hbar\Phi_B}{2\pi b^2}\frac{\partial}{\partial\phi} + \left(\frac{q\Phi_B}{2\pi b}\right)^2\right]\psi = E\psi
\end{aligned} \tag{3.178}$$

We can solve the differential equation above with the boundary conditions that $\psi(\phi) = \psi(\phi + 2\pi)$ to get:

$$\psi = C\exp\left(i\lambda_n\phi\right), \quad n \in \mathbb{Z} \tag{3.179}$$

$$\Rightarrow \quad E_n = \frac{\hbar^2}{2mb^2}\left[n - \frac{q\Phi_B}{2\pi\hbar}\right]^2, \tag{3.180}$$

which shows that the energy of this particle indeed depends on the magnetic field even though there should not be any magnetic field outside the solenoid! If we didn't want to solve the differential equation in its full glory above as we did, we can try to find an ansatz that might simplify our lives. In particular, we want to find an ansatz that removes the vector potential from the Schrödinger's equation. Harkening back to the Berry phase, we recall again the analogy of the Berry connection and the vector potential. As such, we attempt an ansatz of the form:

$$\begin{aligned}
\psi &= e^{ig(\vec{r})}\tilde{\psi} \\
\text{where} \quad g(\vec{r}) &\equiv \frac{q}{\hbar}\int_0^{\vec{r}} \vec{A}(\vec{r})\cdot d\vec{r}.
\end{aligned} \tag{3.181}$$

We notice that taking the gradient of this ansatz gives:

$$\begin{aligned}
\boldsymbol{\nabla}_{\vec{r}}\psi &= i\left[\boldsymbol{\nabla}_{\vec{r}}g(\vec{r})\right]\psi + e^{ig(\vec{r})}\boldsymbol{\nabla}_{\vec{r}}\tilde{\psi} \\
\Rightarrow \quad \left(\frac{\hbar}{i}\boldsymbol{\nabla} - q\vec{A}\right)\psi &= \frac{\hbar}{i}e^{ig(\vec{r})}\boldsymbol{\nabla}_{\vec{r}}\tilde{\psi} \\
\Rightarrow \quad \left(\frac{\hbar}{i}\boldsymbol{\nabla} - q\vec{A}\right)^2\psi &= -\hbar^2 e^{ig(\vec{r})}\boldsymbol{\nabla}^2_{\vec{r}}\tilde{\psi}.
\end{aligned} \tag{3.182}$$

The relations above allows us then to just solve the standard Schrödinger's equation we are familiar with:

$$i\hbar\frac{\partial}{\partial t}\tilde{\psi} = -\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2\tilde{\psi} + V\tilde{\psi} \tag{3.183}$$

where the $\vec{r}$ subscript on the gradient operator is dropped since it is unambiguous in this context. If we can assert such an ansatz, how then are these vector potential dependent phases detected? The idea behind this is by considering the 2 different paths across the solenoid as show in figure 3.6 below.

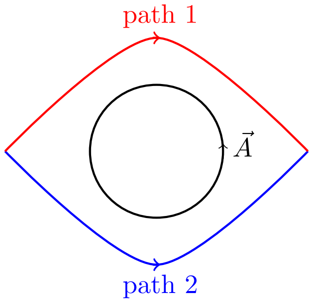

Figure 3.6: The Aharanov-Bohm effect. The paths we want to consider are in fact semicircular arcs despite the illustration above (that is a little more artistic).

Now let's consider the phases accumulated in each path, which we take to be arcs of a circle of some radius $R > b$ for simplicity.

1. Path 1:

   The phase is given by:

$$\begin{aligned} g_1(\vec{r}) &= \frac{q}{\hbar}\int \vec{A}\cdot d\vec{r} \\ &= \frac{q}{\hbar}\int_{\pi}^{2\pi} \frac{\Phi_B}{2\pi R}\hat{\phi}\cdot R d\phi\left(-\hat{\phi}\right) = -\frac{q\Phi_B}{2\pi\hbar}; \end{aligned} \tag{3.184}$$

2. Path 2:

   The phase is given by:

$$\begin{aligned} g_2(\vec{r}) &= \frac{q}{\hbar}\int \vec{A}\cdot d\vec{r} \\ &= \frac{q}{\hbar}\int_{\pi}^{2\pi} \frac{\Phi_B}{2\pi R}\hat{\phi}\cdot R d\phi\hat{\phi} = \frac{q\Phi_B}{2\pi\hbar}. \end{aligned} \tag{3.185}$$

If after traversing these paths, we allow the particles to interfere, we will see an interference pattern due to the phase difference:

$$\boxed{g_2(\vec{r}) - g_1(\vec{r}) = \frac{q\Phi_B}{\pi\hbar}}, \tag{3.186}$$

which indeed admits a means to measure the phase and thus the vector potential effects.

§3.5.3 Synthetic Gauge Fields

In the field of cold atoms, it is possible to engineer systems of neutral particles such they behave as if they were charged and respond to an externally applied magnetic field. Such engineered systems are known as *synthetic gauge fields*. One of the means to do this is via rotating traps and the use of the Coriolis force. Consider a rotating trap with angular frequency:

$$\vec{\Omega}_{\text{rot}} = \Omega_{\text{rot}}\hat{e}_z. \tag{3.187}$$

Recall that given a rotating system, we can move into the rotating frame via the operator:

$$\hat{R}_z = \exp\left(-\frac{i\vec{\Omega}_{\text{rot}} \cdot \hat{\vec{L}}t}{\hbar}\right) \tag{3.188}$$

where $\hat{\vec{L}}$ is the angular momentum vector-operator. In this frame, we consider the "rotated" wavefunction:

$$\left|\tilde{\psi}\right\rangle = \hat{R}_z^\dagger \left|\psi\right\rangle, \tag{3.189}$$

such that we can construct a Hamiltonian in the rotating-frame which works out to be:

$$\begin{aligned} \hat{\tilde{H}} &= \hat{R}_z^\dagger \hat{H} \hat{R}_z + i\hbar\left(\frac{\partial \hat{R}_z^\dagger}{\partial t}\right)\hat{R}_z \\ &= \left[\frac{\hat{p}^2}{2m} + V(\hat{r})\right] + \vec{\Omega}_{\text{rot}} \cdot \hat{\vec{L}} \\ &= \frac{\left(\vec{p} - \vec{A}\right)^2}{2m} + V(\hat{r}) + W_{\text{rot}}(\vec{r}) \end{aligned} \tag{3.190}$$

where

$$\vec{A} \equiv -m\left(\vec{\Omega}_{\text{rot}} \times \hat{\vec{r}}\right), \quad W_{\text{rot}}(\vec{r}) = -\frac{A^2}{2m}. \tag{3.191}$$

So we see that we have effectively introduced a vector potential-like term to the momentum which mimics the Hamiltonian of a charged particle in a magnetic field! However, this method is constrained by the fact that the frequency of rotation cannot be too large such that the particle is no longer confined in the trap (rotation overcomes the trapping potential).

A way to get around this issue but still achieve a synthetic gauge field is by the use of *optical lattices*. Optical lattices are optically generated potential wells that are periodic in space created by standing wave laser beams. The synthetic gauge field is then engineered in these systems as follows. First consider an optical lattice with singlular trapped atoms in each lattice site. The system is then cooled such that the trapped atoms occupy the motional groundstate at the bottom of each optical lattice site. The optical lattice is constructed such that tunneling of the atoms between sites is allowed (the tunneling rate is set by the overlap of the wavefunctions between lattice sites). We can effectively consider the 2 lowest internal states, for which we irradiated the atoms with lasers to excite the second state. The lasers have a detuning from the transition gap by δ and Rabi frequency Ω. The incidence of the laser results in 2 effects:

1. A "kick" in the momentum from $p \to \tilde{p} = p + \hbar k_{\text{photon}}$;
2. An internal state transition $\left|\downarrow\right\rangle \to \left|\uparrow\right\rangle$.

As such, we can consider the basis denoted by $\left|p; s\right\rangle$ where p is the momentum of the atom and $s \in \{\uparrow, \downarrow\}$. We can then write the Hamiltonian as:

$$\hat{H} = \frac{\hat{\tilde{p}}^2}{2m^*}\left|\uparrow\right\rangle\left\langle\uparrow\right| + \frac{\hat{p}^2}{2m^*}\left|\downarrow\right\rangle\left\langle\downarrow\right| + \frac{\delta}{2}\hat{\sigma}_z + \frac{\Omega}{2}\Big(\left|\tilde{p};\uparrow\right\rangle\left\langle p;\downarrow\right| + \left|p;\downarrow\right\rangle\left\langle\tilde{p};\uparrow\right|\Big) \tag{3.192}$$

where m^* is the effective optical lattice mass and the term $|\tilde{p};\uparrow\rangle\langle p;\downarrow|$ is responsible for a transition from the $|p;\downarrow\rangle$ state to the $|\tilde{p};\uparrow\rangle$ state. We can make a change of variable such that the Hamiltonian is now diagonal and written as:

$$\begin{aligned}
\hat{H} &= \frac{\hat{\tilde{p}}^2}{2m^*}|\uparrow\rangle\langle\uparrow| + \frac{\left(\hat{\tilde{p}} - \hbar k\right)^2}{2m^*}|\downarrow\rangle\langle\downarrow| + \frac{\delta}{2}\hat{\sigma}_z + \frac{\Omega}{2}\Big(|\tilde{p};\uparrow\rangle\langle\tilde{p};\downarrow| + |p;\downarrow\rangle\langle\tilde{p};\uparrow|\Big) \\
&= |\tilde{p}\rangle\langle\tilde{p}|\left[\hat{\mathbb{I}}E_{\tilde{p}} + \frac{\hat{\sigma}_z}{2}\left(\delta + \Delta E_{\tilde{p}}\right) + \frac{\hat{\sigma}_x}{2}\Omega\right] \qquad (3.193) \\
\text{where} \quad E_{\tilde{p}} &\equiv \frac{1}{2}\left(\frac{(\tilde{p}+\hbar k)^2}{2m^*} + \frac{\tilde{p}^2}{2m^*}\right), \quad \Delta E_{\tilde{p}} \equiv \left(\frac{(\tilde{p}+\hbar k)^2}{2m^*} - \frac{\tilde{p}^2}{2m^*}\right)
\end{aligned}$$

where we now drop the subscript on k_{photon} as there is no ambiguity. We are now going to treat the spin-degree of freedom as a synthetic spatial dimension which allows the visualization in figure 3.7.

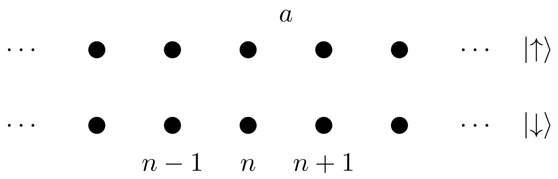

Figure 3.7: Synthetic flux ladder with the black filled circles denoting the atoms in each lattice site. a is the spacing between lattice sites and n is the lattice site index.

With this, we can consider a 4-step process:

1. An atom absorbs a photon and transits from the $|\downarrow\rangle$ to the $|\uparrow\rangle$. This process accumulates a phase $e^{i\phi} = e^{ik(na)}$;
2. the $|\uparrow\rangle$ atoms tunnels from its current site n to site $n+1$. This process does not accumulate a phase;
3. the $|\uparrow\rangle$ atoms then emits a photon and transits back down to the $|\downarrow\rangle$ state. This process also accumulates the phase $e^{-i(\phi+ka)}$;
4. the atom then tunnels back to site n from site $n+1$.

