Quantum Mechanics II

Based on lectures by Dr. Andrei Belitsky

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These notes are not endorsed by the lecturers, and I have modified them (often significantly) after lectures. They are nowhere near accurate representations of what was actually lectured, and in particular, all errors are almost surely mine.

Contents

1 Introduction/Review

1.1 Postulate 1: The State of a System

Every physical state in quantum mechanics is represented by a state vector, $|\psi\rangle$, in the infinite-dimensional linear Hilbert Space. The state vector $|\psi\rangle$ can be represented in different bases expanding them in complete sets of basis elements (that is, functions):

$$\{|\phi_n\rangle \, | n = 1, \dots \infty\}$$

With the orthogonality and completeness conditions

$$\begin{aligned} \langle \phi_n | \phi_m \rangle &= \delta_{nm} \\ \sum_n |\phi_n\rangle \langle \phi_n| &= 1 \end{aligned}$$

Thus,

$$\begin{aligned} |\psi\rangle &= \sum_n |\phi_n\rangle \langle \phi_n | \psi \rangle \\ &= \sum_n a_n |\phi_n\rangle \end{aligned}$$

where

$$a_n = \langle \phi_n | \psi \rangle$$

We then say that the state vector $|\psi\rangle$ is represented by its components a_n in the basis $|\phi_n\rangle$.
We can write this in any other basis, as well. The state of a microsystem is independent of the basis in which it is expanded.

Proof. If we have two bases,

$$\begin{aligned} |\psi\rangle &= \sum_n a_n |\phi_n\rangle \\ &= \sum_n b_n |\chi_n\rangle \end{aligned}$$

Combining these two representations (by setting them equal to each other), we find that

$$\begin{aligned} |\psi\rangle &= \sum_n b_n \sum_m |\phi_m\rangle \langle \phi_m | \chi_n \rangle \\ &= \sum_m \left(\sum_n b_n \langle \phi_m | \chi_n \rangle \right) |\phi_m\rangle \\ a_n &= \sum_m b_m \langle \phi_n | \chi_m \rangle \end{aligned}$$

Thus, we can write a unitary transformation matrix,

$$U_{nm} \equiv \langle \phi_n | \chi_m \rangle$$

with the provable property

$$UU^\dagger = 1$$

□

1.2 Postulate 2: Observables and Operators

An observable is a measurable dynamical variable, like the ones we see in classical mechanics (eg. position/coordinate, momentum, energy). In quantum mechanics, we represent an observable by an operator $\hat{A}$. Because the eigenvalues must be real, $\hat{A}$ for an observable must be Hermitian, that is,

$$\hat{A} = \hat{A}^\dagger$$

1.3 Postulate 3: Measurements in Quantum Mechanics

Quantum theory predicts the result of a measurement. It doesn't make sense to talk about what might happen in the physical world outside the context of measurement. In order to measure an observable, we act on the state (not necessarily an eigenstate) with it. If we write the state in a basis of eigenstates of $\hat{A}$,

$$|\psi\rangle = \sum_n \langle \phi_n | \psi \rangle \, |\phi_n\rangle$$

Then we can use the definition of an eigenstate to see what it means to act on a state by an observable:

$$\hat{A} \, |\phi_n\rangle = a_n \, |\phi_n\rangle$$
$$\hat{A} \, |\psi\rangle = \sum_n a_n \, \langle \phi_n | \psi \rangle \, |\phi_n\rangle$$

And finally, we can show the observation effect:

$$|\psi\rangle \xrightarrow{a_n} \langle \phi_n | \psi \rangle \, |\phi_n\rangle = |\psi_{after}\rangle$$

1.4 Postulate 4: Probabilistic Interpretation

Before a measurement, we don't know with any certainty which eigenstate a system will be in after the measurement, only a probabilistic outcome is possible. The probability of measuring $\hat{A}$ and getting the eigenvalue a_n from the state $|\psi\rangle$ (in the eigenstate basis $\{\phi_n\}$) is

$$P_n = \frac{|\langle \phi_n | \psi \rangle|^2}{\langle \psi | \psi \rangle}$$

For an m-degenerate eigenvalue a_n,

$$P_n = \sum_j^m \frac{|\langle n, j | \psi \rangle|^2}{\langle \psi | \psi \rangle}$$

Where

$$\hat{A}\,|n,j\rangle = a_n\,|n,j\rangle$$

For continuous spectra, the differential element of the probability of measuring $\hat{A}$ and finding a value between $[a, a+\mathrm{d}a]$ in the system $|\psi\rangle$ is

$$\frac{\mathrm{d}P(a)}{\mathrm{d}a} = \frac{|\langle a|\psi\rangle|^2}{\langle\psi|\psi\rangle}$$

1.4.1 Simultaneity of Measurements

If two operators (representing observables), $\hat{A}$ and $\hat{B}$, commute,

$$[\hat{A},\hat{B}] = 0$$

they represent compatible observables, or observables that may be simultaneously measured. In other words, if $\hat{A}$ and $\hat{B}$ commute, then there exists some state $|a,b\rangle$ that is an eigenstate of both operators, such that

$$\hat{A}\,|a,b\rangle = a\,|a,b\rangle$$
$$\hat{B}\,|a,b\rangle = b\,|a,b\rangle$$

If the operators $\hat{A}$ and $\hat{B}$, or

$$[\hat{A},\hat{B}] \neq 0$$

then they obey the uncertainty principle: they can't be measured simultaneously without some minimum uncertainty given by

$$\langle(\Delta\hat{A})^2\rangle\langle(\Delta\hat{B})^2\rangle \geq \frac{1}{4}\left|\langle[\hat{A},\hat{B}]\rangle\right|^2$$

Where

$$\begin{aligned}\Delta\hat{A} &= \hat{A} - \langle\hat{A}\rangle\\ \hat{A} &= \langle\psi|\,\hat{A}\,|\psi\rangle\\ &= \sum_n a_n\,|\langle n|\psi\rangle|^2\end{aligned}$$

1.5 Typical Representations

In quantum mechanics, we often use two representations: coordinate (or position), and (linear) momentum. These representations are achieved by means of using basis vector states. In the coordinate representation, we use the basis $|\mathbf{x}\rangle$ to write a wave function of a system as

$$\psi(\mathbf{x},t) = \langle\mathbf{x}|\psi(t)\rangle$$

And likewise, in the momentum representation, we use the basis $|\mathbf{p}\rangle$ to write the wave function of a system as

$$\psi(\mathbf{p},t) = \langle\mathbf{p}|\psi(t)\rangle$$

We can relate these representations by the Fourier transformation, which acts as a change of basis:

$$\psi(\mathbf{x},t) = \int \frac{\mathrm{d}^3\mathbf{p}}{(2\pi\hbar)^3} e^{\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{x}} \psi(\mathbf{p},t)$$
$$\psi(\mathbf{p},t) = \int \mathrm{d}^3\mathbf{x} e^{\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{x}} \psi(\mathbf{x},t)$$

Properties of the Bases

(i) Transformation "matrix" We want some operator that we can use such that

$$|\mathbf{p}\rangle = \hat{U} \odot |\mathbf{x}\rangle$$

Let's see what that looks like:

$$\begin{aligned} |\mathbf{p}\rangle &= \hat{U} \odot |\mathbf{x}\rangle \\ \langle \mathbf{x}|\mathbf{p}\rangle &= \hat{U} \\ \hat{\mathbf{p}} \langle \mathbf{x}|\mathbf{p}\rangle &= -i\hbar\boldsymbol{\nabla} \langle \mathbf{x}|\mathbf{p}\rangle \\ \mathbf{p}\psi_{\mathbf{p}}(\mathbf{x}) &= -i\hbar\boldsymbol{\nabla}\psi_{\mathbf{p}}(\mathbf{x}) \\ \psi_{\mathbf{p}}(\mathbf{x}) &= e^{\frac{i}{\hbar}\mathbf{x}\cdot\mathbf{p}} \end{aligned}$$

To be short,

$$\begin{aligned} \hat{U} &= \langle \mathbf{x}|\mathbf{p}\rangle \\ &= \psi_{\mathbf{p}}(\mathbf{x}) \\ &= e^{\frac{i}{\hbar}\mathbf{x}\cdot\mathbf{p}} \end{aligned}$$

(ii) Orthogonality

$$\langle \mathbf{x}'|\mathbf{x}''\rangle = \delta^{(3)}(\mathbf{x}' - \mathbf{x}'')$$
$$\langle \mathbf{p}'|\mathbf{p}''\rangle = (2\pi\hbar)^3 \delta^{(3)}(\mathbf{p}' - \mathbf{p}'')$$

(iii) Completeness

$$\int \mathrm{d}^3\mathbf{x} \, |\mathbf{x}\rangle \langle \mathbf{x}| = 1$$
$$\int \frac{\mathrm{d}^3\mathbf{p}}{(2\pi\hbar)^3} \, |\mathbf{p}\rangle \langle \mathbf{p}| = 1$$

Important note: The normalization here is different from Zettili because the physical reality of the volume in phase space: $V\frac{\mathrm{d}^3\mathbf{p}}{(2\pi\hbar)^3}$ is the number of states with momentum between $\mathbf{p}$ and $\mathbf{p} + \mathrm{d}\mathbf{p}$ around $\mathbf{p}$ in volume V. Thus, $(2\pi\hbar)^3$ is free volume occupied by a (something) state.

Also! Note that $\hat{\mathbf{x}}$ and $\hat{\mathbf{p}}$ are not compatible operators and so obey the commutation relations:

$$[\hat{\mathbf{x}}_i, \hat{\mathbf{p}}_j] = i\hbar\delta_{ij}$$
$$\Delta x \Delta p \geq \frac{\hbar}{2}$$
$$\Delta x = \sqrt{\langle \hat{x^2} \rangle - \langle \hat{x}^2 \rangle}$$

1.6 Postulate 5: Time Evolution of a System

The time evolution of the state vector $|\psi(t)\rangle$ of a system is governed by the Schrödinger equation:

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

Given an initial state $|\psi(t_0)\rangle$, it defines the state of the system at a later time $t > t_0$. We can also do this by first looking at a time-independent Hamiltonian and introducing a linear unitary transformation operator, which we call the time-development operator:

$$|\psi(t)\rangle = \hat{U}(t, t_0) |\psi(t_0)\rangle$$

It obeys the equation (again, for a time-independent $\hat{H}$)

$$i\hbar \frac{\partial}{\partial t} \hat{U}(t, t_0) = \hat{H}\hat{U}(t, t_0)$$

We can integrate easily to find that

$$\hat{U}(t, t_0) = e^{-\frac{i}{\hbar}\hat{H}(t-t_0)}$$

This is provably a unitary operator (since the Hamiltonian is Hermitian).

1.7 Typical Applications

1.7.1 Particle in External Electromagnetic Fields

Recall from classic electrodynamics that

$$\mathbf{E} = -\boldsymbol{\nabla}\phi - \frac{\partial}{\partial t}\mathbf{A}$$
$$\mathbf{B} = \boldsymbol{\nabla} \times \mathbf{A}$$

Let's construct the Hamiltonian for a particle in an external field. We'll do this by finding the Lagrangian using the Lorentz force and Newton's third law.

Newton's Law

$$\begin{aligned} m\dot{\mathbf{v}} &= \mathbf{F}_{Lorentz} \\ &= q(\mathbf{E} + \mathbf{v} \times \mathbf{B}) \\ &= q(-\boldsymbol{\nabla}\phi - \frac{\partial}{\partial t}\mathbf{A} + \mathbf{v} \times [\boldsymbol{\nabla} \times \mathbf{A}]) \end{aligned}$$

Working out that last bit,

$$\begin{aligned}[\mathbf{v}\times[\boldsymbol{\nabla}\times\mathbf{A}]]_i &= \epsilon_{ijk}v_j[\boldsymbol{\nabla}\times\mathbf{A}]_k \\ &= \epsilon_{ijk}\epsilon_{k\ell m}v_j\partial_\ell A_m \\ &= [\delta_{i\ell}\delta_{jm}-\delta_{im}\delta_{j\ell}]v_j\partial_\ell A_m \\ &= \partial_i(\mathbf{v}\cdot\mathbf{A})-(\mathbf{v}\cdot\boldsymbol{\nabla})A_i\end{aligned}$$

Bringing this back into our main equation,

$$\begin{aligned}m\dot{\mathbf{v}} &= q\left(-\boldsymbol{\nabla}\phi-\frac{\partial}{\partial t}\mathbf{A}-(\mathbf{v}\cdot\boldsymbol{\nabla})\mathbf{A}+\boldsymbol{\nabla}(\mathbf{v}\cdot\mathbf{A})\right) \\ &= q\left(-\boldsymbol{\nabla}\phi-\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{A}+\boldsymbol{\nabla}(\mathbf{v}\cdot\mathbf{A})\right)\end{aligned}$$

Recall now that the equation(s) of motion arise from the Lagrangian,

$$\frac{\partial L}{\partial\mathbf{x}}-\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L}{\partial\mathbf{v}}=0$$

We can, of course, re-write this and equate it to the equation of motion we just found to find the Lagrangian L:

$$\begin{aligned}\boldsymbol{\nabla}L-\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L}{\partial\mathbf{v}}&=0 \\ q\boldsymbol{\nabla}\phi+\boldsymbol{\nabla}(\mathbf{v}\cdot\mathbf{A})-\frac{\mathrm{d}}{\mathrm{d}t}(m\mathbf{v}+q\mathbf{A})&=0 \\ \frac{m\mathbf{v}^2}{2}+q(\mathbf{v}\cdot\mathbf{A})-q\phi&=L\end{aligned}$$

Note that the final term means that we can't simply write the Lagrangian like we might be used to, as $L=T-V$.
The Hamiltonian, usually written $\hat{H}=T+V$, can be written in terms of the Lagrangian as

$$\begin{aligned}H &= \mathbf{p}\cdot\mathbf{v}-L \\ &= \mathbf{v}\frac{\partial L}{\partial\mathbf{v}}-L \\ &= \mathbf{v}(m\mathbf{v}+q\mathbf{A})-\frac{m\mathbf{v}^2}{2}-q(\mathbf{v}\cdot\mathbf{A})+q\phi \\ &= \frac{m\mathbf{v}^2}{2}+q\phi\end{aligned}$$

We can re-write $\mathbf{v}$ in terms of generalized momentum,

$$m\mathbf{v}=\mathbf{p}-q\mathbf{A}$$

So that

$$H=\frac{1}{2m}(\mathbf{p}-q\mathbf{A})^2+q\phi$$

Since the Lorentz force is not a potential force (ie. it can't be written as the gradient of some potential function), it's not gauge-invariant, so we can't accommodate it in its original form, hence the need for this. But, just because the Hamiltonian is "non-physical," that doesn't necessarily mean that the eigenstates or eigenvalues will be non-physical or non-gauge-invariant.

Proof. We can start with our basic definitions:

$$i\hbar\frac{\partial}{\partial t}\psi(t,\mathbf{x}) = \hat{H}\psi(t,\mathbf{x})$$
$$\hat{H} = \frac{1}{2m}(\mathbf{p} - q\mathbf{A})^2 + q\phi$$
$$\mathbf{p} = -ih\boldsymbol{\nabla}$$

If we transform $\mathbf{A}$ and ϕ, as such:

$$\mathbf{A} \to \mathbf{A}' = \mathbf{A} + \boldsymbol{\nabla} \times \chi$$
$$\phi \to \ \phi' = \phi - \frac{\partial}{\partial t}\chi$$

Then our Schrödinger equation goes from

$$i\hbar\frac{\partial}{\partial t}\psi = \left[\frac{1}{2m}(-i\hbar\boldsymbol{\nabla} - q\mathbf{A})(-i\hbar\boldsymbol{\nabla} - q\mathbf{A}) + q\phi\right]\psi$$

to

$$i\hbar\frac{\partial}{\partial t}\psi' = \left[\frac{1}{2m}(-i\hbar\boldsymbol{\nabla} - q\mathbf{A}')(-i\hbar\boldsymbol{\nabla} - q\mathbf{A}') + q\phi'\right]\psi'$$
$$i\hbar\frac{\partial}{\partial t}\psi' = \left[\frac{1}{2m}(-i\hbar\boldsymbol{\nabla} - q\mathbf{A} - q\boldsymbol{\nabla}\chi)(-i\hbar\boldsymbol{\nabla} - q\mathbf{A} - q\boldsymbol{\nabla}\chi) + q\phi - q\frac{\partial}{\partial t}\chi\right]\psi'$$

In order for the wave function to remain invariant by a change in phase, we need $|\psi|^2 = |\psi'|^2$, so we can write/guess ψ' as ψ with a phase transformation:

$$\psi' = e^{i\alpha}\psi$$

Where $\left|e^{i\alpha}\right|^2 = 1$ and α is a function of t and $\mathbf{x}$. Making this substitution in our gauge-shifted Schrödinger equation:

$$i\hbar\frac{\partial}{\partial t}e^{i\alpha}\psi =$$
$$\left[\frac{1}{2m}(-i\hbar\boldsymbol{\nabla} - q\mathbf{A} - q\boldsymbol{\nabla}\chi)(-i\hbar\boldsymbol{\nabla} - q\mathbf{A} - q\boldsymbol{\nabla}\chi) + q\phi - q\frac{\partial}{\partial t}\chi\right]e^{i\alpha}\psi$$
$$i\hbar\left[i\frac{\partial\alpha}{\partial t}\psi + \frac{\partial\psi}{\partial t}\right] =$$
$$\left[\frac{1}{2m}(-i\hbar\boldsymbol{\nabla} - q\mathbf{A} - q\boldsymbol{\nabla}\chi)(-i\hbar\boldsymbol{\nabla} - q\mathbf{A} - q\boldsymbol{\nabla}\chi) + q\phi - q\frac{\partial}{\partial t}\chi\right]\psi$$

In order for this to be true and gauge-invariant, we must have

$$i\hbar i\frac{\partial a}{\partial t} = -q\frac{\partial\chi}{\partial t}$$

Meaning we can solve for α:

$$\alpha = \frac{q}{\hbar}\chi$$

So

$$\psi' = e^{\frac{q}{\hbar}}\chi$$

If we finish cancelling, we'll end up with just the same Schrödinger equation we started with. □

1.7.2 The One-Dimensional Quantum Harmonic Oscillator; The Ladder Method

Recall that for a one-dimensional simple harmonic oscillator,

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{m\omega^2}{2}\hat{x}^2$$

We can re-write this to make it fit our needs later:

$$\begin{aligned} H &= \hbar\omega\left[\frac{p^2}{2\hbar\omega m} + \frac{m\omega}{2\hbar}x^2\right] \\ &= \hbar\frac{m\omega}{2\hbar}\left[x^2 + \frac{p^2}{(m\omega)^2}\right] \\ &= \hbar\omega\left(\sqrt{\frac{m\omega}{2\hbar}}\right)\left[x + i\frac{p}{m\omega}\right]\left[x - i\frac{p}{m\omega}\right] \end{aligned}$$

We can define two ladder operators, a and $a^\dagger$, which are given by

$$\begin{aligned} a &= \sqrt{\frac{m\omega}{2\hbar}}\left[x + \frac{i}{m\omega}p\right] \\ a^\dagger &= \sqrt{\frac{m\omega}{2\hbar}}\left[x - \frac{i}{m\omega}p\right] \end{aligned}$$

If we do, we can re-write the Hamiltonian as

$$H = \hbar\omega a^\dagger a$$

We can't just define these as operators and be good to go, though. Let's see what happens if we try to re-write this in operators. Recall first that $[\hat{x}, \hat{p}] = i\hbar$.

$$\begin{aligned} \hat{H} &= \hbar\omega\hat{a}^\dagger\hat{a} \\ &= \hbar\omega\frac{m\omega}{2\hbar}\left[\hat{x} - \frac{i}{m\omega}\hat{p}\right]\left[\hat{x} + \frac{i}{m\omega}\hat{p}\right] \\ &= \frac{m\omega^2}{2}\left[\hat{x}^2 + \frac{\hat{p}^2}{(m\omega)^2} + \frac{i}{m\omega}(\hat{x}\hat{p} - \hat{p}\hat{x})\right] \\ &= \frac{m\omega^2}{2}\left[\hat{x}^2 + \frac{\hat{p}^2}{(m\omega)^2} - \frac{\hbar}{m\omega}\right] \end{aligned}$$

This is *almost* what we started with, but we have an extra term added on at the end there. To account for this weird shift, we re-write the quantum Hamiltonian operator as

$$\hat{H} = \hbar\omega\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right)$$

From here, we can start to construct a Hilbert space of states. We start with the lowest possible energy state: the vacuum state (which we'll write as $|0\rangle$). We can start to use the ladder operators we defined before as creation/annihilation

operators:

$$\begin{aligned} \hat{a}\,|0\rangle = 0 \qquad & \hat{H}\,|0\rangle = \frac{\hbar\omega}{2}\,|0\rangle \\ \hat{a}^\dagger\,|0\rangle = |1\rangle \qquad & \hat{H}\,|1\rangle = \frac{\hbar\omega}{2}\left(1+\frac{1}{2}\right)|1\rangle \\ \left(\hat{a}^\dagger\right)^n|0\rangle = |1\rangle \qquad & \hat{H}\,|n\rangle = \frac{\hbar\omega}{2}\left(n+\frac{1}{2}\right)|n\rangle \end{aligned}$$

To normalize, we take

$$\frac{\left(\hat{a}^\dagger\right)^n|0\rangle}{\sqrt{n!}} = |n\rangle$$

2 Time-Dependent Perturbation Theory

2.1 The Pictures of Quantum Mechanics

We've seen that there are a number of ways to represent wave functions and operators in QM, all connected by unitary transformations. Each class of representations is called a picture, and differs from the others primarily by the way it treats the time evolution of a system. There are three pictures we'll be talking about in this class, as they're the three that show up the most often.

2.1.1 The Scchrödinger Picture

The Schroödinger picture is useful for time-independent Hamiltonians. In this piture, the state vetors depend on time, but the operators do not. We write the wave equation in this picture as

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\left|\psi_S(t)\right\rangle = \hat{H}\left|\psi_S(t)\right\rangle$$

Where the S subscript denotes the Schrödinger picture. We relate the initial state at time t_0 to a later state at time t by means of a linear unitary operator we call the propagator, or the time-evolution operator (we already saw this earlier):

$$\left|\psi_S(t)\right\rangle = \hat{U}(t,t_0)\left|\psi_S(t_0)\right\rangle$$

Where

$$\hat{U}(t,t_0) = e^{-i(t-t_0)\hat{H}}$$

The time-evolution operator should satisfy the following properties:

$$\hat{U}^\dagger = \hat{U}^{-1} = \hat{U}$$
$$\hat{U}(t_0,t_0) = 1$$
$$\hat{U}(t_1,t_2)\hat{U}(t_2,t_3) = \hat{U}(t_1,t_3)$$

2.1.2 The Heisenberg Picture

The Heisenberg picture is useful for describing systems with time-dependent Hamiltonians. In this picture, the state vectors don't depend on time, but the operators do.
We can get to this picture by applying $\hat{U}^\dagger$ from the SP onto $\left|\psi_S(t)\right\rangle$:

$$\left|\psi_H(t)\right\rangle = \hat{U}^\dagger(t)\left|\psi_S(t)\right\rangle = \left|\psi_S(0)\right\rangle$$

By extension, this means that

$$\frac{\mathrm{d}}{\mathrm{d}t}\left|\psi_H\right\rangle = 0$$

We can examine, as well, how the expectation value evolves with time, again coming from the Schrödinger picture:

$$\begin{aligned}\left\langle \hat{A}_S \right\rangle &= \langle \psi_S(t)| \hat{A}_S |\psi_S(t)\rangle \\ &= \langle \psi_H| \hat{U}^\dagger \hat{A}_S \hat{U} |\psi_H\rangle \\ &= \langle \psi_H| \hat{A}_H(t) |\psi_H\rangle \\ &= \left\langle \hat{A}_H \right\rangle\end{aligned}$$

Where

$$\hat{A}_H(t) = \hat{U}^\dagger(t)\hat{A}_S\hat{U}(t)$$

We can see here that although we define the operator itself in terms of its time evolution, the expectation value remains the same.

The Heisenberg Equation of Motion

To determine the equation of motion (that is, the equation that regulates the time evolution of operators in the Heisenberg picture), we can take the time derivative of $\hat{A}_H$, assuming that $\hat{A}_S$ does not depend explicitly on time:

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t} &= \frac{\partial \hat{U}^\dagger(t)}{\partial t}\hat{A}\hat{U}(t) + \hat{U}^\dagger(t)\hat{A}\frac{\partial \hat{U}(t)}{\partial t} \\ &= -\frac{1}{i\hbar}(\hat{U}^\dagger\hat{H}\hat{U})(\hat{U}^\dagger\hat{A}_S\hat{U}) + \frac{1}{i\hbar}(\hat{U}^\dagger\hat{A}_S\hat{U})(\hat{U}^\dagger\hat{H}\hat{U})\end{aligned}$$

Since $\hat{U}$ and $\hat{H}$ commute, we can write this as

$$\begin{aligned}&= \frac{i}{\hbar}\left(\hat{H}(\hat{U}^\dagger\hat{A}_S\hat{U}) - (\hat{U}^\dagger\hat{A}_S\hat{U})\hat{H}\right) \\ &= \frac{i}{\hbar}\left[\hat{H}, \hat{U}^\dagger\hat{A}_S\hat{U}\right] \\ &= \frac{i}{\hbar}\left[\hat{H}, \hat{A}_H\right]\end{aligned}$$

In the textbook, this is written as

$$= \frac{1}{i\hbar}\left[\hat{A}_H, \hat{H}\right]$$

This is the Heisenberg picture's equivalent to the Schrödinger equation. In general, it tends to be difficult to solve.

2.1.3 The Dirac (Interaction) Picture

The Dirac (or interaction) picture is useful for describing systems with time-dependent Hamiltonians. In this picture, the state vectors and the operators both depend on time.
A typical Hamiltonian system in the Dirac picture can be taken to be of the form

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

where $\hat{H}_0$ is the time-independent part of the Hamiltonian, or the Hamiltonian in the Schrödinger picture, and $\hat{V}(t)$ is the time-dependent part of the Hamiltonian, a potential which can be considered a small perturbation as long as $|V| \ll H_0$.

State vectors in the Dirac picture can be written in terms of the time-independent (ie. Schrödinger) Hamiltonian and the Schrödinger picture's state vector:

$$|\psi_D(t)\rangle = e^{\frac{i}{\hbar}\hat{H}_0 t}\,|\psi_S(t)\rangle$$

The time evolution of the state vector in the Dirac picture can be given by

$$\begin{aligned} i\hbar\frac{\mathrm{d}}{\mathrm{d}t}|\psi_D(t)\rangle &= -\hat{H}_0 e^{i\hat{H}_0 t/\hbar}\,|\psi_S(t)\rangle + e^{i\hat{H}_0 t/\hbar} i\hbar\frac{\mathrm{d}}{\mathrm{d}t}|\psi_S(t)\rangle \\ &= -\hat{H}_0 e^{it\hat{H}_0/\hbar}\,|\psi_S(t)\rangle + (\hat{H}_0 + \hat{V}_S)e^{it\hat{H}_0/\hbar}\,|\psi_S(t)\rangle \\ &= \left(e^{i\hat{H}_0 t/\hbar}\hat{V}_S(t)e^{-i\hat{H}_0 t/\hbar}\right) e^{i\hat{H}_0 t/\hbar}\,|\psi_S(t)\rangle \\ &= \hat{V}_D\,|\psi_D(t)\rangle \end{aligned}$$

Thus,

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}|\psi_D(t)\rangle = \hat{V}_D(t)\,|\psi_D(t)\rangle$$

This shows us that the time evolution of the state vector is driven by the interaction given by the potential function (hence, we sometimes call this the interaction picture).

We can also find the Dirac representation of an operator in terms of its Schrödinger representation:

$$\hat{A}_D(t) = e^{i\hat{H}_0 t/\hbar}\hat{A}_S e^{-i\hat{H}_0 t/\hbar}$$

Like in the Heisenberg representation, we can also show that the equation of motion for operators in the Dirac picture is

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t}\hat{A}_D(t) &= \frac{1}{i\hbar}\left[\hat{A}_D(t), \hat{H}_0\right] \\ &= \frac{i}{\hbar}\left[\hat{H}_0, \hat{A}_D(t)\right] \end{aligned}$$

2.2 Time-Dependent Perturbation Theory

2.2.1 Time-Dependent Perturbation Theory

Last semester, we only concerned ourselves with Hamiltonians that didn't depend on time, which is useful, but restrictive since most quantum phenomenons are governed by time-dependent Hamiltonians. Right now, we'll concern ourselves with Hamiltonians that can be written as

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

Where the time-dependent part of the Hamiltonian, $\hat{V}(t)$, is small enough compared to the time-independent part, $\hat{H}_0$, that it can be considered a small perturbation.