These steps form a closed-loop in the synthetic flux ladder picture in 3.7 but still results in an overall phase $\phi - (\phi + ka) = -ka$, being picked up which can be taken as the Berry phase. Recall that the gauge field phase we saw in the Aharnov-Bohm effect is given by:

$$\begin{aligned}
g &= \frac{q}{\hbar}\oint \vec{A}\cdot d\vec{r} = \frac{q\Phi_{\text{synth}}}{\hbar} \\
\Rightarrow \quad \frac{q\Phi_{\text{synth}}}{\hbar} &= -ka \qquad (3.194) \\
\Rightarrow \quad \Phi_{\text{synth}} &= \frac{\hbar(-ka)}{q}.
\end{aligned}$$

If we then take Φ_{synth} as effectively being a magnetic flux, we have $\Phi_{\text{synth}} = BA = Ba^2$ which evaluates to:

$$B = \frac{\Phi_{\text{synth}}}{a^2} \approx 1000 \text{ [T]}. \tag{3.195}$$

A magnetic field of 1000 Tesla is effectively impossible to achieve in a lab, so this method of engineering a synthetic gauge field allows for the effective application of an extremely strong magnetic field.

Chapter 4

Quantum Scattering

The study of scattering theory aims to create a formalism to extract the structure about an object known as the scatterer, by scattering other objects on it and observing the products (outgoing objects) of this process. Furthermore, understanding scattering processes often in many-body systems will also allow us to better understand and predict the behavior and dynamics of such systems. We will be starting our discussion with the Lippman-Schwinger equation to formally understand the formalism of things. This is in general difficult to solve exactly, so we will be looking at perturbative and low-energy approaches such as the Born approximation to tackle these problems.

§4.1 Formal Scattering Theory

The starting point here is by considering a Hamiltonian made up of 2 "pieces". The first being the free-particle Hamiltonian and the other a potential term that represents the scatterer which serves to "modify" the plane wave.

$$\hat{H} = \frac{\hat{p}^2}{2\mu} + \hat{V} \equiv \hat{H}_0 + \hat{V} \tag{4.1}$$

where $\mu = m_1 m_2/(m_1 + m_2)$ is the reduced mass. We use the reduced mass because more often than not, moving to the center of mass frame for a scattering process is often easiest for us to perform an analysis of the physics. We are going to assume several things about $\hat{V}$ to simplify the analysis.

1. $\hat{V}$ is time-independent;
2. $\hat{V}$ is short-ranged, that is there is a radius r_0 beyond which we can effectively treat the potential as zero (e.g. Lennard-Jones potential).

Now, the goal is then to solve the time-independent Schödinger's equation:

$$\left(\hat{H}_0 + \hat{V}\right) |\psi\rangle = E |\psi\rangle , \tag{4.2}$$

for which we can recast this problem into one for which we solve for a Greens operator $\hat{G}$ (analogous to the Greens function in operator space) by considering:

$$\begin{aligned} &\left(\hat{H}_0 - E\right)|\psi\rangle = -\hat{V}|\psi\rangle \\ \Rightarrow\quad &\left(\hat{H}_0 - E\right)\hat{G} = -\hat{\mathbb{I}} \\ \Rightarrow\quad &\hat{G} = \left(E - \hat{H}_0\right)^{-1}. \end{aligned} \tag{4.3}$$

Solving for the Greens operator will allow us to construct solutions of the form:

$$|\psi\rangle = |\phi\rangle + \hat{G}\hat{V}|\psi\rangle \tag{4.4}$$

where $|\phi\rangle$ is an arbitrary solution of the homogeneous system $(\hat{H}_0 - E)|\phi\rangle = 0$ (free-particle solutions). Let's now work in the position basis. Inserting the resolution of the identity over position states to the Greens operator solution gives us:

$$\langle x|\psi\rangle = \langle x|\phi\rangle + \int d^3x' \int d^3x'' \langle x|\hat{G}|x'\rangle \langle x'|\hat{V}|x''\rangle \langle x''|\psi\rangle \tag{4.5}$$

where $G(x,x') \equiv \langle x|\hat{G}|x'\rangle$ is the usual Greens function we are familiar with and we often make the approximation:

$$\langle x'|\hat{V}|x''\rangle \approx V(\vec{x}\,')\delta(\vec{x}\,' - \vec{x}\,'') \tag{4.6}$$

to simplify things. The key result is then that for a local (finite-range) potential, we have:

$$\boxed{\psi_E(x) = \phi_E(x) + \int d^3x' G_E(x,x')V(x')\psi_E(x')}, \tag{4.7}$$

which is a reformulation of the Schrödinger's equation as an integral equation known as the *Lippman-Schwinger equation.* This equation however, is not too well defined since the Greens function has singularities by its construction in equation (4.3). To resolve this issue and construct Greens functions that are unique, a trick from complex analysis is used which adds a small imaginary term which we set to 0 at the end of the calculation. That is, we take:

$$E \quad\to\quad E \pm i\varepsilon \tag{4.8}$$

where $\varepsilon > 0$ and then later take the limit as $\varepsilon \to 0$. With this added term, we now have the Greens operator as:

$$\hat{G}^{(\pm)} = \left(E - \hat{H}_0 \pm i\varepsilon\right)^{-1}. \tag{4.9}$$

From here, we are now going to try to derive solutions to the Greens function in the position representation. To do this, we are going to again insert the resolution of the identity but now in the momentum basis since we note that eigenstates of $\hat{H}_0$ are indeed momentum eigenstates:

$$\begin{aligned} G^{(\pm)}(x,x') &= \int d^3p \int d^3p' \langle x|p\rangle \langle p| \left(E - \hat{H}_0 \pm i\varepsilon\right)^{-1} |p'\rangle \langle p'|x'\rangle \\ &= \int \frac{d^3p}{(2\pi\hbar)^3} \left[\frac{\exp\left(\frac{i\vec{p}\cdot(\vec{x}-\vec{x}\,')}{\hbar}\right)}{E - p^2/(2m) \pm i\varepsilon}\right]. \end{aligned} \tag{4.10}$$

Doing a change of variables using the relation $\vec{p} = \hbar\vec{k}$ and defining $\vec{R} \equiv \vec{x} - \vec{x}\,'$, we get:

$$\begin{aligned}
G^{(\pm)}(x, x') &= \frac{1}{(2\pi)^3}\int d\Omega_{k'}\int (k')^2 dk' \left[\frac{\exp\left(ik'R\cos\theta_{k'}\right)}{\frac{\hbar^2 k^2}{2\mu} - \frac{\hbar^2 (k')^2}{2\mu} \pm i\varepsilon}\right] \\
&= \frac{2\mu}{(2\pi\hbar)^2}\left(\frac{1}{iR}\right)\int_0^\infty \frac{k'\left(e^{ik'R} - e^{-ik'R}\right)dk'}{k^2 - (k')^2 \pm i\varepsilon} \\
&= \frac{1}{4\pi^2}\left(\frac{2\mu}{\hbar^2}\right)\frac{1}{iR}\int_{-\infty}^{\infty}\frac{k' e^{ik'R} dk'}{k^2 - (k')^2 \pm i\varepsilon}.
\end{aligned} \tag{4.11}$$

From here, we use the residual theorem with contour integration from complex analysis to get the result:

$$\boxed{G^{(\pm)}(x, x') = -\frac{2\mu}{\hbar^2}\left(\frac{e^{\pm ik|x-x'|}}{4\pi|x - x'|}\right)}, \tag{4.12}$$

where the ± implies that the waves are either incoming (−) or outgoing (+). To be clear, the Greens function we have derived is a solution to the equation:

$$\left(-\frac{\hbar^2}{2\mu}\boldsymbol{\nabla}^2 - E\right)G(x, x') = -\delta(x - x'). \tag{4.13}$$

Plugging this into the Lippman-Schwinger equation for an incoming plane wave gives us:

$$\psi(x) = A\left[e^{i\vec{k}\cdot\vec{x}} - \frac{2\mu}{\hbar^2}\int\left(\frac{e^{\pm ik|x-x'|}}{4\pi|x - x'|}\right)V(x')\psi(x')d^3x'\right] \tag{4.14}$$

where A is a normalization. However, we see that the solution to $\psi(x)$ is itself dependent on $\psi(x)$ (shows up in the integrand). A way to get around this is by making appropriate approximations. First, we assume that we are observing the scattered wave far enough away from the scatterer that we are allowed to write:

$$\psi(x) \approx A\left[e^{i\vec{k}\cdot\vec{x}} - \frac{2\mu}{\hbar^2}\frac{e^{ikr}}{4\pi r}\int \exp\left(-i\vec{k}\,'\cdot\vec{x}\,'\right)V(x')\psi(x')d^3x'\right]. \tag{4.15}$$

It works out that the integral above is what is known as the *scattering amplitude*, but before we get to that, we take a step back to consider the observables of interest that we want measure.

§4.1.1 Differential Scattering Cross-Sections

An observable ubiquitous in scattering theory is known as the *differential scattering cross-section.*

Definition 4.1.1. Differential Cross-Section: *The ratio of the scattered flux to the incident flux on a scatterer* $d\sigma$*, that scatters into a differential solid angle* $d\Omega$:

$$\frac{d\sigma}{d\Omega} = \lim_{r\to\infty} \frac{r^2\left(\hat{r}\cdot\vec{J}_s\right)}{|J_i|}, \tag{4.16}$$

where $\vec{J}_s$ *is the scattered flux and* $\vec{J}_i$ *is the incident flux.*

Recall that in quantum mechanics, we had that the probability flux is given by:

$$\vec{J} = \frac{\hbar}{2\mu i}\left(\psi^*\nabla\psi - \psi\nabla\psi^*\right). \tag{4.17}$$

Going back to the Lippman-Schwinger equation, we have that in the far field limit, we can define a quantity:

$$\begin{aligned} f(\hat{k},\hat{k}') &\equiv -\frac{\mu}{2\pi\hbar^2}\int d^3x' e^{-i\vec{k}'\cdot\vec{x}'}V(\vec{x}')\psi(\vec{x}') && (4.18)\\ \Rightarrow \quad \lim_{r\to\infty}\psi(\vec{x}) &= A\left[e^{i\vec{k}\cdot\vec{x}} + f(\hat{k},\hat{k}')\frac{e^{ikr}}{r}\right]. && (4.19)\end{aligned}$$

To make sense of what $f(\hat{k},\hat{k}')$ is, we consider the case of *elastic* scattering. Since $f(\hat{k},\hat{k}')$ is the coefficient of the scattered wave solution, we can think of it in terms of a probability amplitude. In particular, this is the probability amplitude associated to a particle scattering off the scatterer with a velocity v into some differential solid angle $d\Omega$. So we can write:

$$\begin{aligned} d\mathbb{P} &= |\psi_s|^2 dv \\ &= \frac{|A|^2\left|f(\hat{k},\hat{k}')\right|^2}{r^2} r^2 d\Omega\cdot v dt, \end{aligned} \tag{4.20}$$

where ψ_s is the scattered wave. However, because we are treating the collision process as elasting, this post-scattering outgoing probability flux must equate to the pre-collision incoming probability flux. The incoming flux would then be the probability amplitude associated to an incident particle travelling at speed v, that passes through a differential area $d\sigma$ in time dt:

$$\begin{aligned} d\mathbb{P} &= |\psi_i|^2 dv \\ &= |A|^2 d\sigma\cdot v dt. \end{aligned} \tag{4.21}$$

Equating these 2 differential probability measures, we get:

$$\begin{aligned} &\frac{|A|^2\left|f(\hat{k},\hat{k}')\right|^2}{r^2} r^2 d\Omega\cdot v dt = |A|^2 d\sigma\cdot v dt \\ \Rightarrow \quad &\boxed{\frac{d\sigma}{d\Omega} = \left|f(\hat{k},\hat{k}')\right|^2}, \end{aligned} \tag{4.22}$$

which tells us that the absolute square of the scattering amplitude is indeed the differential cross-section! From the differential cross-section, we can also compute the total cross-section σ defined as:

$$\boxed{\sigma = \int d\Omega \frac{d\sigma}{d\Omega} = \int d\Omega \left| f(\hat{k}, \hat{k}') \right|^2}. \tag{4.23}$$

However, we are still facing the issue of calculating the scattering amplitude from the Lippman-Schwinger equation which seems to require that the solution is already solved for in its formulation. Things brings us to the approximation method known as the *Born approximation.*

§4.2 The Born Approximation

The Born approximation asserts that the scatterer is weak and only perturbs the incoming wave slightly, so the lowest order version of this approximation is done by replacing the wavefunction in the integrand with just the incoming plane wave solution which gives:

$$f^{(1)}(\hat{k}, \hat{k}') = \frac{\mu}{2\pi\hbar^2} \int d^3x' \exp\left(i(\vec{k} - \vec{k}\,') \cdot \vec{x}\,'\right) V(\vec{x}\,'). \tag{4.24}$$

The integral above is in fact just the Fourier transform of the potential! As a first pass, we consider a spherical symmetric potential for which we can write:

$$\begin{aligned} f^{(1)}(\theta) &= -\frac{\mu}{2\pi\hbar^2} \int_0^\infty r^2 dr \int_0^{2\pi} d\phi \int_0^\pi d(\cos\theta) e^{iqr\cos\theta} V(r) \\ &= -\frac{2\mu}{\hbar^2 q} \int_0^\infty r V(r) \sin(qr) dr. \end{aligned} \tag{4.25}$$

where $\vec{q} = \vec{k} - \vec{k}\,'$. An example of a spherically symmetric potential is the *Yukawa potential* written as:

$$V(r) = -\frac{e^2}{r} e^{-\alpha r} \tag{4.26}$$

$$\Rightarrow \quad f^{(1)}(\theta) = \frac{2\mu e^2}{\hbar^2} \left(\frac{1}{q^2 + \alpha^2}\right). \tag{4.27}$$

Even though it may suffice in some cases to only consider the first-order approximation, most actual cases require higher order correction to the lowest-order approximation done above. This is usually done with a *multiple scattering series*:

$$f = f^{(1)} + f^{(2)} + f^{(3)} + \dots. \tag{4.28}$$

for which we can construct a representation of the probability scattering transition terms in what is known as a *T-matrix.* This is a little more involved for which the precursor is first knowing what each of the terms in the multiple scattering series looks like. For starters, the second-order correction above is given by:

$$f^{(2)} = -\frac{\mu}{2\pi\hbar^2} \int d^3x'' e^{-i\vec{k}\,'\cdot\vec{x}\,'} V(\vec{x}\,') \int d^3x G(\vec{x}, \vec{x}\,') V(\vec{x}\,') e^{i\vec{k}\cdot\vec{x}}, \tag{4.29}$$

which accounts for all 2-component scattering processes.

§4.3 Alternative Formulation of Scattering

Here, we are going to consider an alternative approach to scattering problems by directly solving the derivative form of the Schrödinger equation. We again assume that the potential is time-indepdent, for which we want to find solutions to:

$$\left[-\frac{\hbar^2}{2\mu}\boldsymbol{\nabla}^2+V(\vec{r})\right]\psi(\vec{r})=E\psi(\vec{r}) \tag{4.30}$$

such that $\psi(\vec{r})$ is regular as $r\to\infty$ and $r\to 0$. For completeness, let's have a little refresher of the derivations for the *radial solution* $R_{E\ell}$ and *spherical harmonics* $Y_{m\ell}$.

Central Potentials:

In spherical coordinates, the Laplacian on an arbitrary wavefunction ψ is given as:

$$\boldsymbol{\nabla}^2\psi=\frac{1}{r}\frac{\partial^2}{\partial r^2}(r\psi)+\frac{1}{r^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\psi \tag{4.31}$$

As such, the full Schrödinger equation with a central potential in spherical coordinates is given by:

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r}\frac{\partial^2}{\partial r^2}r+\frac{1}{r^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\right]\psi+V(r)\psi=E\psi \tag{4.32}$$

It can be shown that:

$$\hat{\vec{L}}^2=-\frac{\hbar^2}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}-\frac{\hbar^2}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \tag{4.33}$$

where $\hat{\vec{L}}$ is the angular momentum operators with their respective eigenfunctions are then:

$$\hat{\vec{L}}=\left(\hat{L}_x,\hat{L}_y,\hat{L}_z\right) \tag{4.34}$$

$$\hat{L}_x\equiv\hat{y}\hat{p}_z-\hat{z}\hat{p}_y,\quad \hat{L}_y\equiv\hat{z}\hat{p}_x-\hat{x}\hat{p}_z,\quad \hat{L}_z\equiv\hat{x}\hat{p}_y-\hat{y}\hat{p}_x \tag{4.35}$$

$$\hat{L}_z\psi_{\ell m}=\hbar m\psi_{\ell m},\qquad m\in\mathbb{R} \tag{4.36}$$

$$\boxed{\hat{\vec{L}}^2\psi_{\ell m}=\hbar^2\ell(\ell+1)\psi_{\ell m}},\qquad \ell\in\mathbb{R} \tag{4.37}$$

As such, the Schrödinger equation reduces to:

$$-\frac{\hbar^2}{2m}\frac{1}{r}\frac{\partial^2}{\partial r^2}(r\psi)+\frac{\mathbf{L}^2}{2mr^2}\psi+V(r)\psi=E\psi \tag{4.38}$$

for which if we choose a separable ansatz $\psi(r,\theta,\phi)=R_{E\ell}(r)Y_{\ell m}(\theta,\phi)$ with $Y_{\ell m}(\theta,\phi)$ being eigenstates of $\hat{\vec{L}}^2$, we get:

$$-\frac{\hbar^2}{2m}\frac{1}{r}\frac{d^2\left(rR_{E\ell}\right)}{dr^2}Y_{\ell m}+\frac{\hbar^2\ell(\ell+1)}{2mr^2}R_{E\ell}Y_{\ell m}+V(r)R_{E\ell}Y_{\ell m}=ER_{E\ell}Y_{\ell m} \tag{4.39}$$

From here, we see that all the spherical harmonics $Y_{\ell m}$ cancel out to give:

$$-\frac{\hbar^2}{2m}\frac{d^2\left(rR_{E\ell}\right)}{dr^2}+\frac{\hbar^2\ell(\ell+1)}{2mr^2}\left(rR_{E\ell}\right)+V(r)\left(rR_{E\ell}\right)=E\left(rR_{E\ell}\right) \tag{4.40}$$

And if we define $u_{E\ell}(r) \equiv rR_{E\ell}(r)$, we get:

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2u_{E\ell}(r)}{dr^2} + \left[V(r) + \frac{\hbar^2\ell(\ell+1)}{2mr^2}\right]u_{E\ell}(r) = E\cdot u_{E\ell}(r)} \tag{4.41}$$

The 2 boxed results constitute the radial and angular equations for a general central potential.

Back to scattering, we now use asymptotic analysis of the regularity conditions on $\psi(\vec{r})$ to see that we can construct an ansatz far away from the scatterer of the form:

$$\lim_{r\to\infty}\psi(\vec{r}) \sim e^{i\vec{k}\cdot\vec{r}} + f_k(\hat{k},\hat{k}')\frac{e^{ikr}}{r} \tag{4.42}$$

where $k = \sqrt{2\mu E/\hbar^2}$ is the de Broglie wave-vector and primes denote post-scattering variables. We again assert that the potential is short-ranged, where we do not assume any particular form for $V(\vec{r})$. Without loss of generality, we can take $\hat{k} = \hat{z}$. This ansatz is illustrated in figure 4.1 below.

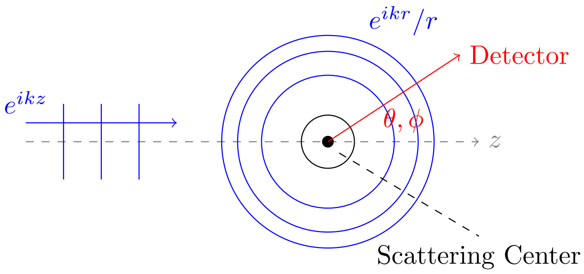

Figure 4.1: Scattering stationary solution.

We can now ask, what are the good quantum numbers to describe our wavefunction? Let's once again consider a spherically symmetric potential for simplicity. For spherically symmetric potentials, we have that the appropriate quantum numbers are $\{E, l, m_l\}$. As such, we can write the wavefunction in terms of a radial part dependent on E and l, and an angular part that depends on l and m_l:

$$\psi(\vec{r}) = R_{E,l}(r)Y_{l,m}(\theta,\phi), \tag{4.43}$$

where $R_{E,l} = u_{E,l}/r$ satisfies the radial Scrödinger equation given as:

$$-\frac{\hbar^2}{2\mu}u''_{E,l}(r) + \left[\frac{\hbar^2 l(l+1)}{2\mu r^2} + V(r)\right]u_{E,l}(r) = Eu_{E,l}(r). \tag{4.44}$$

As such, we can construct a general solution by linear combinations of these separable solutions as:

$$\psi_E(\vec{r}) = \sum_{l,m_l} A^E_{l,m_l}\frac{u_{E,l}(r)}{r}Y_{l,m}(\theta,\phi). \tag{4.45}$$

We notice that the radial equation is in fact a 1-dimensional differential equation, so let's start but first drawing intuition from scattering in 1D.

1D Scattering and Phase Shifts:

Consider the finite-range potential with a hard wall as illustrated below.

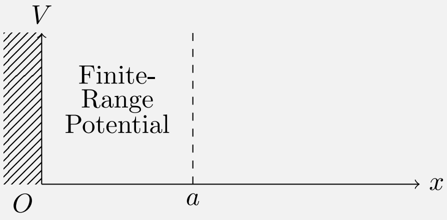

Figure 4.2: 1D Finite-Range Potential with a Hard-Wall

Recall that for the potential above, we required an odd function which vanishes at the origin O. The ansatz for the wavefunction for $r > a$ would thus be:

$$\varphi(x) = N\sin(kx) = \frac{N}{2i}\left(e^{ikx} - e^{-ikx}\right) \tag{4.46}$$

with N being the normalization factor, e^{ikx} the outgoing wave and e^{-ikx} the ingoing wave. This would be fine if there were just a hard-wall potential, but because of the non-trivial finite-range potential in $0 < r < a$, it must be modified. 2 considerations for this:

1. The outgoing term is required to be modified since it scatters off the finite-range potential.
2. Probability must be conserved upon modification of the ansatz.

This leads us to modify the outgoing wave with just a phase shift:

$$\psi(x) = \frac{N}{2i}\left(e^{ikx}e^{2i\delta_k} - e^{-ikx}\right) \tag{4.47}$$

Remember this result as we now look at scattering in 3D. This will be an invaluable tool for us.