Let's start by considering the case where $V = 0$ (ie. the first-order approximation to the perturbed system):

$$\hat{H}_0\,|\psi_n\rangle = E_n\,|\psi_n\rangle$$

The eigenvalues, E_n, and eigenstates, $|\psi_n\rangle$ of this system are known, and its most genera state vectors are given by stationary states,

$$\begin{aligned} |\Psi_n(t)\rangle &= e^{-it\hat{H}_0/\hbar}\,|\psi_n\rangle \\ &= e^{-itE_n/\hbar}\,|\psi_n\rangle \end{aligned}$$

Now, we can switch on a time-dependent perturbation from time $t = 0$ to time $t = \tau$ that looks like:

$$\hat{V}(t) = \begin{cases} \hat{V}(t), & 0 \le t \le \tau \\ 0, & t < 0, t > \tau \end{cases}$$

During this interval, the Schrödinger equation is

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\,|\Psi(t)\rangle = (\hat{H}_0 + \hat{V}(t))\,|\Psi(t)\rangle$$

When the system interacts with $\hat{V}(t)$ between $0 \le t \le \tau$, it either absorbs or emits energy. This forces the system to undergo a transition from one unperturbed eigenstate to another. The main task of time-dependent perturbation theory, then, consists in answering the question: what is the probability of a system initially in a state $|\psi_i\rangle$ and energy E_i undergoing a transition to a state $|\psi_f\rangle$ with E_f?
The general solution to an unperturbed system can be written as

$$|\Psi(t)\rangle = \sum_n c_n\,|\Psi_n(t)\rangle$$

The perturbed problem is solved similarly, by allowing time-dependence of the normalization constants,

$$|\Psi(t)\rangle = \sum_n c_n(t)\,|\Psi_n(t)\rangle$$

And substituting into the Schrödinger equation to find $c_n(t)$ in various orders of approximation.
Instead, we can actually solve the problem exactly in the Dirac picture. Starting with the Schrödinger equation in the Shrödinger picture, we first make the shift to the Dirac picture:

$$\begin{aligned} |\Psi_D(t)\rangle &= e^{i\hat{H}_0 t/\hbar}\,|\Psi(t)\rangle \\ \therefore |\Psi(t)\rangle &= e^{-i\hat{H}_0 t/\hbar}\,|\Psi_D(t)\rangle \end{aligned}$$

So we can write

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\,|\Psi_D(t)\rangle = \hat{V}_D(t)\,|\Psi_D(t)\rangle$$

Where $\hat{V}_D(t)$ has the same relationship to $\hat{V}(t)$ as all operators do when one is in the Schrödinger picture and one is in the Dirac picture.
We can use the time-development operator to re-write the state vector as

$$|\Psi_D(t)\rangle = \hat{U}_D(t, t_0)\,|\Psi_D(t_0)\rangle$$

We can use this to simplify the Schrödinger equation—if we plug this in, since we will have a $|\Psi_D(t_0)\rangle$ (that is, a constant) on either side, and the operators will each apply to $\hat{U}$ instead of the state vector, we can re-write the Schrödinger equation as

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\hat{U}_D(t,t_0) = \hat{V}_D(t)\hat{U}_D(t,t_0)$$

In order to make this look like what we're used to with time-independent perturbation theory, let's introduce a small scalar parameter ϵ, which we can set to $\epsilon = 1$ later when we need to. This is similar to when we did time-independent perturbation theory and we wrote the perturbated Hamiltonian as $\hat{H} = \hat{H}_0 + \lambda\hat{V}$, we're just using ϵ instead. We're just using this to keep track of which order correction we're on.

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\hat{U}_D(t,t_0) = \epsilon\hat{V}_D(t)\hat{U}_D(t,t_0)$$

We can then write our perturbative series for $\hat{U}_D$ as

$$\hat{U}_D(t,t_0) = \epsilon^0\hat{U}_D^{(0)} + \epsilon\hat{U}_D^{(1)}(t,t_0) + \epsilon^2\hat{U}_D^{(2)}(t,t_0) + \cdots$$

So we can write our Schrödinger equation using this series as

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}(1+\epsilon\hat{U}_D^{(1)}(t,t_0)+\epsilon^2\hat{U}_D^{(2)}(t,t_0)+\cdots) = \epsilon\hat{V}_D(t)(1+\epsilon\hat{U}_D^{(1)}(t,t_0)+\epsilon^2\hat{U}_D^{(2)}(t,t_0)+\cdots)$$

Collecting each of our terms:

$$\begin{aligned}
\epsilon^0 : \quad & i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\hat{U}_D^{(0)} = 0 \\
\epsilon^1 : \quad & i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\hat{U}_D^{(1)} = \hat{V}_D\hat{U}_D^{(0)} \\
\epsilon^2 : \quad & i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\hat{U}_D^{(2)} = \hat{V}_D\hat{U}_D^{(1)}
\end{aligned}$$

We can try to solve, very generally, each of these corrections, using $t_0 = 0$:

$$\begin{aligned}
\epsilon^0 : \quad & \hat{U}_D^{(0)}(t,0) = \text{const.} \\
& \hat{U}_D^{(0)}(0,0) = 1 \\
\implies & U_D^{(0)}(t,0) = 1 \\
\epsilon^1 : \quad & i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\hat{U}_D^{(1)} = \hat{V}_D\hat{U}_D^{(0)} \\
\int \mathrm{d}t' \left(i\hbar\frac{\mathrm{d}}{\mathrm{d}t'}\hat{U}_D^{(1)}(t',0)\right) &= \int \mathrm{d}t'\hat{V}_D(t') \\
i\hbar\hat{U}_D^{(1)}(t,0) &= \int_0^t \mathrm{d}t'\hat{V}_D(t') \\
\hat{U}_D^{(1)}(t,0) &= -\frac{i}{\hbar}\int_0^t \mathrm{d}t'\hat{V}_D(t')
\end{aligned}$$

In the name of time, we'll stop there and say that we can repeat this process as much as we'd like. The general form of this is

$$\epsilon^n : \qquad \hat{U}_D^{(n)}(t,0) = \left(-\frac{i}{\hbar}\right)^n \int_0^t \mathrm{d}t' \hat{V}_D(t') \hat{U}_D^{(n-1)}(t',0)$$

Note that this works as well for $t_0 \neq 0$.

2.2.2 Transition Probabilities

Now we can move on to the main question we said we were trying to answer: the probability of finding the state in some final $|\psi_f\rangle$ at time $t > \tau$ from an initial $|\psi_i\rangle$ at time $t < 5_0$. The porbability of this transition (ie. the transition probability) is given to a first-order approximation by

$$\begin{aligned}
P_{if}(t) &= |\langle \psi_{f,D} | \psi_D \rangle|^2 \\
&= \left| \langle \psi_{f,D} | \, \hat{U}_D(t,0) \, | \psi_{i,D} \rangle \right|^2 \\
&= \left| \langle \psi_{f,D} | \left(1 - \frac{i}{\hbar} \int_0^t \mathrm{d}t' \hat{V}_D(t')\right) | \psi_{i,D} \rangle \right|^2 \\
&= \left| \langle \psi_{f,D} | \psi_{i,D} \rangle - \frac{i}{\hbar} \int_0^t \mathrm{d}t' \, \langle \psi_{f,D} | \, \hat{V}_D(t') \, | \psi_{i,D} \rangle \right|^2
\end{aligned}$$

Per the definition of the braket for two state vectors, the first term can be simplified to just δ_{if}, so if we assume the initial and final states are, in fact, different states, then

$$= \left| -\frac{i}{\hbar} \int_0^t \mathrm{d}t' \, \langle \psi_{f,D} | \, \hat{V}_D(t') \, | \psi_{i,D} \rangle \right|^2$$

Remembering that the initial and final states are eigenstates of the unperturbed/time-independent Hamiltonian, we can define transition frequency, ω_{fi} between the initial and final eneergy levels:

$$\begin{aligned}
\omega_{fi} &= \frac{E_f - E_i}{\hbar} \\
&= \frac{1}{\hbar} \left(\langle \psi_f, D | \, \hat{H}_0 \, | \psi_{f,D} \rangle - \langle \psi_{i,D} | \, \hat{H}_0 \, | \psi_{i,D} \rangle \right)
\end{aligned}$$

Recall, also, that we can re-write

$$\hat{V}_D(t) = e^{it'\hat{H}_0/\hbar} \hat{V}_S(t) e^{-it'\hat{H}_0/\hbar}$$

So we can continue this simplification, remembering that the initial and final states are eigenstates of $\hat{H}_0$:

$$\begin{aligned}
P_{fi} &= \left| -\frac{i}{\hbar} \int_0^t \mathrm{d}t' \, \langle \psi_{f,D} | \, e^{it'\hat{H}_0/\hbar} \hat{V}_S(t') e^{it'\hat{H}_0/\hbar} \, | \psi_{i,D} \rangle \right|^2 \\
&= \left| -\frac{i}{\hbar} \int_0^t \mathrm{d}t' \, \langle \psi_{f,D} | \, e^{it'E_f/\hbar} \hat{V}_S(t') e^{it'E_i/\hbar} \, | \psi_{i,D} \rangle \right|^2 \\
&= \left| -\frac{i}{\hbar} \int_0^t \mathrm{d}t' e^{i\omega_{fi}t'} \, \langle \psi_{f,D} | \, \hat{V}_S(t') \, | \psi_{i,D} \rangle \right|^2
\end{aligned}$$

2.2.3 Transition Probability for Constant Perturbation

Consider the case where

$$\hat{V}_S(t) = \hat{V}_0$$

That is, where the perturbation is constant with respect to time. We can find the transition probability

$$\begin{aligned} P_{fi} &= \frac{1}{\hbar^2}\left|\langle\psi_{f,D}|\,\hat{V}_S(t')\,|\psi_{i,D}\rangle\int_0^t \mathrm{d}t' e^{i\omega_{fi}t'}\right|^2 \\ &= \frac{1}{\hbar^2}\left|\langle\psi_{f,D}|\,\hat{V}_S(t')\,|\psi_{i,D}\rangle\right|^2\left|\frac{e^{i\omega_{fi}t}-1}{\omega_{fi}}\right|^2 \end{aligned}$$

We can use a relationship between e and sin to write

$$= \frac{4\left|\langle\psi_{f,D}|\,\hat{V}_S(t')\,|\psi_{i,D}\rangle\right|^2}{(\hbar\omega_{fi})^2}\sin^2\left(\frac{\omega_{fi}t}{2}\right)$$

As a function of t, the transition probability is an oscillating sinusoidal function with a period of $\frac{2\pi}{\omega_{fi}}$. As a function of ω_{fi}, it has a peak at $\omega_{fi}=0$, and an interference pattern surrounding it. This means that the transition probability is greatest when $E_f \approx E_i$. In the limit $t\to\infty$, the transition probability takes the shape of the Dirac delta function.
We can also define the transition rate, or the transition probability per unit time, as

$$\begin{aligned} \Gamma_{fi} &= \lim_{t\to\infty}\frac{P_{fi}(t)}{t} \\ &= \lim_{t\to\infty}\frac{\sin^2(xt)}{x^2t} \\ &= \frac{|\langle V\rangle|^2}{\hbar}\pi\delta(\omega_{fi}/2) \\ &= \frac{2\pi}{\hbar}|\langle V\rangle|^2\,\delta(E_f^{(0)}-E_i^{(0)}) \end{aligned}$$

Where $x=\omega_{fi}/2$. The delta term guarantees the conservation of energy.

2.2.4 Transition Probability for a Harmonic Perturbation

Consider a perturbation which harmonically depends on time:

$$\hat{V}(t) = \hat{v}e^{i\omega t} + \hat{v}^\dagger e^{-i\omega t}$$

Where $\hat{v}$ is a time-independent operator. An example of this perturbation is when charged particles interact with electromagnetic fields.
The transition probability is given by

$$\begin{aligned} P_{fi}(t) &= \frac{1}{\hbar^2}\left|\int_0^t \mathrm{d}t' e^{i\omega_{fi}t}\,\langle\psi_{f,D}|\,(\hat{v}e^{i\omega t}+\hat{v}^\dagger e^{-i\omega t})\,|\psi_{i,D}\rangle\right|^2 \\ &= \frac{1}{\hbar^2}\left|\langle\hat{v}\rangle\,\frac{e^{i(\omega_{fi}+\omega)t}-1}{i(\omega_{fi}+\omega}+\left\langle\hat{v}^\dagger\right\rangle\frac{e^{i(\omega_f i-\omega}-1}{i(\omega_{fi}-\omega)}\right|^2 \\ &= \frac{4}{\hbar^2}\left[|\langle\hat{v}\rangle|^2\,\frac{\sin^2\left(\frac{\omega_{fi}+\omega}{2}t\right)}{\omega_{fi}+\omega)^2}+\left|\left\langle\hat{v^\dagger}\right\rangle\right|^2\frac{\sin^2\left(\frac{\omega_{fi}-\omega}{2}t\right)}{\omega_{fi}-\omega)^2}\right] \end{aligned}$$

2.3 Adiabatic and Sudden Approximations

So far, we've looked time-development perturbations, but we haven't paid any attention to how fast the perturbations are changing. Here, we'll look at what happens if we turn on and off the perturbation slowly vs. quickly. It will help us to re-write the integral in the transition probability equation we found earlier using integration by parts with $u = \left\langle \hat{V}(t') \right\rangle$ and $\mathrm{d}v = \mathrm{d}t' \left(\partial t' e^{i\omega_{fi}t'} \right)$. You know how to do integration by parts, so I'll skip the middle parts and show the answer:

$$\frac{1}{\hbar\omega_{fi}} \int_0^t \mathrm{d}t' e^{i\omega_{fi}t'} \left\langle \frac{\partial}{\partial t'} \hat{V}(t') \right\rangle$$

This is helpful because from now on, evaluating this integral depends on the rate of change of the perturbation.

2.3.1 Adiabatic Approximation

Adiabatic approximations are approximations where the perturbation is not only small, but also very slow—we could say that these perturbations have a weak time-dependence. In this approximation, we essentially estimate the solutions to the Schrödinger equation at every time t by stationary states (that is, ψ_n and E_n) of the instantaneous Hamiltonian such that at every time they are smoothly converted into eigenfunctions of the corresponding Hamiltonian at a later time $t' > t$. This method leads us to the adiabatic theorem:

Theorem (Adiabatic Theorem)**.** If a system is initially in the nth state and if the Hamiltonian evolves slowly with tim, it will be found at a later time in the nth state of the new instantaneous Hamiltonian. That is, the system will make no transitions, it always remains in the nth state of each Hamiltonian.

Proof. If the Hamiltonian is independent of time, then a particle which starts out in the eigenstate of $\hat{H}$

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

changes with time but remains in the eigenstate ψ_n by simply picking up the phase factor

$$\left| \psi_n(t) \right\rangle = \left| \psi_n \right\rangle e^{-iE_n t/\hbar}$$

But if the Hamiltonian changes with time, then its eigenfuntions and eigenvales should also be time-dependent, ie.,

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

But they are still an orthonormal and complete set such that a general solution to the time-dependent Schrödinger equation can be expanded as their linear combination,

$$\left| \psi(t) \right\rangle = \sum_n c_n(t) \left| \psi_n(t) \right\rangle$$

If we substitute this back into the time-dependent Schrödinger equation, we find

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\left|\psi(t)\right\rangle &= \hat{H}(t)\left|\psi_n(t)\right\rangle \\ i\hbar\frac{\partial}{\partial t}\sum_n c_n(t)\left|\psi_n(t)\right\rangle &= \sum_n c_n(t)E_n(t)\left|\psi_n(t)\right\rangle \\ i\hbar\frac{\partial}{\partial t}\sum_n \left(\dot{c}_n(t)\left|\psi_n(t)\right\rangle + c_n\left|\dot{\psi}_n\right\rangle\right) &= \sum_n c_n(t)E_n(t)\left|\psi_n(t)\right\rangle \end{aligned}$$

Thus,

$$\sum_n \dot{c}_n\left|\psi_n\right\rangle = -\sum_n c_n\left(\left|\dot{\psi}_n\right\rangle - E_n\left|\psi_n\right\rangle\right)$$

We can form an inner product with $|\psi_m\rangle$ and solve:

$$\begin{aligned} \left\langle\psi_m\right|\left[\sum_n \dot{c}_n\left|\psi_n\right\rangle\right] &= \left\langle\psi_m\right|\left[\sum_n c_n\left|\dot{\psi}_n\right\rangle - E_n\left|\psi_n\right\rangle\right] \\ \sum_n \dot{c}_n\delta_{mn} &= -\sum_n c_n\left(\left\langle\psi_m\middle|\dot{\psi}_n\right\rangle - E_n\delta_{nm}\right) \\ \dot{c}_m &= -\sum_n c_n\left\langle\psi_m\middle|\dot{\psi}_n\right\rangle + c_m E_m \end{aligned}$$

In order to figure out the braket term, let's differentiate our Schrödinger equation with respect to t, and form an inner product with $|\psi_m\rangle$:

$$\begin{aligned} \hat{H}\left|\psi_n\right\rangle &= E_n\left|\psi_n\right\rangle \\ \dot{\hat{H}}\left|\psi_n\right\rangle + \hat{H}|\dot{\psi_n}\rangle &= \dot{E}_n\left|\psi_n\right\rangle + E_n|\dot{\psi_n}\rangle \\ \left\langle\psi_m\right|\dot{\hat{H}}\left|\psi_n\right\rangle + \left\langle\psi_m\right|\hat{H}|\dot{\psi_n}\rangle &= \dot{E}_n\delta_{nm} + \left\langle\psi_m\middle|\dot{\psi}_n\right\rangle E_n \\ \left\langle\psi_m\right|\dot{\hat{H}}\left|\psi_n\right\rangle &= E_n\delta_{nm} + (E_n - E_m)\left\langle\psi_m\middle|\dot{\psi}_n\right\rangle \end{aligned}$$

So that for $n \neq m$:

$$\begin{aligned} \left\langle\psi_m\right|\dot{\hat{H}}\left|\psi_n\right\rangle &= (E_n - E_m)\left\langle\psi_m\middle|\dot{\psi}_n\right\rangle \\ \left\langle\psi_m\middle|\dot{\psi}_n\right\rangle &= \frac{\left\langle\psi_m\right|\dot{\hat{H}}\left|\psi_n\right\rangle}{(E_n - E_m)} \end{aligned}$$

Going back to our equation for $\dot{c}_m$,

$$\begin{aligned} \dot{c}_m &= c_m E_m - c_m\left\langle\psi_m\middle|\dot{\psi}_m\right\rangle - \sum_{n\neq m} c_n\left\langle\psi_m\middle|\dot{\psi}_n\right\rangle \\ \dot{c}_m &= c_m\left(E_m - \left\langle\psi_m\middle|\dot{\psi}_m\right\rangle\right) - \sum_{n\neq m} c_n\frac{\left\langle\psi_m\right|\dot{\hat{H}}\left|\psi_n\right\rangle}{E_n - E_m} \end{aligned}$$

This is an exact result. Now, the adiabatic approximation consists in assuming that

$$\left(\frac{\hbar}{E_n - E_m}\right)\left\langle\psi_m\right|\dot{\hat{H}}\left|\psi_n\right\rangle \ll E_n - E_m$$

The term in front there is to match (I can't tell what this word is). Recall that the second term after that is the time change of the Hamiltonian. If we make this approximation, then

$$\dot{c}_m = c_m \left(E_m - \left\langle \psi_m \middle| \dot{\psi}_m \right\rangle \right)$$
$$\therefore c_m = c_m(0) e^{\int_0^t \mathrm{d}t' \left(E_m(t') - \langle \psi_m | \dot{\psi}_m \rangle \right)}$$

Such that the evolution is diagonal.
I don't understand the final example, but basically, we can use some examples to show that this shows that the state will always stay the same relative to the Hamiltonian.

Let's go back to the transition probability from earlier. Since the perturbation is slowly turned on/off, the rate of change of the perturbation changes slower than the exponential in the integral, so we can approximately pull it out:

$$\int_0^t \mathrm{d}t' \left\langle \frac{\partial \hat{V}(t')}{\partial t'} \right\rangle e^{i\omega_{fi}t'} \approx \left\langle \frac{\partial \hat{V}(t)}{\partial t} \right\rangle \int_0^t \mathrm{d}t' e^{i\omega_{fi}t'}$$

Applying what we found earlier,

$$\frac{1}{\omega_{fi}} \left\langle \frac{\partial V}{\partial t} \right\rangle \ll E_f - E_i$$

to the transition probability, we can find the probability of the state transitioning to... any other state:

$$P_{fi} = \frac{1}{\hbar^2 \omega_{fi}^2} \left| \left\langle \frac{\partial V}{\partial t} \right\rangle \right|^2 \frac{4 \sin^2(\omega_{fi} t/2)}{\omega_{fi}^2}$$
$$= \frac{4}{\hbar^2} \frac{\left| \left\langle \frac{\partial V}{\partial t} \right\rangle \right|^2}{\omega_{fi}^4} 4 \sin^2(\omega_{fi} t/2) \approx 0$$

□

2.3.2 Sudden Approximation

Again, let's start without needing to look at perturbation theory. Consider a system at $t = 0$ in an eigenstate $|\psi_n\rangle$ of $\hat{H}_0$, that is,

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

And at time t,

$$\left| \psi_n^{(0)}(t) \right\rangle = e^{-iE_n t/\hbar} \left| \psi_n^{(0)} \right\rangle$$

Let's say that at time $t = 0$, $\hat{H}_0 \to \hat{H}$, where $\hat{H} - \hat{H}_0$ does not have to be small. Let $|\phi_n\rangle$ be the eigenfunctions of $\hat{H}$:

$$\hat{H} |\psi_n\rangle = E_n |\phi_n\rangle$$

where at time t,

$$|\phi_n(t)\rangle = e^{iE_n t/\hbar} |\phi_n\rangle$$

The state of the system for $t > 0$ is thus given by

$$|\Phi(t)\rangle = \sum_n c_n e^{iE_n t/\hbar} |\phi_n\rangle$$

If the system is initially in an eigenstate $|\psi_m\rangle$ of $\hat{H}_0$, the continuity condition at $t = 0$ means that the system must remain in this state just after the change:

$$|\Phi(0)\rangle = \sum_n c_n |\phi_n\rangle = |\psi_m\rangle$$
$$\implies c_n = \langle\phi_n|\psi_m\rangle$$

The probability that a sudden change in the system's Hamiltonian from $\hat{H}_0$ to the nth state of $\hat{H}$ (as long as we're talking about discrete states) is

$$P_{nm} = |\langle\phi_n|\psi_m\rangle|^2$$

Now, let's look at this in the context of perturbation theory. We'll start with the thing in the larger section:

$$P_{fi} = \frac{1}{\hbar^2\omega_{fi}} \left| \int_0^t \mathrm{d}t' e^{i\omega_{fi}t'} \left\langle \frac{\partial \hat{V}}{\partial t'} \right\rangle \right|^2$$

If we very suddenly switch on our perturbation, we can approximate the rate of change of the perturbation to be like a delta function. So the exponential term is very slowly changing compared to the *very* sudden change of $\frac{\partial V}{\partial t}$, and can thus be approximately pulled out of the integral:

$$\int_0^t \mathrm{d}t' e^{i\omega_{fi}t'} \left\langle \frac{\partial \hat{V}}{\partial t} \right\rangle \approx e^{i\omega_{fi}t} \int_0^t \left\langle \frac{\partial V}{\partial t'} \right\rangle \mathrm{d}t'$$
$$= e^{i\omega_{fi}t} \left\langle \hat{V}(0) \right\rangle$$

Where $t = 0$, recall, is just the time the interaction was switched on.

$$P_{fi} = \frac{\left|\left\langle \hat{V} \right\rangle\right|^2}{\hbar^2\omega_{fi}^2}$$

Note here that although we write the expectation value, we really mean

$$\left\langle \hat{V} \right\rangle = \langle\psi_f| \hat{V} |\psi_i\rangle$$

2.4 Absorption and Emission of Radiation

Time-dependent perturbation theory is very useful to study the way that atoms (and, more specifically, their electrons) interact with external electromagnetic radiation. We'll assume that there's only one electron involved with the interaction, and that the nucleus is infinitely heavy.
The "free" Hamiltonian of the atomic electron is

$$\hat{H}_0 = \frac{\hat{\mathbf{p}}^2}{2m} + \hat{V}_0(\hat{\mathbf{x}})$$

where $\hat{V}_0(\hat{\mathbf{x}})$ is the static potential of the electron with the atomic nucleus and other electrons in the atom. We found before that when an atom is placed in an external field, the Hamiltonian becomes

$$\hat{H} = \frac{(\hat{\mathbf{p}} - q\mathbf{A})^2}{2m} + q\phi + V_0(\hat{\mathbf{x}})$$

Where ϕ and $\mathbf{A}$ are the scalar and vector potentials. Let's work it out and see what we get, plugging in $q = -e$:

$$\hat{H} = \frac{1}{2m_e}(\hat{\mathbf{p}}^2 - q\hat{\mathbf{p}} \cdot \mathbf{A} - q\mathbf{A} \cdot \hat{\mathbf{p}} + q^2\mathbf{A}^2) + q\phi + \hat{V}_0(\hat{\mathbf{x}})$$

We can simplify using the following identities:

$$\begin{aligned} \hat{\mathbf{p}} &= -i\hbar\boldsymbol{\nabla} \\ \hat{\mathbf{p}} \cdot \mathbf{A} &= (\hat{\mathbf{p}} \cdot \mathbf{A}) + \mathbf{A} \cdot \hat{\mathbf{p}} \\ &= -i\hbar(\boldsymbol{\nabla} \cdot \mathbf{A}) + \mathbf{A} \cdot \hat{\mathbf{p}} \end{aligned}$$

We can thus plug in

$$\hat{H} = \frac{1}{2m_e}(\hat{\mathbf{p}}^2 + qi\hbar(\boldsymbol{\nabla} \cdot A) - 2q\mathbf{A} \cdot \hat{\mathbf{p}} + q^2\mathbf{A}^2) + q\phi + \hat{V}_0(\hat{\mathbf{x}})$$

We can choose the Coulomb gauge such that $\boldsymbol{\nabla} \cdot \mathbf{A} = 0$, meaning $\phi = 0$, so that

$$\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m_e} + \frac{e}{m_e}\mathbf{A} \cdot \mathbf{p} + \hat{V}_0(\hat{x}) = \hat{H}_0 + \hat{V}_i(\hat{x})$$

Note that we also neglected the squared term because it was signifiantly smaller than the others. Recall that q, along with a bunch of other fundamental constants, will form the fine structure constant. We can prove that $q\mathbf{A}$ will be significantly larger than $q^2\mathbf{A}^2$ this way.
The way that we've defined this,

$$\hat{V}_i(\hat{x}) = \frac{e}{m_e}\mathbf{A} \cdot \mathbf{p}$$

is the perturbation. We can't go any further without an explicit form of $\mathbf{A}(\mathbf{x})$, though.

2.4.1 Classical Treatment of Radiation

Classically, electric and magnetic fields and their potentials are described by continuous fields. Recall Maxwell's equations:

$$\begin{aligned} \boldsymbol{\nabla} \cdot \mathbf{E} &= 0 & \boldsymbol{\nabla} \cdot \mathbf{B} &= 0 \\ \boldsymbol{\nabla} \times \mathbf{E} &= -\frac{\partial}{\partial t}\mathbf{B} & \boldsymbol{\nabla} \times \mathbf{B} &= \mu_0\epsilon_0\frac{\partial}{\partial \mathbf{E}} \end{aligned}$$

We can substitute into the electric field curl and the magnetic field divergence and solve in terms of potentials:

$$\begin{aligned} \mathbf{E} &= -\boldsymbol{\nabla}\phi - \frac{\partial}{\partial t}\mathbf{A} \\ \mathbf{B} &= \boldsymbol{\nabla} \times \mathbf{A} \end{aligned}$$

We can then use the others to find that

$$\boldsymbol{\nabla}^2\phi + \frac{\partial}{\partial t}\boldsymbol{\nabla}\cdot\mathbf{A} = 0$$
$$\left(\mu_0\epsilon_0\frac{\partial^2}{\partial t^2} - \boldsymbol{\nabla}^2\right)\mathbf{A} = -\mu_0\epsilon_0\frac{\partial}{\partial t}\boldsymbol{\nabla}\phi - \boldsymbol{\nabla}(\boldsymbol{\nabla}\cdot\mathbf{A})$$

Recall that in the Coulomb gauge, $\boldsymbol{\nabla}\cdot\mathbf{A} = 0$ and $\boldsymbol{\nabla}^2\phi = 0$, so

$$\left(\mu_0\epsilon_0\frac{\partial^2}{\partial t^2} - \boldsymbol{\nabla}^2\right)\mathbf{A} = 0$$

We can find the solution to this differential equation in terms of plane waves. In general, for a monochromatic wave:

$$\mathbf{A}(t,\mathbf{x}) = \mathbf{A}_0^* e^{i(\omega t - \mathbf{k}\cdot\mathbf{x})} + \mathbf{A}_0 e^{-i(\omega t - \mathbf{k}\cdot\mathbf{x})}$$

If the light has polarization $\boldsymbol{\varepsilon}$, then we can re-write this using the relation $\mathbf{A}_0 = A_0\boldsymbol{\varepsilon}$.
But not all solutions to wave equations are solutions to Maxwell's equations. Namely, we have to impose the gauge again:

$$\boldsymbol{\nabla}\cdot\mathbf{A} = 0 \implies \mathbf{k}\cdot\mathbf{A}_0 = 0$$

Physically, this means that that $\mathbf{A}$ lies in a plane perpendicular to the wave's direction of propagation. We can apply this definition of $\mathbf{A}$ to our Maxwell's equations to find the the electric and magnetic fields:

$$\begin{aligned}\mathbf{E} &= -\frac{\partial}{\partial t}\mathbf{A}\\ &= -i\omega\mathbf{A}_0 e^{i(\omega t - \mathbf{k}\cdot\mathbf{x})} + +i\omega\mathbf{A}_0^* e^{-i(\omega t - \mathbf{k}\cdot\mathbf{x})}\\ \mathbf{B} &= \boldsymbol{\nabla}\times\mathbf{A}\\ &= -i(\mathbf{k}\times\mathbf{A}_0)e^{i(\omega t - \mathbf{k}\cdot\mathbf{x})} + i(\mathbf{k}\times\mathbf{A}_0)e^{-i(\omega t - \mathbf{k}\cdot\mathbf{x})}\end{aligned}$$

Or, using the substitution we defined for polarization,

$$\mathbf{E} = -i\omega\boldsymbol{\varepsilon}A_0\left(e^{i(\omega t - \mathbf{k}\cdot\mathbf{x})} - e^{-i(\omega t - \mathbf{k}\cdot\mathbf{x})}\right)$$
$$\mathbf{B} = -i(\mathbf{k}\times\boldsymbol{\varepsilon})A_0\left(e^{i(\omega t - \mathbf{k}\cdot\mathbf{x})} - e^{-i(\omega t - \mathbf{k}\cdot\mathbf{x})}\right)$$

So that, as expected,

$$\begin{aligned}\mathbf{B} &= \frac{\mathbf{k}}{\omega}\times\mathbf{E}\\ &= \frac{k}{\omega}(\mathbf{n}\times\mathbf{E})\\ &= \frac{1}{c}(\mathbf{n}\times\mathbf{E})\end{aligned}$$

So they havee the same magnitude, mediated by $1/c$ (note again that this is different than the textbook).
Now, let's find the normalization constant A_0 by finding the energy of a single

photon in terms of $\mathbf{E}$ and $\mathbf{B}$.
Recall that the energy of the field is

$$\begin{aligned} W &= \frac{1}{2}\int \mathrm{d}^3\mathbf{x}\left(\epsilon_0\mathbf{E}^2 + \frac{1}{\mu_0}\mathbf{B}^2\right) \\ &= \frac{\epsilon_0}{2}\int \mathrm{d}^3\mathbf{x}(\mathbf{E}^2 + c^2\mathbf{B}^2) \end{aligned}$$

The energy density (energy per unit volume) is

$$w = \frac{\epsilon_0}{2}(\mathbf{E}^2 + c^2\mathbf{B}^2)$$

The time-averaged value is

$$\langle w\rangle = \frac{\hbar\omega}{V}$$

We can expand the expression for w:

$$\begin{aligned} w &= \frac{\epsilon_0}{2}\left(2\cdot 4\omega^2 A_0^2\sin^2(\mathbf{k}\cdot\mathbf{x}-\omega t)\right) \\ &= 4\epsilon_0\omega^2 A_0^2\sin^2(\mathbf{k}\cdot\mathbf{x}-\omega t) \end{aligned}$$

To find the time-averaged value, we average over one period, $T = 2\pi/\omega$:

$$\begin{aligned} \langle w\rangle &= \frac{0}{T}\int_0^T \mathrm{d}t w \\ &= 4\epsilon_0\omega^2 A_0^2\left\langle\sin^2(\mathbf{k}\cdot\mathbf{x}-\omega t)\right\rangle \\ &= 2\epsilon_0\omega^2 A_0^2 \end{aligned}$$

For the final bit there, we used the fact that $\left\langle\sin^2\right\rangle = 1/2$. Combining these two things that we have for describing the time-averaged value of w, we can solve for A_0:

$$A_0 = \sqrt{\frac{\hbar}{2\epsilon_0\omega V}}$$

Therefore,

$$\mathbf{A}(t,\mathbf{x}) = \boldsymbol{\varepsilon}\sqrt{\frac{\hbar}{2\epsilon_0\omega V}}\left(e^{i(\omega t-\mathbf{k}\cdot\mathbf{x})} + e^{-i(\omega t-\mathbf{k}\cdot\mathbf{x})}\right)$$

We can substitute this into the "perturbation:"

$$\begin{aligned} \hat{V}_i &= \frac{e}{m_e}\mathbf{A}\cdot\hat{\mathbf{p}} \\ &= \frac{e}{m_e}\sqrt{\frac{\hbar}{2\epsilon_0\omega V}}\left(e^{i(\omega t-\mathbf{k}\cdot\mathbf{x})} + e^{-i(\omega t-\mathbf{k}\cdot\mathbf{x})}\right)\boldsymbol{\varepsilon}\cdot\mathbf{p} \end{aligned}$$

So it has the form of an interaction potential with a harmonic dependence on time. We can define our annihilation/creation operators then as

$$\begin{aligned} \hat{v} &= \frac{e}{m_e}\sqrt{\frac{\hbar}{2\epsilon_0\omega V}}e^{+i\mathbf{k}\cdot\mathbf{x}}(\boldsymbol{\varepsilon}\cdot\hat{\mathbf{p}}) \\ \hat{v}^\dagger &= \frac{e}{m_e}\sqrt{\frac{\hbar}{2\epsilon_0\omega V}}e^{-i\mathbf{k}\cdot\mathbf{x}}(\boldsymbol{\varepsilon}\cdot\hat{\mathbf{p}}) \end{aligned}$$

So that

$$\hat{V} = \hat{v}e^{-i\omega t} + \hat{v}^\dagger e^{+i\omega t}$$

We can say that in line with the harmonic perturbation we saw earlier, the term with $\hat{v}$ is representative of the absorption of the incident photon on the atom, whereas the term with $\hat{v}^\dagger$ is representative of the stimulated emission of the photon from the atom. The transition rates of these are now

$$\Gamma_{fi}^{emi} = \frac{2\pi}{\hbar} \left|\left\langle \hat{v}^\dagger \right\rangle\right|^2 \delta(E_f - E_i + \hbar\omega)$$
$$\Gamma_{fi}^{abs} = \frac{2\pi}{\hbar} \left|\langle \hat{v} \rangle\right|^2 \delta(E_f - E_i - \hbar\omega)$$

For more information: if an atom absorbs a photon, then as its energy level decays, it will emit two photons with the same energy. This is why we call it stimulated emission. This leads to an amplification of the electromagnetic field. This is how stuff like masers and lasers.

2.4.2 Spontaneous Emission (Einstein's A & B Coefficients)

There's another way that radiation interacts with matter: spontaneous emission. An atom makes a transition from a higher state to a lower state with a release of a photon. Classically, it doesn't make sense for an atom to make a transition from a stationary state on its own without some perturbation. The resolution of this lies in the quantum nature of light. Quantumly, an electromagnetic wave is a collection of oscillators, as we will discuss next. Quantum mechanically, an oscillator, even one in the ground state, possesses an energy $\frac{\hbar\omega}{2}$. Even at $t = 0$, and with "switched" off light, there are still zero-point fluctuations. Thus this nonzero energy serves as a perturbation which "stimulates" spontaneous emission.
Recall that for an incoherent prturbation, i.e., a non-monochromatic wave with a range of frequencies $\mathrm{d}\omega$, the transition rate is given by

$$\begin{aligned} w_{fi} &= \int \mathrm{d}\Gamma_{fi} \\ &= \int \mathrm{d}\omega \rho(\omega) \Gamma_{fi}(\omega) \\ &= B\rho(\omega_{fi}) \\ &: \omega_{fi} = E_f - E_i; \\ &: B = \frac{2\pi}{\hbar} \left|\langle \hat{v} \rangle\right|^2 \end{aligned}$$

Where, again, $\langle \hat{v} \rangle = \langle f | \hat{v} | i \rangle$. This describes absportion and stimulated emission.

Consider a container of N atoms. with N_a atoms in the lower state $|\psi_a\rangle$ and N_b atoms in the higher state $|\psi_b\rangle$. In this container, there is some ambient field, described by $\rho(\omega)$.
For stimulated emission, the transition rate is

$$B_{b\to a}\rho(\omega)$$

So the number of particles leaving the $|\psi_b\rangle$ state is

$$N_b B_{b\to a}\rho(\omega)$$

And the absorption adds particles to $|\psi_b\rangle$ equal to

$$N_a B_{a\to b}\rho(\omega)$$

So with these two processes, the total change of particles in the $|\psi_b\rangle$ state is

$$\frac{\mathrm{d}N_b}{\mathrm{d}t} = N_a B_{a\to b}\rho(\omega) - N_b B_{b\to a}\rho(\omega)$$

If the atoms are in thermal equilibrium with the ambient field, then we must have

$$\begin{aligned} &\frac{\mathrm{d}N_b}{\mathrm{d}t} = 0 \\ \implies\ &\rho(\omega) = 0 \end{aligned}$$

This, however, contradicts the blackbody radiation formula. To fix that, we (following Einstein) must one more term to the above formula to represent spontaneous emission:

$$\frac{\mathrm{d}N_b}{\mathrm{d}t} = N_a B_{a\to b}\rho(\omega) - N_b B_{b\to a}\rho(\omega) - N_b A$$

Where A is the transition rate of spontaneous emission. This way, at thermal equilibrium,

$$0 = \frac{\mathrm{d}N_b}{\mathrm{d}t} = -N_b A + \rho(\omega)(N_a B_{a\to b} - N_b B_{b\to a})$$

Thus

$$\begin{aligned} \rho(\omega) &= \frac{N_b A}{N_a B_{a\to b} - N_b B_{b\to a}} \\ &= \frac{A}{\frac{N_a}{N_b} B_{a\to b} - B_{b\to a}} \end{aligned}$$

Recall from statistical mechanics that the number of particles is proportional to te Bolzmann factor (with energy E in thermal equilibrium at T):

$$N_i \propto e^{-E_i i/k_B T}$$

So

$$\frac{N_a}{N_b} = e^{-(E_a - E_b)/k_B T}$$

And

$$\begin{aligned} \rho(\omega) &= \frac{A}{B_{a\to b} e^{-(E_a - E_b)/k_B T} - B_{b\to a}} \\ &= \frac{A}{B_{a\to b} e^{\hbar\omega/k_B} - B_{b\to a}} \end{aligned}$$

Where

$$E_a - E_b = -\hbar\omega$$

Compare this to Planck's blackbody formula (the energy density of thermal radiation),

$$\rho(\omega) = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\hbar\omega/k_B T} - 1}$$

We can easily conclude two things: firstly, that the B coefficints must be equal. Second,

$$A = \frac{\hbar\omega^3}{\pi^2 c^3} B_{a\to b}$$

2.4.3 Quantization of the Electromagnetic Field

We've seen that the classical treatment accounts only for absorption and stimulated emission, but not spontaneous emission. This is because, as you may remember, the classical treatment is only valid/useful when the intensity (ie. the number of photons) is very large—that is, when the it's so high that the wave nature of radiation is important/dominating. At low intensities, the particle nature becomes non-negligible, so we have to start looking at a quantum mechanical treatment of radiation instead. This means that we need to promote $\mathbf{E}$ and $\mathbf{B}$ to hermitian operators.
Precisely, in the past, we found that a monochromatic plane wave satisfies Maxwell's equations in the Coulomb gauge, and we were able to fully specify it in $\mathbf{A}$. $\mathbf{A}$ describes a wave propagating along the vector $\mathbf{k}$ and oscillating in the plane perpendicular to it. We define two orthogonal unit vectors defining states of linear polarization, $\boldsymbol{\varepsilon}_1$ and $\boldsymbol{\varepsilon}_2$. Thus,

$$\mathbf{A}_0 = A_0 \boldsymbol{\varepsilon}_\lambda$$

Where $\lambda = 1, 2$.
If we place our EM field in a large volume V with sides L_x, L_y, and L_z, then the momentum of the field takes quantized, discrete values:

$$k_i = \frac{2\pi}{L_i} n_i$$

Thus a monochromatic wave can be expanded in a Fourier series (noting that if the volume were infinite, we would make this an integral):

$$\mathbf{A} \sum_{\mathbf{k}} \sum_{\lambda=1}^{2} \left[\boldsymbol{\varepsilon}_\lambda A_{\lambda,\mathbf{k}} e^{-i(\omega_k t - \mathbf{k}\cdot\mathbf{x})} + \boldsymbol{\varepsilon}_\lambda A^*_{\lambda,\mathbf{k}} e^{-i(\omega_k t - \mathbf{k}\cdot\mathbf{x})} \right]$$

Where

$$\sum_{\mathbf{k}} = \sum_{k_x} \sum_{k_y} \sum_{k_z}$$
$$|\mathbf{k}| = \frac{\omega_k}{c}$$

To figure out the physical meaning of the amplituds $A_{\mathbf{K},\lambda}$ and $A^*_{\mathbf{k},\lambda}$, let's try to write the Hamiltonian of the electromagnetic field in their terms. We found the energy of an electromagnetic field earlier, and for a conservative system, that's the same as the Hamiltonian:

$$H = \frac{\epsilon_0}{2} \int \mathrm{d}^3\mathbf{x} [\mathbf{E}^2 + c^2 \mathbf{B}^2]$$

We can also define this as the sum of the electric and magnetic field Hamiltonians. To write these individually, we're going to want to look at them separately. Let's start with $H_E = H_1$:

$$H_1 = \frac{\epsilon_0}{2}\int \mathrm{d}^3\mathbf{x}\mathbf{E}^2$$

Recall that we know what $\mathbf{E}$ looks like with respect to $\mathbf{A}$:

$$\begin{aligned}\mathbf{E} &= -\frac{\partial}{\partial t}\mathbf{A} \\ &= \sum_{\lambda,\mathbf{k}}[i\omega_{\mathbf{k}}\boldsymbol{\varepsilon}_\lambda A_{\mathbf{k},\lambda}e^{-i(\omega t-\mathbf{k}\cdot\mathbf{x})} - i\omega_{\mathbf{k}}\boldsymbol{\varepsilon}_\lambda A^*_{\mathbf{k},\lambda}e^{i(\omega t-\mathbf{k}\cdot\mathbf{x})}]\end{aligned}$$

In the name of simpler notation, we'll absorb the time-dependence into the amplitudes, such that

$$A_{\mathbf{k},\lambda}e^{-i\omega t} = A_{\mathbf{k},\lambda}(t)$$

So that

$$\mathbf{E} = \sum_{\lambda,\mathbf{k}} i\omega_{\mathbf{k}}\boldsymbol{\varepsilon}_\lambda[A_{\mathbf{k},\lambda}(t)e^{i\mathbf{k}\cdot\mathbf{x}} - A^*_{\mathbf{k},\lambda}(t)e^{-i\mathbf{k}\cdot\mathbf{x}}$$

If we do this, then we plug in to find the Hamiltonian H_1, then... we'll have to do a lot of math and simplification. I'll skip most of the simplification because it's really not particularly worth discussing and write the result. Note that I've omitted the time-dependence for the sake of brevity, but it is, in fact, still there.

$$H_1 = -V\frac{\epsilon_0}{2}\sum_{\lambda,\mathbf{k}}\omega^2_{\mathbf{k}}[A_{\lambda,\mathbf{k}}A_{\lambda,-\mathbf{k}} + A^*_{\lambda,\mathbf{k}}A^*_{\lambda,-\mathbf{k}} - A_{\lambda,\mathbf{k}}A^*_{\lambda,\mathbf{k}} - A^*_{\lambda,\mathbf{k}}A_{\lambda,\mathbf{k}}-]$$

We can do an analagous procedure for H_2:

$$\begin{aligned}\mathbf{B} &= \boldsymbol{\nabla}\times\mathbf{A} \\ &= \sum_{\lambda,\mathbf{k}} i(\mathbf{k}\times\boldsymbol{\varepsilon}_\lambda[A_{\lambda,\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{x}} - A^*_{\lambda,\mathbf{k}}e^{-i\mathbf{k}\cdot\mathbf{x}}]\end{aligned}$$

So, if

$$H_2 = \frac{\epsilon_0}{2}c^2\int \mathrm{d}^3\mathbf{x}\mathbf{B}^2$$

The, again, skipping the really hard and sorta pointless math,

$$= -\frac{\epsilon_0}{2}Vc^2\sum_{\lambda,\mathbf{k}}\mathbf{k}^2[-A_{\lambda,\mathbf{k}}A_{\lambda,-\mathbf{k}} - A^*_{\lambda,\mathbf{k}}A^*_{\lambda,-\mathbf{k}} - A^*_{\lambda,\mathbf{k}}A_{\lambda,\mathbf{k}} - A_{\lambda,\mathbf{k}}A^*_{\lambda,\mathbf{k}}]$$

If we put all this together and simplify, we find that

$$H = \epsilon_0 V\sum_{\lambda,\mathbf{k}}\omega^2_{\mathbf{k}}[A^*_{\mathbf{k},\lambda}A_{\mathbf{k},\lambda} + A_{\mathbf{k},\lambda}A^*_{\mathbf{k},\lambda}]$$

This result reminds us of a one-dimensional oscillator written in terms of independent vibrational modes. We can introduce a set of conjugate variables resembling coordinate and momentum:

$$\begin{aligned}Q_{\lambda,\mathbf{k}} &= \sqrt{\epsilon_0 V}(A_{\lambda\mathbf{k}} + A^*_{\lambda\mathbf{k}}) \\ P_{\lambda,\mathbf{k}} &= -i\omega\mathbf{k}\sqrt{\epsilon_0 V}(A_{\lambda\mathbf{k}} - A^*_{\lambda\mathbf{k}})\end{aligned}$$

If we do this, we can re-write the Hamiltonian as

$$H = \frac{1}{2}\sum_{\lambda,\mathbf{k}} \left(\omega_{\mathbf{k}}^2 Q_{\lambda,\mathbf{k}}^2 + P_{\lambda,veck}^2\right)$$

And wow! Now we're looking at something with the sae structure as the Hamiltonian of a collection of independent harmonic oscillators with unit pass. This makes sense—electromagnetic waves in a vacuum result from harmonic oscillations of the electromagnetic field. To quantize the Hamiltonian, we need to promote Q and P to operators with

$$[\hat{Q}_{\lambda_1,\mathbf{k}_1}, \hat{P}_{\lambda_2,\mathbf{k}_2}] = i\hbar\delta_{\lambda_1,\lambda_2}\delta_{\mathbf{k}_1,\mathbf{k}_2}$$

Following the same procedure as we do for the classical harmonic oscillator, let's introduce the creation/annihilation operators, and write the normalization of $A_{\lambda,\mathbf{k}}$ in terms of them:

$$\sqrt{2V\epsilon_0\omega_k}\hat{A}_{\lambda,\mathbf{k}} = \sqrt{\hbar}\hat{a}_{\lambda,\mathbf{k}}$$
$$\sqrt{2V\epsilon_0\omega_k}\hat{A}^\dagger_{\lambda,\mathbf{k}} = \sqrt{\hbar}\hat{a}^\dagger_{\lambda,\mathbf{k}}$$

So that

$$\hat{H} = \sum_{\lambda,\mathbf{k}} \frac{\hbar\omega_k}{2}(\hat{a}^\dagger_{\lambda,\mathbf{k}}\hat{a}_{\lambda,\mathbf{k}} + \hat{a}_{\lambda,\mathbf{k}}\hat{a}^\dagger_{\lambda,\mathbf{k}})$$

If we try to find the commutation relation for these operators, we'll find that it's exactly the same as we would expect for the classical harmonic oscillator, meaning we can re-write this as

$$\begin{aligned}\hat{H} &= \sum_{\lambda,\mathbf{k}}\left[\hat{a}^\dagger_{\lambda,\mathbf{k}}\hat{a}_{\lambda,\mathbf{k}} + \frac{1}{2}\right] \\ &= \sum_{\lambda,\mathbf{k}}\left[\hat{n}_{\lambda,\mathbf{k}} + \frac{1}{2}\right]\end{aligned}$$

Where $\hat{n}$ is the number-of-particles operator. The eigenvector of that operator is

$$\hat{n}_{\lambda,\mathbf{k}}\left|n_{\lambda,\mathbf{k}}\right\rangle = n_{\lambda,\mathbf{k}}\left|n_{\lambda,\mathbf{k}}\right\rangle$$

with

$$\left|n_{\lambda,\mathbf{k}}\right\rangle = \frac{1}{\sqrt{n_{\lambda,\mathbf{k}}!}}$$

Recall what the ladder operators do:

$$\hat{a}^\dagger\left|n\right\rangle = \sqrt{n+1}\left|n+1\right\rangle$$
$$\hat{a}\left|n\right\rangle = \sqrt{n-1}\left|n-1\right\rangle$$

And that the eigenstate of the Hamiltonian is built from the number-of-particles states:

$$\left|n_{\lambda_1,\mathbf{k}_1}, n_{\lambda_1,\mathbf{k}_1}, \ldots\right\rangle = \prod_j \left|n_{\lambda_j,\mathbf{k}_j}\right\rangle$$

With the predictable energy eigenvalues

$$E_r = \sum_{\lambda,\mathbf{k}} \left[n_{\lambda,\mathbf{k}} + \frac{1}{2} \right]$$

Next, we want to find the interaction potential, $\mathbf{V}$. Re-writing, we can say that

$$\begin{aligned} \hat{A}_{\lambda,\mathbf{k}} &= \sqrt{\frac{\hbar}{2\epsilon_0 V \omega_k}} \hat{a}_{\lambda,\mathbf{k}} \\ \hat{\mathbf{A}}(t,\mathbf{x}) &= \sum_{\lambda,\mathbf{k}} \sqrt{\frac{\hbar}{2\epsilon_0 V \omega_k}} \boldsymbol{\varepsilon}_{\boldsymbol{\lambda}} \left[\hat{a}_{\lambda,\mathbf{k}}(t) e^{i\mathbf{k}\cdot\mathbf{x}} + \hat{a}^\dagger_{\lambda,\mathbf{k}}(t) e^{i\mathbf{k}\cdot\mathbf{x}} \right] \end{aligned}$$

Using the same time-development shortcut as earlier. Thus,

$$\begin{aligned} \hat{V} &= \frac{e}{m_e} (\hat{\mathbf{A}} \cdot \hat{\mathbf{p}}) \\ &= \sum_{\lambda,\mathbf{k}} \left(\hat{v}_{\lambda,\mathbf{k}} e^{-i\omega_k t} + \hat{v}^\dagger_{\lambda,\mathbf{k}} e^{i\omega_k t} \right) \end{aligned}$$

Where

$$\hat{v}_{\lambda,\mathbf{k}} = \frac{e}{m_e} \sqrt{\frac{\hbar}{2\epsilon_0 V \omega_k}} e^{i\mathbf{k}\cdot\mathbf{x}} (\boldsymbol{\varepsilon} \cdot \mathbf{p}) \hat{a}_{\lambda,\mathbf{k}} \hat{v}^\dagger_{\lambda,\mathbf{k}} \quad = \frac{e}{m_e} \sqrt{\frac{\hbar}{2\epsilon_0 V \omega_k}} e^{-i\mathbf{k}\cdot\mathbf{x}} (\boldsymbol{\varepsilon} \cdot \mathbf{p}) \hat{a}^\dagger_{\lambda,\mathbf{k}}$$

These correspond respectfully to the absorption (annihilation) and emission (creation) of a photon by the atom. This process is known as the formalism of the second quantization.

2.4.4 Transition Rates for Absorption and Emission

Pre-interaction, the syatem (atom + radiation) is in the state

$$|\Phi_i\rangle = |\psi_i\rangle \left| n^{(i)}_{\lambda,\mathbf{k}} \right\rangle$$

And after the interaction, it's in the state

$$|\Phi_i\rangle = |\psi_f\rangle \left| n^{(f)}_{\lambda,\mathbf{k}} \right\rangle$$

We'll address absorption and emission separately.

Emission

In this case, we can write the initial and final states as follows:

$$\begin{aligned} |\Phi_i\rangle &= |\psi_i\rangle \, |n_{\lambda,\mathbf{k}}\rangle \\ |\Phi_f\rangle &= |\psi_f\rangle \, |n_{\lambda,\mathbf{k}} + 1\rangle \end{aligned}$$

The state of the photon increases by one, since the electromagnetic field gains a photon from emission. Formally, we can achieve this by creating a photon—applying the creation operator to the photonic state. We must do this by

applying the creation interaction potential, $\hat{v}^\dagger_{\lambda,\mathbf{k}}$:

$$\begin{aligned}\langle\Phi_f|\,\hat{v}^\dagger_{\lambda,veck}\,|\Phi_i\rangle &= \frac{e}{m_e}\sqrt{\frac{\hbar}{2\epsilon_0 V\omega_k}}\,\langle\psi_f|\,e^{-i\mathbf{k}\cdot\mathbf{x}}\boldsymbol{\varepsilon}_\lambda\cdot\hat{\mathbf{p}}\,|\psi_i\rangle\,\langle n_{\lambda,\mathbf{k}}+1|\,\hat{a}^\dagger_{\lambda,\mathbf{k}}\,|n_{\lambda,\mathbf{k}}\rangle \\ &= \frac{e}{m_e}\sqrt{\frac{\hbar}{2\epsilon_0 V\omega_k}}\sqrt{n_{\lambda,\mathbf{k}}+1}\,\langle\psi_f|\,e^{-i\mathbf{k}\cdot\mathbf{x}}\boldsymbol{\varepsilon}_\lambda\cdot\hat{\mathbf{p}}\,|\psi_i\rangle\end{aligned}$$

Thus, we find

$$\Gamma^{emi}_{fi} = \frac{e^2}{m_e^2}\frac{\pi}{\epsilon_0 V\omega_k}(n_{\lambda,\mathbf{k}}+1)\left|\langle\psi_f|\,e^{-i\mathbf{k}\cdot\mathbf{x}}\boldsymbol{\varepsilon}_\lambda\cdot\mathbf{p}\,|\psi_i\rangle\right|^2\delta(E_f-E_i+\hbar\omega_k)$$

Absorption

We can perform a remarkably similar analysis for absorption of photons:

$$\begin{aligned}\langle\Phi_f|\,\hat{v}_{\lambda,veck}\,|\Phi_i\rangle &= \frac{e}{m_e}\sqrt{\frac{\hbar}{2\epsilon_0 V\omega_k}}\,\langle\psi_f|\,e^{i\mathbf{k}\cdot\mathbf{x}}\boldsymbol{\varepsilon}_\lambda\cdot\hat{\mathbf{p}}\,|\psi_i\rangle\,\langle n_{\lambda,\mathbf{k}}-1|\,\hat{a}_{\lambda,\mathbf{k}}\,|n_{\lambda,\mathbf{k}}\rangle \\ &= \frac{e}{m_e}\sqrt{\frac{\hbar}{2\epsilon_0 V\omega_k}}\sqrt{n_{\lambda,\mathbf{k}}}\,\langle\psi_f|\,e^{i\mathbf{k}\cdot\mathbf{x}}\boldsymbol{\varepsilon}_\lambda\cdot\hat{\mathbf{p}}\,|\psi_i\rangle\end{aligned}$$

And thus,

$$\Gamma^{abs}_{fi} = \frac{e^2}{m_e^2}\frac{\pi}{\epsilon_0 V\omega_k}n_{\lambda,\mathbf{k}}\left|\langle\psi_f|\,e^{i\mathbf{k}\cdot\mathbf{x}}\boldsymbol{\varepsilon}_\lambda\cdot\mathbf{p}\,|\psi_i\rangle\right|^2\delta(E_f-E_i-\hbar\omega_k)$$

2.4.5 Dipole Approximation

A typial quantum mechanical system is much smaller than the wavelength of emitted radiation.