Back to the radial equation, remember again that we are looking for solutions where $r \gg r_0$. In this regime, we can look for solutions where $V(r) = 0$ and $E = \frac{\hbar^2 k^2}{2m}$:

$$\begin{aligned} &-\frac{\hbar^2}{2m}\frac{d^2u_{E\ell}(r)}{dr^2} + \frac{\hbar^2\ell(\ell+1)}{2mr^2}u_{E\ell}(r) = \frac{\hbar^2k^2}{2m}u_{E\ell}(r) \\ \Rightarrow\quad &\left[-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2}\right]u_{E\ell}(r) = k^2u_{E\ell}(r) \\ \Rightarrow\quad &\boxed{\left[-\frac{d^2}{d\rho^2} + \frac{l(l+1)}{\rho^2}\right]u_{E\ell}(\rho) = u_{E\ell}(\rho)}, \qquad \rho \equiv kr \end{aligned} \tag{4.48}$$

Since we can do a change of variable to eliminate k^2, the energy for this system is **not** quantized.

It works out that solutions to the boxed equation (4.48) above are linear combinations of spherical Bessel functions:

$$u_{E\ell}(\rho) = A_\ell \rho j_\ell(\rho) + B_\ell \rho n_\ell(\rho) \tag{4.49}$$

remembering that ρ is already a function of k which directly related to the energy E, hence the subscripts in $u_{E\ell}$.

Spherical Bessel Functions:

Spherical Bessel functions are canonical solutions to solving the radial portion of the *Helmholtz equation*, $\left(\nabla^2 + k^2\right) A = 0$:

$$\begin{aligned} r^2 \frac{d^2 f(r)}{dr^2} + 2r \frac{df(r)}{dr} + \left[r^2 - l(l+1)\right] f(r) = 0 \\ \Rightarrow \quad \left[-\frac{d^2}{dr^2} - \frac{2}{r}\frac{d}{dr} + \frac{l(l+1)}{r^2}\right] f(r) = f(r) \end{aligned} \tag{4.50}$$

These solutions have the form:

$$\begin{aligned} j_l(r) &= (-r)^l \left(\frac{1}{r}\frac{d}{dr}\right)^l \frac{\sin(r)}{r}, \quad \text{“\textit{Spherical Bessel Functions}”} \\ n_l(r) &= -(-r)^l \left(\frac{1}{r}\frac{d}{dr}\right)^l \frac{\cos(r)}{r}, \quad \text{“\textit{Spherical Neumann Functions}”} \end{aligned} \tag{4.51}$$

and are related to the ordinary Bessel functions of the first kind by the relations:

$$\begin{aligned} j_l(r) &= \sqrt{\frac{\pi}{2r}} J_{l+\frac{1}{2}}(r) \\ n_l(r) &= (-1)^{l+1} \sqrt{\frac{\pi}{2r}} J_{-l-\frac{1}{2}}(r) \end{aligned} \tag{4.52}$$

Note that $n_l(r)$ diverges / is *singular* at the origin ($r = 0$) while $j_l(r)$ does not / is *non-singular*. The large radius limit ($r \to \infty$) of these functions go like:

$$\begin{aligned} j_l(r) &\to \frac{1}{r} \sin\left(r - \frac{l\pi}{2}\right) \\ n_l(r) &\to -\frac{1}{r} \cos\left(r - \frac{l\pi}{2}\right) \end{aligned} \tag{4.53}$$

We will now see that scattering amplitudes can actually be computed in terms of *phase shifts*. Knowing that the plane wave $e^{ikz} = e^{ikr\cos\theta}$ is a solution to equation (4.48), it must then be constituted of linear combinations of spherical Bessel functions:

$$e^{ikrcos\theta} = \sum_{\ell=0}^{\infty} a_{\ell m} \left[A_\ell j_\ell(kr) + B_\ell n_\ell(kr)\right] Y_{\ell m}(\theta, \phi). \tag{4.54}$$

A few things to notice before we proceed.

- Remembering that we are working with a spherically symmetric potential, and since we have chosen an axis for the incoming wave to propagate (z-axis), we can deduce that the ϕ (azimuthal) dependence is irrelevant ($z = r\cos\theta$ is independent of $\phi \Rightarrow m = 0$).
- Plane wave solutions have no divergences at the origin, so we cannot include the spherical Neumann functions in the solution for e^{ikz}.

With these in mind, our expansion simpifies to:

$$e^{ikrcos\theta} = \sum_{\ell=0}^{\infty} a_{\ell 0} A_\ell j_\ell(kr) Y_{\ell 0}(\theta). \tag{4.55}$$

It then works out that the $a_{\ell 0}A_\ell$ coefficients work out to give:

$$\boxed{e^{ikrcos\theta} = \sqrt{4\pi}\sum_{\ell=0}^{\infty}(i)^l\sqrt{2l+1}\ Y_{\ell 0}(\theta) j_\ell(kr)} \tag{4.56}$$

So we see that a plane wave can be built as in infinite sum of *partial waves* (Each term in ℓ) where each partial wave is an exact solution to (4.48).

§4.3.1 Low-Energy Scattering

We are now going to look at scattering that occurs specifically in the low-energy limit (all scattering that occurs is elastic / *single-channel scattering*). We start by again asserting that $r \gg r_0$ has $V(r) \approx 0$. That renders our radial equation as:

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + \frac{l(l+1)\hbar^2}{2\mu r^2} - \frac{\hbar^2 k^2}{2m}\right] u_{E,l}(r) = 0 \tag{4.57}$$

This produces 2 possible solutions which are spherical Bessel and Neumann functions:

$$f_{El}(r) = \sqrt{\frac{2\mu}{\pi\hbar^2 k}}(kr) j_l(kr), \quad \text{regular at } r = 0 \tag{4.58}$$

$$g_{El}(r) = \sqrt{\frac{2\mu}{\pi\hbar^2 k}}(kr) n_l(kr), \quad \text{irregular at } r = 0 \tag{4.59}$$

Bessel and Neumann functions are really just oscillatory functions with a decay envelop. These solutions are **not** normalizable since they are scattering solutions, and so the pre-factors ($\sqrt{2\mu/\pi\hbar^2 k}$) in front of these solutions are there for *energy normalization.* These solutions are orthonormal with respect to different energies:

$$\begin{aligned} &\int f_{El}(r) f_{E'l}(r) dr = \delta(E - E') \\ &\int g_{El}(r) g_{E'l}(r) dr = \delta(E - E'). \end{aligned} \tag{4.60}$$

In the region where $r \gg r_0$, there will be a regime whereby $kr \ll 1$ (low-energy and $r \gg r_0$ but not large enough to make kr large) and another where $kr \gg 1$ (low-energy and r large enough to make kr large). This is illustrated in figure 4.3 below.

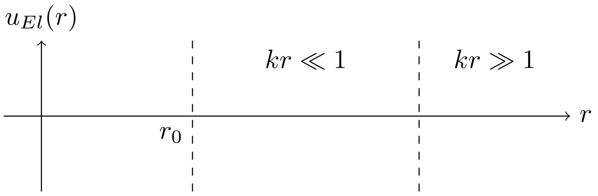

Figure 4.3: Regions of interest for $u_{El}(r)$.

In both these regimes, we can find very good approximate analytical solutions to f_{El} and g_{El}. First note that our radial solution can then be written as:

$$\begin{aligned} u_{El} &= A_l f_{El}(r) + B_l g_{El}(r) \\ &= C_l \left[f_{El}(r)\cos\delta_l - g_{El}(r)\sin\delta_l \right] \end{aligned} \tag{4.61}$$

where $a_l = \sqrt{A_l^2 + B_l^2}$ and $\tan\delta_l = -B_l/A_l$. It turns out that the 2 forms above are completely equivalent.

> **Note**: The zero energy solution of the radial equation is given by:
>
> $$u_{0l}(r) = \alpha r^{l+1} + \frac{\beta}{r^l}. \tag{4.62}$$

Now we list the solutions in the corresponding regimes below.

1. $kr \ll 1$ regime:

$$(kr)j_l(kr) \approx \frac{(kr)^{l+1}}{(2l+1)!!} \tag{4.63}$$

$$(kr)n_l(kr) \approx -\frac{(2l-1)!!}{(kr)^l} \tag{4.64}$$

Substituting our analytical approximations, we get:

$$\boxed{u_{El}(r) \approx C_l \sqrt{\frac{2\mu}{\pi\hbar^2 k}} \left[\frac{(kr)^{l+1}}{(2l+1)!!}\cos\delta_l + \frac{(2l-1)!!}{(kr)^l}\sin\delta_l \right]} \tag{4.65}$$

Then if we impose $u_{El}(kr \ll 1) = u_{0l}$, we arrive at:

$$\alpha = C_l \frac{(k)^{l+1}}{(2l+1)!!}\cos\delta_l, \quad \beta = -C_l \frac{(2l-1)!!}{(k)^l}\sin\delta_l \tag{4.66}$$

$$\Rightarrow \quad \tan\delta_l = -\frac{\beta}{\alpha}\left(\frac{k^{2l+1}}{(2l+1)!!(2l-1)!!} \right) \tag{4.67}$$

where we have $k^{2l+1}/(2l+1)!!(2l-1)!!$ is universal whereas β/α depends on the regime we are in. This dependence on k is known as the *Wigner's threshold law.*

2. $\underline{kr \gg 1 \text{ regime}}$:

$$(kr)j_l(kr) \approx \sin\left(kr - \frac{\pi l}{2}\right) \tag{4.68}$$

$$(kr)n_l(kr) \approx -\cos\left(kr - \frac{\pi l}{2}\right) \tag{4.69}$$

Substituting our analytical approximations, we get:

$$\boxed{u_{El} = C_l\sqrt{\frac{2\mu}{\pi\hbar^2 k}}\sin\left(kr - \frac{\pi l}{2} + \delta_l\right)} \tag{4.70}$$

Which are oscillatory solutions, much like a plane wave scattering off a hard wall in 1D.

We call δ_l the *scattering phase shift*, because this just tells us that at large distances, scattering off the scattering center simply results in a phase shift between the incoming and outgoing wavefunction. Looking again at the $kr \ll 1$ regime, we had:

$$u_{El} \sim \frac{1}{(2l+1)!!} - \frac{\tan\delta_l/k^{2l+1}}{r^{2l+1}} \tag{4.71}$$

$$\Rightarrow \quad \boxed{(a_l)^{2l+1} = -\lim_{k\to 0}\frac{\tan\delta_l}{k^{2l+1}}} \tag{4.72}$$

where in the boxed equation above, we call a_l the *l-wave scattering length* (l is a variable and could represent any order of scattering, $s, p, d, f, ...$), with the definition simply stemming from the fact that we notice a length dimensional quantity and take the low-energy limit of it. A commonly used result is the s-wave ($l = 0$) scattering length which is then just:

$$\boxed{a_0 = -\lim_{k\to 0}\frac{\tan\delta_0}{k}}. \tag{4.73}$$

Let's now look at the general form of these low-energy, single-channel scattering solutions. The first bit of intuition is that when we have a very deep potential well, the wavefunction would oscillate greatly ($\sim$ due to high kinetic energies). Let's look again at our radial solutions at long ranges in the 2 possible regimes of kr:

$$(kr \ll 1): \quad u_{El}(r) \sim \left[\frac{1}{(2l+1)!!} + \frac{a_l^{2l+1}}{r^{2l+1}}\right] r^{l+1} \tag{4.74}$$

$$(kr \gg 1): \quad u_{El} \sim \sin\left(kr - \frac{\pi l}{2} + \delta_l\right) \tag{4.75}$$

So we can look at the $l = 0$ case, and have a solution that which takes a form that looks something that presented in figure 4.4 below.