2.4.6 Spontaneous Emission (Differential Rate)

We found before the transition probability for spontaneous emission:

$$\Gamma^{sp.\ emi}_{fi} = \frac{\pi\omega_k}{\epsilon_0 V}\left|\langle\psi_f|\,(\boldsymbol{\varepsilon_\lambda}(\mathbf{k}\cdot\hat{\mathbf{d}}\,|\psi_i\rangle\right|^2\delta E_f - E_i + \hbar\omega_k$$

Where $\mathbf{d} = q\mathbf{x} = -e\mathbf{x}$ is the operator of the dipole moment. This describes the probability of spontaneous emission og a photon with the transition of the system in a discrete state $|\psi_i\rangle$ into another state $|\psi_f\rangle$ on the discrete spectrum. The photon is emitted on a continuum of final states, though (that is, its energy is continuous). The photon will be detected by measuring its momentim on the interval $[\mathbf{p}, \mathbf{p}+\mathrm{d}\mathbf{p}]$ Therefore the transition probabiity must be summed over the ontinuum of final-state photons.
The number of photons in the volume V possessing momenta within the interval

$[\mathbf{p}, \mathbf{p} + \mathrm{d}\mathbf{p}]$ is

$$\begin{aligned}
\mathrm{d}N &= V \frac{\mathrm{d}^3\mathbf{p}}{(2\pi\hbar)^3} \\
&= 4\pi \left(\frac{L}{2\pi\hbar}\right)^3 p^2 \mathrm{d}p \\
&= \left(\frac{L}{2\pi\hbar}\right)^3 \mathrm{d}^3\mathbf{p} \\
&= \left(\frac{L}{2\pi c}\right)^3 \omega_k^2 \mathrm{d}\omega_k \mathrm{d}\Omega
\end{aligned}$$

We can make the substitution for $\mathrm{d}^3\mathbf{p}$ because

$$\begin{aligned}
\mathrm{d}^3\mathbf{p} &= p^2 \mathrm{d}p \mathrm{d}\Omega; \\
p &= \hbar k = \frac{\hbar\omega_k}{c} \\
\implies \mathrm{d}^3\mathbf{p} &= \left(\frac{\hbar}{c}\right)^3 \omega_k^2 \mathrm{d}\omega_k \mathrm{d}\Omega
\end{aligned}$$

Thus, the transition rate corresponding to the emission of the photon in the soid angle $\mathrm{d}\Omega$ (that is,the differential emission rate) is

$$\begin{aligned}
\mathrm{d}W_{fi,\lambda}^{sp.\ em} &= P^{sp.\ em} \mathrm{d}N \\
&= \frac{\omega_k^3}{8\pi\hbar c^3} \left| \langle\psi_f| \left(\boldsymbol{\varepsilon}_\lambda \cdot \hat{\mathbf{d}}\right) |\psi_i\rangle \right|^2 \mathrm{d}\Omega
\end{aligned}$$

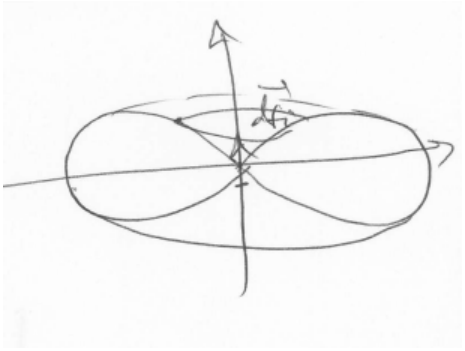
Where we are detecting the photon from the solid angle $\mathrm{d}\Omega$ from a large distance away from the system.
For unpolarized light (that is, where both $\lambda = 1$ and $\lambda = 2$ are in use),

$$\begin{aligned}
\mathrm{d}W_{fi}^{sp.\ em} &= \sum_{\lambda=1}^{2} \mathrm{d}W_{fi,\lambda}^{sp.\ em} \\
&= \frac{\omega_k^3}{8\pi^2\epsilon_0 c^3} \left(|\mathbf{d}_{fi}|^2 - |\mathbf{d}_{fi} \cdot \mathbf{n}|^2 \right) \mathrm{d}\Omega \\
&= \frac{\omega_k^3}{8\pi\epsilon_0 c^3} |\mathbf{d}_{fi}|^2 \sin^2\theta \mathrm{d}\Omega
\end{aligned}$$

In this simplification, we make use of two things:

$$\begin{aligned}
\mathrm{d}\Omega &= \sin\theta \mathrm{d}\theta \mathrm{d}\varphi \\
|\mathbf{d_{fi}}|^2 \sin^2\theta &= |\mathbf{d_{fi}}|^2 - |\mathbf{d_{fi}}|^2 \cos^2\theta
\end{aligned}$$

The differential emission rate thus has an angular distribution that looks like this:



The total rate for a differential solid angle is given by the interval of this:

$$\begin{aligned}
W_{fi}^{sp.em} &= \int_{4\pi} \mathrm{d}W_{fi}^{sp.\ em} \\
&= \frac{\omega_k^3}{8\pi^2\epsilon_0 c^3} \int_{4\pi} \mathrm{d}\Omega \left(|\mathbf{d}_{fi}|^2 - |\mathbf{d}_{fi} \cdot \mathbf{n}|^2 \right) \\
&= \frac{\omega_k^3}{8\pi^2\epsilon_0 c^3} \int_{4\pi} \mathrm{d}\Omega \left(|\mathbf{d}_{fi}|^2 - (d_{fi})_k (d_{fi})_k n_k n_e ll \right) \\
&= \frac{\omega_k^3}{8\pi^2\epsilon_0 c^3} |\mathbf{d}_{fi}|^2 \left(4\pi - \frac{4\pi}{3} \right) \\
W_{fi}^{sp.em} &= \frac{\omega_k^3}{8\pi^2\epsilon_0 c^3} |\mathbf{d}_{fi}|^2
\end{aligned}$$

And the intensity (or power) is given by

$$I_{fi} = \hbar\omega_{fi} W_{fi}$$

2.4.7 Lyman Transitions

Consider a hydrogen aton in the $2p$ excited state, such that

$$\begin{aligned}
\psi_i \to \psi_{n,\ell,m} &= R_n(2) i Y_{\ell m}(\Omega) \\
\psi_f \to \psi_{n',\ell',m'} &= R_{n'}(2) i Y_{\ell' m'}(\Omega)
\end{aligned}$$

For any $n \to 1$ (ie. from any n value going to $n = 1$), we call the Lyman series

$$\mathbf{d}_{fi} = \int \mathrm{d}^3\mathbf{x} \psi_{1\ell' m'}(\mathbf{x}) \mathbf{d} \psi_{n\ell m}(\mathbf{x})$$

This will all be in the UV spectrum. We call $n = 2 \to 1$ the Lyman-α transition, we call the $n = 3 \to 1$ the Lyman-β, etc.
For any $n \to 2$, we call the Balmer series

$$\mathbf{d}_{fi} = \int \mathrm{d}^3\mathbf{x} \psi_{2\ell' m'}(\mathbf{x}) \mathbf{d} \psi_{n\ell m}(\mathbf{x})$$

This will, finaly, be in the visible range.

2.4.8 Selection Rules for Electric Dipole Transitions

We want to look at the matrix elements for the expectation value given by

$$\langle f|\,\mathbf{x}\,|i\rangle \to \langle n', m', \ell'|\,\mathbf{x}\,|n, m, \ell\rangle$$

In order to talk about which of these matrix elements are zero and which are nonzero, we need to talk about the $\hat{\mathbf{L}}$ operator:

$$\hat{\mathbf{L}}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$
$$\hat{\mathbf{L}}_i = [\hat{\mathbf{x}}, \hat{\mathbf{p}}] = \epsilon_{ijk}\hat{x}_j \cdot \hat{p}_k$$

Recall as well that

$$\hat{L}_z\,|m, \ell\rangle = \hbar m\,|m, \ell\rangle$$

We will also need to construct the commutators between the L operator's components and the x operator's components:

$$[\hat{L}_i, \hat{x}_\ell] = i\hbar\epsilon_{i\ell j}\hat{x}_j$$

Now, we can go back to our question about the matrix elements that we're looking for, using these relationships:

$$\langle m', \ell'|\,[\hat{L}_i, \hat{x}_j]\,|m, \ell\rangle = \langle m', \ell'|\,i\hbar\epsilon_{i\ell j}\hat{x}_j\,|m, \ell\rangle$$
$$\langle m', \ell'|\,\hat{L}_z\hat{x}_j - \hat{x}_j\hat{L}_z\,|m, \ell\rangle = i\hbar\epsilon_{ijk}\,\langle m', \ell'|\,\hat{x}_k\,|m, \ell\rangle$$

Let's first look at the case where $i = z = 3$.

$$\hbar m'\,\langle m', \ell'|\,\hat{x}_j\,|m, \ell\rangle - \hbar m\,\langle m', \ell'|\,\hat{x}_j\,|m, \ell\rangle = i\hbar\epsilon_{ijk}\,\langle m', \ell'|\,\hat{x}_k\,|m, \ell\rangle$$
$$(m' - m)\,\langle m', \ell'|\,\hat{x}_j\,|m, \ell\rangle = i\epsilon_{zjk}\,\langle m', \ell'|\,\hat{x}_k\,|m, \ell\rangle$$
$$(m' - m)\,\langle m', \ell'|\,\hat{z}\,|m, \ell\rangle = 0$$

Therefore, for the case $j = z$, we have found our first rule:

$$m' = m \qquad \langle m', \ell'|\,\hat{z}\,|m, \ell\rangle \neq 0$$
$$m' \neq m \qquad \langle m', \ell'|\,\hat{z}\,|m, \ell\rangle = 0$$

Now, let's look at what happens if $j = x, y$ (we'll combine them into a single set of calculations since we'll find that they just repeat if we do them individually):

$$(m' - m)^2\,\langle m', \ell'|\,\hat{x}_j\,|m, \ell\rangle = (m' - m)i\epsilon_{zjk}\,\langle m', \ell'|\,\hat{x}_k\,|m, \ell\rangle$$
$$(m' - m)^2\,\langle m', \ell'|\,\hat{x}_j\,|m, \ell\rangle = i\epsilon_{zjk}\epsilon_{zkm}\,\langle m', \ell'|\,\hat{x}_m\,|m, \ell\rangle$$

We can use the rules for multiplication of Levi-Civita (sp?) tensors to simplify this:

$$(m' - m)^2\,\langle m', \ell'|\,\hat{x}_j\,|m, \ell\rangle = \langle m', \ell'|\,\hat{x}_j\,|m, \ell\rangle$$
$$[(m' - m)^2 - 1]\,\langle \ell', m'|\,\hat{x}_j\,|\ell, m\rangle = 0$$

So, for $j = x, y$, we get this new set of selection rules:

$$m' = m \pm 1 \qquad \langle m', \ell'|\,\hat{x}_j\,|m, \ell\rangle \neq 0$$
$$m' \neq m \pm 1 \qquad \langle m', \ell'|\,\hat{x}_j\,|m, \ell\rangle = 0$$

Now, let's look at selection rules that involve ℓ since we've exhausted all of the possible m values. To do this, we'll need to know that

$$\begin{aligned}
[\hat{\mathbf{L}}^2, \hat{L}_i] &= 0 \\
[\hat{L}_i, \hat{L}_j] &= i\epsilon_{ijk}\hat{L}_k \\
[\hat{\mathbf{L}}^2, \hat{x}_j] &= 2\hbar^2\hat{x}_i + 2i\hbar\epsilon_{ijk}\hat{x}_k\hat{L}_j
\end{aligned}$$

Note that for this last one, there's a *lot* of algebra, but I don't have the time to keep up with the lecture right now. I don't think the algebra itself is particularly important. Recall also how we can relate these to the ℓ index:

$$\hat{\mathbf{L}}^2 |m, \ell\rangle = \hbar\ell(\ell+1) |m, \ell\rangle$$

We now want to look at something real intense:

$$\begin{aligned}
\left[\hat{\mathbf{L}}^2, [\hat{\mathbf{L}}^2, \hat{x}_j]\right] &= 2\hbar[\hat{\mathbf{L}}^2, \hat{x}_j] + 2i\hbar^2\epsilon_{ijk}[\hat{\mathbf{L}}^2, \hat{x}_k]\hat{L}_j \\
&= 2\hbar^2[\hat{\mathbf{L}}^2, \hat{x}_j] + 2i\hbar\epsilon_{ijk}\left(2\hbar\hat{x}_k + 2i\hbar\epsilon_{mk\ell}\hat{x}_\ell\hat{L}_m\right)\hat{L}_j \\
&= 2\hbar^2[\hat{\mathbf{L}}^2, \hat{x}_j] + 2i\hbar\left(2\hbar\epsilon_{ijk}\hat{x}_k\hat{L}_j - 2i\hbar\epsilon_{ijk}\epsilon_{m\ell k}\hat{x}_\ell\hat{L}_m\hat{L}_j\right) \\
&= 2\hbar^2[\hat{\mathbf{L}}^2, \hat{x}_j] + 2i\hbar\left(2\hbar\epsilon_{ijk}\hat{x}_k\hat{L}_j - 2i\hbar(\hat{x}_j\hat{L}_i\hat{L}_j - \hat{x}_i\hat{\mathbf{L}}^2)\right)
\end{aligned}$$

There's some simplification here I'm not understanding so I'll skip to the end

$$\left[\hat{\mathbf{L}}^2, [\hat{\mathbf{L}}^2, \hat{x}_j]\right] = 2\hbar^2\left[\hat{\mathbf{L}}^2\hat{x}_j + \hat{x}_j\hat{\mathbf{L}}^2\right]$$

Now, we can apply this to the transitions we care about to find the selection rules:

$$\begin{aligned}
\langle m', \ell'| 2\hbar^2(\hat{\mathbf{L}}^2\hat{x}_j + \hat{x}_j\hat{\mathbf{L}}^2) &= [\hat{\mathbf{L}}^2, [\hat{\mathbf{L}}^2, \hat{x}_j]] |m, \ell\rangle \\
2\hbar^2\left(\hbar^2\ell'(\ell'+1) + \hbar^2\ell(\ell+1)\right)\langle m', \ell'| \hat{x}_j |m, \ell\rangle &= \hbar^{2(?)}\left(\hbar\ell'(\ell'+1) - \hbar\ell(\ell+1)\right)^2\langle m', \ell'| \hat{x}_j |m, \ell\rangle \\
2(\ell'(\ell'+1) + \ell(\ell+1))\langle m', \ell'| \hat{x}_j |m, \ell\rangle &= (\ell'-\ell)^2(\ell+\ell'+1)^2\langle m', \ell'| \hat{x}_j |m, \ell\rangle
\end{aligned}$$

Moving everything to the same side:

$$\begin{aligned}
\left((\ell'+\ell+1)^2 - 1 - (\ell'-\ell)^2(\ell'+\ell+1)^2\right)\langle m', \ell'| \hat{x}_j |m, \ell\rangle &= 0 \\
\left((\ell'-\ell)^2 - 1\right)\left((\ell'+\ell+1)^2 - 1\right)\langle m', \ell'| \hat{x}_j |m, \ell\rangle &= 0
\end{aligned}$$

From this, we can make our ℓ selection rules. Assuming that we're not talking about $\ell = 0$ or $\ell' = 0$, noting that this works for any $j = x, y, z$:

$$\begin{aligned}
(\ell'-\ell)^2 \neq 1 \qquad & \langle m', \ell'| \hat{x}_j |m, \ell\rangle = 0 \\
(\ell'-\ell)^2 = 1 \qquad & \langle m', \ell'| \hat{x}_j |m, \ell\rangle \neq 0
\end{aligned}$$

Note that we could re-write $(\ell'-\ell)^2 = 1$ a $\ell' = \ell \pm 1$. I'm going to just re-write all of the selection rules just to be safe:

$$\begin{aligned}
m' = m \qquad & \langle m', \ell'| \hat{z} |m, \ell\rangle \neq 0 \\
m' = m \pm 1 \qquad & \langle m', \ell'| \hat{x,y} |m, \ell\rangle \neq 0 \\
\ell' \neq \ell \pm 1 \qquad & \langle m', \ell'| \hat{x}_j |m, \ell\rangle = 0 \\
\ell' = \ell \pm 1 \qquad & \langle m', \ell'| \hat{x}_j |m, \ell\rangle \neq 0
\end{aligned}$$

2.4.9 Lifetime of an Excited State

3 Scattering and Born Approximations

3.1 Classical Scattering Theory

Let's say we have some object centered on the origin and we send a projectile towards the object along the z direction. According to Classical theory, the projectile will hit the object and bounce off in some other direction at an angle θ from the z axis, called the scattering angle. We also define a parameter b, called the the impact parameter, which I think represents the distance of the projectile from the z axis. The question we want to ask is: what is the dependance of θ on b?
In 3 dimensions, let's define an annulus with an inner radius b and a thickness $\mathrm{d}b$, with a projectile being projected on the differential azimuthal angle $\mathrm{d}\phi$ (ie. between ϕ and $\phi + \mathrm{d}\phi$). The projectile will be scattered somewhere into the solid angle $\mathrm{d}\Omega$ (composed of $\mathrm{d}\phi$, the polar angle, and $\mathrm{d}\phi$, the azimuthal angle). We can find two differential values and combine, using σ for cross secion.

$$\begin{aligned}
\mathrm{d}\sigma &= b\mathrm{d}b\mathrm{d}\phi \\
\mathrm{d}\Omega &= \sin\theta \mathrm{d}\theta\mathrm{d}\phi \\
\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} &= \text{diff. cross section}
\end{aligned}$$

The total cross section is thus given by

$$\sigma = \int_{4\pi} \mathrm{d}\Omega \frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}$$

Example (Hard-sphere scattering)**.**

3.1.1 Impact Parameter

3.1.2 Differential Cross Section

3.1.3 Scattering on a Sphere

Let's say we have a bullet that we're shooting at a large, hard ball with radius R, with impact parameter b, scatteering angle θ, and angle α which is one half of the complememntary angle to θ (wrong word? The one that's 180-θ. We can thus say

$$\begin{aligned}
b &= R\sin\alpha \\
2\alpha + \theta &= \pi \\
\implies \theta &= \pi - 2\alpha \\
b &= R\sin((\pi-\theta)/2) \\
&= R\cos(\theta/2) \\
\theta &= 2\arccos\left(\frac{b}{R}\right)
\end{aligned}$$

Note that this works as ong as $b \leq R$. For $b > r$, the bullet doesn't directly hit the ball, so there is no scattering.

Now let's look at this in terms of differential cross-section:

$$\begin{aligned}
\left|\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right| &= \left|\frac{b\mathrm{d}b\mathrm{d}\phi}{\sin\theta\mathrm{d}\theta\mathrm{d}\phi}\right| \\
&= \frac{b}{\sin\theta}\left|\frac{\mathrm{d}b}{\mathrm{d}\theta}\right| \\
&= \frac{R\cos(\theta/2)\frac{R}{2}\sin(\theta/2)}{\sin\theta} \\
&= \frac{R^2}{4}\frac{2\cos(\theta/2)\sin(\theta/2)}{\sin\theta} \\
&= \frac{R^2}{4} \\
\implies \frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} &= \frac{R^2}{4} \\
\sigma &= \int_{4\pi}\mathrm{d}\Omega\frac{R^2}{4} \\
&= \pi R^2
\end{aligned}$$

3.2 Quantum Scattering Theory

3.2.1 Differential Cross-Section

We're going to use the same picture/setup as before (ie. an annulus projecting particles at an object between some differential azimuthal angle, towards some differential solid angle, etc.). Let's define J_{in}, the number of particles throughout σ in $1/t$ (also called the incident flux, incident current density, or the luminocity). We can define $\mathrm{d}N$, the differential number of particles recorded in the differentia solid angle $\mathrm{d}\Omega$ per unit time, and to talk about $\mathrm{d}\sigma$, we will normalize it according to J_{in}:

$$\mathrm{d}\sigma = \frac{1}{J_{in}}\mathrm{d}N$$

Such that

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \frac{1}{J_{in}}\frac{\mathrm{d}N}{\mathrm{d}\Omega}$$

3.2.2 Scattering Amplitude

In quantum, it's often more convenient to operate with waves than with particles. So let's do that. We can imagine a solid object in a boxwith propagating waves (eg. a rock in a ripple tank). We'll define the vertical axis as x and the horizontal axis as z (I don't know why but... here we are). When the waves hit the rock, they will diffuse circularly around the rock, propagating outwards. The function that we can use to describe the waves (assuming they don't change frequency) as

$$\psi = e^{ikz} + f(\theta)\frac{e^{ikr}}{\sqrt{r}}$$

Where the first term represents the plane (initial) waves, and the second term represents the spherical (scattered) waves, and $f(\theta)$ is the scattering amplitude.

Our goal right now is to find the scattering amplitude. We can easily generalize this into 3 dimensions:

$$\psi = e^{ikz} + f(\theta, \phi)\frac{e^{ikr}}{r}$$

To test whether or not this is kosher with quantum theory, let's test it with the Schrödinger equation, using $V = V(\mathbf{r})$ as our potential, which must be a finite-range potential (ie. must be only active within a range, so no Coulomb potential):

$$\left[-\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + V(\mathbf{r})\right]\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

When we're very far away from the scattering center ($r \to -\infty$), if the potential is a finite-range potential, then we can take $V \to 0$ and re-write the Schrödinger equation as

$$-\frac{\hbar}{2m}\boldsymbol{\nabla}^2\psi = E\psi$$

And simplify:

$$(\boldsymbol{\nabla}^2 + k^2)\psi = 0$$

Using the magnitude of k that we know,

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

Where

$$\mathbf{k} = k\mathbf{n}$$

Where $\mathbf{n}$ is the unit vector in the direcction of r. We will thus write our wave equation solution to this as

$$\psi = Ae^{i\mathbf{k}\cdot\mathbf{z}} + Be^{-i\mathbf{k}\cdot\mathbf{z}}$$

We'll still be discussing waves that are propagating along the z axis, such that $\mathbf{k} = k\hat{\mathbf{e}}_z$.
Before scattering, the wave equation can be written

$$\psi_{in} = e^{ikz}$$

After scattering, the outgoing wave can be written as

$$\psi_{out} = f\frac{e^{ikr}}{r}$$

The total wave equation must then be

$$\begin{aligned}\psi &= \psi_{in} + \psi_{out} \\ &= e^{ikz} + f(\theta, \phi)\frac{e^{ikr}}{r}\end{aligned}$$

3.2.3 Differential Cross Section in terms of f

We want to find a continuity equation from the Schrödinger equation. Remember that the traditional continuity equation in electrodynamics is

$$\frac{\partial}{\partial t}\rho + (\boldsymbol{\nabla} \cdot \mathbf{J}) = 0$$

Note that we will have to work with the full time-dependent Schrödinger equation here. Recall that density (probability density, in this case) is the probability density, $|\psi|^2$. Let's try to get the Schrödinger equation in the right form to be able to use ρ:

$$\psi^* \left(i\hbar \frac{\partial}{\partial t}\psi \right) = \psi^* \left(-\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2\psi \right)$$
$$\psi \left(i\hbar \frac{\partial}{\partial t}\psi^* \right) = \psi \left(-\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2\psi^* \right)$$

If we add these together, we get

$$i\hbar \frac{\partial}{\partial t}(\psi\psi^*) = -\frac{\hbar^2}{2m}\left(\psi^*\boldsymbol{\nabla}^2\psi + \psi\boldsymbol{\nabla}^2\psi^*\right)$$

If we choose to simplify this, noting our previous definition for ρ, we can find the probability current density:

$$\mathbf{J} = -i\frac{\hbar}{2}\left[\psi^*\boldsymbol{\nabla}\psi - \psi\boldsymbol{\nabla}\psi^*\right]$$

For the incoming wave, we have

$$\begin{aligned} J_{in} &= -i\frac{\hbar}{2m}[ik - (-ik)] \\ &= \frac{k\hbar}{m} \end{aligned}$$

For the outcoming wave,

$$\psi_{out} = f(\theta, \phi)\frac{e^{ikr}}{r}$$

So the $\boldsymbol{\nabla}$ operator will only care about the r component, meaning

$$\begin{aligned} J_{out} &= \frac{k\hbar}{m} frac f f^* r^2 \\ &= \frac{k\hbar}{me^2}\left|f\right|^2 \end{aligned}$$

Thus, if we say intuitively that $\mathrm{d}N = J_{out} r^2 \mathrm{d}\Omega$, then

$$\begin{aligned} d\sigma &= frac r^2 J_{out} \mathrm{d}\Omega J_{in} \\ &= \left|f\right|^2 \mathrm{d}\Omega \\ \frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} &= \left|f(\theta, \phi)\right|^2 \end{aligned}$$

3.2.4 Integral Form of the Schrödinger Equation

If we look at the Schrödinger equation,

$$\left[-\frac{\hbar}{2m}\boldsymbol{\nabla}^2 + V(\mathbf{r})\right]\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

It's difficult to see a way to be able to easily find f. So we want to change this to make our job a little easier. We can do this by using an inhomogeneous Helmholtz operator

$$\frac{2m}{\hbar^2}$$

To get an inhomogeneous Helmholtz equation:

$$\left[\boldsymbol{\nabla}^2 + \frac{2mE}{\hbar^2}\right]\psi(\mathbf{r}) = -\frac{2m}{\hbar^2}V(\mathbf{r})\psi(\mathbf{r})$$
$$\left[\boldsymbol{\nabla}_r^2 + k^2\right]\psi(\mathbf{r}) = -\frac{2m}{\hbar^2}V(\mathbf{r})\psi(\mathbf{r})$$

This equation now describes 2 wave fronts, one moving to the right and one to the left. Let's try to find the general solution to this, which will be in the form $\psi(\mathbf{r}) = \psi_0(\mathbf{r}) + \tilde{\psi}(\mathbf{r})$. First,

$$[\boldsymbol{\nabla}_r^2 + k^2]\psi_0(\mathbf{r}) = 0$$
$$\psi_0(\mathbf{r}) = Ae^{ikz} + Be^{-ikz}$$
$$\psi_0(\mathbf{r}) = e^{ikz}$$

More difficultly,

$$[\boldsymbol{\nabla}_r^2 + k^2]\tilde{\psi}(\mathbf{r}) = -\frac{2m}{\hbar^2}V(\mathbf{r})\psi(\mathbf{r})$$

This is difficult to solve, but we can make it easier for ourselves using the Green's function method, making the shift $\mathbf{r} \to \mathbf{r} - \mathbf{r}'$:

$$[\boldsymbol{\nabla}_r^2 + k^2]G(\mathbf{r}) = \delta^{(3)}(\mathbf{r})$$

Thus,

$$\tilde{\psi}(\mathbf{r}) = \int \mathrm{d}^3\mathbf{r}' G(\mathbf{r} - \mathbf{r}')\left[-\frac{2m}{\hbar^2}V(\mathbf{r}')\psi(\mathbf{r}')\right]$$
$$\text{LHS} = \int \mathrm{d}^3\mathbf{r}' [\boldsymbol{\nabla}_r^2 + k^2]G(\mathbf{r} - \mathbf{r}')\left[-\frac{2m}{\hbar^2}V(\mathbf{r}')\psi(\mathbf{r}')\right]$$

From the relationship above, we can say then that

$$= -\frac{2m}{\hbar}V(\mathbf{r})\psi(\mathbf{r}) = \text{RHS}$$

We need to do a Fourier transformation to deal with the right-hand side of the equation in order to smooth out the delta function:

$$\begin{aligned}
\delta^{(3)}(\mathbf{r}) &= \int \frac{\mathrm{d}^3\mathbf{q}}{(2\pi)^3} e^{i\mathbf{q}\cdot\mathbf{r}} \\
G(\mathbf{r}) &= \int \frac{\mathrm{d}^3\mathbf{q}}{(2\pi)^3} e^{i\mathbf{q}\cdot\mathbf{r}} \tilde{G}(\mathbf{q}) \\
\text{LHS} &= \int \frac{\mathrm{d}^3\mathbf{q}}{(2\pi)^3} \left[[\boldsymbol{\nabla}_r^2 + k^2] e^{i\mathbf{q}\cdot\mathbf{r}} \right] \tilde{G}(\mathbf{q}) \\
&= \int \frac{\mathrm{d}^3\mathbf{q}}{(2\pi)^3} \left[[k^2 - \mathbf{q}^2] e^{i\mathbf{q}\cdot\mathbf{r}} \right] \tilde{G}(\mathbf{q}) \\
\text{LHS} = \text{RHS} &= \int \frac{\mathrm{d}^3\mathbf{q}}{(2\pi)^3} e^{i\mathbf{q}\cdot\mathbf{r}}
\end{aligned}$$

Note that we can do this because of the following properties:

$$\begin{aligned}
[k^2 - \mathbf{q}^2]\tilde{G}(\mathbf{q}) &= 1 \\
\tilde{G}(\mathbf{q}) &= \frac{1}{k^2 - \mathbf{q}^2}
\end{aligned}$$

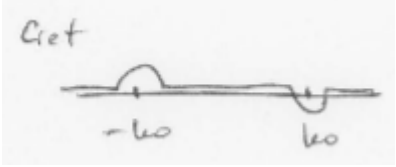
This is a deceptively complicated integral. To make it easier to solve it, let's make a transition into spherical coordinates. We will take

$$\begin{aligned}
\mathrm{d}^3\mathbf{q} &= q^2 \mathrm{d}q \sin\theta \mathrm{d}\theta \mathrm{d}\phi \\
q_z &= q\cos\theta
\end{aligned}$$

If we do this, then

$$\begin{aligned}
G(\mathbf{r}) &= \frac{1}{(2\pi)^3} \int_0^\infty \frac{q^2 \mathrm{d}q}{k^2 - q^2} \int_0^{2\pi} \mathrm{d}\phi \int_0^\pi \sin\theta \mathrm{d}\theta e^{iqr\cos\theta} \\
&= \frac{1}{(2\pi)^3} \int_0^\infty \frac{q^2 \mathrm{d}q}{k^2 - q^2} \left(2\pi \frac{e^{iqr} - e^{-iqr}}{2qr} \right) \\
&= \frac{1}{(2\pi)^2} \frac{1}{ir} \int_0^\infty \frac{q^2 \mathrm{d}q}{k^2 - q^2} \left[e^{iqr} - e^{-iqr} \right] \\
&= \frac{1}{i(2\pi)^2 r} \int_{-\infty}^\infty \frac{\mathrm{d}q q e^{iqr}}{k^2 - q^2}
\end{aligned}$$

We used antisymmetry rules in that last bit to make it work and change the limits.
We'll define just the integral there as I_{ret}. There's a problem: this integral is not well-defined. That is, it has a pole on the integration axis. In order to figure out how, we need to look at the complex plane and use Cauchy's theorem. The option in the complex plane for Cauchy's theorem that we want to use is the retarded one (as opposed to advanced, etc.)



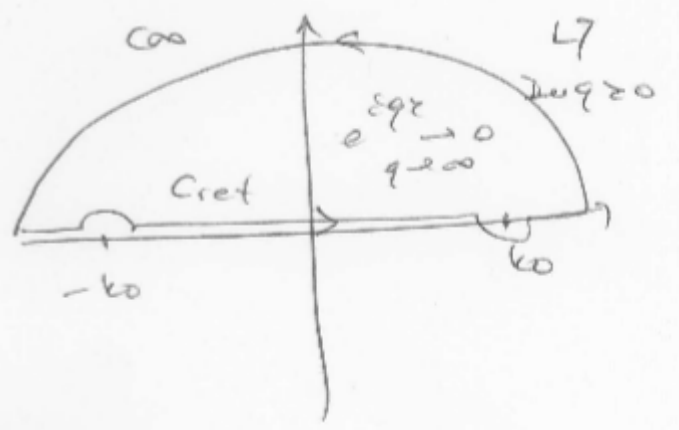
Just to confirm:

$$I_{ret} = \int_{C_{ret}} q \frac{\mathrm{d}q}{k^2 - q^2} e^{ikr}$$

Recall that Cauchy's theorem says that for a closed loop around a pole z_0,

$$\oint_{z_0} \mathrm{d}z \frac{f(z)}{z - z_0} = 2\pi i f(z_0)$$

But the contour we've looked at isn't a closed loop. Should we close the loop above or below the contour? The answer is above. If we try to close it below, we would find that the way we would have to write the integrand would mean that it would diverge at $q \to \infty$. So, we close it above, as such:



If we do this, then

$$\begin{aligned}
\int C_{ret} \frac{\mathrm{d}qq}{k^2 - q^2} e^{ikq} &= \oint_C \frac{\mathrm{d}qq}{k^2 - q^2} e^{ikr} \\
&= 2\pi \operatorname*{res}_{q=k} \frac{qe^{ikr}}{(q-k)(k+q)} \\
&= -2\pi i \frac{ke^{ikr}}{2k} \\
&= -\pi i e^{ikr}
\end{aligned}$$

Plugging this back into our Green's function, we find that

$$G_{ret}(\mathbf{r}) = -\frac{e^{ikr}}{4\pi r}$$

This is called a standard Green's function, and it describes an outgoing spherical wave. Similarly, had we chosen G_{adv}, we would have gotten

$$G_{adv} = -\frac{e^{-ikr}}{4\pi r}$$

We can use either Green's function, or a linear combination of them, but we wan to use the one which is more intuitive, which is the retarded function. We

can plug this back into the thing we were looking at earlier, the solution to the Schrödinger equation that we needed:

$$\begin{aligned}\psi(\mathbf{r}) &= e^{ikr} - \frac{2m}{\hbar^2}\int \mathrm{d}^3\mathbf{r}' G(\mathbf{r}-\mathbf{r}')V(\mathbf{r}') \\ &= e^{ikr} - \frac{m}{2\pi\hbar^2}\int \mathrm{d}^3\mathbf{r}' \frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}V(\mathbf{r}')\psi(\mathbf{r}')\end{aligned}$$

This final equation that we found is called the Lippmann-Schrödinger Equation (or the integral form of the Schrödinger equation).

3.2.5 Asymptotic Form of the Wave Function

Recall that $\mathbf{r}'$ is the vector inside of the potential, where the atom is affected. However, $\mathbf{r}$ is the vector representing the location of the detector, far away from $\mathbf{r}'$, and no longer in the potential. That is, $|\mathbf{r}| \gg |\mathbf{r}'|$. Because of this, we can simplify the second term in the Lippmann-Schrödinger equation by expanding the denominator:

$$\begin{aligned}\frac{1}{|\mathbf{r}-\mathbf{r}'|} &= \frac{1}{\sqrt{(\mathbf{r}-\mathbf{r}')^2}} \\ &= \frac{1}{\sqrt{\mathbf{r}^2 - 2\mathbf{r}\cdot\mathbf{r}' + \mathbf{r}'^2}} \\ &= |\mathbf{r}|\,\frac{1}{\sqrt{1 - \frac{2\mathbf{r}\cdot\mathbf{r}'}{\mathbf{r}^2} + \frac{\mathbf{r}'^2}{\mathbf{r}^2}}}\end{aligned}$$

We can define some $\epsilon \equiv \frac{|\mathbf{r}'|}{|\mathbf{r}|}$, which is approximately $\frac{a}{r} \ll 1$, so that

$$\begin{aligned}&= |\mathbf{r}|\,\frac{1}{\sqrt{q - \epsilon^1 - 2\epsilon^2}} \\ &\approx |\mathbf{r}|\left(1 - \frac{\mathbf{r}\cdot\mathbf{r}'}{\mathbf{r}^2}\right) \\ &= |\mathbf{r}| - \frac{\mathbf{r}}{|\mathbf{r}|}\cdot\mathbf{r}' \\ &= |\mathbf{r}| - \hat{\mathbf{n}}\mathbf{r}'\end{aligned}$$

We can use $\mathbf{k} = k\hat{\mathbf{n}}$ to simplify the exponential to

$$e^{ik|\mathbf{r}-\mathbf{r}'|} = e^{ik|r| - i\mathbf{k}\cdot\mathbf{r}'}$$

And we can go back to the asymptotic wave function and write

$$\begin{aligned}\psi(\mathbf{r}) &= e^{ikz} - \frac{m}{2\pi\hbar^2}\frac{e^{ikr}}{r}\int d^3\mathbf{r}' e^{-i\mathbf{k}\cdot\mathbf{r}'}V(\mathbf{r})\psi(\mathbf{r}') \\ &= e^{ikz} + f(\theta,\phi)\frac{e^{ikr}}{r}\end{aligned}$$

3.3 The Born Approximation

3.3.1 The First Born Approximation

We wrote the Schrödinger equation in the form of the Lippman-Schrödinger equation, where it took the form

$$\psi(\mathbf{r}) = \psi_0(\mathbf{r}) - \frac{m}{2\pi\hbar^2}\int \mathrm{d}^3\mathbf{r}' \frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}V(\mathbf{r}')\psi(\mathbf{r}')$$

And we look where the obeservation point is very far from the scattering, ie, $|\mathbf{r}| \gg |\mathbf{r}'|$. We also found the asymptotic form of the wave function, as seen in the last section. Also recall that

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = |f(\theta,\phi)|^2$$

If V is small, then we can use a systematic expansion to try to solve the asymptotic equation:

$$\begin{aligned} 0^{th} \text{ order}: &\quad \psi(\mathbf{x}) = \psi_0(\mathbf{x}) \\ 1^{st} \text{ order}: &\quad \psi(\mathbf{x}) = \psi_0(\mathbf{x}) + \frac{e^{ikr}}{r}\left(-\frac{m}{2\pi\hbar^2}\int d^3\mathbf{r}' e^{-i(\mathbf{k}\cdot\mathbf{r}')}V(\mathbf{r}')\psi_0(\mathbf{r}')\right) \end{aligned}$$

And so on, but we'll only concern ourselves with the first-order approximation. Thus, we can write the Born approximation for f as

$$f_{Born} = -\frac{m}{2\pi\hbar^2}\int d^3\mathbf{r}' e^{ikr'-i(\mathbf{k}\cdot\mathbf{r}')}V(\mathbf{r}')$$

We can define some new variables to write

$$f_{Born}(\theta,\phi) = -\frac{m}{2\pi\hbar^2}\int \mathrm{d}^3\mathbf{r}' e^{i(\mathbf{q}\cdot\mathbf{r}')/\hbar}V(\mathbf{r}')$$

Note that here, V is not central. Where

$$\begin{aligned} |\mathbf{q}| &= \hbar\,|k\hat{\mathbf{e}}_z - \mathbf{k}| \\ &= \hbar\sqrt{k^2+k^2-2k(\hat{\mathbf{e}}_z\cdot\mathbf{k})} \\ &= \hbar k\sqrt{2(1-\cos\theta} \\ &= 2\hbar k\sin\left(\frac{\theta}{2}\right) \end{aligned}$$

In the cae where V is a central potential, that is, $V(\mathbf{x}) = V(|\mathbf{x}|) = V(r')$, we can write this as

$$\begin{aligned} f_{Born}(\theta,\phi) &= -\frac{m}{2\pi\hbar^2}\int_0^\infty r'^2\mathrm{d}r'\int \mathrm{d}\Omega' e^{iqr'\cos\theta'/\hbar}V(r') \\ &= -\frac{m}{2\pi\hbar^2}\int_0^\infty \mathrm{d}r'(r')^2V(r')2\pi\int_\pi^0 2\cos\theta' e^{iqr'\cos\theta'/\hbar} \\ &= -\frac{2m}{q\hbar}\int_0^\infty \mathrm{d}r'r'\sin\left(\frac{qr'}{\hbar}\right)V(r') \end{aligned}$$

3.3.2 The Validity of the First Born Approximation

Now that we have this approximation, we needto know how and when this will be applicable (ie. what restrictions we must impose on V to make this valid). To determine this, let's not worry about the asymptotic wave function. That is, we can take $\mathbf{r} \to 0$. The wave function is thus

$$\psi(\mathbf{r}=0) = 1 - \frac{m}{2\pi\hbar^2}\int \mathrm{d}^3\mathbf{r}' \frac{e^{ik|\mathbf{r}'|}}{|\mathbf{r}'|} V(\mathbf{r}')\psi(\mathbf{r}')$$

The Born inequality must only be true if the second term is much less than the first term, so that the wave function doesn't deviate too much from the incident plane wave. Mathematically,

$$1 \gg \left| \frac{m}{2\pi\hbar^2}\int \mathrm{d}^3\mathbf{r}' \frac{e^{ik|\mathbf{r}'|}}{|\mathbf{r}'|} V(\mathbf{r}')\psi(\mathbf{r}') \right|$$

In the case of a central potential,

$$1 \gg \frac{m}{2\pi\hbar^2}\left| \int_0^\infty \mathrm{d}r' r' \int \mathrm{d}\Omega' e^{ik(r'+r'\cos\theta')} V(r') \right|$$
$$1 \gg \frac{m}{k\hbar^2}\left| \int_0^\infty \mathrm{d}r' (e^{2ikr'-q}) V(r') \right|$$

Recall that

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

In the case of very small (ie. slow) , $ka \ll 1$, and in the case of very large (ie. fast), $ka \gg 1$. where a is the range of the interaction potential.
For slow particles, where $ka \ll 1$,

$$\begin{aligned} 1 &\gg \frac{m}{k\hbar^2}\left| \int_0^\infty \mathrm{d}r' V(r') 2ikr' \right| \\ &\gg \frac{m}{\hbar^2}\left| \int_0^\infty \mathrm{d}r' V(r') \right| \\ 1 &\gg \frac{ma^2}{\hbar^2} V \end{aligned}$$

By extension, and according to the uncertainty principle,

$$\begin{aligned} \frac{m}{p^2} V &\ll 1 \\ V &\ll \frac{p^2}{2m} = E_{kin} \end{aligned}$$

Now, let's look at fast particles, where $ka \gg 1$. We can ignore the term with the highly oscillating exponential in the inequality, therefore it reads

$$1 \gg \frac{m}{k\hbar^2}\left| \int_0^\infty \mathrm{d}r' V(r') \right|$$

The integral is approximately aV, so

$$1 \gg \frac{ma}{k\hbar^2}$$
$$V \ll \frac{\hbar^2}{ma^2}(ak)$$
$$V \ll \frac{m}{p^2} = E_{kin}(ak)$$

3.3.3 Born Approximation Estimate for the Coulomb Potential

Recallthat the Coulomb potential is a long-range central potential,

$$V(r) = \frac{e^2}{4\pi\epsilon_0}\frac{1}{r} \approx \frac{e^2}{4\pi\epsilon_0}\frac{1}{a}$$

Because it's a long-range potential, we can imagine that we will run into a lot of problems. But for now, we'll ignore those problems and just use the equation(s) we found for a short-range potential using the approximation above. The inequality we found before means that we can write

$$1 \gg \frac{m}{k\hbar}\frac{e^2}{4\pi\epsilon_0}$$

If we multiply and divide by c and shift around the $\hbar$, we can replace the RH fraction with the fine structure constant. We can also say that

$$\frac{k\hbar}{m} = \frac{p}{m} = v$$

To simplify this immensely and say that

$$\frac{v}{c} = \alpha$$

Recall that $\alpha \approx \frac{1}{137}$. If we include the Z factor, such that we can say we're looking at a large object with more particles, $\frac{v}{c} \gg Z\alpha$, which can quickly blow up. The relativistic contraction factor, $\gamma = \sqrt{1-(v/c)^2}$ is small in the case of, say, the hydrogen atom, but will quickly blow up for larger atoms. The Born approximation thus works for Coulomb potentials for small atoms.

3.4 Partial Wave Analysis

3.4.1 Partial Wave Analysis

We've discussed only approximate calculations so far for differential cross sections when the interaction potential is sufficiently small. Now, we're going to break free from that limitation and solve scattering for arbitrarily-strong V. We will only discuss spherically symmetric potentials, where $V(\mathbf{r}) = V(r)$ and $r = |\mathbf{r}|$. We can separate the variables in the Schrödinger equation using spherical coordinates. Recall that in spherical coordinates,

$$\boldsymbol{\nabla}^2 = \frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2}\boldsymbol{\nabla}^2_\Omega$$
$$\boldsymbol{\nabla}^2_\Omega = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\theta^2}$$

The separable form for the solution will be

$$\psi(\mathbf{r}) = R(r) + Y_{\ell m}(\Omega)$$

With the spherical harmonics obeying the equation

$$\boldsymbol{\nabla}^2_\Omega Y_{\ell m}(\Omega) = -\ell(\ell+1)Y_{\ell m}(\Omega)$$

So! The Schrödinger equation for the radial wave function is, plugging this in, given by

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r}\frac{\partial^2}{\partial r^2}(rR(r)) - \frac{\ell(\ell+1)}{r^2}R(r)\right] + V(r)R(r) = ER(r)$$

As always, we'll ahve to consider only potentials with a finite range of interaction (ie. $V(r \leq a) \neq 0$, $V(r > a) = 0$). If we do this, we have 3 regions. In order of decreasing r, these are:

(i) The far region/radiation region ($V = 0$, $\frac{\ell(\ell+1)}{r^2} = 0$):

$$-\frac{\hbar^2}{2m}\frac{1}{r}\frac{\partial^2}{\partial r^2}(rR(r)) = ER(r)$$

If we define $U(r) = rR(r)$ and $k^2 = \frac{2mE}{\hbar^2}$, then

$$\left(\frac{\partial^2}{\partial r^2} + k^2\right)U(r) = 0$$

The solution is clearly

$$U_i(r) = Ae^{ikr} + Be^{-ikr}$$
$$R(r) = A\frac{e^{ikr}}{r} + B\frac{e^{-ikr}}{r}$$

This describes both an incoming and an outgoing spherical wave, but we know that for the scattering case, we only have outgoing waves, so $B = 0$:

$$R_i(r) = A\frac{e^{ikr}}{r}$$

(ii) The intermediate region ($V = 0$, $\frac{\ell(\ell+1)}{r^2} \neq 0$)

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r}\frac{\partial^2}{\partial r^2}(rR(r)) - \frac{\ell(\ell+1)}{r^2}R(r)\right] + V(r)R(r) = ER(r)$$
$$\frac{\partial^2}{\partial r^2}U(r) - \frac{\ell(\ell+1)}{r^2}U(r) + k^2U(r) = 0$$

In reality, we can use something like Mathematica for this, but we'll solve it analytically for the math. We can start by solving for the case $\ell = 0$:

$$\frac{\partial^2}{\partial r^2}U_0(r) + k^2U_0(r) = 0$$

This has solutions, like last time, of

$$U_0(r) = Ae^{ikr} + Be^{-ikr}$$
$$R_0(r) = A\frac{e^{ikr}}{r} + B\frac{e^{ikr}}{r}$$

In ordr to have a finite R at $r = 0$, we must have $B = -A$, so that, simplifying a lot,

$$R_0(r) = \tilde{A}\frac{\sin(kr)}{r}$$

To solve for $\ell \neq 0$, we have to do a bit more work. There's a couple ways of doing this, but they all require a *lot* more work, so we'll try to brute-force a Rodriguez formula, which won't give us an actual answer, but will give us a relationship to be able to work from. We need to define our U this time as

$$U_\ell(r) = e^{\ell+1}\chi_\ell(r)$$

The second derivative of U is thus

$$\frac{\partial^2}{\partial r^2}U_\ell(r) = \ell(\ell+1)r^{\ell-1}\chi_\ell(r) + 2(\ell+1)r^\ell\chi'_\ell(r) + r^{\ell+1}\chi''_\ell(r)$$

Such that, going back to the Schrödinger equation,

$$\ell(\ell{+}1)r^{\ell-1}\chi_\ell(r){+}2(\ell{+}1)r^\ell\chi'_\ell(r){+}r^{\ell+1}\chi''_\ell(r){-}\ell(\ell{+}1)r^{\ell-1}\chi_\ell(r){+}k^2r^{\ell+1}\chi_\ell(r) = 0$$

Or, simplifying,

$$\chi''_\ell(r) + \frac{2(\ell+1)}{r}\chi'_\ell(r) + k^2\chi_\ell(r) = 0$$

If we differentiate this function with respect to r, we get

$$\chi'''_\ell(r) - \frac{2(\ell+1)}{r^2}\chi'_\ell + \frac{2(\ell+1)}{r}\chi''_\ell(r) + k^2\chi'_\ell(r) = 0$$

If we define $\chi'_\ell(r) = r\phi_\ell(r)$, then

$$\chi'_\ell(r) = r\phi_\ell(r)$$
$$\chi''_\ell(r) = \phi_\ell(r) + r\phi'_\ell(r)$$
$$\chi'''_\ell(r) = 2\phi'_\ell(r) + r\phi''_\ell(r)$$

Such that

$$2\phi'\ell(r) + r\phi''_\ell + \frac{2(\ell+1)}{r}[\phi_\ell(r) + r\phi'_\ell(r)] + [k^2 - \frac{2(\ell+1)}{r^2}]r\phi_\ell = 0$$
$$r\phi_\ell(r) + 2(\ell+2)\phi'_\ell + rk^2\phi_\ell = 0A$$
$$\phi_\ell(r) + \frac{2(\ell+2)}{r}\phi'_\ell(r) + k^2\phi_\ell = 0$$

We can see that this is exactly the equation for χ_ℓ, with ℓ shifted by one, so that

$$\phi_\ell(r) = \chi_{\ell+1}(r)$$

Thus, we can relate the two as

$$\begin{aligned}\chi_\ell &= \frac{1}{r}\frac{\partial}{\partial r}\chi_{\ell-1} \\ &= \frac{1}{r}\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial}{\partial r}\chi_{\ell-2}\right) \\ &= \left(\frac{1}{r}\frac{\partial}{\partial r}\right)^\ell \chi_0 \\ &= \left(\frac{1}{r}\frac{\partial}{\partial r}\right)^\ell \frac{\sin(kr)}{r}\end{aligned}$$

Finally, this means

$$\begin{aligned}U_\ell &= r^{\ell+1}\left(\frac{1}{r}\frac{\partial}{\partial r}\right)^\ell \frac{\sin(kr)}{r} \\ R_\ell(r) &= A_\ell r^\ell \left(\frac{1}{r}\frac{\partial}{\partial r}\right)^\ell \frac{\sin(kr)}{r}\end{aligned}$$

If we arbitrarily choose $A_\ell = (-1)^\ell/k^\ell$, then we can express this in terms of spherical bessell functions. We'll also choose $x = kr$ for simplicity.

$$\begin{aligned}R_\ell(r) &= k(-1)^\ell x^\ell \left(\frac{1}{x}\frac{\partial}{\partial x}\right)^\ell \frac{\sin(x)}{x} \\ &= kj_\ell(x)\end{aligned}$$

Remember that

$$j_\ell(x) = \sqrt{\frac{\pi}{2x}}J_{\ell+1/2}(x)$$

We've now found a solution, but it's not the solution we want. We found spherical waves, not standing waves like we'd hoped. Also, we'd have to account for the second linearly independent solution to the spherical Bessel equations. If we instead define $A_\ell^\pm = \mp i(-1)^\ell \frac{1}{k^\ell}$, then the solutions become

$$R_\ell^\pm(r) = kh_\ell^{(1)}(kr)$$

Where, explicitly, Hankel functions of the first kind are given by

$$h_\ell^{(1)}(x) = -i(-1)^\ell x^\ell \left(\frac{1}{x}\frac{\partial}{\partial x}\right)^\ell \frac{e^{ix}}{x}$$

We can therefore write th solution to the Schrödinger equation in the intermediate region as

$$\psi(\mathbf{r}) = \sum_{l=0}^{\infty}\sum_{m=-\ell}^{\ell} A_{\ell m}kh^{(1)}(kr)Y_{\ell m}(\theta,\phi)$$

There is no ϕ dependence because it's spherically symmetric, so $m = 0$:

$$= k\sum_\ell A_\ell\sqrt{\frac{2\ell+1}{4\pi}}h_\ell^{(1)}(kr)P_\ell(\cos\theta)$$

If we define $A_\ell = \sqrt{4\pi(2\ell+1)}i^{\ell+1}a_\ell$, then

$$\psi_{ii}(\mathbf{r}) = k\sum_\ell i^{\ell+1}(2\ell+1)a_\ell h_\ell^{(1)}(kr)P_\ell(\cos\theta)$$

For very large r, I'm going to skip a lot of the really terrible derivations and just write

$$h_\ell^{(1)}\Big|_{x\to\infty} = (-i)^{\ell+1}\frac{e^{ix}}{x}$$
$$\psi_{ii}(\mathbf{r})|_{r\to\infty} = e^{ikr} + f(\theta,\phi)\frac{e^{ikr}}{r}$$

Where

$$f(\theta,\phi) = \sum_{\ell=0}^{\infty} a_\ell(2\ell+1)P_\ell(\cos\theta)$$

This is the best we can do for now.
But, we can say that the differential an total cross sections are given by

$$\begin{aligned}\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} &= |f(\theta)|^2\\ \sigma &= \int_{4\pi}\mathrm{d}\Omega\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\\ &= \sum_{\ell,\ell'=0}(2\ell+1)(2\ell'+1)a_\ell a_\ell^*\int_{4\pi}\mathrm{d}\Omega P_\ell(\cos\theta)P_{\ell'}(\cos\theta)\\ &= 4\pi\sum_{\ell=0}^{\infty}(2\ell+1)\left|a_\ell\right|^2\end{aligned}$$

(iii) The scattering region ($V \neq 0$, $\frac{\ell(\ell+1)}{r^2} \neq 0$) We won't actually talk about this right now.

3.4.2 Determination of Partial Waves

In ordr to find the partial waves a_ℓ, we need to solve the Schrödinger equation in the scattering region and sew it with the solution in the intermediate region using the boundar conditions. The uniform representation for the wave function in the intermediate region is given by

$$\psi(\mathbf{r}) = e^{ikz} + k\sum_{\ell=0}^{\infty} a_\ell e^{\ell+1}(2\ell+1)h_\ell^{(1)}(kr)P_\ell(\cos\theta)$$

Where $z = r\cos\theta$. We can write the first term as a linear superposition of the spherical Bessel function(s), so that

$$e^{ikz} = e^{ikr\cos\theta} = \sum_{\ell=0}^{\infty}[A_\ell j_\ell(kr) + B_\ell n_\ell(kr)]P_\ell(\cos\theta)$$

On $r \to 0$, we must be finite, so $B = 0$:

$$e^{ikr\cos\theta} = \sum_{\ell=0}^{\infty} A_\ell j_\ell(kr)P_\ell(\cos\theta)$$

We can expand each side by a Taylor expansion around $r \to 0$ to find the coefficient A_ℓ. To do that, we need to extract the leading power of the RHS when it's expanded with the Rodriguez formula:

$$\begin{aligned}
P_\ell(x) &= \frac{1}{2^\ell(\ell!)}\frac{\partial^\ell}{\partial x^\ell}(x^2-1)^\ell = C_\ell x^\ell + \cdots \\
&= \frac{1}{2^\ell(\ell!)}\frac{\partial^\ell}{\partial x^\ell}x^{2\ell} + \cdots \\
&= \frac{1}{2^\ell(\ell!)}\frac{\partial^{\ell-1}}{\partial x^{\ell-1}}2\ell x^{2\ell-1} + \cdots \\
&= \frac{1}{2^\ell(\ell!)}\frac{\partial^{\ell-2}}{\partial x^{\ell-2}}2\ell(2\ell-1)x^{2\ell-2} + \cdots \\
&= \frac{1}{2^\ell(\ell!)}\frac{2\ell(2\ell-1)(\ell+1)\ell x^\ell}{(\ell!)} + \cdots \\
&= \frac{(2\ell)!}{2^\ell(\ell!)^2}x^\ell + \cdots
\end{aligned}$$

Similarly, for j:

$$\begin{aligned}
j_\ell(x)|_{x\to 0} &= (-1)^\ell x^\ell \left(\frac{1}{x}\frac{\partial}{\partial x}\right)^\ell \frac{\sin x}{x} \\
&= (-1)^\ell x^\ell \left(\frac{1}{x}\right)^\ell \frac{1}{x}\frac{1}{x}\frac{(-1)^\ell x^{2\ell+1}}{(2\ell+1)!} \\
&= \frac{x^2}{(2\ell+1)}\left(\frac{1}{x}\frac{\partial}{\partial x}\right)^\ell x^{2\ell} \\
&= \left(\frac{1}{x}\frac{\partial}{\partial x}\right)^{\ell-1} 2\ell x^{2\ell-2} \\
&= \left(\frac{1}{x}\frac{\partial}{\partial x}\right)^{\ell-2} 2\ell(2\ell-2)x^{2\ell-4} \\
&= \frac{x^2 2\ell(2\ell-2)\ldots 2}{(2\ell+1)!} \\
&= x^\ell \frac{2^\ell \ell!}{(2\ell+1)!}
\end{aligned}$$

So, in total, we can write the expansions of each side as

$$\begin{aligned}
\sum_{\ell=0}^{\infty}\frac{i^\ell}{\ell!}k^\ell(r\cos\theta)^\ell &= \sum_{\ell=0}^{\infty} A_\ell \frac{2^\ell\ell!}{(2\ell+1)!}(kr)^\ell\frac{(2\ell)!}{2^\ell(\ell!)^2}(\cos\theta)^\ell \\
\frac{i^\ell}{\ell!} &= \frac{A_\ell}{\ell!}\frac{1}{2\ell+1} \\
A_\ell &= i^\ell(2\ell+1)
\end{aligned}$$

And thus,

$$e^{ikz} = \sum_{\ell=0}^{\infty} i^\ell(2\ell+1)j_\ell(kr)P_\ell(\cos\theta)$$

and

$$\psi_{ii}(\mathbf{r}) = \sum_{\ell=0}^{\infty} i^{\ell} \left[j_{\ell}(kr) + ika_{\ell} h_{\ell}^{(1)}(kr) \right] P_{\ell}(\cos\theta)$$

3.4.3 Hard Sphere Scattering

The potential for thi sphere will be similar to an inifite well, that is,

$$V(r) = \begin{cases} \infty, & r \leq R \\ 0, & r > R \end{cases}$$

The paricle can't move past the infinite wall, so $\psi_{ii}(r = R) = 0$. The wave function in th eintermediate region is bounded by this boundary condition:

$$j_{\ell}(kR) + ika_{\ell} h_{\ell}^{(1)}(kR) = 0$$
$$a_{\ell} = \frac{i}{k} \frac{j_{\ell}(kR)}{h^{(1)}(kR)}$$

Where the total cross section is

$$4\pi \sum_{\ell=0}^{\infty} |a_{\ell}|^2 (2\ell + 1)$$

On the low energy limit (where $kR \ll 1$), we can find a useful equation of the total cross section. On this limit,

$$\begin{aligned} h^{(1)}(x \to 0) &= i(-1)^{\ell} x^{\ell} \left(\frac{1}{x} \frac{\partial}{\partial x} \right)^{\ell} \frac{e^{ix}}{x} \\ &\quad + i(-1)^{\ell} e^{ix} x^{\ell} \left(\frac{1}{x} \frac{\partial}{\partial x} \right)^{\ell} \frac{1}{x} \\ &= i(-1)^{\ell} e^{ix} x^{\ell} \left(\frac{1}{x} \frac{\partial}{\partial x} \right)^{\ell-1} \frac{1}{x^3}(-1) \\ &= i(-1)^{\ell} e^{ix} x^{\ell} \left(\frac{1}{x} \frac{\partial}{\partial x} \right)^{\ell-2} \frac{1}{x^5}(-1)(-3) \\ &= (-1)^{\ell} e^{ix} x^{\ell} (-1)^{\ell} \frac{(2\ell - 1)^{2\ell}}{2^{\ell} \ell! x^{2\ell+1}} \\ &= ie^{ix} \frac{(2\ell)!}{2^{\ell} \ell!} \frac{1}{x^{\ell+1}} \end{aligned}$$

Thus, we can write the total cross section as

$$\begin{aligned} \sigma &= 4\pi k^{-2} \sum_{\ell=1}^{\infty} (2\ell + 1) \left| \frac{(kR)^{\ell} 2^{\ell} \ell!}{(2\ell + 1)!} \frac{2^{\ell}(\ell!)}{(2\ell)!} (kR)^{\ell+1} \right|^2 \\ &= 4\pi k^{-2} \sum_{\ell=0}^{\infty} \frac{(2^{\ell} \ell!)^4}{(2\ell + 1)(2\ell!)^4} (kR)^{4\ell+2} \end{aligned}$$

For the low energy approximation, we can keep only the leading ($\ell = 0$) term:

$$= 4\pi R^2 + \mathcal{O}\left((kR)^6\right)$$

3.5 Phase Shifts

3.5.1 Phase Shifts

We'll start by looking at a simple(r) one-dimensional example. Consider a one-dimensional plane wave incoming on an infinite wall at $x = 0$. Hitting the infinite wall, the plan wave will reflect, such that the complete wave function is given by

$$\psi(x) = e^{ikx} + Ae^{-ikx}$$

Where the first term represents the incoming, the second represents the outgoing, and $k = \frac{\sqrt{2mE}}{\hbar}$. We must have $\psi(x = 0) = 0$, which means that $A = -1$, so

$$\psi(x) = e^{ikx} - e^{-ikx}$$

Now, if instead, we have a nonzero potential just before the wall, such that $V(-a \leq x \leq 0) \neq 0$, the reflected wave function can differ from th initial by an overal phase. But, by th conservation of probability, we must still have

$$|\psi_{in}|^2 = |\psi_{out}|^2$$

So if we can write

$$\psi_{out} = Ae^{-ikx}$$

Then this means that $|A|^2 = 1$, and the only possible solution to this is

$$A = e^{2i\delta}$$

Where $2i\delta$ represents the phase shift (and the factor of 2 is just to stay consistent with the litrature). Thus, the reflected wave function is

$$\psi_{out} = e^{-ikx+2i\delta}$$

Therefore, the scattering is encoded in the phase.
We can extend this back into 3 dimensions. Because of the conservation of angular momentum, each partial wave scatters independently. For the incoming plane wave,

$$e^{ikz} = \sum_{\ell=0}^{\infty} i^\ell (2\ell + 1) j_\ell(kr) P_\ell(\cos\theta)$$

We can take the limit where $r \to \infty$, so that

$$j_\ell(x \to \infty) = \frac{1}{2x}\left[(-i)^{\ell+1}e^{ix} + i^{\ell+1}e^{-ix}\right]$$

And, by extension,

$$\begin{aligned} e^{ikz} &= \sum_{\ell=0}^{\infty} \frac{i^\ell}{2(kr)}(2\ell + 1)P_\ell(\cos\theta)\left[(-i)^{\ell+1}e^{ikr} + i^{\ell+1}e^{-ikr}\right] \\ &= \frac{1}{2kri}\sum_{\ell=0}^{\infty}(2\ell + 1)P_\ell(\cos\theta)\left[e^{ikr} - (-1)^\ell e^{-ikr}\right] \end{aligned}$$

Thus, for $V = 0$,

$$\psi = \frac{1}{2kri}\sum_{\ell=0}^{\infty}(2\ell+1)P_\ell(\cos\theta)\left[e^{ikr} - (-1)^\ell e^{-ikr}\right]$$

We can find δ_ℓ in terms of a_ℓ by matching this to a known expression with a_ℓ:

$$\psi = \frac{1}{2kri}\sum_{\ell=0}^{\infty}(2\ell+1)P_\ell(\cos\theta)\left[j_\ell(kr) + ia_\ell k h_\ell^{(1)}(kr)\right]$$

Where

$$h_\ell^{(1)}(kr)|_{r\to\infty} = (-i)^{\ell+1}\frac{e^{ikr}}{kr}$$

So that, taking $r \to \infty$ for ψ, we can find that

$$a_\ell = \frac{e^{i\delta_\ell \sin\delta_\ell}}{k}$$

The sccattering amplitude is

$$\begin{aligned} f(\theta) &= \sum_{\ell=0}^{\infty}(2\ell+1)a_\ell P_\ell(\cos\theta) \\ &= \frac{1}{k}\sum_{\ell=0}^{\infty}(2\ell+1)e^{i\delta_\ell}\sin\delta_\ell P_\ell(\cos\theta) \end{aligned}$$

And thus the total cross-section is

$$\sigma = \frac{4\pi}{k^2}\sum_{\ell=0}^{\infty}(2\ell+1)\sin^2\delta_\ell$$

We can compare the forward scattering amplitude (ie., where $\theta = 0$) to the total cross-section to establish a relation between them:

$$\begin{aligned} f(\theta=0) &= \frac{1}{k}\sum_{\ell=0}^{\infty}(2\ell+1)\sin\delta_\ell\left[\cos\delta_\ell + i\sin\delta_\ell\right] \\ \implies \mathrm{Im}[f(\theta=0)] &= \frac{k}{4\pi}\sigma \end{aligned}$$

This is called the optical theorem, and the phsical origin of theis equation is the conservation of probability for particles.