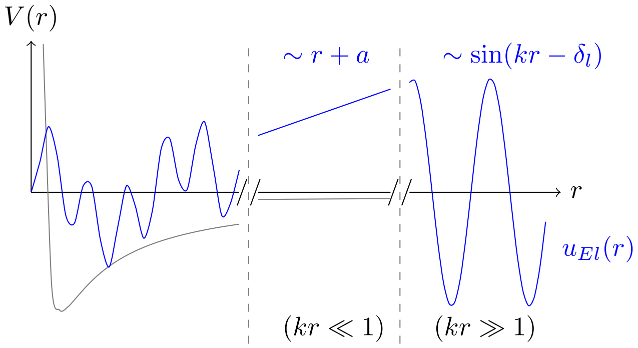

Figure 4.4: $l = 0$ form of solution

where in the case of negative scattering length ($a < 0$, corresponding to attractive potentials), we just have the slope in the region where $kr \ll 1$ being negative (downward sloping). In practice, to get solutions to the wavefunction in the region where r is around the range of r_0, we use numerical methods (e.g. Runge-Kutta 4th order solver) given initial conditions $\{u_{El}, u'_{El}\}$. In general, we have the expression:

$$\frac{u'_{El}(r)}{u_{El}(r)} = \left.\frac{f'_{El}(r)\cos\delta_l - g'_{El}\sin\delta_l}{f_{El}(r)\cos\delta_l - g_{El}\sin\delta_l}\right|_{r=r^*} \tag{4.76}$$

$$\Rightarrow \boxed{\tan\delta_l = \left.\frac{W[f_{El}, u_{El}]}{W[g_{El}, u_{El}]}\right|_{r=r^*}} \tag{4.77}$$

where $W[\ ,\ ]$ is the *Wronskian* defined as $W[a, b] = ab' - a'b$ and r^* is known as the *matching distance*, that is the distance beyond which the asymptotic solutions become good approximations.

> **Note**: With this, we can prove the *Wigner threshold law* which tells us that as $k \to 0$, then $\tan\delta_l \sim k^{2l+1}$.

We are now going to consider the problem of scattering off a finite-square well. Before we get to this, it is worth while taking an aside to consider the concept of an *effective range* of the potential. We start from the definition of the scattering length (equation 4.72) and add correction terms without taking the limit of $k \to \infty$ and consider terms in varying order of k:

$$-k\cot\delta = \frac{1}{a} - \frac{1}{2}r_{\text{eff}}k^2 + \ldots \tag{4.78}$$

where r_{eff} is defined as the effective range. This is a quantity that tells us how much our observable will change when we vary the energy (what the energy dependence of the system is since it is attached to k^2). The effective range will also allow us a way to characterize resonances (e.g. Feshbach resonances).

Example:

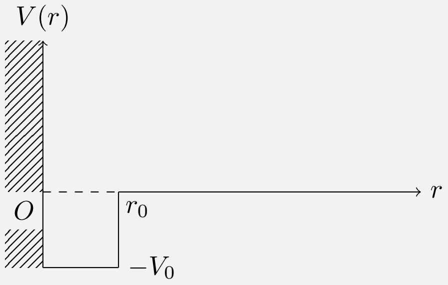

Figure 4.5: 1D Square-Well Scattering Potential

Consider the potential now with a hard wall and attractive square-well:

$$V(r) = \begin{cases} \infty, & r < 0 \\ -V_0, & r \leq r_0 \\ 0, & r > r_0 \end{cases} \tag{4.79}$$

For this question, we will be looking at the analysis for $l = 0$. Before we dive into solving this problem, we remark that there is often times a regime where parameters can be tuned such that the s-wave scattering becomes extremely large. This interestingly can lead to a bound state. To see this, we first get intuition by considering a repulsive potential:

$$V(r) = \begin{cases} \infty, & r < 0 \\ +V_0, & r \leq r_0 \\ 0, & r > r_0 \end{cases} \tag{4.80}$$

with *effective range* r_0, such that within this range, we have:

$$E - V_0 = \frac{\hbar^2 q^2}{2\mu}, \tag{4.81}$$

where q is the wave-vector that is less than k (the wave-vector of a free particle with energy E). This suppression of the wave-vector within the potential range causes the wavelength of the wavefunction in this region to increase. The s-wave scattering length turns out to be the radius at which free-particle wavefunction is projected into the region $r < r_0$, given that the wavefunctions within and external to the potential are continuous at $r = r_0$. Now we can ask, what if we were able to engineer the system such that we instead had an attractive potential? In this case, the matching described above to get the s-wave scattering length then increases the scattering length as the well gets deeper!

We now solve this system formally. We will split analysis for this into 2 parts, one where $E > 0$ and the other for $E < 0$. Consider first the case where the energy is $E > 0$.

1. $\underline{E > 0}$:

   For this problem, we will have 2 wave numbers:

$$r > r_0: \quad k^2 = \frac{2\mu E}{\hbar^2} \tag{4.82}$$

$$r \leq r_0: \quad \kappa^2 = \frac{2\mu(E + V_0)}{\hbar^2} \tag{4.83}$$

So we have that:

$$r \leq r_0 : \quad u_{E0}(r) = \sqrt{\frac{2\mu}{\pi\hbar^2\kappa}}(\kappa r)j_0(\kappa r) \tag{4.84}$$

$$\begin{aligned} r > r_0 : \quad f_{E0}(r) &= \sqrt{\frac{2\mu}{\pi\hbar^2 k}}(kr)j_0(kr) \\ g_{El}(r) &= \sqrt{\frac{2\mu}{\pi\hbar^2 k}}(kr)n_0(kr) \end{aligned} \tag{4.85}$$

because in the $r < r_0$ region, we must have that the wavefunction be regular at $r = 0$. So taking the Wronskian formula once again to find the phase shift, we get the expression for $k \to 0$ to be:

$$\tan\delta_0 = -kr_0 + \frac{k}{\kappa_0}\tan(\kappa_0 r_0) \tag{4.86}$$

$$\Rightarrow \quad \boxed{a = r_0 - \frac{\tan(\kappa_0 r_0)}{\kappa_0}} \tag{4.87}$$

where $\kappa_0^2 = 2\mu V_0/\hbar^2$. This expression tells us that a diverges whenever $\kappa_0 r_0 = n\pi + \pi/2$, which indeed corresponds to creation of bound states in the potential well! Note that increasing values of κ_0 implies that we are making the potential well deeper.

2. $\underline{E < 0}$:
Now we consider $E < 0$ solutions (when $l = 0$). We use the same procedure but now:

$$r \leq r_0 : \quad u_{E0}(r) = A\sin(\kappa r) \tag{4.88}$$

$$r > r_0 : \quad h_{E0}(r) = Be^{-kr} \tag{4.89}$$

where now, $k^2 = 2\mu|E|/\hbar^2$ and we just named another function h_{E0} since it is not the Bessel function solution. Then plugging into the Wronskian formula for the phase shift, we get:

$$\sqrt{\kappa_0^2 - k^2}\cot\left[r_0\sqrt{\kappa_0^2 - k^2}\right] = -k \tag{4.90}$$

This is a transcendental equation and number of intersections between the functions on the RHS and LHS of the expression above gives us the number of bound states. Notice that in the limit where $\kappa_0 \gg k$, we get:

$$\begin{aligned} & -k \approx \kappa_0 \cot\left[\kappa_0 r_0\right] \\ \Rightarrow \quad & \tan(\kappa_0 r_0) \approx -\frac{\kappa_0}{k} \\ \Rightarrow \quad & a \approx r_0 - \frac{1}{\kappa_0}\left(-\frac{\kappa_0}{k}\right) \\ \Rightarrow \quad & k \approx \frac{1}{a - r_0} \end{aligned} \tag{4.91}$$

From this, we plug this into the equation for the energy involving k which gives us:

$$\begin{aligned} E &= -\frac{\hbar^2 k^2}{2\mu} \\ &\approx -\frac{\hbar^2}{2\mu(a-r_0)^2} \end{aligned} \tag{4.92}$$

Then if we further assert that the s-wave scattering length a is much larger than the range of the potential r_0, we get:

$$\boxed{E = -\frac{\hbar^2}{2\mu a^2}} \tag{4.93}$$

This is in fact a "*universal*" result.

That is to say, whenever we have a single channel scattering system which incoming particle having an energy close to zero in relation to the depth of the potential well, then the energy would go like $\sim 1/a^2$ as long as the scattering length is much greater than the range of the potential.

States with $l = 0$ for which majority of the wavefunction exists outside the classically forbidden region (due to the lack of an angular momentum barrier) despite having insufficient energy classically are known as *halo states.*

Note: We can actually compute this analytically for the square-well scattering problem. This works out to be:

$$r_{\text{eff}} = r_0 \left[1 - \frac{r_0^2}{3a^2} - \frac{1}{\kappa_0^2 a r_0}\right] \tag{4.94}$$

§4.3.2 Scattering Cross-Sections

Earlier we have seen that to derive scattering, we first look at the wavefunction in the very large limit ($kr \gg 1$), where we arrived at the partial wave expansion expression:

$$\psi_E \approx \frac{1}{r}\sum_{l,m} A_{l,m} Y_l^m(\theta,\phi)\left(\frac{2\mu}{\pi\hbar^2 k}\right)^{1/2} \sin\left(kr - \frac{l\pi}{2} + \delta_l\right). \tag{4.95}$$

The goal of writing this was to compare this result to specific scattering problems (also in the $kr \gg 1$ regime) which would take the general form:

$$\psi_E = e^{i\vec{k}\cdot\vec{r}} + f(\hat{k}',\hat{k})\frac{e^{ikr}}{r}. \tag{4.96}$$

The scattering amplitude function would now have matrix elements $\left\langle \hat{k}' \middle| f(\hat{k}',\hat{k}) \middle| \hat{k} \right\rangle$. We now note the very useful identity:

$$e^{i\vec{k}\cdot\vec{r}} = 4\pi \sum_{l,m} i^l Y^*_{lm}(\hat{k}) Y_{lm}(\hat{r}) j_l(kr), \tag{4.97}$$

which, in the $kr \gg 1$ regime, simplifies to:

$$e^{i\vec{k}\cdot\vec{r}} \approx 4\pi \sum_{l,m} i^l Y^*_{lm}(\hat{k}) Y_{lm}(\hat{r}) \frac{\sin\left(kr - \frac{l\pi}{2}\right)}{kr}. \tag{4.98}$$

Substituting this into the general scattering solution and equating it to the partial wave expansion, we get:

$$\begin{aligned}
&4\pi \sum_{l,m} i^l Y^*_{lm}(\hat{k}) Y_{lm}(\hat{r}) \frac{\sin\left(kr - \frac{l\pi}{2}\right)}{kr} + f(\hat{k}', \hat{k}) \frac{e^{ikr}}{r} \\
&= \frac{1}{r} \sum_{l,m} A_{l,m} Y_l^m(\theta, \phi) \left(\frac{2\mu}{\pi\hbar^2 k}\right)^{1/2} \sin\left(kr - \frac{l\pi}{2} + \delta_l\right).
\end{aligned} \tag{4.99}$$