3.6 Scattering from a Delta Function Potential

Consider a scattering from a spherical delta function potential,

$$V(r) = V_0\delta(r-a)$$

at small velocities (that is, low energies). Find the differential and total cross-sections.

As we found for hard-sphere scattering, we can approximate low energy cross sections by the s wave contribution, ie.,

$$\begin{aligned}\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} &= |f_0(\theta)|^2 = \frac{1}{k^2}\sin^2\delta_0 \\ \sigma &= \frac{4\pi}{k^2}\sin^2\delta_0\end{aligned}$$

The only thing we have to do is find the phase shift δ_0. To do this, we're going to take the Schödinger equation, using the separation of variables for the solution such that $\psi(\mathbf{x}) = rU_\ell(r)Y_{\ell m}(\Omega)$, where $rU_\ell(r) = R(r)$. Thus,

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2} + \frac{\hbar^2}{2m}\ell(\ell+1) + V_0\delta(r-a)\right]U_\ell(r) = EU_\ell(r)$$

On the low-energy limit, where $\ell = 0$ (I think that's why we choose $\ell = 0$, at least),

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2} + V_0\delta(r-a)\right] = EU_0(r)$$

Our two boundary conditions are:

$$\begin{aligned} r \to 0 &: \qquad R_0(r)|_{r\to 0} = \text{Finite} \\ r \to \infty &: \qquad R(r)|_{r\to\infty} \to 0\end{aligned}$$

The first boundary condition means that

$$U(r \to 0) \to \infty$$

For the second boundary condition, we need some more space to work. For $r \neq a$, we have

$$\left(\frac{\partial^2}{\partial r^2} - k^2\right)U_0(r) = 0$$

Where

$$k^2 = \frac{2mE}{\hbar^2} > 0$$

Between 0 and a, the solution to this Schrödinger equation (which we'll write as $\overset{<}{U}_0(r)$) is

$$\begin{aligned}\overset{<}{U}_0(r) &= A\left(e^{ikr} - e^{-ikr}\right) \\ &= \tilde{A}\sin(kr)\end{aligned}$$

Similarly, the solution for $r > a$ is

$$\overset{>}{U}_0(r) = \tilde{B}\sin(kr + \delta_0)$$

We just need to sew these together at $r = a$. We need the function to be continuous at the boundary, so

$$\tilde{A}\sin(ka) = \tilde{B}\sin(ka + \delta_0)$$

We need a similar condition on the first derivative, which we'll find using the Schrödinger equation, integrating in the vicinity of $r = a$ (that is, between $a + \epsilon$ and $a - \epsilon$ at the limit $\epsilon \to 0$):

$$\int_{a-\epsilon}^{a+\epsilon} \mathrm{d}r \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2} + V_0\delta(r-a) \right] U_0(r) = E\int_{a-\epsilon}^{a+\epsilon} \mathrm{d}r U_0(r)$$
$$-\frac{\hbar^2}{2m}\left[\left(\overset{>}{U_0}(a)\right)' - \left(\overset{<}{U_0}(a)\right)' \right] + V_0 U_0(a) = 0$$

The U connected to the potential V_0 could really be either of the ones we found, since we have the condition that they must be the same at $r = a$, but we'll just arbitrarily pick one of them moving forward:

$$\left(\overset{>}{U_0}(a)\right)' - \left(\overset{<}{U_0}(a)\right)' = \frac{2mV_0}{\hbar^2}\overset{>}{U_0}(a)$$
$$\tilde{B}k\cos(ka+\delta_0) - \tilde{A}k\cos(ka) = \frac{2mV_0}{\hbar^2}\tilde{B}\sin(ka+\delta_0)$$
$$\tilde{B}\left[k\cos(ka+\delta_0) - \frac{2mV_0}{\hbar^2}\sin(ka+\delta_0) \right] = \tilde{A}k\cos(ka)$$

If we divide this by our other boundary condition, we find

$$k\cot(ka+\delta_0) - \frac{2mV_0}{\hbar^2} = k\cot(ka)$$

So, as anticipated, when $V_0 = 0$, $\delta_0 = 0$ (or multiples of 2π, but 0 is the useful one). When $V_0 \neq 0$, however, we need to use our low-energy approximation ($ka \ll 1$):

$$k\cot(\delta_0) - \frac{2mV_0}{\hbar^2} \approx \frac{k}{ka} = \frac{1}{a}$$

So that

$$\cot(\delta_0) = \frac{1}{ka} + \frac{2mV_0}{\hbar^2 k}$$

So using our low-energy approximations for the differential cross-section,

$$\begin{aligned}
\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} &= \frac{1}{k^2}\sin^2\delta_0 \\
&= \frac{1}{k^2}\frac{1}{1+\cot^2\delta_0} \\
&= \frac{1}{k^2}\frac{1}{1+\frac{1}{(ka)^2}\left[1+\frac{2mV_0a}{\hbar^2}\right]^2} \\
&= \frac{a^2}{(ka)^2+\frac{2mV_0a}{\hbar^2}+1} \\
\sigma &= \frac{4\pi a^2}{(ka)^2+\frac{2mV_0a}{\hbar^2}+1}
\end{aligned}$$

3.7 Scattering of Identical Particles

In the case of 1-dimensional identical and indistnguishable, recall that we cannot write the total wave function of the system as the multiplicative sum of the individual particles, that is,

$$\psi(x_1, \ldots, x_N) \neq \Pi_{i=1}^{N} \psi(x_i)$$

And recall that we've already seen the [switching] operator, where

$$P_{ij}\psi(x_1, \ldots, x_i, \ldots, x_j, \ldots, x_N) = \psi(x_1, \ldots, x_j, \ldots, x_i, \ldots, x_N) =$$

Where squaring the operator gets us back to the original wave function. Thus, $P_{ij}^2 = 1 \implies P_{ij} = \pm 1$. One (+/-) is for bosons, one is for fermions.
Recall that the wave functions for bosons and fermions are given by:

$$\begin{aligned} \text{Bosons:} \quad & \psi(x_1, x_2) = \psi_{n_1}(x_1)\psi_{n_2}(x_2) + \psi_{n_1}(x_2)\psi_{n_2}(x_1) \\ \text{Fermions:} \quad & \psi(x_1, x_2) = \psi_{n_1}(x_1)\psi_{n_2}(x_2) - \psi_{n_1}(x_2)\psi_{n_2}(x_1) \end{aligned}$$

Where bosons have integer spin and a symmetric wf, and fermions have half-integer spin and antisymmetric wf.

3.7.1 Scattering of Spin-0 Bosons

The initial-state wave function for two identical particles approaching each other at the same speeds on the z axis is

$$\psi_{in} = e^{ikz} + e^{-ikz}$$

After scattering/collision, they will be sent in different directions—one above axis by the angle θ and one below at the angle $\pi - \theta$. We can't necessarily distinguish which one goes in which direction though, if we put a detector, say, above the axis and wait for something to hit it.
The outgoing wave must be symmetric:

$$\psi_{out} = \frac{e^{ikr}}{r}[f(\theta) + f(\pi - \theta)]$$

The differential cross-section is thus

$$\begin{aligned} \frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} &= |f_{sym}|^2 \\ &= |f(\theta) + f(\pi - \theta)|^2 \\ &= |f(\theta)|^2 + |f(\pi - \theta)|^2 + 2\mathrm{Re}[f^*(\theta)f(\pi - \theta)] \end{aligned}$$

This differs from the calssical model by the final term, the interference term.

3.7.2 Scattering of Spin-1/2 Fermions

The wave function will be written in terms of its spatial and spin coordinates, ie.,

$$\psi(x_1, s_1; x_2, s_2)$$

Where we have

$$|\mathbf{s}| = |\mathbf{s}_1 + \mathbf{s}_2| = \begin{cases} 1 \\ 0 \end{cases}$$

$$|\mathbf{s}_1| = |\mathbf{s}_2| = \frac{\hbar}{2}$$

In the case that the total spin is 0, $|\mathbf{s}| = 0$,

$$\psi(x_1, s_1; x_2, s_2) = X_a(s_1, s_2)\psi_s(x_1, x_2)$$

Such that spin wave function is antisymmetric, but the spatial one is symmetric. This is a singlet state, as it's only singly-degenerate (or not dgenerate? Whatever the terminology is):

$$X_a(s_1, s_@) = \frac{1}{\sqrt{2}}\left(\left|\frac{\hbar}{2}\right\rangle_1 \left|-\frac{\hbar}{2}\right\rangle_2 - \left|-\frac{\hbar}{2}\right\rangle_1 \left|\frac{\hbar}{2}\right\rangle_2\right)$$

In th case of the total spin being 1, the position is antisymmetric, but the spin wave function is not, and we have a triplet state, as s_z can now be any of 1, 0, or -1.

$$X_s(s_1, s_2) = \begin{cases} |\hbar/2\rangle_1 |\hbar/2\rangle_2 \\ \frac{1}{\sqrt{2}}\left(|\hbar/2\rangle_1 |-\hbar/2\rangle_2 + |-\hbar/2\rangle_1 |\hbar/2\rangle_2\right) \\ |-\hbar/2\rangle_1 |-\hbar/2\rangle_2 \end{cases}$$

Thus, for a singlet state, the differential cross-section is that for the symmetric wave function, and for the triplet state, for the antisymmetric. If the incident particle is unpolarized, all states are equally likely, so

$$\begin{aligned} \frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} &= \frac{3}{4}\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\bigg|_a + \frac{1}{4}\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\bigg|_s \\ &= |f(\theta)|^2 + |f(\pi - \theta)|^2 - \mathrm{Re}[f^*(\theta)f(\pi - \theta)] \end{aligned}$$

4 Quasiclassical (WKB) Approximation

The WKB approximation is an approximation technique to find solutions to the Schrödinger equation when the quantum system is nearly classical (ie. when quantum numbers are very very large). In other words, it's treating systems with slowly verying potentials. We take the point-like limit, when the de Broglie wavelength $\lambda \to 0$. This approximation will work for us so long as the real λ is much, much smaller than the size of the region we're looking at along the whole region. This means that in the case of, say, a positive quadratic potential, this won't work at the turning points.
In the case where the potential is flat, we have

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

Where E is the energy of the particle and V is the energy of the potential. In the case where $\hbar \to 0$, $k \to \infty$. The solution to this Schrödinger equation is

$$\psi = e^{ikx} = e^{ix\sqrt{2m(E-V_0)}/\hbar}$$

But what if the potential is not flat? We will write the solution instead in the still-justifiable form

$$\psi = e^{iS(x)/\hbar}$$

Where $S(x)$ is some complex function. To approximate this classically, we want to find the expansion of $S(x)$:

$$S(x) = S_0(x) + \hbar S_1(x) + \hbar^2 S_2(x) + \cdots$$

This converges very slowly. The calculation of more than just these first few leading terms is incredible complicated and we won't really go into it, even though it only converges slowly. To try to do this, let's start with the Schrödinger equation with a one-dimensional potential, substituting our wave function:

$$\begin{aligned}
-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) + V(x)\psi(x) &= E\psi(x) \\
-\frac{\hbar^2}{2m}\frac{\partial}{\partial x}\left[\frac{i}{\hbar}S' e^{iS/\hbar}\right] &= E\psi(x) \\
-\frac{\hbar^2}{2m}\left[\frac{i}{\hbar}S'' e^{iS/\hbar} + \left(\frac{i}{\hbar}\right)^2 (S')^2 e^{iS/\hbar}\right] &= E\psi(x) \\
\frac{i}{\hbar}S' + \left(\frac{i}{\hbar}\right)^2 (S')^2 + \frac{2m}{\hbar^2}(E - V(x)) &= 0 \\
(S')^2 - 2m(E - V(x)) - i\hbar S'' &= 0
\end{aligned}$$

Substituting the first few terms of th approximation into this, we get

$$\begin{aligned}
(S_0' + \hbar S_1')^2 - 2m(E - V(x)) - i\hbar(S_0'' + \hbar S_1'') &\approx 0 \\
(S_0')^2 + 2\hbar S_0' S_1' - 2m(E - V(x)) - i\hbar S_0'' &\approx 0
\end{aligned}$$

We can separate and align these by powers of $\hbar$:

$$\begin{aligned}
\hbar^0: \quad (S_0')^2 &= 2m(E-V(x)) \\
&= p^2(x) \\
S_0' &= \pm p(x) \\
S_0(x) &= \pm \int^x \mathrm{d}x' p(x') \\
\hbar^1: \quad 2S_0'S_1' &= iS_0'' \\
S_1' &= \frac{i}{2}\frac{S_0''}{S_0'} \\
S_1 &= \frac{i}{2}\ln(S_0') \\
S_1 &= \frac{i}{2}\ln(p(x))
\end{aligned}$$

There is a missing constant in both of these that we will absorb into the overall multiplier.
Together, the wave function must then be

$$\begin{aligned}
\psi(x) &\approx e^{i(S_0+\hbar S_1)/\hbar} \\
&= Ce^{\frac{i}{\hbar}\left(\pm\int^x \mathrm{d}x' p(x') + \hbar\frac{i}{2}\ln(p(x))\right)} \\
&= \frac{C}{\sqrt{p(x)}} e^{\pm\frac{i}{\hbar}\int^x \mathrm{d}x' p(x')}
\end{aligned}$$

This gives us a linear combination of solutions:

$$\psi(x) = \frac{A}{\sqrt{p(x)}} e^{\frac{i}{\hbar}\int^x \mathrm{d}x' p(x')} + \frac{B}{\sqrt{p(x)}} e^{-\frac{i}{\hbar}\int^x \mathrm{d}x' p(x')}$$

Where

$$|p(x)| = \sqrt{2m(V-E)}$$

Note that this is only in the classically-allowed region. In the classically-forbidden region (ie. $E < V$), the signs in the exponentials swap, and the integrand must take an absolute value.

4.1 The Applicability of the WKB Approximation

We said before that this is applicable when p is not small. This means that, based on the solutions we found, the approximations are valid provided

$$\left|(S')^2\right| \gg \hbar\,|S''|$$

Since $S' = \pm p$ and $p/\hbar = k = 2\pi/\lambda = 1/\bar{\lambda}$, we can write this instead as

$$\begin{aligned}
\left|p^2\right| &\gg \hbar\,|p'| \\
1 &\gg \left|\frac{p'}{p^2}\right| \\
1 &\gg \left|\frac{\partial}{\partial x}\frac{1}{p}\right| \\
1 &\gg \left|\frac{\mathrm{d}\bar{\lambda}}{\mathrm{d}x}\right|
\end{aligned}$$

That is, the wavelength of the particle can change infinitesimale on the distance scale of order of its size.
We can write this condition in terms of p to see what exactly we mean by "small p." If

$$\begin{aligned} p' &= -\frac{mF}{p} \\ p &= \sqrt{2m(E-V)} \\ \implies p' &= -\frac{1}{2}\frac{2m(-V')}{\sqrt{2m(E-V)}} = -\frac{mF}{p} \end{aligned}$$

Then we can write this as

$$\begin{aligned} 1 &\gg \hbar m\frac{|F|}{p^3} \\ p &\gg \sqrt[3]{\hbar m\,|F|} \end{aligned}$$

We can also make sure the WKB is applicable by using very large quantum numbers, so that we have a nearly-continuous spectrum of energy levels.

4.2 Connection Formulas

Consider a potential well with non-rigid walls. We have two turning points, x_1 and x_2, beyond which is the classically-forbidden region, and between which is the classically allowed region. Our aim is to find the energy levels in this well. Along the way, we'll also find how to determine the wave function at the turning points. Note that the WKB applies everywhere in this region except the turning points.

In region I ($x < x_1$):

$$\psi_I(x) = \frac{A}{\sqrt{|p(x)|}} e^{-\frac{1}{\hbar}\int_x^{x_1} \mathrm{d}x' |p(x')|}$$

In region II ($x_1 < x < x_2$):

$$\psi_{II}(x) = \frac{B}{\sqrt{|p(x)|}} e^{\frac{i}{\hbar}\int_x^{x_2} \mathrm{d}x' |p(x')|} + \frac{C}{\sqrt{|p(x)|}} e^{-\frac{i}{\hbar}\int_x^{x_2} \mathrm{d}x' |p(x')|}$$

In region III ($x > x_2$):

$$\psi_{III}(x) = \frac{D}{\sqrt{|p(x)|}} e^{-\frac{1}{\hbar}\int_{x_2}^{x} \mathrm{d}x' |p(x')|}$$

We still need to determine the unknown coefficints. To do this, we have to connect the 3 regions at the turning points. The problem is, the approximation fails right at the turning points, so we'd have to solve the Schrödinger equation exactly, at least at first glance. We'll try to avoid that as much as possible. Instead, we're going to look at another way of doing this. Using x_2 as the first turning point to look at, we can deform x in the complex plane in order to avoid

reaching x_2 exactly. We'll deform it as a circle. We can parameterize x in the complex plane as

$$x = x_2 + \rho e^{i\theta}$$

So we start and end the circular deformation of x at a distance ρ from x_2. Approaching the region of the turning point, we can use the approximation

$$V(x) = V(x_2) + (x - x_2)V'(X_2) + \cdots = E - (x - x_2)F_2 + \cdots$$

So,

$$E - V(x) \approx -(x - x_2)F_2$$

So the wave function in region III in the vicinity of the turning point is

$$\psi_{III}(x)|_{x\to x_2} = \frac{D}{\sqrt[4]{2m\left|F_2\right|(x - x_2)}} e^{-\frac{1}{\hbar}\int_{x2}^{x_2+\rho e^{i\theta}} \mathrm{d}x' |p(x')|}$$

Taking a look at just the exponential integral,

$$\begin{aligned} I(\rho,\theta) &= \int_{x_2}^{x_2+\rho e^{i\theta}} \mathrm{d}x' \, |p(x')| \\ &= \int_{x_2}^{x_2+\rho e^{i\theta}} \mathrm{d}x' \sqrt{2m\left|F_2\right|(x - x_2)} \\ &= \sqrt{2m\left|F_2\right|}\frac{2}{3}(x - x_2)^{3/2}\Big|_x^2 \, e^{x_2+\rho e^{i\theta}} \\ &= \sqrt{2m\left|F_2\right|}\frac{2}{3}\left(\rho e^{i\theta}\right)^{3/2} \end{aligned}$$

The two endpoints of this are at $\theta = 0$ and $\theta = \pi$:

$$\begin{aligned} I(\rho,0) &= \sqrt{2m\left|F_2\right|}\frac{2}{3}\rho^{3/2} \\ I(\rho,\pi) &= \sqrt{2m\left|F_2\right|}\frac{2}{3}\rho^{3/2}e^{3i\pi/2} \\ &= -\sqrt{2m\left|F_2\right|}\frac{2i}{3}\rho^{3/2} \end{aligned}$$

$\theta = \pi$ is in region II, so we can stitch it together with those. For completeness, we'll write

$$\psi_{III}(x)|_{x\to\hat{\mathbf{x}}_2,\theta\to\pi} = \frac{De^{-i\pi/4}}{\sqrt{p(x)}} e^{\frac{i}{\hbar}\int_x^{x_2} \mathrm{d}x' p(x')}$$

This must be equal to the solution in region 2 in the vicinity of the turning point. When going through the turning point, the asymptotic behavior of the two region II solutions are vastly different, and it turns out that one becomes very large and the other very small, so that we can ignore one of them moving forward. If we ignore the C term, then

$$B = De^{-i\pi/4}$$

But what if we had gone under the axis instead of over? Well, then the opposite one would be true, and

$$C = De^{i\pi/4}$$

Thus, we find

$$\begin{aligned}\psi_I I(x) &= \frac{2D}{\sqrt{p(x)}}\left[e^{-i\pi/4}e^{i/\hbar\int_x^{x_2}\mathrm{d}x' p(x')}e^{i\pi/4}e^{i/\hbar\int_x^{x_2}\mathrm{d}x' p(x')}\right] \\ &= \frac{2D}{\sqrt{p(x)}}\cos(\frac{1}{\hbar}\int_x^{x_2}\mathrm{d}x' p(x') - \frac{\pi}{4}\end{aligned}$$

Had we done this around the turning point x_1 instead, we would have found a very similar solution:

$$\psi_I I(x) = \frac{2A}{\sqrt{p(x)}}\cos(\frac{1}{\hbar}\int_{x_1}^{x}\mathrm{d}x' p(x') - \frac{\pi}{4}$$

4.3 The Bohr-Sommerfeld Quantization Condition

Since th two solutions in the allowed region have to coincide, the sum of the phases must be a multiple of *pi*:

$$\begin{aligned}\frac{1}{\hbar}\left(\int_x^{x_2}+\int_{x_1}^{x}\right)\mathrm{d}x' p(x') - \frac{\pi}{2} &= n\pi \\ \frac{1}{\hbar}\int_{x_1}^{x_2}\mathrm{d}x' p(x) &= \pi(n+1/2)\end{aligned}$$

And we also find that

$$A = (-1)^n D$$

We've ignored some terms on the order of $\hbar$.

4.4 Energy Levels of the Harmonic Oscillator

The one-dimensional harmonic oscillator has the Hamiltonian

$$H = \frac{p^2}{2m} + \frac{m\omega^2}{2}x^2$$

So the momentum is

$$p(x) = \sqrt{2m - m^2\omega^2 x^2}$$

The turning points (ie. where $p = 0$) are where $E = V$, or where

$$E = \frac{m\omega^2}{2}x^2$$

So, the two turning points are

$$\begin{aligned}x_+ &= \sqrt{\frac{2E}{m\omega^2}} \\ x_- &= -\sqrt{\frac{2E}{m\omega^2}}\end{aligned}$$

So using the Bohr-Sommerfeld quantization condition.

$$\frac{1}{\hbar}\int_{x_-}^{x_+} \mathrm{d}x' \sqrt{2m(E - m\omega^2 x^2/2)} = \pi(n + 1/2)$$
$$m\omega\frac{1}{\hbar}\int_{x_-}^{x_+} \mathrm{d}x' \sqrt{2E/(m\omega^2) - x'^2} = \pi(n + 1/2)$$
$$m\omega\frac{1}{\hbar}\int_{x_-}^{x_+} \mathrm{d}x' \sqrt{x_+^2 - x'^2} = \pi(n + 1/2)$$

If we define $x' = x + y$, then

$$m\omega\frac{1}{\hbar}\int_{x_-}^{x_+} \mathrm{d}x' \sqrt{1 - y^2} = \pi(n + 1/2)$$

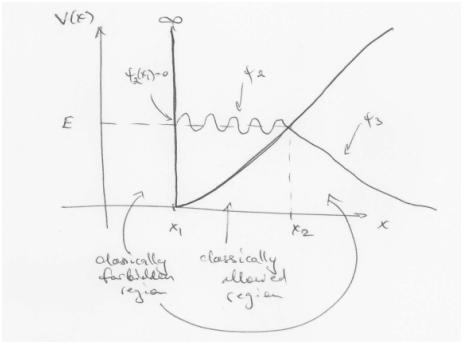
I won't go through the exact derivation, but it's simple to prove that the integral is simply $\pi/2$. Skipping some basic agebra simplification,

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

In this case, it reproduces the exact energy levels. This is an exception, but it is a pretty cool exception.

4.5 Bound States in the Potential with One Rigid Wall

Consider a particle in the potential $V(x)$ with a single infinite wall at $x = x_1$. To findthe energylevels in it (ie. the quantization condition), we have to find the expansion for the WKB wave function in the domain $x_1 < x < x_2$, where x_2 is the turning point, by going through the turning points on the left and the right, as below:



We found before that generaically, in the range $x < x_2$,

$$\psi_{III}(x) = \frac{D}{\sqrt{|p|}} e^{-\frac{1}{\hbar}\int_{x_2}^{x} \mathrm{d}x|p(x')|}$$

And in the range $x_1 < x < x_2$,

$$\psi_{II}(x) = \frac{2C}{\sqrt{p(x)}} \cos\left(\frac{1}{\hbar}\int_x^{x_2} \mathrm{d}x' p(x') - \frac{\pi}{4}\right)$$
$$\psi_{II}(x) = \frac{2C}{\sqrt{p(x)}} \cos\left(\frac{1}{\hbar}\int_{x_1}^{x} \mathrm{d}x' p(x') + \alpha\right)$$

The only difference now is the boundary condition at x_1, where the solution for $x < x_1$, $\psi_I(x) = 0$ since the wall is infinitely large. We can match either of the above solutions at $x = x_1$, but we'll choose the one that already involves x_1:

$$0 = \frac{2C}{\sqrt{|p(x)|}} \cos(\alpha)$$
$$\alpha = -\frac{\pi}{2} + m\pi$$

where m can be positive or negative odd integers. If we add the two psi_{II} wave functions together to try to find the full wave function in the classically-allowed region, we find that

$$\frac{1}{\hbar}\int_{x_1}^{x_2} \mathrm{d}x' p(x') = \pi\left(n + \frac{3}{4}\right)$$

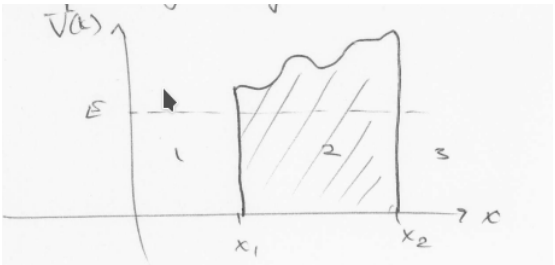
4.6 Bound States in the Potential with Two Rigid Walls

In the case that we have two rigid walls, we the solution is pretty simple. Now, in the classically-forbidden region, we have $\psi_1 = \psi_3 = 0$, and in the classically-allowed region, we can have an arbitrarily-complex potential. Matching at $x = x_2$ and $x = x_1$, we find that the phase shift for both is $-\frac{\pi}{2}$, so we can write

$$\frac{1}{\hbar}\int_{x_1}^{x_2} \mathrm{d}x' p(x') = \pi(n+1)$$

4.7 Tunneling through a Potential Barrier

Nowe we'll be looking at the opposite of a potential well. COnsider a potential barrier with square walls and a bumpy top. The limitation of the current consideration of square wlls is for the sake of simplification, so that we can have clearly-defined classically allowed and forbidden regions.



In the region $x < x_1$, we have both an incoming and outgoing wave. Remembering that we can define $k = \sqrt{2mE}$, we can write the wave function in region I as

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

In the region $x > x_2$, we similarly have a free wave function, but this time only a transmitted wave, with the wave function

$$\psi_{III}(x) = F^{ikx}$$

Finally, we need to look in the region $x_1 < x < x_2$. In the WKB approximation,

$$\psi_{II}(x) = \frac{C}{\sqrt{|p(x)|}} e^{-\frac{1}{\hbar}\int_{x_1}^{x} \mathrm{d}x' |p(x)|} + \frac{D}{\sqrt{|p(x)|}} e^{\frac{1}{\hbar}\int_{x_1}^{x} \mathrm{d}x' |p(x)|}$$

When the barrier becomes infinitly wide ($x \to \infty$), the second of these grows exponentially, and we need a normalizable wave function, so we can call this unphysical and say $D = 0$, so what we're left with is

$$\psi_{II}(x) = \frac{C}{\sqrt{|p(x)|}} e^{-\frac{1}{\hbar}\int_{x_1}^{x} \mathrm{d}x' |p(x)|}$$

We can write the transmission/tunneling probability as

$$T = \frac{|F|^2}{|A|^2}$$

Our goal is to find F in terms of A by relating them through C. We can sew the solutions at x_1 and x_2. We're going to ignore the pre-factors a little bit to make our lives a little easier. So we'll look just at the leading terms. Matching the wave functions and their derivatives at $x = x_1$,

$$\begin{aligned} Ae^{ikx_1} + Be^{-ikx_1} &= C \\ ikAe^{ikx_1} - ikBe^{-ikx} &= aC \\ Ae^{ikx_1} - Be^{-ikx_1} &= \tilde{a}C \end{aligned}$$

If we add this third line to the first line, we find

$$\begin{aligned} \left|2Ae^{ikx_1}\right| &= (1 + \tilde{a})C \\ |A| &\propto |C| \end{aligned}$$

Now, matching at x_2,

$$\begin{aligned} Ce^{-\frac{1}{\hbar}\int_{x_1}^{x_2} \mathrm{d}x' \left|p(x')\right|} &= \left|Fe^{ikx_2}\right| \\ |C|\, e^{-\frac{1}{\hbar}\int_{x_1}^{x_2} \mathrm{d}x' \left|p(x')\right|} &= |F| \end{aligned}$$

Therefore, the leading WKB result for the transmission probability is

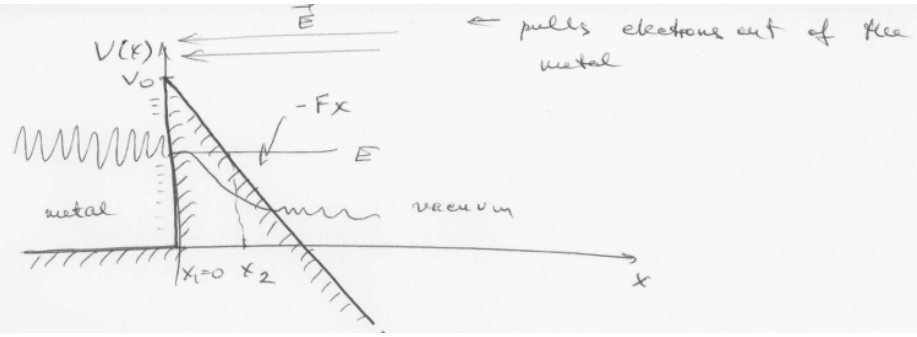
$$\begin{aligned} T &\propto e^{-2\gamma} \\ \gamma &= \frac{1}{\hbar}\int_{x_1}^{x_2} \mathrm{d}x' \, |p(x')| \end{aligned}$$

4.8 Cold Emission of Electrons from Metal

Consider a chunk of metal with free-to-move electrons inside of it. The potential for the electrons should be a step function, such that the electrons are free inside, but face some barrier (at the size of the work function V_0) to get out:

$$V(x) = \begin{cases} V_0, & x > 0 \\ 0, & x < 0 \end{cases}$$

If we turn on an electric field $\mathcal{E}$ outside the metal, a force will be exerted on the electrons with magnitude $F = e\mathcal{E}$ (assuming there's no electric field inside the metal). For $x > 0$, we now have $V(x) = V_0 - e\mathcal{E}x$. The barrier now looks like this:



The electrons are now able to tunnel out through the barrier. $x_1 = 0$, and we can find x_2 by discovering where the energy of the electron is equal to the value of the potentialm or $x_2 = \frac{V_0 - E}{e\mathcal{E}}$. Now, we just need to calculate γ:

$$\begin{aligned} \gamma &= \frac{1}{\hbar}\int_0^{\frac{V_0-E}{e\mathcal{E}}} \mathrm{d}x' \sqrt{2m(V_0 - E - e\mathcal{E}x)} \\ &= \frac{\sqrt{2me\mathcal{E}}}{\hbar}\int_0^{\frac{V_0-E}{e\mathcal{E}}} \mathrm{d}x' \sqrt{\frac{V_0 - E}{e\mathcal{E}} - x} \\ &= \frac{\sqrt{2me\mathcal{E}}}{\hbar}\frac{2}{3}\left(\frac{V_0 - E}{e\mathcal{E}} - x\right)\Bigg|_0^{\frac{V_0-E}{e\mathcal{E}}} \\ &= \frac{2}{3}\frac{\sqrt{2m}}{\hbar e\mathcal{E}}(V_0 - E)^{3/2} \end{aligned}$$

So that the probability of tunneling out of the metal is

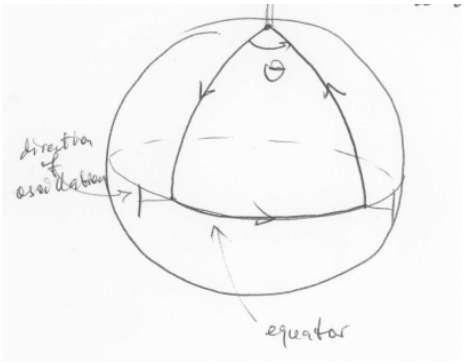
$$T \propto e^{-\frac{4}{3}\frac{\sqrt{2m}}{\hbar e\mathcal{E}}(V_0-E)^{3/2}}$$

This is used in scanning tunneling microscopes to construct accureate maps of the suface under investigation. This is the end of what will be covered on the exams.

5 Berry's Phase

5.1 Nonholonomic Process

Onsider a pendulum mounted on a ball and moved around a closed path. Like, let's say you and some friends on another continent asked Santa for a pendulum for Christmas.



It's hard to see from the picture, but if the direction of the pendulum is originally in the direction of the first path, when we return to the starting point, it will be in the opposite direction—that is, in the direction of the third path. More generally, it will have changed such that the planes of oscillation are separated by some angle θ. This is an example of a nonholonomic process. Note that this only works for a slow path. That means that we can talk about this in the same way we talked about things in the Adiabatic approximation.
The angle θ is equal to the solid angle Ω subtended by the path. Recall that

$$\mathrm{d}\Omega = \mathrm{d}\phi \sin\vartheta \mathrm{d}\vartheta$$

For us,

$$\Omega = \int_0^\theta \mathrm{d}\vartheta \int_0^{\pi/2} \mathrm{d}\vartheta \sin\vartheta = \theta$$

This is a nice result becaue it doesn't depend on the shape of the path.

5.2 Geometric Phase

According to the Adiabatic theorem, a particle that starts in the n^{th} eigenstate of $\hat{H}(t)$ at $t = 0$ remains in it at $t > 0$:

$$\psi_n(t) = \psi_n(0) e^{-i\Theta_n(t) + i\gamma_n(t)} \psi_n(t)$$

With the dynamic phase being

$$\Theta_n(t) = \frac{1}{\hbar} int_0^t \mathrm{d}t' E_n(t')$$

And the geometric phase being

$$\gamma_n(t) = -\int_0^t \mathrm{d}t' \left\langle \psi_n(t') \middle| \dot{\psi}_n(t') \right\rangle$$

If the Hamiltonian is time-dependent, it has some factor in it $\mathbf{x}(t)$, such that $|\psi_n(t)\rangle = |\psi_n(\mathbf{x}(t))\rangle$, and therefore

$$\frac{\partial}{\partial t}|\psi_n(t)\rangle = \frac{\mathrm{d}\mathbf{x}}{\mathrm{d}t}\cdot\boldsymbol{\nabla}|\psi_n(\mathbf{x}(t))\rangle$$

So we can write the geometric phase as

$$\gamma_n(t) = \int_{\mathbf{x}(0)}^{\mathbf{x}(t)} \mathrm{d}\mathbf{x}\cdot\langle\psi_n|\boldsymbol{\nabla}\psi_n\rangle$$

We can often write this in terms of a constant, so that

$$\gamma_n(t) = \int_{\mathbf{x}(0)}^{\mathbf{x}(t)} \mathrm{d}\mathbf{x}\cdot\mathbf{A}(\mathbf{x})$$

If the Hamiltonian refers to the same form at $t = T$ as it did at $t = 0$, the geometric phase doesn't vanish (but I think it does any other time), and

$$\begin{aligned}\gamma_n(T) &= i\oint \mathrm{d}\mathbf{x}\cdot\langle\psi_n|\boldsymbol{\nabla}\psi_n\rangle \\ &= i\int_S \mathrm{d}\mathbf{S}\cdot[\boldsymbol{\nabla}\times\mathbf{A}]\end{aligned}$$

This looks a lot like a flux through a magnetic induction—it's not really, but we'll write it like it is

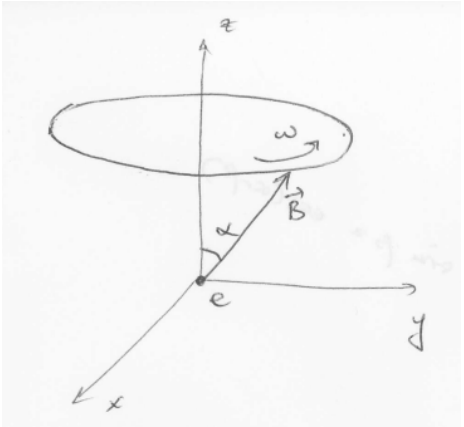
$$= i\int \mathrm{d}\mathbf{S}\cdot\mathbf{B}$$

Note that this depends only on the path taken, not on how fast it's transversed (ie. there's no explicit time-dependence). This gamma in this form is known as Berry's phase (where the $\mathbf{B}$ comes from). Note that to make this happen, we've had to define a "magnetic field" as

$$\mathbf{B} = \boldsymbol{\nabla}\times\langle\psi_n|\boldsymbol{\nabla}\psi_n\rangle$$

5.2.1 Electron in a Slowly Changing Magnetic Field

Let' discuss the problem of a magnetic moment $\boldsymbol{\mu}$ in a time-varying magnetic field $\mathbf{B}(t)$. We can define the field very basically below



Where there is two types of procession, with

$$\begin{aligned}\omega &= |\boldsymbol{\omega}| \\ \boldsymbol{\omega} &= \omega\hat{\mathbf{z}} \\ \boldsymbol{\omega}_B &= \omega_B \frac{\mathbf{B}}{|\mathbf{B}|}\end{aligned}$$

We can write $\mathbf{B}$, using the restriction that $|\mathbf{B}| = B_0$, as

$$\mathbf{B(t)} = B_0 \left(\sin\alpha\cos(\omega t), \sin\alpha\sin(\omega t), \cos\alpha\right)$$

The Hamiltonian is defined by

$$\begin{aligned}H &= \boldsymbol{\mu}\cdot\mathbf{B} \\ &= \frac{e}{m}\mathbf{B}\cdot\mathbf{S} \\ &= \frac{e\hbar}{2m}\boldsymbol{\sigma}\cdot\mathbf{B}(t)A \\ &= \frac{e\hbar B_0}{2m}\begin{pmatrix}\cos\alpha & \sin\alpha e^{-i\omega t} \\ \sin\alpha e^{i\omega t} & -\cos\alpha\end{pmatrix}\end{aligned}$$

In order to write this whole thing as a linear algebra problem, we'll have to define

$$\psi = \begin{pmatrix}a \\ b\end{pmatrix}$$

So the Schrödinger equation is

$$\frac{\hbar}{2}\frac{eB_0}{m}\begin{pmatrix}\cos\alpha & \sin\alpha e^{-i\omega t} \\ \sin\alpha e^{i\omega t} & -\cos\alpha\end{pmatrix}\begin{pmatrix}a \\ b\end{pmatrix} = E\begin{pmatrix}a \\ b\end{pmatrix}$$

We can diagonalize the matrix here, calling it $M = UDU^\dagger$, where D is a diagonal matrix with elements corresponding to M's eigenvalues, which we'll call d_1 and d_2. We know that $\det(M) = -1$, so

$$\det(UDU^\dagger) = \det(D) = d_1 d_2 = -1$$

Which gives us the solutions

$$\begin{aligned}E &= \pm\frac{\hbar}{2}\frac{eB_0}{m} \\ &= \frac{\hbar\omega_B}{2} \\ \omega_B &= \frac{eB_0}{2}\end{aligned}$$

Now, we need to solve the matrix equation

$$\begin{pmatrix}\cos\alpha & \sin\alpha e^{-i\omega t} \\ \sin\alpha e^{i\omega t} & -\cos\alpha\end{pmatrix}\begin{pmatrix}a \\ b\end{pmatrix} = \begin{pmatrix}a \\ b\end{pmatrix}$$

This is not super difficult and we'll skip the full derivation to just get the answers (note that there's 2, one for each of the eigenvalues):

$$\psi_+ = \begin{pmatrix}a_+ \\ b_+\end{pmatrix} = \begin{pmatrix}\cos\frac{\alpha}{2} \\ \sin\frac{\alpha}{2}\ e^{i\omega t}\end{pmatrix}\ \psi_+ = \begin{pmatrix}a_- \\ b_-\end{pmatrix} = \begin{pmatrix}\sin\frac{\alpha}{2}\ e^{-i\omega t} \\ -\cos\frac{\alpha}{2}\end{pmatrix}$$

We now need to find the solution to the time-dependent Schrödinger equation, where we'll write

$$\psi(t) = C_+(t)\psi_+(t) + C_-(t)\psi_-(t)$$

We can define a vector $\boldsymbol{\lambda} = \boldsymbol{\omega} - \boldsymbol{\omega}_B$, such that

$$|\boldsymbol{\lambda}| = \lambda = \sqrt{\omega^2 + \omega_B^2 - 2\omega\omega_B \cos\alpha}$$

When we can (skipping a few steps that are calculatable in, say, Mathematica or something) say that

$$C_+(t) = \left[\cos\frac{\lambda t}{2} - i\frac{\omega_B - \omega\cos\alpha}{\lambda}\sin\frac{\lambda t}{2}\right] e^{i\omega t/2}$$
$$C_-(t) = i\frac{\omega}{\lambda}\sin\alpha\sin\frac{\lambda t}{2}e^{i\omega t/2}$$

In the adiabatic assumption, $\omega \ll \omega_B$, meaning that

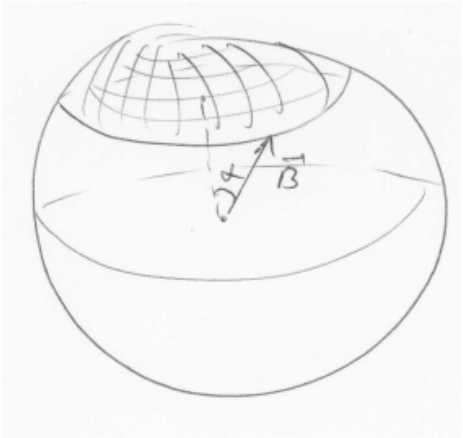
$$\begin{aligned}\lambda &\approx \omega_B - \omega\cos\alpha \\ C_- &\approx 0 \\ C_+ &\approx e^{-i\omega_B t/2}e^{-i\omega t(1-\cos\alpha)/2} \\ &= e^{i\Theta(t)}e^{\gamma(t)}\end{aligned}$$

Such that

$$\gamma(t) = -i\frac{\omega t}{2}(1-\cos\alpha)$$

For a complete processional cycle, as below, we can find that

$$\gamma(T) = -i\pi(1-\cos\alpha)$$



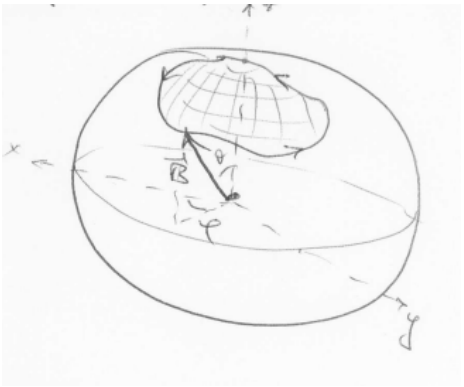
In doing this, more generally, we took the solid angle,

$$\Omega = \int_0^{2\pi} \mathrm{d}\phi \int_0^{\alpha} \mathrm{d}\theta \sin\theta = 2\pi(1-\cos\theta)$$

So it is equally accurate to write

$$\gamma_+(T) = \frac{1}{2}\Omega$$

But let's take it more generally—what if the procession wasn't solid like that, as in the path below:



We have a problem: we don't know the form of **B**. So how can we solve it? Well, let's use Berry's phase, because that'll tell us a lot. We know that generally,

$$\begin{aligned}\gamma(T) &= i \oint_C \mathrm{d}\mathbf{x} \cdot \langle \psi_+ | \boldsymbol{\nabla} \psi_+ \rangle \\ &= i \int_S \mathrm{d}\mathbf{S} \left[\boldsymbol{\nabla} \times \mathbf{A} \right]\end{aligned}$$

We need to find **A**, considering α as the generic polar angle θ, and ωt as our azimuthal angle ϕ. We know **A** from our definition, which we'll mildly re-write as

$$\mathbf{A} = \psi_+^\dagger \boldsymbol{\nabla} \psi_+$$

and ψ_+ from earlier in this section, and we know that in spherical coordinates,

$$\boldsymbol{\nabla} = \hat{\mathbf{r}} \frac{\partial}{\partial r} + \frac{1}{r} \hat{\boldsymbol{\theta}} \frac{\partial}{\partial \theta} + \frac{1}{r \sin\theta} \hat{\boldsymbol{\phi}} \frac{\partial}{\partial \phi}$$

The radius isn't changing, so that term will go to 0, and we can write **A**, skipping the simplification, as

$$\mathbf{A} = \hat{\boldsymbol{\phi}} \frac{i}{2r} \tan \frac{\theta}{2}$$

The curl of **A** is thus (again, I'm not going to do the simplification, this is super possible on my own with just some trig tricks)

$$\frac{i\hat{\mathbf{r}}}{2r^2}$$

So, going back to the very beginning, this means that we can write

$$\begin{aligned}\gamma(T) &= -\frac{1}{2} \int_\Omega \mathrm{d}\Omega \\ &= -\frac{1}{2} \Omega\end{aligned}$$

5.3 The Aharamov-Bohm Effect

The Berry's phase has measureable physical consequences. A typical setup to measure this is the following:

The signal we detect will be a linear superposition of the original and the Berrry's phase-shifted wave functions,

$$\left|\tilde{\psi}\right|^2 = \frac{1}{4}\left|\psi\right|^2\left|1+e^{i\gamma}\right|^2 = \left|\psi\right|^2\sin\left(\frac{\gamma}{2}\right)^2$$

5.3.1 Particle in the Vicinity of a Solenoid

We've already discussed that in an electromagnetic field, the Hamiltonian is written in terms of $\mathbf{A}$ and ϕ, rather than $\mathbf{E}$ and $\mathbf{B}$,

$$\hat{H} = \frac{1}{2m}\left(\hat{\mathbf{p}} - q\hat{\mathbf{A}}\right)^2 + q\phi$$

But also recall that the theory is gauge-invariant, so we can make the transformation

$$\mathbf{A} \to \mathbf{A}' = \mathbf{A} + \boldsymbol{\nabla}\chi$$
$$\phi \to \phi'\phi - \frac{\partial}{\partial t}\chi$$

Aharamov and Bohm showed that the vector potential can affect the quantum behavior of a charged particle even when it is moving through a vanishing field. We'll take a look at an example with a charged oarticle near an infinitely-long solenoid with current I. The magnetic field inside of the solenoid is uniform, and we expect it to be 0 on the outside. We can find a more exact solution by integrating the following expression over the section of the solenoid subtended by a circular contour of radius r:

$$\int_S \mathrm{d}\mathbf{S}\cdot\boldsymbol{\nabla}\times\mathbf{A} = \int_S \mathrm{d}\mathbf{S}\mathbf{B}$$
$$\oint_C \mathrm{d}\mathbf{r}\cdot\mathbf{A} =$$
$$abs\mathbf{B}\pi a^2\ 2\pi r\left|\mathbf{A}\right| = \Phi$$
$$\left|\mathbf{A}\right| = \frac{\Phi}{2\pi r}$$

We can also find that, due to the directional necessity of the curl

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

$\mathbf{A}$ must be in the direction $\hat{\boldsymbol{\phi}}$. The solenoid itself is uncharged, so $\phi = 0$, meaning we can re-write the Hamiltonian as

$$\hat{H} = \frac{1}{2m}\left[-i\hbar\boldsymbol{\nabla} - \frac{q\Phi}{2\pi r}\hat{\boldsymbol{\phi}}\right]^2$$

Note that the ϕ direction is the only thing that's changing in this, so we can replace $\boldsymbol{\nabla}$ with $\frac{\hat{\boldsymbol{\phi}}}{r}\frac{\partial}{\partial\phi}$, and use this in the Schrödinger equation:

$$\frac{1}{2m}\left[-\frac{i\hbar}{r}\frac{\partial}{\partial\phi} - \frac{q\Phi}{2\pi 4}\right]^2\psi(\phi) = E\psi(\phi)$$

We can write the sollution to this, very generally, as

$$\psi(\phi) = A_+ e^{i\lambda+\phi} + A_- e^{-i\lambda-\phi}$$

So we can plug in and simplify, to find that

$$\begin{aligned}
\frac{1}{2m}\left[\frac{\hbar\lambda}{r} - \frac{q\Phi}{2\pi r}\right]^2 &= E \\
\sqrt{\left[\lambda - \frac{q\Phi}{2\pi\hbar}\right]^2} &= \pm\sqrt{\frac{2mEr^2}{\hbar^2}} \\
\lambda_\pm &= \frac{q\Phi}{2\pi\hbar} \pm \frac{r}{\hbar}\sqrt{2mE}
\end{aligned}$$

We also have a boundary condition (of sorts), that

$$\psi(\phi) = \psi(\phi + 2\pi)$$

So that we should be able to replace ϕ with $\phi + 2\pi$ at any point without changing anything. To stay consistent with the literature, it is common to re-write $A_\pm$ as n (which makes sense if we do the algebra of the above equality), so that

$$n = \frac{q\Phi}{2\pi\hbar} \pm \frac{r}{\hbar}\sqrt{2mE_n}$$

5.3.2 Gauge Transformation of a Wave Function

More generally, when a particle moves through a region of vanishing field $\mathbf{B} = \boldsymbol{\nabla} \times \mathbf{A} = 0$, but the potential itself is nonzero (again, taking the electric potential to be 0), we can eliminate the potential from the Schrödinger equation. Starting out, the Schrödinger equation in this situation can be written by

$$\frac{1}{2m}(-i\hbar\boldsymbol{\nabla} - q\mathbf{A})^2\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

The solution will be in the form

$$\psi(\mathbf{r}) = e^{ig(\mathbf{r})}\psi'(\mathbf{r})$$

Plugging this in,

$$\begin{aligned}
\frac{1}{2m}\left(-i\hbar\boldsymbol{\nabla}_\mathbf{r} - q\mathbf{A}(\mathbf{r})\right)^2 e^{ig(\mathbf{r})}\psi'(\mathbf{r}) &= Ee^{ig(\mathbf{r})}\psi'(\mathbf{r}) \\
\frac{e^{ig(\mathbf{r})}}{2m}(\hbar\boldsymbol{\nabla}_\mathbf{r} g(\mathbf{r}) - i\hbar\boldsymbol{\nabla}_\mathbf{r} - q\mathbf{A}(\mathbf{r}))^2\psi'(\mathbf{r}) &= Ee^{ig(\mathbf{r})}psi'(\mathbf{r})
\end{aligned}$$

We can write some things that show up a lot in simpler forms:

$$\begin{aligned}
\boldsymbol{\nabla}_\mathbf{r} g(\mathbf{r} &= \frac{q}{\hbar}\mathbf{A}(\mathbf{r}) \\
g_0(\mathbf{r}) &= \frac{q}{\hbar}\oint_{\mathbf{r}_0}^{\mathbf{r}} \mathrm{d}\mathbf{r}' \cdot \mathbf{A}(\mathbf{r}')
\end{aligned}$$

It's provable that g is only a funtion of $\mathbf{r}$ in the case of a vanishing $\mathbf{B}$. For proof, consider two alternative paths, and we'll try to find $g_C - g_{C'}$:

$$\begin{aligned} g_C(\mathbf{r}) - g_{C'}(\mathbf{r}) &= \frac{q}{\hbar}\left[\int_{\mathbf{r}_0[C]}^{\mathbf{r}} \mathrm{d}\mathbf{r}' \cdot \mathbf{A}(\mathbf{r}') - \int_{\mathbf{r}_0[C']}^{\mathbf{r}} \mathrm{d}\mathbf{r}' \cdot \mathbf{A}(\mathbf{r}') -\right] \\ &= \frac{q}{\hbar}\left[\int_C \mathrm{d}\mathbf{S} \cdot \boldsymbol{\nabla} \times \mathbf{A} - \int_{C'} \mathrm{d}\mathbf{S} \cdot \boldsymbol{\nabla} \times \mathbf{A}\right] \end{aligned}$$

And this will only be for different paths if $\boldsymbol{\nabla} \times \mathbf{A}$, or $\mathbf{B}$ is equal to 0. So, we can write the Schrödinger equation without A:

$$\frac{1}{2m}(-i\hbar\boldsymbol{\nabla}_{\mathbf{r}})^2 = E\psi'$$

5.3.3 Aharamov-Bohm Experiment

Aharamov and Bohm proposed and experiment where an electron beam splits into two and each passes on wither side of a solenoid in the $\mathbf{B} = 0$ region. The phase is

$$g(\mathbf{r}) = \frac{q}{\hbar}\int \mathrm{d}\mathbf{r} \cdot \mathbf{A}$$

With the $\mathbf{A}$ that we found earlier. For electrons passing below and above,

$$\begin{aligned} g_{top} &= \frac{q}{\hbar}\int_{C_{top}} \mathrm{d}\mathbf{r} \cdot \mathbf{A} \\ &= -\frac{q\Phi}{2\hbar} \\ g_{bottom} &= \frac{q}{\hbar}\int_{C_{bottom}} \mathrm{d}\mathbf{r} \cdot \mathbf{A} \\ &= \frac{q\Phi}{2\hbar} \end{aligned}$$

5.3.4 AB Effect = Berry's Phase

6 Magnetic Monopoles

There's no current experimental evidence for magnetic charges. However, Dirac pointed out that the existebce if one magnetic monopole in the unniverse yields the electric charge quantization. Let's review that argument.
The field of a magnetic monopole is analogous to the electric field of an electric charge:

$$\mathbf{B} = \frac{g\mu_0}{4\pi}\frac{\hat{\mathbf{n}}}{r^2}$$

Notice that the existence of magnetic monopoles would mean symmetric Maxwell's equations, eg.

$$\boldsymbol{\nabla}\cdot\mathbf{E} = \frac{\rho}{\epsilon_0}$$
$$\boldsymbol{\nabla}\cdot\mathbf{B} = \mu_0\rho_\mu$$

Let's find the gauge potential corresponding to $\mathbf{B}$:

$$\oint_{L=\partial S} \mathrm{d}\mathbf{r}\cdot\mathbf{A} = \int_S \mathrm{d}\mathbf{S}\cdot\mathbf{B}$$

Where S could either be S_1 (the upper part of the surface defined by a sphere of radius g, at the θ an ϕ angles defined by $\mathbf{B}$), or S_2 (the lower part of the surface).
In the case that $S = S_1$,

$$\begin{aligned}\int_{S_1}\mathrm{d}\mathbf{S}\cdot\mathbf{B} &= \frac{g\mu_0}{4\pi}\int_{\Omega_1}\mathrm{d}\Omega\\ &= \frac{g\mu_0}{4\pi}\Omega_1\\ &= \frac{g\mu_0}{2}(1-\cos\theta)\end{aligned}$$

Then

$$\oint_L \mathrm{d}\mathbf{r}\cdot\mathbf{A} = A_\phi r\sin\theta 2\pi$$
$$\mathbf{A}^\uparrow = \frac{g\mu_0}{4\pi}\frac{1-\cos\theta}{r\sin\theta}\hat{\boldsymbol{\phi}}$$

This one diverges at $\theta = \pi$.
In the case that $S = S_2 = S_{sphere} - S_1$, the orientation of the surface means that we have a change of sign:

$$\int_{S_2}\mathrm{d}\mathbf{S}\cdot\mathbf{B} = \frac{g\mu_0}{2}(1+\cos\theta)$$
$$\mathbf{A}^\downarrow = -\frac{g\mu_0}{4\pi}\frac{1+\cos\theta}{r\sin\theta}\hat{\boldsymbol{\phi}}$$

This one diverges at $\theta = 0$.
Outside the sphere, where $\mathbf{B} = \boldsymbol{\nabla}\times\mathbf{A} = 0$,

$$\psi(\mathbf{x}) = e^{\frac{ig}{\hbar}\int^{\mathbf{x}}\mathrm{d}\mathbf{r}'\cdot\mathbf{A}(\mathbf{r}')}\psi'(\mathbf{x})$$

Where ψ' is the field-independent wave function. Inside the sphere, we have to use one of the $\mathbf{A}$ functions that we found earlier:

$$\psi^{\uparrow}(\mathbf{x}) = e^{\frac{iq}{\hbar}\int^{\mathbf{x}} \mathrm{d}\mathbf{r}'\mathbf{A}^{\uparrow}(\mathbf{r}')}\psi'(\mathbf{x})$$
$$\psi^{\downarrow}(\mathbf{x}) = e^{\frac{iq}{\hbar}\int^{\mathbf{x}} \mathrm{d}\mathbf{r}'\mathbf{A}^{\downarrow}(\mathbf{r}')}\psi'(\mathbf{x})$$

Where, of course, these are related by a simple transformation (I won't show it here, just set them equal and solve).
We know that the phase has to be the gauge function χ:

$$\begin{aligned}\boldsymbol{\nabla}\chi &= \mathbf{A}^{\uparrow} - \mathbf{A}^{\downarrow} \\ &= \frac{g\mu_0}{4\pi}\frac{\hat{\boldsymbol{\phi}}}{r\sin\theta} \\ \hat{\boldsymbol{\phi}}\frac{1}{r\sin\theta}\frac{\partial\chi}{\partial\phi} &= \frac{g\mu_0}{4\pi}\frac{\hat{\boldsymbol{\phi}}}{r\sin\theta} \\ \chi &= \frac{g\mu_0}{2\pi}\phi\end{aligned}$$

We can find the phase

$$\int^{\mathbf{x}} \mathrm{d}\mathbf{x}' \cdot \boldsymbol{\nabla}'\chi = \frac{g\mu_0}{2\pi}\phi$$

And we can use this in our relationship between the two inner wave functions (I, again, for time's sake, won't show this here). Both functions have to be unique, ie.,

$$\psi^{\uparrow\downarrow}(\phi) = \psi^{\uparrow\downarrow}(\phi + 2\pi)$$

So,

$$e^{2iq'g'2\pi/\hbar c} = 1$$

Given that

$$q' = \frac{q}{\sqrt{4\pi\epsilon_0}}$$
$$g' = \sqrt{\frac{\mu_0}{4\pi}}g$$

We find that

$$q'g' = n\frac{\hbar c}{2}$$

So that the existence of magnetic monopoles menas that the product $q'g'$ is quantized, meaning all electric charges will be multiples of the smallest one.