Now we also note the identites:

$$\begin{aligned}
&Y_l^m(\hat{r}) \equiv \left\langle \hat{k}' \middle| l, m \right\rangle, \quad Y^*_{lm}(\hat{k}) \equiv \left\langle l, m \middle| \hat{k} \right\rangle \\
\Rightarrow \quad & f(\hat{k}', \hat{k}) \frac{e^{ikr}}{r} = \frac{1}{r} \sum_{l,m} \left\langle \hat{k}' \middle| l, m \right\rangle \\
& \times \left[A_{l,m} \left(\frac{2\mu}{\pi\hbar^2 k}\right)^{1/2} \sin\left(kr - \frac{l\pi}{2} + \delta_l\right) - 4\pi i^l \left\langle l, m \middle| \hat{k} \right\rangle \frac{\sin\left(kr - \frac{l\pi}{2}\right)}{kr} \right].
\end{aligned} \tag{4.100}$$

In the above expression, the left-hand side only has outgoing waves whereas on the right-hand side, there are both incoming and outgoing waves, which we can force to vanish. This grants us that:

$$A_{lm} = 4\pi i^l e^{i\delta_l} \left\langle l, m \middle| \hat{k} \right\rangle \left(\frac{2\mu}{\pi\hbar^2 k}\right)^{-1/2} \tag{4.101}$$

which now allows us to find the scattering amplitude:

$$\begin{aligned}
\left\langle \hat{k}' \middle| f(\hat{k}', \hat{k}) \middle| \hat{k} \right\rangle &= \sum_{lm} \left\langle \hat{k}' \middle| l, m \right\rangle \frac{4\pi}{2ik} i^l (e^{2i\delta_l} - 1) \left\langle l, m \middle| \hat{k} \right\rangle \\
&= \frac{1}{2ik} \sum_l (2l+1) P_l(\cos\theta)(e^{2i\delta_l} - 1) \\
\Rightarrow \quad & \boxed{\sum_l f_l(\theta) = \sum_l (2l+1) P_l(\cos\theta) \left(\frac{e^{2i\delta_l} - 1}{2ik}\right)}.
\end{aligned} \tag{4.102}$$

So this allows us to compute the distribution of scattered particles based on phase shifts! With this, we define the outgoing flux of scattered waves through a solid angle $d\Omega$ as:

$$\frac{\hbar k}{\mu}|f(\Omega)|^2 d\Omega, \tag{4.103}$$

with units of [$\sim L^3/T$] where $\hbar k/\mu$ acts as a velocity term. The incoming flux through a solid angle $d\Omega$ would then simply be $\hbar k/\mu$ [$\sim L/T$]. The differential cross section $d\sigma$ is then:

$$d\sigma = \frac{\text{outgoing flux}}{\text{incoming flux}} = |f(\Omega)|^2 d\Omega, \tag{4.104}$$

and total cross-section given as:

$$\begin{aligned} \sigma &= \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta |f(\Omega)|^2 d\theta \\ &= \frac{\pi}{k^2}\sum_l (2l+1)\left|e^{2i\delta_l}-1\right|^2 \\ \Rightarrow \quad &\boxed{\sigma = \frac{4\pi}{k^2}\sum_l (2l+1)\sin^2\delta_l \equiv \sum_l \sigma_l} \end{aligned} \tag{4.105}$$

This allows us another means to see why only s-wave scattering is dominant in the low energy ($k \ll 1$) limit. We saw earlier that $\delta_l \sim k^{2l+1}$ in the low energy regime, so we get;

$$\sigma = \sum_l \sigma_l \sim 1 + c_1 k^4 + c_2 k^8 + \dots \tag{4.106}$$

and since $k \ll 1$, all the higher order terms drop out and only the $l = 0$ term is relevant. Now consider the probability flux:

$$\vec{J} = \frac{\hbar}{2\mu i}\left[\psi \boldsymbol{\nabla}\psi^* - \psi^* \boldsymbol{\nabla}\psi\right], \tag{4.107}$$

the incoming flux for $\psi_{\text{incoming}} = e^{ikz}$ would be given by:

$$\vec{J}_{\text{incoming}} = -\frac{\hbar k}{2\mu}\hat{z}, \tag{4.108}$$

whereas for the outgoing wave $\psi_{\text{outgoing}} = f(\theta,\phi)e^{ikr}/r$, the flux would be:

$$\vec{J}_{\text{outgoing}} = |f(\theta,\phi)|^2 \frac{\hbar k}{2\mu r^2}\hat{r}, \tag{4.109}$$

so we get:

$$\boxed{\frac{d\sigma}{d\Omega} = \frac{r^2\left|\vec{J}_{\text{outgoing}} \cdot \vec{r}\right|}{\left\|\vec{J}_{\text{incoming}}\right\|}}. \tag{4.110}$$

§4.3.3 The Fermi Pseudopotential

We are now going to discuss a useful approximation of the potential function of scatterers in certain regimes. A useful references on this concept can be found in the journal articles Am. J. Phys. 52, 695 (1984). Enrico Fermi proposed (which was later experimentally verified) that scatterers in the ultracold (low-energy) regime can actually just be modeled by a δ-function along with an associated s-wave scattering length. Under this approximation scheme, having just the scattering length is extremely useful for simplifying scattering problems with complicated scattering geometries (potential functions are complicated). This model was first proposed when Fermi was modeling the perturbative effects of a foreign gas (e.g. He) on Rydberg atoms (large alkali atoms, e.g. Na) and its line spectra. This was in light of the experiments done by Amaldi and Segre. It was found that in the presence of foreign gases with no permanent electric dipole moments, the line spectra experienced blue shifting, which could only be a result of scattering processes.

The physical picture is as follows. Firstly, Rydberg atoms are large with a single outermost electron. Due to the effective charge screening effects the electronic configuration has on the outermost electron, the outermost electron feels a potential likened to that of a Hydrogen atom which some effective nuclear charge (figure 4.6). The size of the atom however, causes the Coulombic attraction on the outermost electron to be suppresed, hence it is weakly bound. This implies than the electron wavefunction has a very large de Broglie wavelength. The Rydberg atoms are taken to be far spaced from each other, so the potential landscape U, experienced by the outermost electrons due to other Rydberg atoms is slowly varying. However, the foreign gas atoms have deep and narrow potentials V_i, with effective range ρ, when these Rydberg atoms scatter off them (*contact interactions*). This renders the Schrödinger equation:

$$\boldsymbol{\nabla}^2\psi + \frac{2m}{\hbar^2}\left[E - U - \sum_i V_i\right]\psi = 0. \tag{4.111}$$

Since the electrons have a long de Broglie wavelength λ_{dB}, we then consider an approximate wavefunction $\overline{\psi}$ that is constant over spatial regions much smaller than λ_{dB}, but large enough that there are a significant number of foreign gas atoms. In this region, we move into the frame of one of these foreign atoms which renders the radial solution a complicated function in the region $r < \rho$, but roughly constant outside. Radial solutions are usually considered via $u(r) = rR(r)$, so the constant region is now linear in r, for which we extrapolate it illustrated in figure 4.7.

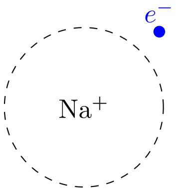

Figure 4.6: Outermost electron of a sodium Rydberg atom.

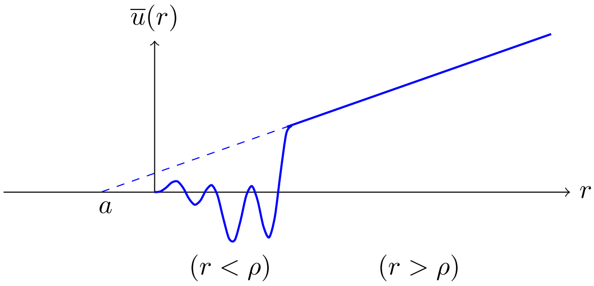

Figure 4.7: Sketch of the radial solution $\overline{u}(r)$, in the scatterer frame.

The solution can now be written as:

$$u(r) \approx (r+a)\overline{\psi}. \tag{4.112}$$

The radial Schrödinger equation now becomes:

$$\begin{aligned} u''(r) &= \frac{2m}{\hbar^2}\left[(U-E)+\sum_i V_i\right]u(r) \\ &\approx -\frac{2m}{\hbar^2}\sum_i V_i u(r). \end{aligned} \tag{4.113}$$

Consider just one foreign atom, we can integrate the equation above, considering a spatial average over the scattering potential and wavefunction $\overline{V\psi}$ and plug in the linear ansatz to get:

$$\begin{aligned} 4\pi u'(r) &= \frac{2m}{\hbar^2}\int d^3r\overline{V\psi} \\ \Rightarrow \quad \int d^3r\overline{V\psi} &= \frac{2\pi a\hbar^2}{m}\overline{\psi} \\ \Rightarrow \quad V_F(r) &= \frac{2\pi a\hbar^2}{m}\delta^3(\vec{r}). \end{aligned} \tag{4.114}$$

This is the resulting form of the Fermi-pseudopotential. More generally, a system with multiple scatterers is given as:

$$\boxed{V_F(r) = \frac{2\pi a\hbar^2}{m}\sum_i \delta^3(\vec{r}-\vec{r}_i)}. \tag{4.115}$$

In summary, the Fermi-pseudopotential is a simplified model of the potential function designed to satisfy the scattering phase-shift and energy properties of the true potential function within the relevant low-energy regime.

Note: This potential leads to some less than desirable behaviours (too singular) in certain applications. This was fixed by Huang and Yang in 1957 (Phys. Rev. 105, 767) via the form:

$$V(r) = \frac{4\pi\hbar^2 a}{2\mu}\delta(\vec{r})\frac{d}{dr}(r), \tag{4.116}$$

where the parenthesis on the r after the derivative indicates that the derivative and r act together as an operator:

$$V(r)\psi(r) = \frac{4\pi\hbar^2 a}{2\mu}\delta(\vec{r})\frac{d}{dr}\Big(r\psi(r)\Big). \tag{4.117}$$

This is known as a *regularized Fermi pseudopotential.*

§4.3.4 Feshbach Resonances

Feshbach resonances arise in low-energy collisions of atoms / molecules. Under certain conditions, the colliding atoms will "stick together" in an unstable compound for a finite lifetime (known as a resonance). In particular, a Feshbach resonance is said to occur when the kinetic energy of the incoming scatterer matches the bound state of an interatomic potential of the colliding pair.

To understand this, we first notice that there are 2 potential energy curves we need to consider in this process.

1. The potential energy associated to the free atom, without the presence of any other scatterers in the vicinity. This is known as the *background potential.*
2. The potential energy that arises from exchange interactions of 2 atoms close together, resulting in a hyperfine structure.

The language used to refer to these potentials is "*channels*". Channels which have energy (in the region $r \gg r_{\text{eff}}$) larger than the energy of the incoming scatterer as said to be *closed.* Whereas channels with lower energies are said to be *open.* An illustration of the potential energy functions for 2-channels is given in figure 4.8.

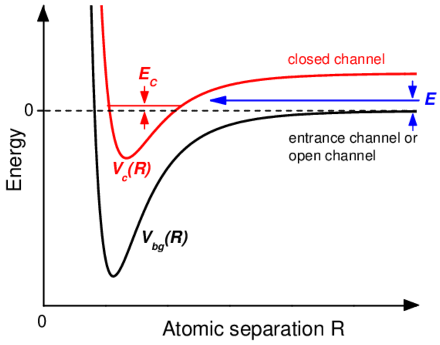

Figure 4.8: Potential energies for a 2-channel scattering process. V_{c} is the closed channel potential whereas V_{bg} the background (open) channel.