7 Basics of the Path Integral

7.1 Propagator

Consider the following transition amplitude:

$$K(\mathbf{x}', t'; \mathbf{x}, t) = \begin{cases} \langle \mathbf{x}', t' | \mathbf{x}, t \rangle, & t' > t \\ 0, & t' < t \end{cases}$$
$$= \langle \mathbf{x}', t' | \mathbf{x}, t \rangle \, \theta(t - t')$$

constructed in terms of basis kets $|\mathbf{x}, t\rangle$. For stationary states (ie., states where the Hamiltonian is time-independent),

$$|\mathbf{x}, t\rangle \equiv e^{+\frac{i}{\hbar}\hat{H}t} |\mathbf{x}\rangle$$

So that the transition amplitude (where $t' > t$),

$$K = \langle \mathbf{x}' | \, e^{-\frac{i}{\hbar}\hat{H}(t'-t)} \, |\mathbf{x}\rangle$$

is the matrix element of the time-evolution operator

$$U(t', t) \equiv e^{-\frac{i}{\hbar}\hat{H}(t'-t)}$$

This transition amplitude to go from $\mathbf{x}, t$ to $\mathbf{x}', t'$ is called the propagator.
Let's discuss the interpretation of K.
Consider a state $|\alpha\rangle$ for an observable $\hat{A}$. Its coordinate-space wave function is

$$\psi_\alpha(vecx, t) = \langle \mathbf{x}, t | \alpha \rangle$$

Then for $t' > t$, we can write this as

$$\psi_\alpha(\mathbf{x}', t') = \langle vecx', t' | \alpha \rangle$$
$$= \int \mathrm{d}^3\mathbf{x} \, \langle \mathbf{x}', t' | \mathbf{x}, t \rangle \, \langle \mathbf{x}, t | \alpha \rangle$$
$$= \int \mathrm{d}^3\mathbf{x} K(\mathbf{x}', t'; \mathbf{x}, t) \psi_\alpha(\mathbf{x}, t)$$

Thus, K propagates the wave function in space-time from $\mathbf{X}, t$ to $\mathbf{x}', t'$.

Properties of K

(i) Causality (obvious from the definition)

$$K(\mathbf{x}', t'; \mathbf{x}, t) = 0, \qquad t' < t$$

(ii) $K(\mathbf{x}', t'; \mathbf{x}, t) = \langle \mathbf{x}', t' | \mathbf{x}, t \rangle = \delta^{(3)}(\mathbf{x}' - \mathbf{x})$

(iii) Composition (will be very important for the definition of the path integral). Choosea point $\mathbf{x}'', t''$ with $t < t'' < t'$. Then

$$\langle \mathbf{x}', t' | \mathbf{x}, t \rangle = \int \mathrm{d}^3\mathbf{x}'' \, \langle \mathbf{x}', t' | \mathbf{x}'', t'' \rangle \, \langle \mathbf{x}'', t'' | \mathbf{x}, t \rangle$$
$$K(\mathbf{x}', t'; \mathbf{x}, t) = \int \mathrm{d}^3\mathbf{x}'' K(\mathbf{x}', t'; \mathbf{x}'', t'') K(\mathbf{x}'', t''; \mathbf{x}, t)$$

(iv) Representation through a complete set of states.
Let $\phi_\alpha(\mathbf{x}, t)$ be an energy eigenstate, so that

$$\phi_\alpha(\mathbf{x}, t) = \phi_\alpha(\mathbf{x}) e^{iE_\alpha t/\hbar}$$

Then at time t',

$$\phi_\alpha(\mathbf{x}, t') = \phi_\alpha(\mathbf{x}) e^{iE_\alpha t'/\hbar} = \int \mathrm{d}^3 x K(\mathbf{x}', t'; \mathbf{x}, t) \phi_\alpha(\mathbf{x}) e^{iE_\alpha t/\hbar}$$

If we multiply by the complex conjugate and sum over α,

$$\begin{aligned}\sum_\alpha \psi_\alpha^*(\mathbf{x}'') \psi_\alpha(\mathbf{x}') e^{iE_\alpha (t-t')/\hbar} & \\ &= \int \mathrm{d}^3 x K(\mathbf{x}', t'; \mathbf{x}, t) \sum_\alpha \psi_\alpha^*(\mathbf{x}'') \psi_\alpha(\mathbf{x}) \\ &= K(\mathbf{x}', t'; \mathbf{x}'', t)\end{aligned}$$

(v) From here it is clear that K is the Green's function for the Schrödinger equation.

7.2 Propagator for a Free System

Let's try to calculate the propagator for $V = 0$. Ie, where

$$\hat{H} = \frac{\hat{p}^2}{2m}$$

Recall that the complete set of eigenstates is formed by eigenstates of $\hat{p}$:

$$\begin{aligned}\hat{p} \left|p\right\rangle &= p \left|p\right\rangle \\ \hat{H} \left|p\right\rangle &= \frac{p^2}{2m} \left|p\right\rangle\end{aligned}$$

Then, assuming as alway that $t' > t$,

$$\begin{aligned}K(\mathbf{x}', t'; \mathbf{x}, t) &= \langle \mathbf{x}', t' | \mathbf{x}, t \rangle \\ &= \int \frac{\mathrm{d}^3 \mathbf{p}}{(2\pi\hbar)^3} \langle \mathbf{x}', t' | p \rangle \langle \mathbf{p} | \mathbf{x}, t \rangle \\ &= \int \frac{\mathrm{d}^3 \mathbf{p}}{(2\pi\hbar)^3} e^{-i\frac{p^2}{2m\hbar}(t'-t) + \frac{i}{\hbar}\mathbf{x}\cdot(\mathbf{x}'-\mathbf{x})}\end{aligned}$$

This integral, as it stands, is not convergent. In order to make it convergent, we need to add a negative addendum to the exponent:

$$\begin{aligned}&= \int \frac{\mathrm{d}^3 \mathbf{p}}{(2\pi\hbar)^3} e^{-i\frac{p^2}{2m\hbar}(t'-t-i_0) + \frac{i}{\hbar}\mathbf{x}\cdot(\mathbf{x}'-\mathbf{x})} \\ &= e^{i\frac{m}{2\hbar}\frac{(\mathbf{x}'-\mathbf{x})^2}{t'-t-i_0}} \int \frac{d^3\mathbf{p}'}{(2\pi\hbar)^3} e^{-i\frac{t'-t-i_0}{2m\hbar}\mathbf{p}'^2}\end{aligned}$$

This is just a Gaussian integral, so our final solution for K is

$$K(\mathbf{X}', t'; \mathbf{x}, t) = \frac{1}{(2\pi\hbar)^3} \left(\frac{2m\hbar\pi}{i(t'-t-i_0)} \right)^{3/2} e^{\frac{im}{2\hbar}\frac{(\mathbf{x}'-\mathbf{x})^2}{t'-t-i_0}} \theta(t'-t)$$

7.3 Feynman Path Integral

Let's divide the space-time interval $(t' - t, \mathbf{x}' - \mathbf{x})$ into infinitesimally small intervals, ie.,

$$[t', t] = [t_N, t_{N-1}] \cup [t_{N-1}, t_{N-2}] \ldots \cup [t_1, t_0]$$

Such that $\Delta t = \frac{t_N - t_0}{N}$. To relate this back to our original proposition, $t_N = t'; t_0 = t$. The propagator for this interval is thus

$$K(\mathbf{x}', t'; \mathbf{x}, t) = \int \mathrm{d}\mathbf{x}_1 \mathrm{d}\mathbf{x}_2 \ldots \mathrm{d}\mathbf{x}_{N-1} K(\mathbf{x}', t'; \mathbf{x}_{N-1} t_{N-1}) \ldots K(\mathbf{x}_1, t_1; \mathbf{x}, t)$$

In the limit that $N \to \infty, \Delta t \to 0$, this becomes an integral over all possible paths between $(\mathbf{x}, t)$ and $(\mathbf{x}', t')$. Such an integral is called the path integral.
Let's calculate the propagator for a system with an arbitrary time-independent Hamiltonian,

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

7.4 Stationary Phase

7.5 Tunneling and Instantons

7.6 Propagator for a Quantum Mechanical Oscillator

8 Homework and Solutions

8.1 Homework 1 (1.1 - 2.1.3)

(i) A particle in a one-dimensional harmonic oscillator potential with mass m and frequency ω is in the state

$$|\psi(t=0)\rangle = |a\rangle$$

at time $t = 0$, whih is the eigenstate of the operator or the coordinate $\hat{x}\,|a\rangle = a\,|a\rangle$ with eigenvalue a (do not confuse with the annihilation operator!). Find the expectation value of the Heisenberg operators $\hat{x}_H(t)$ and $\hat{p}_H(t)$ in this state.

Answer.

$$\langle \hat{x}_H \rangle = a\cos(\omega t)$$
$$\langle \hat{p}_H \rangle = -m\omega a \sin(\omega t)$$

Proof. Recall that the relationship between Heisenberg operators and standard(Schrödinger) operators is

$$\hat{A}_H(t) = e^{i\hat{H}t/\hbar}\hat{A}_S e^{-i\hat{H}t/\hbar}$$

Recall also that the Hamiltonian for a harmonic oscillator is given by

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{m\omega^2\hat{x}^2}{2}$$

We first have to find the Heisenberg representation of the position and momentum operators, using a truncated Taylor series representation of e^x:

$$\begin{aligned}
\hat{x}_H(t) &= e^{i\hat{H}t/\hbar}\hat{x}e^{i\hat{H}t/\hbar} \\
&= \left(1 + \frac{i}{\hbar}\hat{H}t + \frac{1}{2!}\left(\frac{i}{\hbar}\right)^2\hat{H}^2t^2 + \cdots\right)\hat{x}\left(1 - \frac{i}{\hbar}\hat{H}t + \frac{1}{2!}\left(\frac{i}{\hbar}\right)^2\hat{H}^2t^2 - \cdots\right) \\
&= \hat{x} + \frac{i}{\hbar}t(\hat{H}\hat{x} - \hat{x}\hat{H}) + \frac{1}{2!}\left(\frac{i}{\hbar}\right)^2(\hat{H}^2\hat{x} - 2\hat{H}\hat{x}\hat{H} + \hat{x}\hat{H}^2) + \cdots \\
&= \hat{x} + \frac{i}{\hbar}t[\hat{H},\hat{x}] + \frac{1}{2!}\left(\frac{i}{\hbar}\right)^2\left[\hat{H},[\hat{H},\hat{x}]\right] + \frac{1}{3!}\left(\frac{i}{\hbar}\right)^3\left[\hat{H}\left[\hat{H}[\hat{H},\hat{x}]\right]\right] + \cdots
\end{aligned}$$

We can calculate the commutators here:

$$\begin{aligned}
[\hat{H},\hat{x}] &= \frac{1}{2m}[\hat{p}^2,\hat{x}] \\
&= \frac{1}{2m}\left(\hat{p}[\hat{p},\hat{x}] + +[\hat{p},\hat{x}]\hat{p}\right) \\
&= -\frac{i\hbar}{m}\hat{p} \\
\left[\hat{H},[\hat{H},\hat{x}]\right] &= -\frac{i}{\hbar}m[\hat{H},\hat{p}] \\
&= -(i\hbar)^2\omega^2\hat{x}
\end{aligned}$$

We can go on, but the pattern is clear enough that we'll skip to putting it all together and simplifying using the Taylor series for sines and cosines:

$$\begin{aligned}\hat{x}_H(t) &= \hat{x} + \frac{i}{\hbar}t\left(-\frac{i}{\hbar}\right)\hat{p} + \frac{1}{2!}\left(\frac{i}{\hbar}\right)^2 t^2(-(i\hbar\omega)^2)\hat{x} + \cdots \\ &= \hat{x}\left(1 - \frac{(\omega t)^2}{2!} + \cdots\right) + \frac{p}{m\omega}\left(t\omega - \frac{(\omega t)^3}{3} + \cdots\right) \\ &= \hat{x}\cos(\omega t) + \frac{\hat{p}}{m\omega}\sin(\omega t)\end{aligned}$$

We could use an analagous process to show also that

$$\hat{p}_H(t) = \hat{p}\cos(\omega t) - m\omega\hat{x}\sin(\omega t)$$

Now, we can do the easy(er) part: finding the expectation value of each operator. Because $|a\rangle$ is an eigenstate of $\hat{x}$, as long as we assume that $|a\rangle$ is normalized, we can find that

$$\begin{aligned}\langle a|\,\hat{x}\,|a\rangle &= a\,\langle a|a\rangle \\ &= a\end{aligned}$$

The p expectation value is a little more difficult:

$$\begin{aligned}\langle a|\,\hat{p}\,|a\rangle &= \int_{-\infty}^{\infty}\frac{\mathrm{d}p}{2\pi\hbar}\,\langle a|\,\hat{p}\,|p\rangle\,\langle p|a\rangle \\ &= \int_{-\infty}^{\infty}\frac{\mathrm{d}p}{2\pi\hbar}p\,|\langle a|p\rangle|^2 \\ &= \int_{-\infty}^{\infty}\frac{\mathrm{d}p}{2\pi\hbar}p \\ &= 0\end{aligned}$$

So in all, plugging this into what we found as the Heisenberg represntation of each of these,

$$\begin{aligned}\langle a|\,\hat{x}_H(t)\,|a\rangle &= a\cos(\omega t) \\ \langle a|\,\hat{p}_H(t)\,|a\rangle &= -m\omega a\sin(\omega t)\end{aligned}$$

□

(ii) The Hamiltonian of a spin-$\frac{1}{2}$ particle is given by a two-by-two matrix

$$\frac{\omega\hbar}{2}\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix},$$

where ω is a constant (having the units of inverse seconds).

– Find the time evolution operator which relates states of the system at initial time $t = 0$ to a later time $t > 0$ in the matrix form

Answer.

$$\hat{U}(t) = \begin{pmatrix}\cos\left(\frac{\omega t}{2}\right) & -\sin\left(\frac{\omega t}{2}\right)\\ \sin\left(\frac{\omega t}{2}\right) & \cos\left(\frac{\omega t}{2}\right)\end{pmatrix}$$

Proof. We can re-write the Hamiltonian, for the sake of ease, as

$$\hat{H} = \frac{\hbar\omega}{2}\sigma_y$$

where σ_y is the y Pauli matrix.
The time evolution operator is given by

$$\begin{aligned}\hat{U}(t) &= e^{-i\hat{H}t/\hbar} \\ &= e^{-i\omega t\sigma_y/2}\end{aligned}$$

We can re-write this using a Taylor series:

$$= 1 - \frac{i}{2}\omega t\sigma_y + \frac{1}{2!}\left(-\frac{i}{2}\omega t\right)^2\sigma_y^2 + \frac{1}{3!}\left(-\frac{i}{2}\omega t\right)^3 + \cdots$$

We know/can find that $\sigma_y^2 = 1$, so

$$\begin{aligned}&= 1 - \frac{i\omega t}{2}\sigma_y + \frac{1}{2!}\left(\frac{i\omega t}{2}\right)^2 - \frac{1}{3!}\left(\frac{i\omega t}{2}\right)^3\sigma_y + \cdots \\ &= \left(1 + \frac{1}{2!}\left(\frac{i\omega t}{2}\right)^2 + \cdots\right) - i\left(\left(\frac{\omega t}{2}\right) - \frac{1}{3!}\left(\frac{\omega t}{2}\right)^3 + \cdots\right)\sigma_y\end{aligned}$$

Again, we can use what we know about Taylor series to write

$$= \cos\left(\frac{\omega t}{2}\right) - i\sin\left(\frac{\omega t}{2}\right)\sigma_y$$

noting that cos is being multiplied by the identity matrix, so

$$\hat{U}(t) = \begin{pmatrix}\cos\left(\frac{\omega t}{2}\right) & -\sin\left(\frac{\omega t}{2}\right) \\ \sin\left(\frac{\omega t}{2}\right) & \cos\left(\frac{\omega t}{2}\right)\end{pmatrix}$$

□

– If the initial state $|\hbar/2, t = 0\rangle$ at time $t = 0$ is an eigenstate of the operator

$$\frac{\hbar}{2}\begin{pmatrix}1 & 0 \\ 0 & -1\end{pmatrix}$$

with the eigenvalue $\hbar/2$, find the matrix form of the evolved state $|\hbar/2, t\rangle$ at $t > 0$

Answer.

$$|\hbar/2, t\rangle = \begin{pmatrix}\cos\left(\frac{\omega t}{2}\right) \\ \sin\left(\frac{\omega t}{2}\right)\end{pmatrix}$$

Proof. The operator in question is simply $\hat{s}_z$. We can write the relationship between the operator and the initial state as

$$\hat{s}_z\,|\hbar/2, t = 0\rangle = \frac{\hbar}{2}\,|\hbar/2, t = 0\rangle$$

We can solve this linear equation to find that

$$|\hbar/2, t=0\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

The evolved state of this at time t is thus given by the time-development operator from the previous part applied to the initial state:

$$\begin{aligned} |\hbar/2, t\rangle &= \hat{U}(t)\,|\hbar/2, t=0\rangle \\ &= \begin{pmatrix} \cos\left(\frac{\omega t}{2}\right) \\ \sin\left(\frac{\omega t}{2}\right) \end{pmatrix} \end{aligned}$$

□

– Find the expetation values of all spin operators $\hat{s}_x$, $\hat{s}_y$, and $\hat{s}_z$ in the above state $|\hbar/2, t\rangle$

Answer. All of these can be found with simple linear algebra:

$$\begin{aligned} \langle \hbar/2, t|\, \hat{s}_x\, |\hbar/2, t\rangle &= \frac{\hbar}{2}\sin(\omega t) \\ \langle \hbar/2, t|\, \hat{s}_y\, |\hbar/2, t\rangle &= 0 \\ \langle \hbar/2, t|\, \hat{s}_z\, |\hbar/2, t\rangle &= \frac{\hbar}{2}\cos(\omega t) \end{aligned}$$

(iii) Solve the Heisenberg equations of motion for the time-dependent spin operators $\hat{s}_i$ (with $i = x, y, z$) evolving with the Hamiltonian $H = \hbar\omega\sigma_z/2$, where σ_z is the third Pauli matrix.

Answer.

$$\begin{aligned} \hat{s}_x(t) &= \\ \hat{s}_y(t) &= \\ \hat{s}_z(t) &= \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \end{aligned}$$

Proof. We can re-write the Hamiltonian here as $\hat{H} = \omega\hat{s}_z$. The Heisenberg equation(s) of motion for the operators $\hat{s}_i$ are given by

$$\begin{aligned} i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\hat{s}_i(t) &= [\hat{s}_i(t), \hat{H}] \\ &= \omega[\hat{s}_i(t), \hat{s}_z] \end{aligned}$$

We know of the spin operators that

$$\begin{aligned} [\sigma_i, \sigma_j] &= 2i\epsilon_{ijk}\sigma_k \\ [\hat{s}_i, \hat{s}_j] &= i\hbar\epsilon_{ijk}\hat{s}_k \end{aligned}$$

So each equation of motion can be given by

$$\begin{aligned} i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\hat{s}_x(t) &= \omega[\hat{s}_x(t), \hat{s}_z] \\ &= -i\hbar\omega\hat{s}_y(t) \\ i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\hat{s}_y(t) &= \omega[\hat{s}_y(t), \hat{s}_z] \\ &= i\hbar\omega\hat{s}_x(t) \\ i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\hat{s}_z(t) &= \omega[\hat{s}_z(t), \hat{s}_z] \\ &= 0 \end{aligned}$$

The final equation gives us

$$\hat{s}_z(t) = \hat{s}_z(0) = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

The first and second equations form a linear combination for

$$\hat{s}_\pm(t) = \hat{s}_x(t) + i\hat{s}_y(t)$$

Where

$$\begin{array}{rl} & \dfrac{\mathrm{d}}{\mathrm{d}t}\hat{s}_x(t) = -\omega\hat{s}_y\hat{s}_y(t) \\ + & \dfrac{\mathrm{d}}{\mathrm{d}t}i\hat{s}_y(t) = i\omega\hat{s}_y\hat{s}_y(t) \\ \hline & \dfrac{\mathrm{d}}{\mathrm{d}t}\hat{s}_\pm(t) = \pm i\omega\hat{s}_\pm(t) \end{array}$$

So we need to solve the system given by

$$\hat{s}_\pm(t) = \hat{s}_\pm(0)e^{\pm i\omega t}$$

Where

$$\begin{aligned} \hat{s}_+(0) &= \frac{\hbar}{2}\begin{pmatrix} 0 & 2 \\ 0 & 0 \end{pmatrix} \\ \hat{s}_-(0) &= \frac{\hbar}{2}\begin{pmatrix} 0 & 0 \\ 2 & 0 \end{pmatrix} \end{aligned}$$

That's pretty trivial, if we do, we'll find the answers above. □

8.2 Homework 2 (2.2.1 - 2.2.4)

(i) A spin-1/2 particle is originally in the ground state of the Hamiltonian

$$H_0 = \omega_0 S_z$$

At time $t = 0$ the system is perturbed by

$$H_1(t \geq 0) = \omega_1 S_x e^{-t\tau}$$

Here and above S_j are the spin matrices. Consider H_1 as a small perturbation of H_0, i.e., $\omega_0 \gg \omega_1$. Find the probability for the particle to flip its spin under the perturbation at $t \to \infty$.

Answer.

$$P_{\uparrow\downarrow}(t \to \infty) = \frac{(\omega_1 \tau)^2}{4(\tau^2 \omega_0^2 + 1)}$$

Proof. A spin-1/2 particle described by the given Hamiltonian (assuming $\omega_0 > 0$ can be in one of two states: either spin-up, or spin-down. We can write these as

$$\begin{array}{lll} \text{Spin up} & |\uparrow\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} & H_0 |\uparrow\rangle = \dfrac{\omega_0 \hbar}{2} |\uparrow\rangle \\ \text{Spin down} & |\downarrow\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} & H_0 |\downarrow\rangle = -\dfrac{\omega_0 \hbar}{2} |\downarrow\rangle \end{array}$$

The ground state of a particle is the particle with the lowest energy. Since we said ω_0 is positive, that measn that $|\downarrow\rangle$ must be ge ground state. The transition probability for the particle to flip its spin is

$$P_{\uparrow\downarrow}(t \to \infty) = \left| -\frac{i}{\hbar} \int_{-\infty}^{\infty} \mathrm{d}t' e^{i\omega_{\uparrow\downarrow} t'} \langle\uparrow| H_1 |\downarrow\rangle \right|^2$$

Note that $\omega_{\uparrow\downarrow} = \omega_\uparrow - \omega_\downarrow = \omega_0$, so we can re-write this as

$$= \left| -\frac{i}{\hbar} \int_{-\infty}^{\infty} \mathrm{d}t' e^{i\omega_0 t'} \langle\uparrow| \omega_1 e^{-t'/\tau} (\hbar/2) \sigma_x |\downarrow\rangle \right|^2$$

The σ_x term is the only one which we can't pull out of the braket, but we can simplify it:

$$\langle\uparrow| \sigma_x |\downarrow\rangle = \begin{pmatrix} 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = 1$$

Thus, we can continue our simplification:

$$\begin{aligned} P_{\uparrow\downarrow}(t \to \infty) &= \frac{\omega_1^2}{4} \left| \int_0^{\infty} e^{-t'\left(\frac{1}{\tau} - i\omega_0\right)} \right|^2 \\ &= \frac{\omega_1^2}{4} \frac{1}{\left|\frac{1}{\tau} - i\omega_0\right|^2} \\ P_{\uparrow\downarrow}(t \to \infty) &= \frac{(\omega_1 \tau)^2}{4(\tau^2 \omega_0^2 + 1)} \end{aligned}$$

□

(ii) A one-dimensional quantum mechanical harmonic oscillator (possessing the electric charge q) in its ground state is suddenly immersed in a constant homogeneous electric field E (i.e., the change in the Hamiltonian is not (!) small, that is, the electric field is large!). Find the probability of its transition to an arbitrary excited state $|n\rangle$ [Hint: You will need the Gaussian integral $\int_{-\infty}^{\infty} \mathrm{d}x e^{-x^2} = \sqrt{\pi}$.]

Answer.

$$P_{n0} = \frac{1}{n!}\left(\frac{\xi_0^2}{2}\right)^n e^{-(\xi_0^2/2)}$$

Proof. □

(iii) A charged particle in n-th excited state of the one-dimensional harmonic osillator potential at $t = -\infty$ is subject to a small perturbation of the form

$$V(t) = qExe^{-t^2/\tau^2},$$

where x is the coordinates and its prefactors are constants. Find probability amplitudes for all possible transitions at $t \to \infty$.

Answer.

$$P_{nm} = \frac{(qE\tau)^2\pi}{2m\omega\hbar} e^{-\omega^2\tau^2/2}\left[(m+1)\delta_{n,m+1} + m\delta_{n,m-1}\right]$$

Proof. □

8.3 Homework 3 (2.3 - 2.4.5)

(i) A particle of mass m is bound to a one-dimensional infinite square well potential of width L. One of the walls movese to a new position such that the length of the box becomes $8L$. Find the probability for the particle to stay in the ground state when the above move is done (i) adiabatically and (ii) suddenly. In the case of the adiabatic change, find the work done to move the wall.

Answer. *Proof.* □

(ii) A particle of mass m and electric charge q is confined to move in an infinitely deep one-dimensional square well of width a. Calculate the rate of spontaneous emission during the quantum transition from nth to mth ($n > m$) excited state in the dipole approximation. Provide numerical values for $(n = 2) \to (m = 1)$ and $(n = 3) \to (m = 2)$.

(iii) Consider $2p \to 1s$ transitions in the hydrogen atom in the dipole approximation.

- Calculate values (i.e., numerical factor times Bohr radius a_B) for the components of the electric dipole moment operator $\mathbf{d} = -e\mathbf{r}$, where $\mathbf{r} = x\mathbf{e}_x + u\mathbf{e}_y + z\mathbf{e}_z$, corresponding to three transitions (in the notation $|n\ell m\rangle$)

$$\langle 210|\,\mathbf{d}\,|100\rangle\,, \qquad \langle 211|\,\mathbf{d}\,|100\rangle\,, \qquad \langle 21,-1|\,\mathbf{d}\,|100\rangle\,.$$

Answer. *Proof.* □

- Find the lifetimes for the three excited states. Make numerical estimates.

Answer. *Proof.* □