> **Note**: In general, systems can have several closed and open channels, for which the spectrum can be very complicated. However, we will restrict our study to 2 channels for the purposes of understanding Feshbach resonances at the most basic level.

Now consider 2 scatterers, both of which incoming in the open channel (sometimes also referred to as the *entrance channel*). Each of these channels of course obey the Schrödinger's equation, but can have channel couplings between them, so we write:

$$\left[\hat{T} + V_{\text{bg}}(r) - E\right]\psi_{\text{bg}}(r) + g(r)\psi_{\text{c}}(r) = 0 \tag{4.118}$$

$$\left[\hat{T} + V_{\text{c}}(r) - E\right]\psi_{\text{c}}(r) + g(r)\psi_{\text{bg}}(r) = 0, \tag{4.119}$$

where $\hat{T}$ is the kinetic energy operator. We now consider a complete set of solutions for the closed channel potential $\{\psi_{\mathrm{c}}^m\}$, each solution denoted by m. In other words, we have:

$$\begin{aligned} \left[\hat{T} + V_{\mathrm{c}}(r) - E_m\right]\psi_{\mathrm{c}}^m(r) &= 0 \\ \Rightarrow \quad \psi_{\mathrm{c}}(r) &= \sum_m \alpha_m \psi_{\mathrm{c}}^m(r). \end{aligned} \tag{4.120}$$

Plugging this expansion solution into the couple equation gives:

$$\begin{aligned} (E_m - E)\alpha_m &= -\left\langle \psi_{\mathrm{c}}^m(r)\right| g(r) \left|\psi_{\mathrm{c}}(r)\right\rangle \\ \Rightarrow \quad \alpha_m &= -\frac{\left\langle \psi_{\mathrm{c}}^m(r)\right| g(r) \left|\psi_{\mathrm{c}}(r)\right\rangle}{E_m - E}. \end{aligned} \tag{4.121}$$

As mentioned, a resonance occurs when the entrance channel energy matches one of the closed channel boundstates, for which if we assume this, this implies that the boundstate associated to this energy will be amplified. As such, a resonance implies one value of $\alpha_m = \alpha^*$ will contribute most significantly to the solution, giving us:

$$\psi_{\mathrm{c}}(r) \approx -\frac{\left\langle \psi_{\mathrm{c}}^*(r)\right| g(r) \left|\psi_{\mathrm{c}}(r)\right\rangle}{E^* - E}\psi_{\mathrm{c}}^*(r), \tag{4.122}$$

indeed showing that on resonance (when E matches E^*), we get that the amplitude becomes unboundedly large. Of course in a actuality, the wavefunction remains finite even on resonance when we include the other correction terms. Attempting to plug this solution back into the coupled system would leave us with a difficult equation to solve comprehensively, instead it is better to model the effects of the resonance by choosing an ansatz which gives rise to the expected behaviors and ensuring that it mathematically satisfies the Schödinger equation.

We can characterize a resonance in terms of its phase shift (which leads to things like the time-delay and scattering lengths). Ideally, we want to separate the phase shift into 2 parts:

$$\delta = \delta_{\mathrm{bg}} + \delta_{\mathrm{res}}, \tag{4.123}$$

where δ_{bg} is the phase-shift expected from non-resonant scattering (in the presence of the background channel) and δ_{res} is the resonance associated phase shift. It turns out that a good model for the phase shifts near resonances is known as the *Breit-Wigner lineshape*:

$$\boxed{\delta(E) = \delta_{bg} + \tan^{-1}\left(\frac{\Gamma/2}{E - E^*}\right)}. \tag{4.124}$$

Γ corresponds to the lifetime of the molecular (resonance) state which is proportional to the matrix element $\left\langle \psi_{\mathrm{c}}^*(r)\right| g(r) \left|\psi_{\mathrm{c}}(r)\right\rangle$. From this, we can get the s-wave scattering length a using the formula:

$$\begin{aligned} a &= -\lim_{k\to 0}\frac{\tan\delta}{k} \\ &\approx -\lim_{k\to 0}\left[\frac{\tan\delta_{\mathrm{bg}}}{k} - \frac{\Gamma/2}{k(E^* - E)}\right] \\ \Rightarrow \quad &\boxed{a = a_{\mathrm{bg}}\left(1 + + \frac{\Delta}{E^* - E}\right)}, \end{aligned} \tag{4.125}$$

defining $a_{\mathrm{bg}} = -\lim_{k\to 0} \frac{\tan\delta_{\mathrm{bg}}}{k}$ and once again defining Δ such that it is proportional to matrix element $\langle\psi_c^*(r)|\, g(r)\, |\psi_c(r)\rangle$. In the low energy regime, we have that this result reduces to

$$a = a_{\mathrm{bg}}\left(1 + + \frac{\Delta}{E^*}\right). \tag{4.126}$$

In experimental set-ups, the energy of the entrance channel can be tuned via varying the external magnetic field or optical methods. For magnetic field methods, we get the plot in figure 4.9.

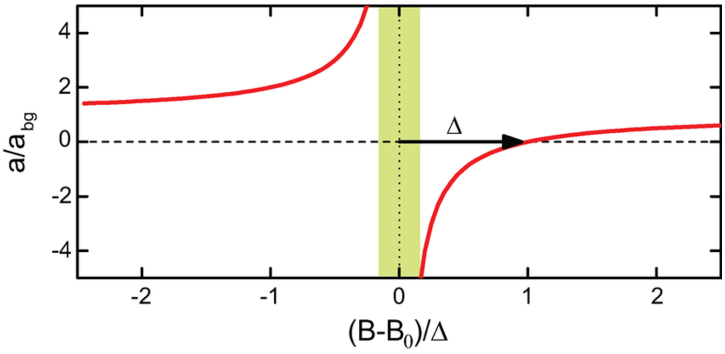

Figure 4.9: Plots of scattering vs magnetic field.

Keep in mind that this is a model, in actual experimental results, the plot is not discontinuous at the resonant value of B_0, but follows the Breit-Wigner lineshape solution behavior elsewhere.

§4.4 Matter Waves

In the proceeding discussions, we are going to consider a low-temperature regime whereby we enter a regime where quantum statistics are significant. Such systems are experimentally achievable due to advances in laser cooling and trapping (which won the Nobel prize in 1997). In sufficiently cold regimes, we observe new phases of matter such as the *Bose-Einstein condensate* (BEC).

Before we get to this, we first consider a classical gas at room temperature. At such high temperatures, the gas consists of classical atoms that move at around 300 m/s, and interact via hardsphere contact interactions. However, if we decrease the temperature to the point where $p^2/2m \approx k_B T$, we need to start considering the wave (quantum) behaviour of the constituent particles. We characterize this with the thermal de Broglie wavelength of the particles goes like:

$$\lambda_{dB} = \sqrt{\frac{2\pi\hbar^2}{mk_B T}}, \tag{4.127}$$

for which if this becomes on the order of the particle separation ($n\lambda_{dB}^3 \approx 1$), the system exhibits exotic behaviors (e.g. Bose-Einstein condensation for a system of bosons). The BEC is as mentioned, a phase of matter and manifest below a transition temperature T_c. More specifically, a BEC is defined by the system having a macroscopic number of particles in the quantum groundstate (first proposed by Bose and Einstein in 1924 and 1925 respectively, then realized experimentally by Cornell, Wieman and Ketterle in 1995). Rb and Na atoms were the first to be condensed to the BEC phase.

Of course, creating a BEC is an extremely difficult task. A major challenge is that we require a very high phase-space density of the gas ($n\lambda_{dB}^3 \approx 1$) but simultaneously, we also require that the gas is sufficiently dilute so that the particles are weakly interacting (to prevent the formation a solid or superfluid instead, which has *large quantum depletion*). Another concern of the diluteness is that we want to minimize the presence of molecular resonances and 3-body recombination effects. To prevent this, we want to spin-polarize the atoms to limit the availability of such bound states. This thus necessitates that the system be below the critical temperature to even consider just a metastable BEC. Such critical temperatures are on the order of nano-Kelvin temperatures, which are extremely low (temperature of deep space is around 3K). To achieve this, there are several techniques.

1. Laser Cooling (Doppler Cooling):

   This technique allows for cooling of a system to the micro-Kelvin scale. The premise of this is process is that we first radiate the atoms with photons such that they resonantly absorb them. By conservation of momentum, this causes the atoms to slow down. So if we precisely and systematically repeat this process, we can progressively cool this system. By construction of the process, this process is also known as *Doppler cooling.*

   However, this cooling process is limited due to the fact that these atoms would radiate the absorbed photons stochastically. This stochastic process on average would result in some minimum thermal energy, so the minimum temperature of laser cooling is set by this process.

2. Evaporative Cooling:

   Another cooling process is known as *evaporative cooling.* To do this, we first trap the atoms in an optical trap. We then change the magnetic field applied such that the atoms with higher momentum escape from the trap, leaving atoms that have a lower energy on average.

In practice, a BEC is actualized using both the cooling processes above, starting with laser cooling then applying evaporative cooling techniques. Now we can ask, how do we detect a BEC? There are 2 commonly adopted techniques which we briefly talk about below.

1. Time-of-Flight Imaging:

   The first way is by observing the expansion of the gas when we release it from the trap. If the gas would be thermal, the gas constituents would have very high momenta and so would cause the gas to expand rapidly. However, a BEC on the other hand would remain much more localized after the trap is turned off. So what we can do is image the gas over time after the release of the trap and measure the the rate of expansion, known as its *time-of-flight.*

2. Persistence of Anisotropy:

   Another means to observe that a system has phased transitioned to a BEC is by imaging the density profile after confinement in an anisotropic trap. To do this, the BEC is initially trapped anisotropically (such as a cylindrically symmetric trap), then let to freely evolve (trap is turned off). If the gas were to be thermal, the expansion would quickly become isotropic following the Boltzmann H-theorem. However, a BEC would retain the trap anisotropy for longer times.

§4.4.1 Bose-Einstein Statistics

We are now going to study a little more formally the properties of a BEC. To begin, the assertion of quantum statistics (bosons vs fermions) is that all identical particles are indistinguishable. Bosons are characterized by having integer spins, whereas fermions having half-integer spins. The assertion of indistinguishability has profound implications on the statistics of the system, such as the permutation statistics of particle configurations. For instance, consider consider grouping 10 particles evenly into 2 boxes. If the particles are distinguishable, there are ${}^{1}0C_5$ ways to do this. On the other hand, there is only **one** way of doing so if the particles are indistinguishable!

In the setting of statistical mechanics, we have that indistinguishable bosons will have a distribution of being in some given energy state as:

$$n_i = \frac{1}{e^{\beta(E_i-\mu)}-1}, \tag{4.128}$$

where $\beta = 1/(k_B T)$. This is known as a *Bose-Einstein distribution.* In the limit of high temperatures, this distribution simplifies to just a Boltzmann factor. However, if we consider a system where we lower the chemical potential such that it reaches the lowest possible energy E_0 (groundstate energy), this in facts leads to a macroscopic population of particles in the groundstate. This occurs when the temperature falls below a critical temperature T_c, and results in a Bose-Einsten condensation.

Definition 4.4.1. Critical Temperature, T_c: The temperature above which, all particles are in an excited state.

To actually calculate this critical temperature so we know what fraction of particles we can get into the BEC state, a key concept for us is the density of state, which we have derived to be:

$$\begin{aligned} D(E)dE &= \frac{4\pi V p^2 dp}{\hbar^3} \\ \Rightarrow \quad D(E) &= \frac{4\pi V p^2 dp}{\hbar^3 dE}, \end{aligned} \tag{4.129}$$

where V is the volume. With this, we can consider the total number of states with all energies above the groundstate energy is given by:

$$N_{\text{ex}} = \frac{4\pi V}{\hbar^3}\int_{E_0}^{\infty}\frac{\sqrt{E}dE}{e^{\beta E}-1}, \tag{4.130}$$

then with the appropriate change of variables, we can get:

$$\begin{aligned} N_{\text{ex}} &= \frac{4\pi V}{\hbar^3}T^{3/2}\int_0^{\infty}\frac{u^2du}{\exp(u)-1} = \frac{4\pi V}{\hbar^3}T^{3/2}\Gamma(3)\epsilon(3) \\ \Rightarrow \quad N_{\text{ex}} &= N\left(\frac{T}{T_c}\right)^{3/2}, \end{aligned} \tag{4.131}$$

where Γ is the gamma function, ϵ is the Rieman-Zeta function and T_c is defined by the evaluation of the integral and parameters of the physical system. As such, we get that the number of particles in the groundstate, computed by $N - N_{\text{ex}}$, is given by:

$$\boxed{N_{\text{g}} = N\left[1 - \left(\frac{T}{T_c}\right)^{3/2}\right]}. \tag{4.132}$$

Harmonically Trapped BECs

Now let us consider a BEC in a harmnonic trap:

$$U(\vec{r}) = \frac{1}{2}m\left(\omega_x x^2 + \omega_y y^2 + \omega_z z^2\right). \tag{4.133}$$

To get the density of states, we consider the volume this system would occupy in phase-space. We see from the form of the conjugate variables, that the volume would be a hyper-ellipsoid. So the phase-space hyper-volume, and hence density of states would be proportional to:

$$\begin{aligned} & D(E) \propto \frac{E^2}{\omega_x\omega_y\omega_z} \\ \Rightarrow \quad & N_{\text{ex}} \propto T^3 \int_0^\infty \frac{u^2 du}{\exp(u) - 1} \\ \Rightarrow \quad & N_{\text{ex}} = N\left(\frac{T}{T_c}\right)^3 \\ \Rightarrow \quad & \boxed{N_{\text{g}} = N\left[1 - \left(\frac{T}{T_c}\right)^3\right]}. \end{aligned} \tag{4.134}$$

There also exists other interesting trapping geometries which can lead to the number of particles in the groundstate having different temperature dependencies (e.g. box traps).

§4.4.2 Quantum Theory of an Interacting Bose Gas

Now, we consider a system in which all particles have reached a bose-condensed state. We are now going to try and write down a Hamiltonian that describes the dynamics of this system. In general, we can write the Hamiltonian in terms of its first quantization formalism as:

$$\hat{H} = \sum_{i=1}^{N}\left[\frac{\hat{p}_i^2}{2m} + V(\hat{\vec{r}}_i)\right] + \sum_{i,j} V_{\text{int}}(\hat{\vec{r}}_i - \hat{\vec{r}}_j), \tag{4.135}$$

with solutions $\psi = \psi(\hat{\vec{r}}_1, \ldots, \hat{\vec{r}}_N)$. The first simplification is to approximate the interaction potential $V_{\text{int}}(\hat{\vec{r}}_i - \hat{\vec{r}}_j)$, with the Fermi-pseudopotential. To make further progress however, we require the formalism of *second quantization*, in which we use *quantum fields operators.* Second quantization reframes the problem from traditional quantum mechanics by asking "how many particles occupy a particular quantum state/mode", instead of "how many quantum states can we retrieve from a given quantum system".

The first step is to construct operators that "create" particles in a particular state as $\hat{b}^\dagger(\vec{r})$, and an operators that "annihilate" particle in that state as $\hat{b}(\vec{r})$. These operators have commutation relations which are governed by the quantum statistics of the particles.

1. Bosons: $\left[\hat{b}_\zeta, \hat{b}^\dagger_{\zeta'}\right] = \delta_{\zeta,\zeta'}$;

   These act on states as:

$$\hat{b}^\dagger_\zeta \left|n_1, n_2, \ldots, n_\zeta, \ldots\right\rangle = \sqrt{n_\zeta + 1}\ \hat{b}^\dagger_\zeta \left|n_1, n_2, \ldots, n_\zeta + 1, \ldots\right\rangle \tag{4.136}$$

$$\hat{b}_\zeta \left|n_1, n_2, \ldots, n_\zeta, \ldots\right\rangle = \sqrt{n_\zeta}\ \hat{b}^\dagger_\zeta \left|n_1, n_2, \ldots, n_\zeta - 1, \ldots\right\rangle. \tag{4.137}$$

2. Fermions: $\left\{\hat{f}_\zeta, \hat{f}^\dagger_{\zeta'}\right\} = \delta_{\zeta,\zeta'}$,

where the subscript ζ denotes the mode index and we adopt the notation of $\hat{f}$ for fermions instead of $\hat{b}$ that is for bosons. The commutator relations above encode the Pauli exclusion principle for fermions, so this is implicit in its construction. From now on, we will be working with bosons. At this points, we can then define a field operator over real-space by a Fourier transform which annihilates a particle in state $|k\rangle$:

$$\hat{\psi}(\vec{r}) = \frac{1}{\sqrt{V}} \sum_k e^{i\vec{k}\cdot\vec{r}} \hat{b}_k. \tag{4.138}$$

The creating version of this is just its dagger. These follow the commutation relation:

$$\left[\hat{\psi}(\vec{r}), \hat{\psi}^\dagger(\vec{r})\right] = \delta^3(\vec{r} - \vec{r}\,'). \tag{4.139}$$

The operators follow the completeness relation:

$$\int d^3r\ \hat{\psi}^\dagger(\vec{r})\hat{\psi}(\vec{r}) = \sum_\zeta \hat{b}^\dagger_\zeta \hat{b}_\zeta = \hat{N}, \tag{4.140}$$

and the Heisenberg equation of motion:

$$i\hbar\frac{\partial}{\partial t}\hat{\psi} = \left(-\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + V + V_{\text{int}}\hat{\psi}^\dagger\hat{\psi}\right)\hat{\psi}. \tag{4.141}$$

With this, we can then recast the first-qunatization Hamiltonian into second-quantized form as:

$$\boxed{\hat{H} = \int d^3r\ \hat{\psi}^\dagger(\vec{r}) \left[\frac{\hat{p}^2}{2m} + V(\hat{\vec{r}})\right] \hat{\psi}(\vec{r}) + \frac{1}{2}\int d^3r \int d^3r'\ \hat{\psi}^\dagger(\vec{r})\hat{\psi}^\dagger(\vec{r}\,')\hat{V}_{\text{int}}(\hat{\vec{r}} - \hat{\vec{r}}\,')\hat{\psi}(\vec{r}\,')\hat{\psi}(\vec{r})}. \tag{4.142}$$

This Hamiltonian is a real beast to solve exactly, however the dilute limit of a gas allows us to assert certain approximations which makes things easier to deal with. A relative simple case is considering the zero-temperature limit. In this case, we have that all particle will occupy the same quantum groundstate. So if we have a harmonically trapped gas, all particles will have the position-space wavefunction written as:

$$\phi_0(\vec{r}) = \frac{1}{\pi^{3/4}\sqrt{a_x a_y a_z}} \exp\left(-\frac{x^2}{2a_x^2} - \frac{y^2}{2a_y^2} - \frac{z^2}{2a_z^2}\right), \tag{4.143}$$

where $a_i = \sqrt{\hbar/(m\omega_i)}$ are the harmonic oscillator length scales. So in the second quantization picture, we have a non-interacting gas being solved by the wavefunction:

$$|\Psi\rangle = \frac{(\hat{b}_0^\dagger)^N}{\sqrt{N!}} |\text{vac}\rangle . \tag{4.144}$$

Now to include interactions for a zero-temperature dilute gas, we will use a mean-field approach. This is valid in the regime where $na^3 \ll 1$, with n being the average density of the gas. This approximates the interaction potential by a mean-field potential U_0, rendering the equation of motion as:

$$i\hbar\frac{\partial}{\partial t}\hat{\psi} = \left(-\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + V_{\text{trap}} + U_0\hat{\psi}^\dagger\hat{\psi}\right)\hat{\psi}. \tag{4.145}$$

Furthermore, we expect that in this regime, the field operator should be well approximated by a classical coherent field, $\hat{\psi} = \psi + \delta\hat{\psi}$. This approximation results in a nonlinear equation of motion:

$$\boxed{i\hbar\frac{\partial}{\partial t}\psi = \left(-\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + V_{\text{trap}} + U_0|\psi|^2\right)\psi}, \tag{4.146}$$

known as the *Gross-Pitaevski equation.* Counter to what traditional quantum mechanics asserts, this is a nonlinear equation! This nonlinearity arises from the approximations made and turns out to model a BEC exceedingly well. We note that the terms in this Hamiltonian have energy scalings that go like:

$$-\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + V_{\text{trap}} \sim \hbar\omega_{\text{trap}} \tag{4.147}$$

$$U_0|\psi|^2 \sim \frac{Na}{a_{\text{trap}}}\hbar\omega_{\text{trap}}. \tag{4.148}$$

The second energy scaling tells us that even in a weakly interaction bose gas, there can be significant mean-field effects!

Appendices

§.1 Evaluation of the Integral in Fermi's Golden Rule

Recall that for the derivation of Fermi's golden rule, we started with a harmonic perturbation which led to an integral of the form:

$$I = \int_{-\infty}^{\infty} \frac{\sin^2(xt)}{x^2 t} dx \tag{149}$$

To evaluate this, we first do a change of variable $u \equiv xt$ which gives:

$$\begin{aligned} \int_{-\infty}^{\infty} \frac{\sin^2 u}{u^2} du &= \int \frac{1 - \cos(2u)}{2u^2} du \\ &= \mathrm{Re}\left(P \int \frac{1 - e^{2iu}}{2u^2} du \right) \end{aligned} \tag{150}$$

where P is the *Cauchy-principle value*. We see that the integrand is ill-defined at $u = 0$, so we are going to do a contour integral by considering a closed contour S that wraps around the point $u = 0$ by an interval $[-\delta, \delta]$, and makes a large arc at infinity. This gives us:

$$I_S = \oint_S \frac{1 - e^{2iu}}{2u^2} du = 0 \tag{151}$$

We refer to the contour over the small arc around $u = 0$ as S_2 and the contour at infinity (great arc) as S_1. So we have:

$$I_S = I_{S_1} + I_{S_2} + I_{S'} = 0 \tag{152}$$

where S' accounts for all other contour segments. First we note that I_{S_1} and $I_{S'}$ vanish, so we just need to consider I_2 in the limit where $\delta \to 0$ (compute the Cauchy principle value). To do so, we define $u \equiv \delta e^{i\theta}$ which gives us:

$$\begin{aligned} I_{S_2} &= \lim_{\delta \to 0} \int \frac{1 - e^{2iu}}{2u^2} du \\ &= \lim_{\delta \to 0} i \int_{\pi}^{0} \frac{1 - 2i\delta e^{i\theta}}{2\delta^2 e^{2i\theta}} \delta e^{i\theta} d\theta = -\pi, \end{aligned} \tag{153}$$

indeed giving us the π that we hoped for (yum).